



Chemical Kinetic Modelling for Combustion

Prof. Henry Curran

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Overview/Aims

➤ 5 days / 15 lectures

➤ Day 1

➤ (1-3) Basic thermodynamic principles

➤ Day 2

➤ (4) Basic kinetic principles

➤ (5,6) Experimental JSR, FR, RCM & ST contribution to kinetics

➤ Day 3

➤ (7-9) Small species mechanism development





Overview/Aims

➤ 5 days / 15 lectures

➤ Day 4

➤ (10-12) Large hydrocarbon mechanism development

➤ Day 5

➤ (13-15) Oxygenated hydrocarbon mechanism development



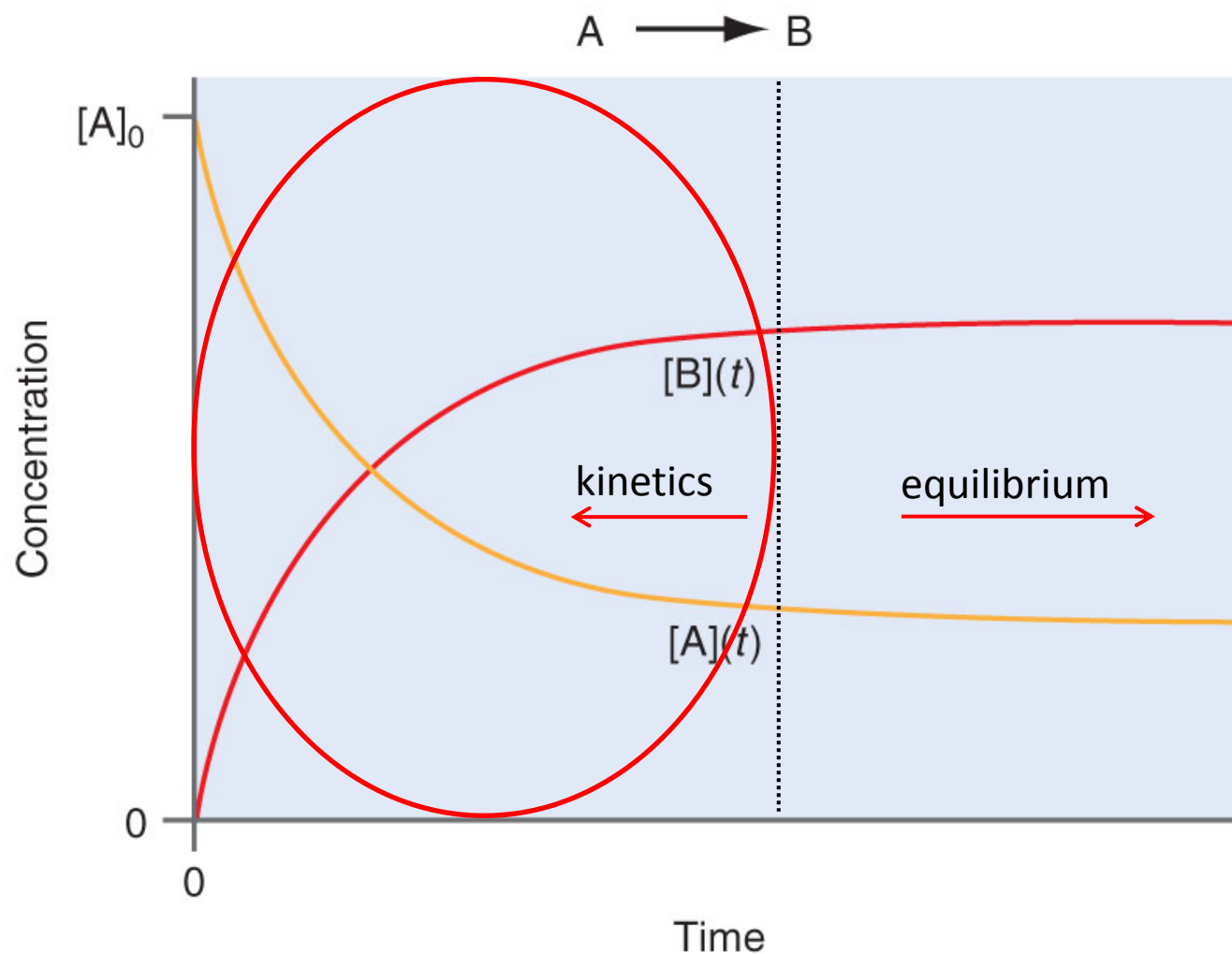


Basic kinetic and thermodynamic principles





Kinetics and equilibrium



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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.

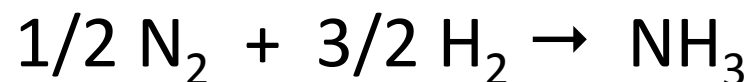


Enthalpy of Formation

Molar standard enthalpy of formation $\Delta_f H^\circ$:

- 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



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



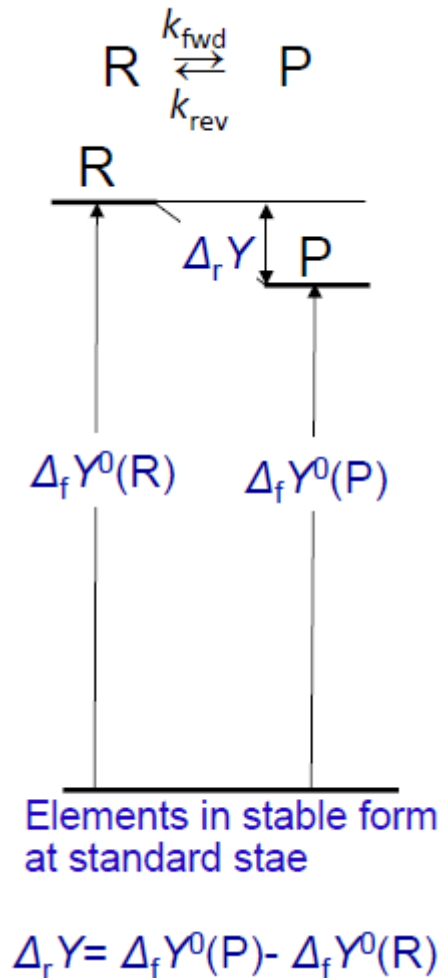
Thermodynamic data

Tabulated data

Standard enthalpy of formation, $\Delta_f H^0$
Standard entropy of formation, $\Delta_f S^0$
Specific heat capacity, $C_p(T)$

Sources of data

Experiments
Ab initio calculations
Empirical schemes based on
observed rules in experimental or ab initio data



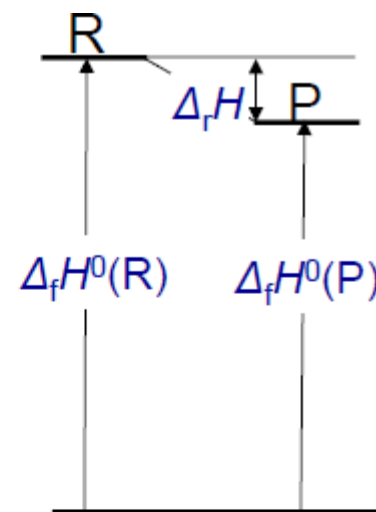


Thermodynamic data: Experimental sources

Enthalpy of formation, $\Delta_f H$

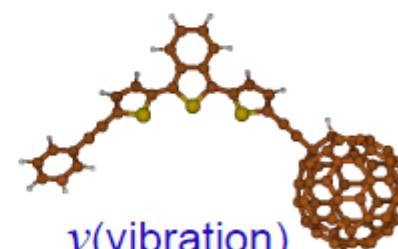
Determine the enthalpy change of any reaction $\Delta_r H$
Calculate enthalpy of formation from $\Delta_r H$
and those of known reaction partners

$$\Delta_f H^0(R) = \Delta_r H + \Delta_f H^0(P)$$



Entropy of formation, $\Delta_f S$

Rarely measured directly
(from temperature dependence of K_r)
Calculated from experimental molecular parameters
using statistical thermodynamics



ν (vibration)
 Θ (inertia)

Specific heat capacities, C_p

Can be measured directly for stable species
Calculated from experimental molecular parameters
using statistical thermodynamic

generally simplified
formulas of statistical
thermodynamics



Enthalpy of Formation

Variation with temperature:

- At constant pressure:

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

- 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:

$$\Delta_f H_{(T)}^\circ = \Delta_f H_{298\text{ K}}^\circ + \int_{298}^T \Delta_r C_P^\circ dT = \Delta_f H_{298\text{ K}}^\circ + \int_{298}^T (C_{P_{\text{molecule}}}^\circ - C_{P_{\text{elements}}}^\circ) dT$$

- Permits derivation an analytic expression as a function of T



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

$$G = H - TS$$

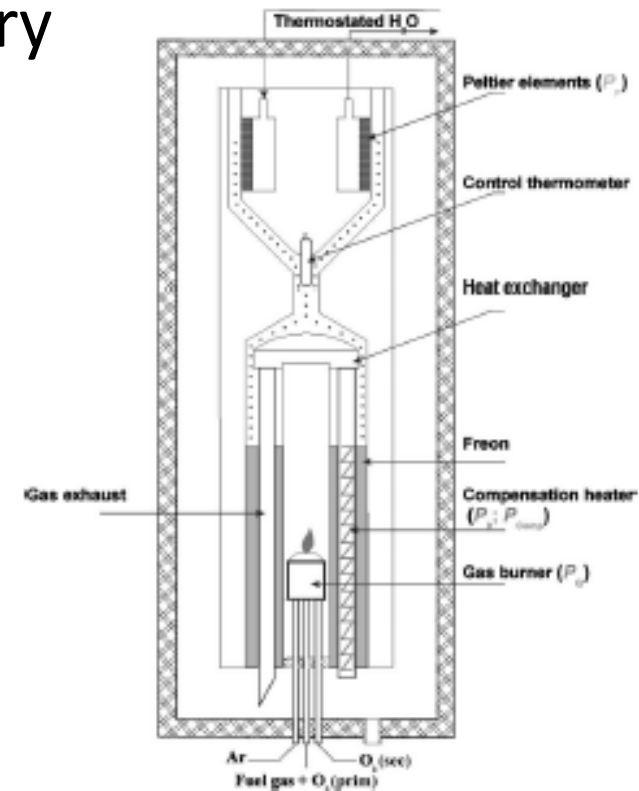


Thermodynamics

How do we determine C_p , S , H ?

- Experiment—Combustion Calorimetry
 - Foundation of thermodynamics BUT....
 - Time consuming
 - Difficult/expensive
 - Fine for stable species, what about radicals?

Modern design



Y.I. Alexandrov *Thermochim. Acta* **382**, 55



Non-experimental methods

Ab initio quantum chemistry

Solving the Schrödinger equation for a molecule provides its energy and its thermodynamic properties

In principle.

In fact, the methods of ab initio quantum chemistry are approximate

Estimation of thermodynamic parameters based on empirical rules

Group additivity method

Ab initio methods

are based on a few approximations

and a real effort to fix the problems of the approximations

Group additivity

within certain limits of accuracy the thermodynamic properties of properly selected groups add up to that of a molecule

data can be borrowed from information on one or more similar molecules

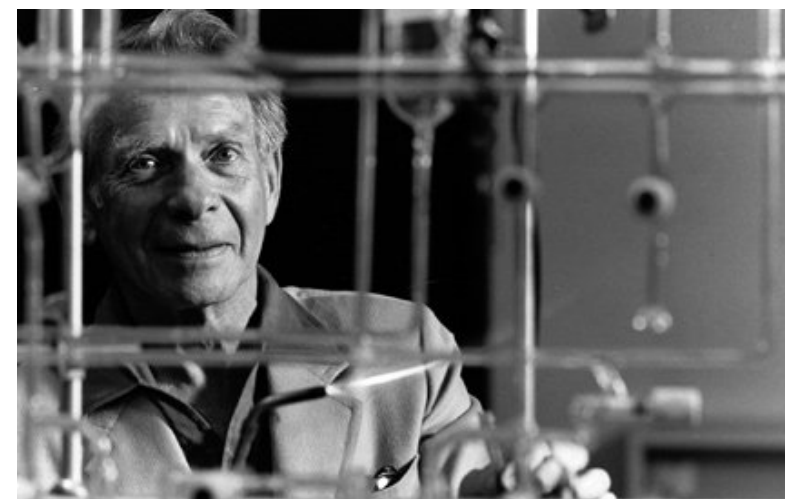
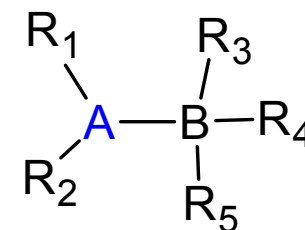
the question is the “limit of accuracy”.



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





Group Additivity

Consider Ethane:

- Simple molecule with **2 identical groups** (C/C/H₃)



- Thermodynamics well known
- $\Delta_f H = -84. \pm 0.4 \text{ kJ/mol}$ (NIST)
 - Contribution of each group = -42.0 kJ/mol
- $C_p \text{ 298.15 K} = 52.49 \text{ J/mol}$ (NIST)
 - Contribution of each group = 26.25 J/mol
- $S \text{ 298.15 K} = 229.28 \text{ J/mol}$
 - 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:

$$\delta S^\circ = -R \ln \sigma$$

➤ σ = number of symmetries in the molecule = $\sigma_{\text{ext}} \times \sigma_{\text{int}}$

— σ_{ext} number of external symmetries (rotation of molecule)

— σ_{int} number of internal symmetries (rotations around single bonds)

➤ Ethane $\sigma_{\text{ext}} = 2$, $\sigma_{\text{int}} = 9$, total correction = $-R \ln(18)$

➤ Similar corrections for optical isomers = $+R \ln(\# \text{ of OI})$



Group Additivity

What about free radicals?

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

➤ $\Delta_f H (\text{R}\cdot) = \text{BDE} + \Delta_f H (\text{RH}) - \Delta_f H (\text{H}\cdot)$

Varies based on
type of C-H bond
broken

Heat of
formation
of 'parent'
species

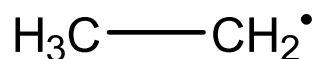
Well known
 $\Delta_f H = 52.1$
kcal/mol



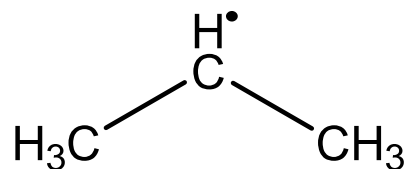
Group Additivity

BDE Groups

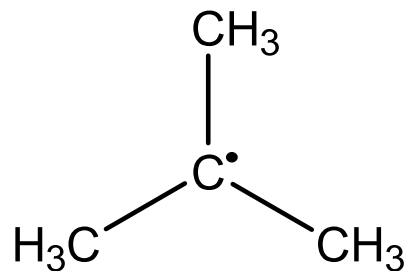
- Strength of C–H bond depends on stability of radical



Type = primary, 101.1 kcal/mol



Type = secondary, 98.45 kcal/mol



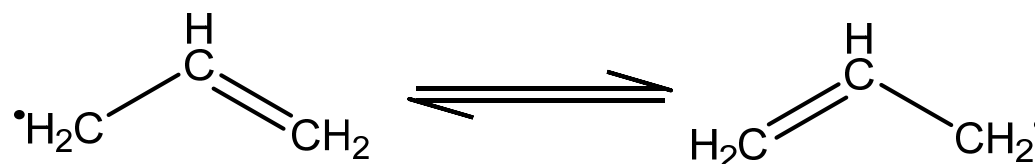
Type = tertiary, 96.50 kcal/mol



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

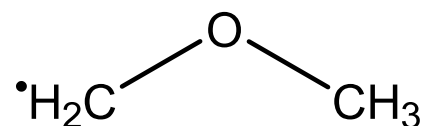
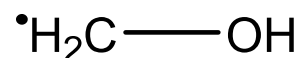
Compare with primary alkane (101.1 kcal/mol)



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, $\equiv$ divalent atom

C_t : sp carbon atom, 1 triple bond, 1 single, $\equiv$ monovalent atom

C_a : allene-like carbon atom, $C=\textcolor{red}{C}=C$, ending atoms are C_d

C_B : carbon-atom in aromatic rings, $\equiv$ trivalent atom

C_{BF} : “fused carbon” carbon-atom belonging to several aromatic rings, $\equiv$ trivalent atom

Super-atoms:

$C=O$, carbonyl group $\equiv$ (CO) divalent

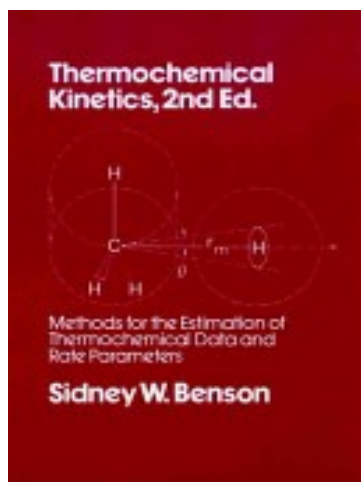
NO , NO_2 , SO_2 , $PO\ldots$



Benson's groups

Table A.1. Group Values for ΔH_f° , S_{int}° , and C_p° , Hydrocarbons

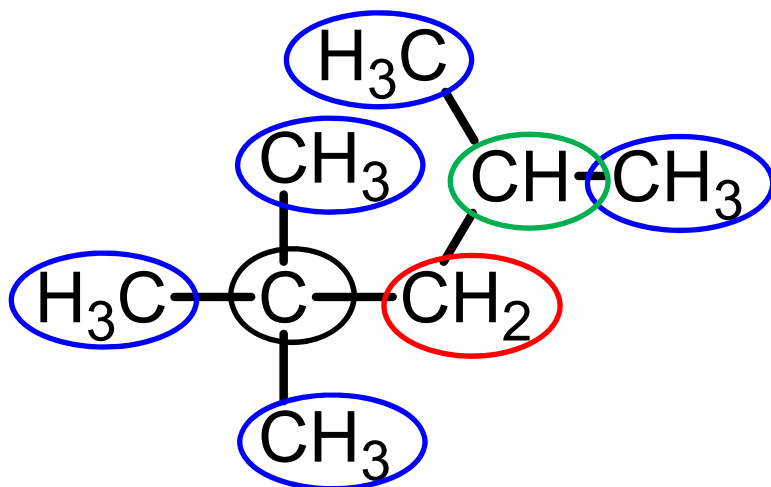
Group	ΔH_f° 298	S_{int}° 298	C_p°					
			300	400	500	600	800	1000
$C-(H)_3(C)$	-10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77
$C-(H)_2(C)_2$	-4.93	9.42	5.50	6.95	8.25	9.35	11.07	12.34
$C-(H)(C)_3$	-1.90	-12.07	4.54	6.00	7.17	8.05	9.31	10.05
$C-(C)_4$	0.50	-35.10	4.37	6.13	7.36	8.12	8.77	8.76
$C_d-(H)_2$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





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

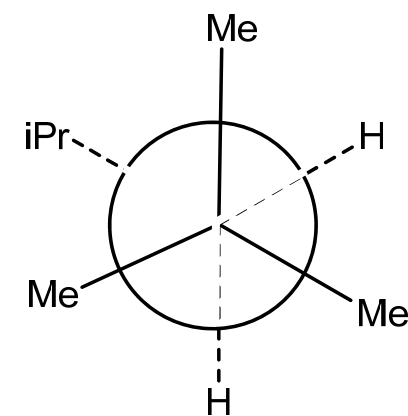
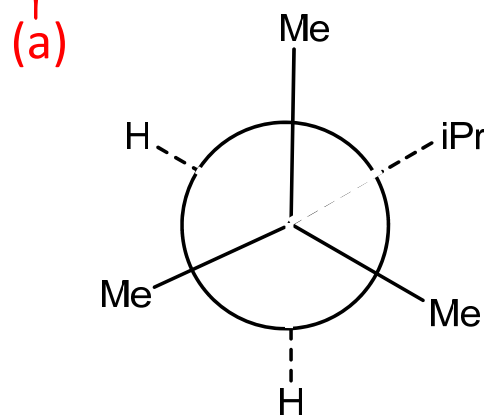
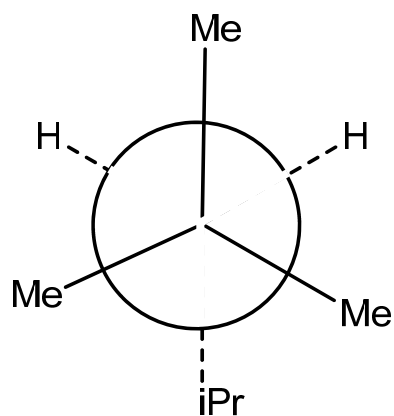
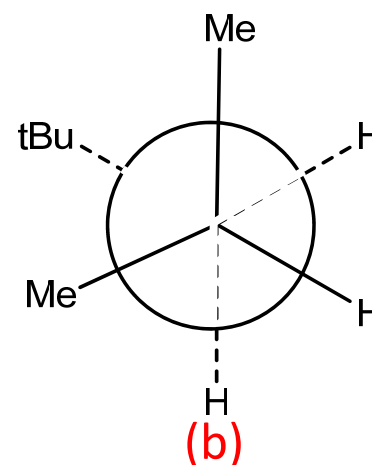
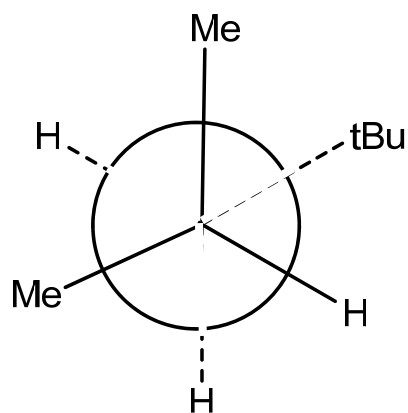
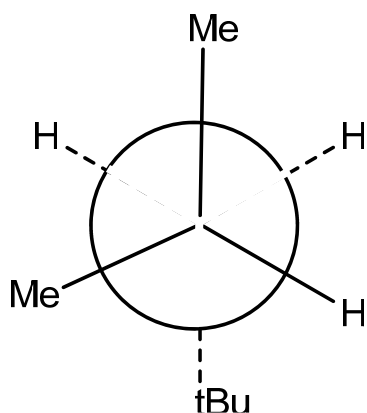
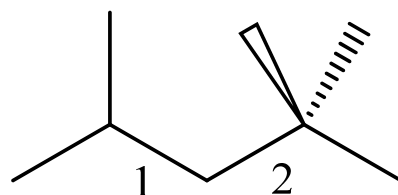
$$\sigma_{\text{ext}} = 1, \sigma_{\text{int}} = 729$$

Correction to symmetry

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

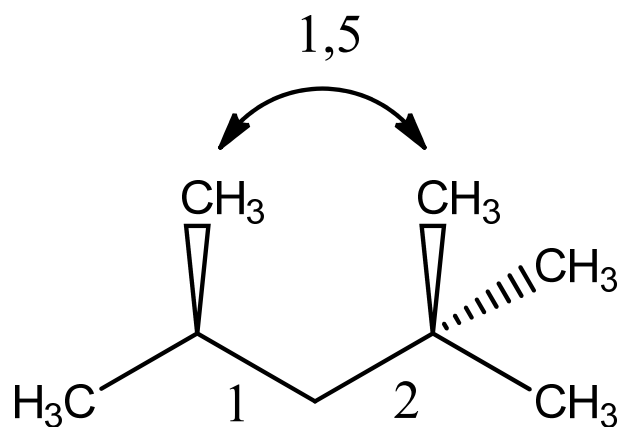


Gauche (C–C) interactions

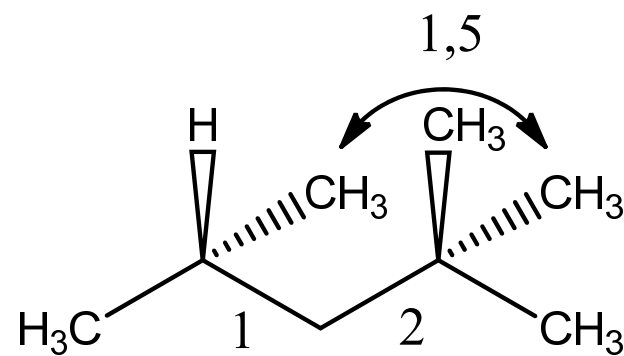




1,5 (H–H) Interaction



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	C_p° (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

$(T_{\text{eb}}, T_{\text{fus}}, T_{\text{c}}, P_{\text{c}} \dots)$

Quantum Chemistry softwares

Semi-empirical approach: MOPAC...

Ab initio : Gaussian, Spartan, Jaguar, Molpro, ...



Thermochemistry in Chemkin

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

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

$$H_k^o = \int_0^T C_p^o dT$$

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

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

$$S_k^o = \int_0^T \frac{C_{p^k}^o}{T} dT$$
$$\frac{S_k^o}{R} = a_{1k} \ln T + \sum_{n=2}^N \frac{a_{nk} T^{(n-1)}}{(n-1)} + a_{N+2,k}$$

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

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

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

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

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   50   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   60   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
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column numbers:

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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.



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>



Basic Chemical Kinetic Principles I



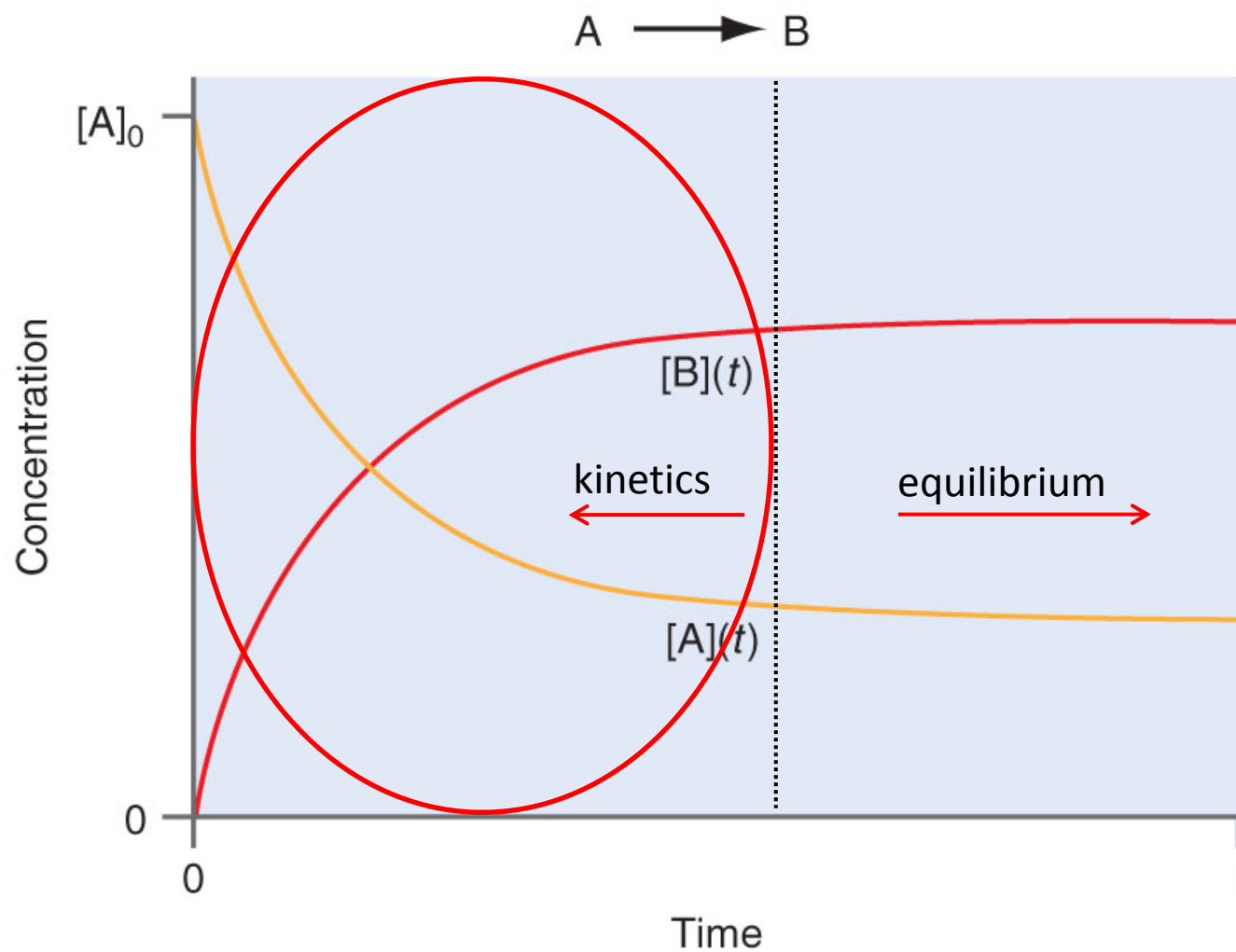


Chemical Kinetics

- 1st and 2nd Order reactions
- Kinetics in flow reactors; plug vs stirred
- Temperature dependence; *Arrhenius equation*
- Complex reactions
 - chain reactions
 - polymerisations
 - explosions; branching chain reactions



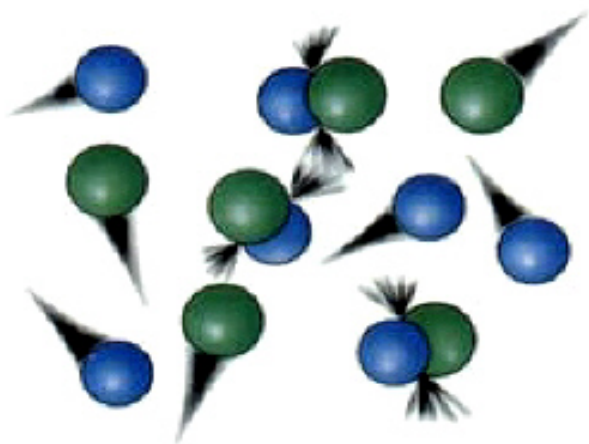
Kinetics and equilibrium



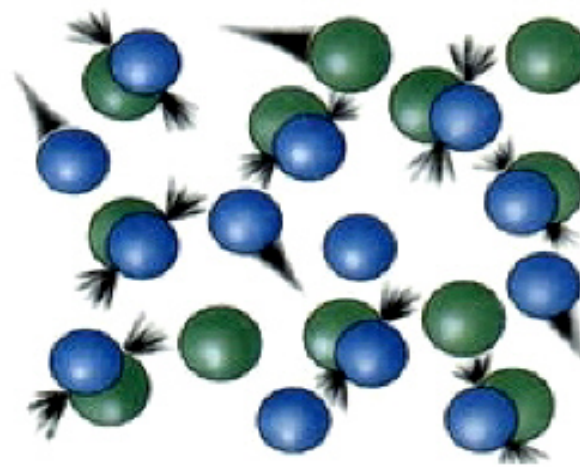
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Rate of reaction depends on concentration of reactants



Low concentration = Few collisions



High concentration = More collisions



Rate of reaction {symbol: R,n, ..}



Rate? conc/time or in SI $\text{mol dm}^{-3} \text{s}^{-1}$

$$\begin{aligned} - (1/5)(d[\text{Br}^-]/dt) &= - (1/6) (d[\text{H}^+]/dt) = \\ (1/3)(d[\text{Br}_2]/dt) &= (1/3)(d[\text{H}_2\text{O}]/dt) \end{aligned}$$

Rate law? *Comes from experiment*

$$\text{Rate} = k [\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2$$

where k is the *rate constant* (variable units)



Rate of reaction

Stoichiometric equation



- $\text{Rate} = - (1/m) \, d[\text{A}]/dt$
- $\quad = - (1/n) \, d[\text{B}]/dt$
- $\quad = + (1/p) \, d[\text{X}]/dt$
- $\quad = + (1/q) \, d[\text{Y}]/dt$
- Units: (concentration/time)
- in SI $\text{mol}/\text{m}^3/\text{s}$, more practically $\text{mol dm}^{-3} \text{ s}^{-1}$



Rate Law

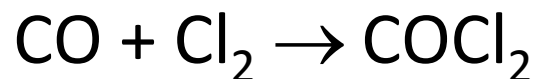
- How does the rate depend upon []s?
- Find out by experiment

The Rate Law equation

- $R = k_n [A]^\alpha [B]^\beta \dots$ (for *many* reactions)
 - order, $n = \alpha + \beta + \dots$ (dimensionless)
 - rate constant, k_n (units depend on n)
 - Rate = k_n when each [conc] = unity

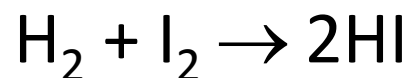


Experimental rate laws?



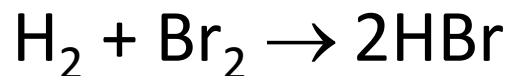
➤ Rate = $k [\text{CO}][\text{Cl}_2]^{1/2}$

– Order = 1.5 or one-and-a-half order



➤ Rate = $k [\text{H}_2][\text{I}_2]$

– Order = 2 or second order



➤ Rate = $k [\text{H}_2][\text{Br}_2] / (1 + k' \{[\text{HBr}]/[\text{Br}_2]\})$

– Order = *undefined* or none



Integration of rate laws

➤ Order of reaction

For a reaction $aA \rightarrow \text{products}$, the rate law is:

$$r = -\frac{1}{a} \frac{d[A]}{dt} = k[A]^n$$

$$\Rightarrow \frac{d[A]}{dt} = -ak[A]^n$$

**rate of change in the
concentration of A**

defining $k_A = ak$

$$r = \frac{d[A]}{dt} = -k_A[A]^n$$



First-order reaction



$$r = \frac{d[A]}{dt} = -k_A [A]^1$$

$$\frac{d[A]}{[A]} = -k_A dt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k_A \int_0^t dt$$

$$\ln[A]_t - \ln[A]_0 = -k_A (t - t_0)$$



First-order reaction

$$\ln[A]_t - \ln[A]_0 = -k_A(t - t_0)$$

$$\ln[A]_t = \ln[A]_0 - k_A t$$

A plot of $\ln[A]$ versus t gives a straight line of slope $-k_A$ if $r = k_A[A]^1$



First-order reaction

$$\ln[A]_t - \ln[A]_0 = -k_A(t - t_0)$$

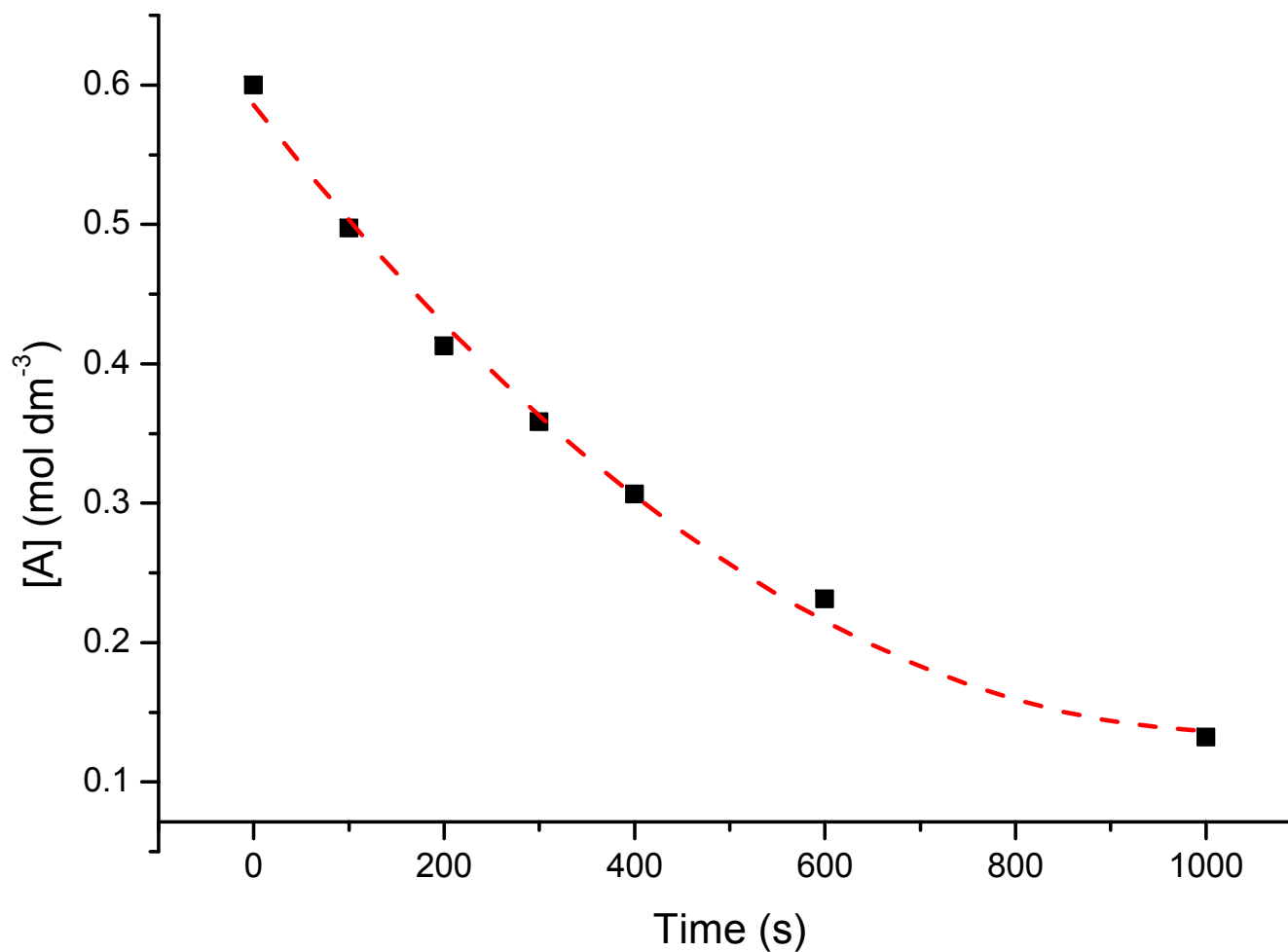
$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -k_A t$$

$$\frac{[A]_t}{[A]_0} = e^{-k_A t}$$

$$[A]_t = [A]_0 e^{-k_A t}$$



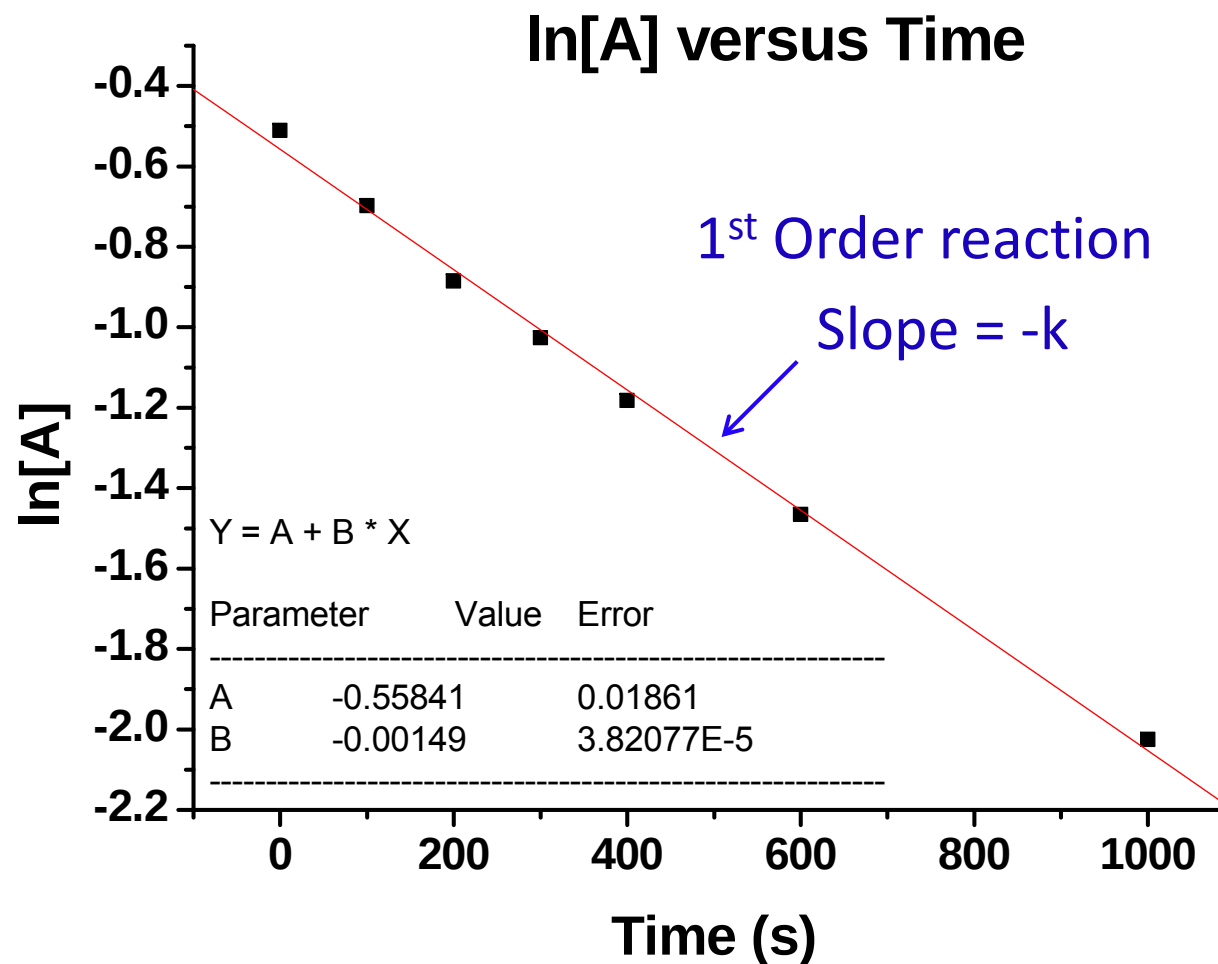
$A \rightarrow P$ assume that $-(d[A]/dt) = k [A]^1$





Integrated rate equation

$$\ln [A] = -k t + \ln [A]_0$$





Half life: first-order reaction

- The time taken for [A] to drop to half its original value is called the reaction's **half-life**, $t_{1/2}$. Setting $[A] = \frac{1}{2}[A]_0$ and $t = t_{1/2}$ in:

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -k_A t$$

$$\ln\left(\frac{\frac{1}{2}[A]_0}{[A]_0}\right) = -k_A t_{1/2}$$



Half life: first-order reaction

$$\ln\left(\frac{1}{2}\right) = -k_A t_{1/2} = -0.693$$

$$\Rightarrow t_{1/2} = \frac{0.693}{k_A} \quad \text{or} \quad k_A = \frac{0.693}{t_{1/2}}$$



When is a reaction over?

➤ $[A] = [A]_0 \exp\{-kt\}$

Technically $[A]=0$ only after *infinite* time



Second-order reaction



$$r = \frac{d[A]}{dt} = -k_A [A]^2$$

$$\frac{d[A]}{[A]^2} = -k_A dt$$

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k_A \int_0^t dt$$



Second-order reaction

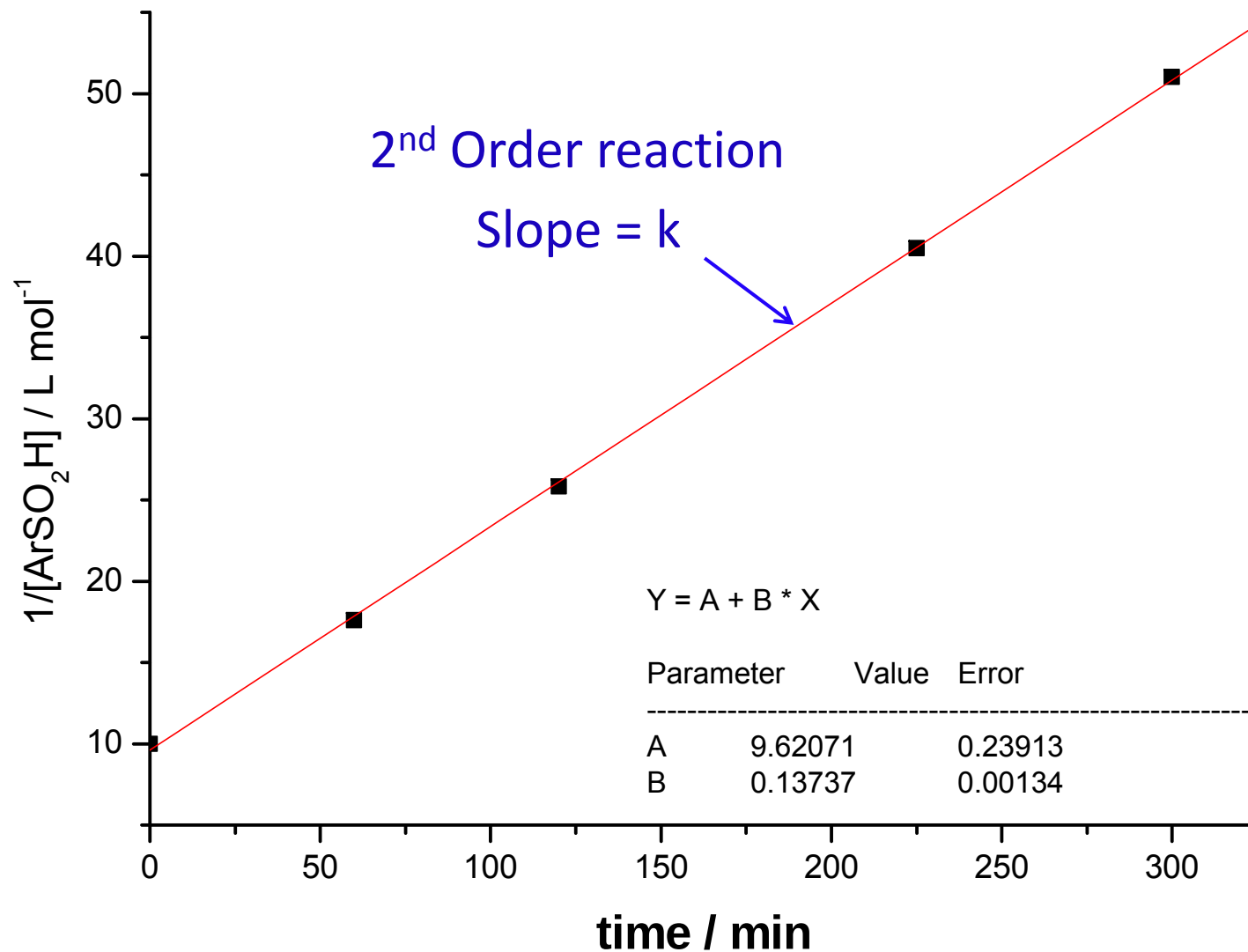
$$\frac{1}{[A]_0} - \frac{1}{[A]_t} = -k_A(t - t_0)$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k_A t$$

A plot of $1/[A]$ versus t gives a straight line of slope k_A if $r = k_A[A]^2$



Second order test: $A + A \rightarrow P$





Half-life: second-order reaction

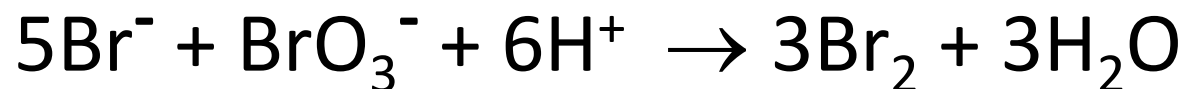
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = k_A t$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = k_A t_{1/2}$$

$$\frac{1}{[A]_0} = k_A t_{1/2} \quad \text{or} \quad \frac{1}{k_A [A]_0} = t_{1/2}$$



Initial Rate Method



General example: $A + B + \dots \rightarrow P + Q + \dots$

➤ Rate law: $\text{rate} = k [\text{A}]^\alpha [\text{B}]^\beta \dots??$

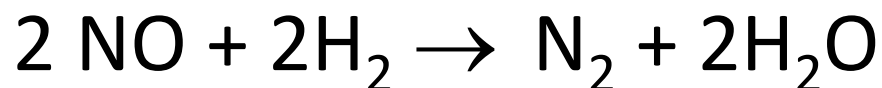
$$\log R_0 = \alpha \log [\text{A}]_0 + (\log k + \beta \log [\text{B}]_0 + \dots)$$

$$y = mx + c$$

- Do series of expts. in which all $[\text{B}]_0$, etc are constant and only $[\text{A}]_0$ is varied; measure R_0
- Plot $\log R_0$ (Y-axis) *versus* $\log [\text{A}]_0$ (X-axis)
- Slope $\Rightarrow \alpha$



Example: $R_0 = k [\text{NO}]^\alpha [\text{H}_2]^\beta$



➤ Expt.	$[\text{NO}]_0$	$[\text{H}_2]_0$	R_0
– 1	25	10	2.4×10^{-3}
– 2	25	5	1.2×10^{-3}
– 3	12.5	10	0.6×10^{-3}

Deduce orders wrt NO and H₂ and calculate k.

➤ *Compare* experiments #1 and #2 $\Rightarrow \beta$

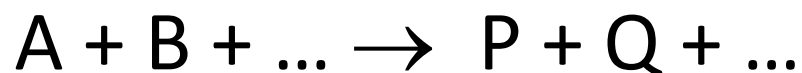
➤ *Compare* experiments #1 and #3 $\Rightarrow \alpha$

Now, solve for k from $k = R_0 / ([\text{NO}]^\alpha [\text{H}_2]^\beta)$



How to measure initial rate?

➤ Key: $-(d[A]/dt) \approx -(\delta[A]/\delta t) \approx (\delta[P]/dt)$



t=0 100 100 $\rightarrow$ 0 0 mol m⁻³

10 s 99 99 $\rightarrow$ 1 1 ditto

➤ Rate?

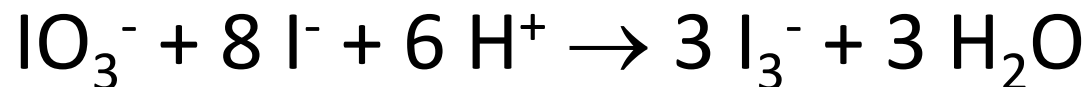
$$-(100-99)/10 = -0.10 \text{ mol m}^{-3} \text{ s}^{-1}$$

$$+(0-1)/10 = -0.10 \text{ mol m}^{-3} \text{ s}^{-1}$$

➤ Conclusion? *Use product analysis for best accuracy.*



Isolation / flooding



- **Rate = $k [\text{IO}_3^-]^\alpha [\text{I}^-]^\beta [\text{H}^+]^\gamma \dots$**
 - Add excess iodate to reaction mix
 - Hence $[\text{IO}_3^-]$ is *effectively* constant
 - **Rate = $k' [\text{I}^-]^\beta [\text{H}^+]^\gamma \dots$**
 - Add excess acid
 - Therefore $[\text{H}^+]$ is *effectively* constant
- **Rate $\approx k'' [\text{I}^-]^\beta$**
- Use integral or initial rate methods *as desired*



Rate law for elementary reaction

- Law of Mass Action applies:
 - rate of rxn $\propto$ product of active masses of reactants
 - “active mass” molar concentration raised to power of number of species
- Examples:
 - $A \rightarrow P + Q$ rate = $k_1 [A]^1$
 - $A + B \rightarrow C + D$ rate = $k_2 [A]^1 [B]^1$
 - $2A + B \rightarrow E + F + G$ rate = $k_3 [A]^2 [B]^1$



Rate law for elementary reaction

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 - $A \rightarrow P + Q$ rate = $k_1 [A]^1$
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 - $2A + B \rightarrow E + F + G$ rate = $k_3 [A]^2 [B]^1$

Molecularity of elementary reactions?

- Unimolecular (decay) $A \rightarrow P$

$$-(d[A]/dt) = k_1 [A]$$

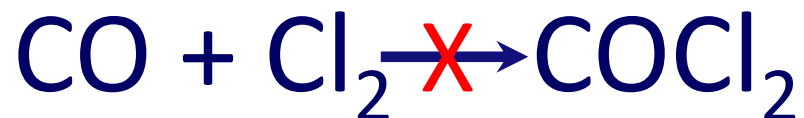
- Bimolecular (collision) $A + B \rightarrow P$

$$-(d[A]/dt) = k_2 [A] [B]$$

- Termolecular (collision) $A + B + C \rightarrow P$

$$-(d[A]/dt) = k_3 [A] [B] [C]$$

- No other are feasible! *Statistically highly unlikely.*



- Experimental rate law: $-(d[\text{CO}]/dt) = k [\text{CO}] [\text{Cl}_2]^{1/2}$
 - Conclusion?: reaction does *not* proceed as written
 - “Elementary” reactions; rxns. that proceed as written at the *molecular level*.
- $\text{Cl}_2 \rightarrow \text{Cl} + \text{Cl}$ (1) ➤ decay
- $\text{Cl} + \text{CO} \rightarrow \text{COCl}$ (2) ➤ collisional
- $\text{COCl} + \text{Cl}_2 \rightarrow \text{COCl}_2 + \text{Cl}$ (3) ➤ collisional
- $\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$ (4) ➤ collisional
- Steps 1 thru 4 comprise the “mechanism” of the reaction.



$$- (d[\text{CO}]/dt) = k_2 [\text{Cl}] [\text{CO}]$$

If steps 2 & 3 are **slow** in comparison to 1 & 4

then, $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$ or $K = [\text{Cl}]^2 / [\text{Cl}_2]$

So $[\text{Cl}] = \sqrt{K} \times [\text{Cl}_2]^{1/2}$

Hence:

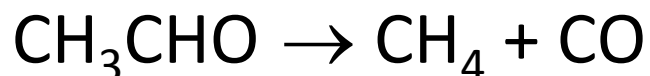
$$\text{➤ } -(d[\text{CO}] / dt) = k_2 \times \sqrt{K} \times [\text{CO}][\text{Cl}_2]^{1/2}$$

Predict that: *observed* $k = k_2 \times \sqrt{K}$



Complex (non-elementary) rxns

Chain reactions



in over 90% yield

Traces of C_2H_6 , H_2 , CH_3COCH_3 , etc.

Rate law $\text{rate} = k[\text{CH}_3\text{CHO}]^{3/2}$

Possible mechanism?

- $\text{CH}_3\text{CHO} \rightarrow \dot{\text{C}}\text{H}_3 + \text{H}\dot{\text{C}}\text{O}$ initiation
- $\dot{\text{C}}\text{H}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\dot{\text{C}}\text{O}$ propagation
- $\text{CH}_3\dot{\text{C}}\text{O} \rightarrow \dot{\text{C}}\text{H}_3 + \text{CO}$ propagation
- $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 (+\text{M}) \rightarrow \text{C}_2\text{H}_6 (+\text{M})$ termination



Basic Chemical Kinetic Principles II





Temperature dependence?



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 $\approx$ doubles for a 10K rise**



Details of T dependence

Hood (1878)

➤ $k = A \exp\{-B/T\}$

Arrhenius (1899)

➤ $k = A \exp\{-E / RT\}$

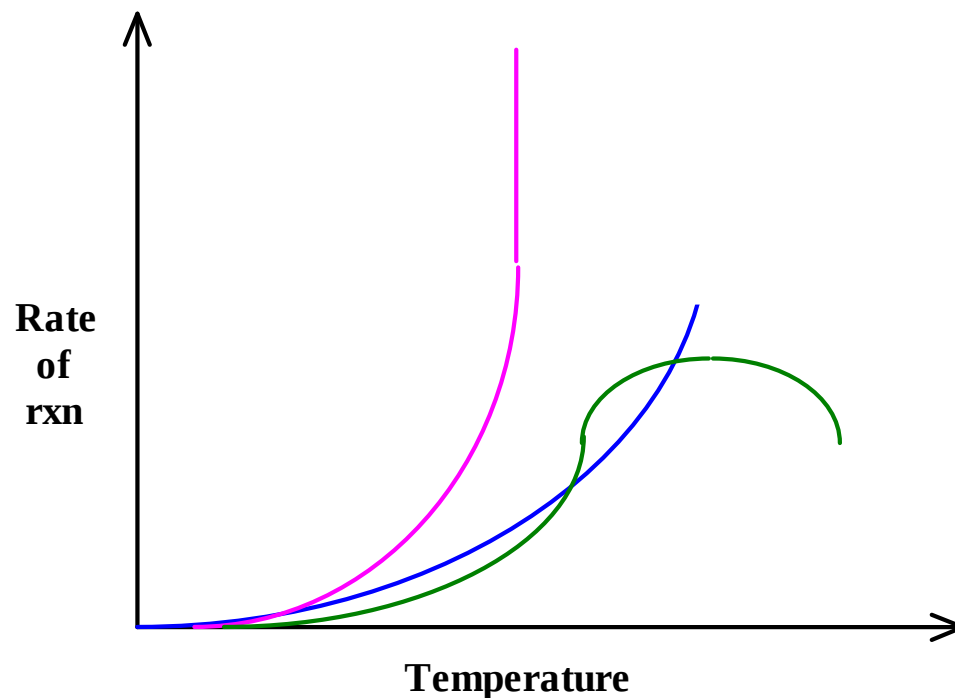
A pre-exponential factor
or A -factor

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

E activation energy

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

R gas constant.





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

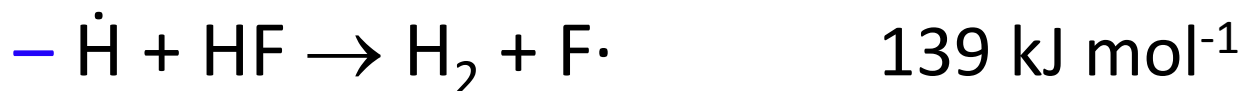
Useful *linear* form: $\ln k = \ln A - (E/R)(1/T)$

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

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

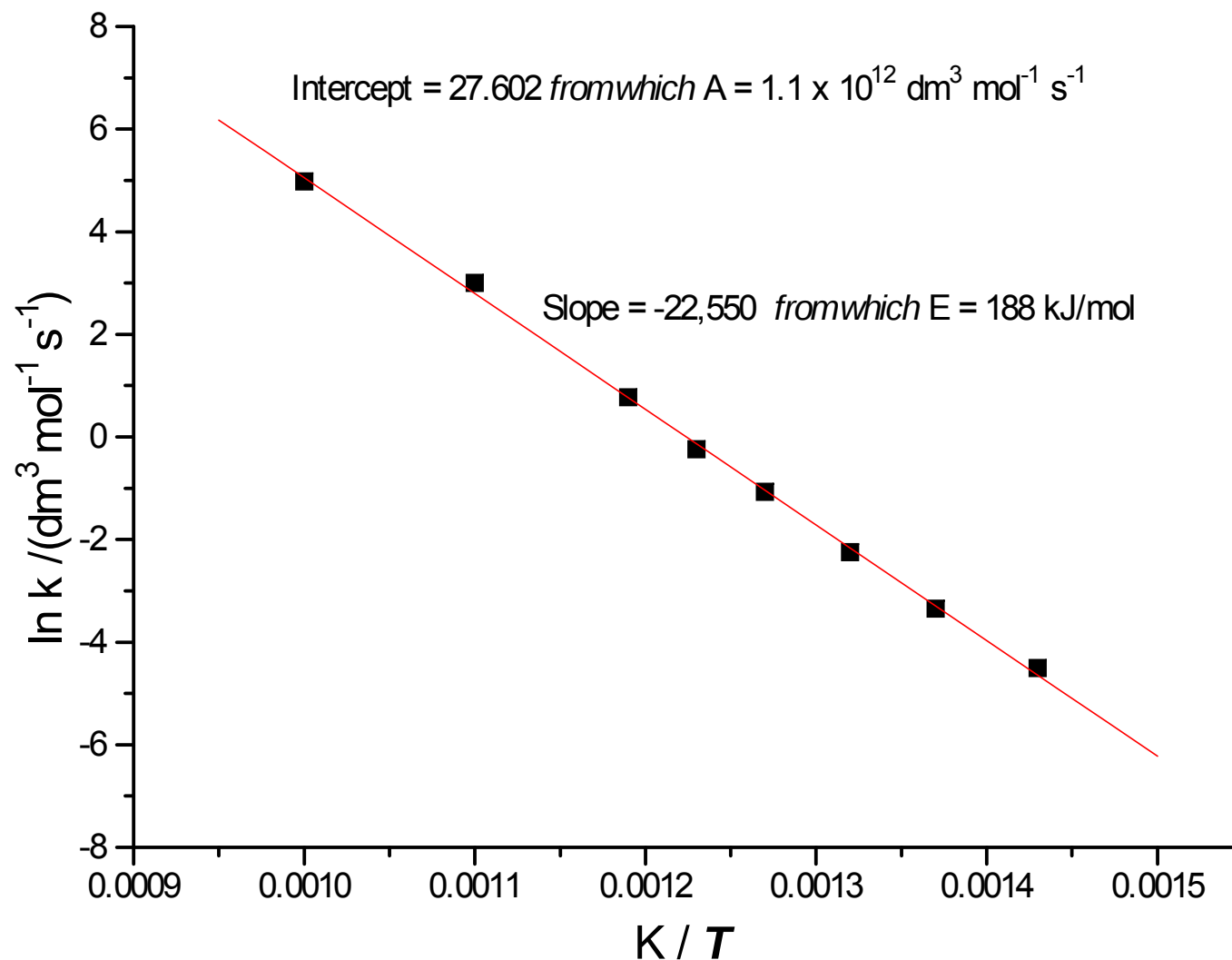
➤ Experimental E s range from 0 to +400 kJ mol⁻¹

Examples:





Practical Arrhenius plot, origin not included





Problem

- In consecutive rxns the slower step usually determines the overall rate of rxn. Diethyl adipate (DA) is hydrolysed in 2 steps as:



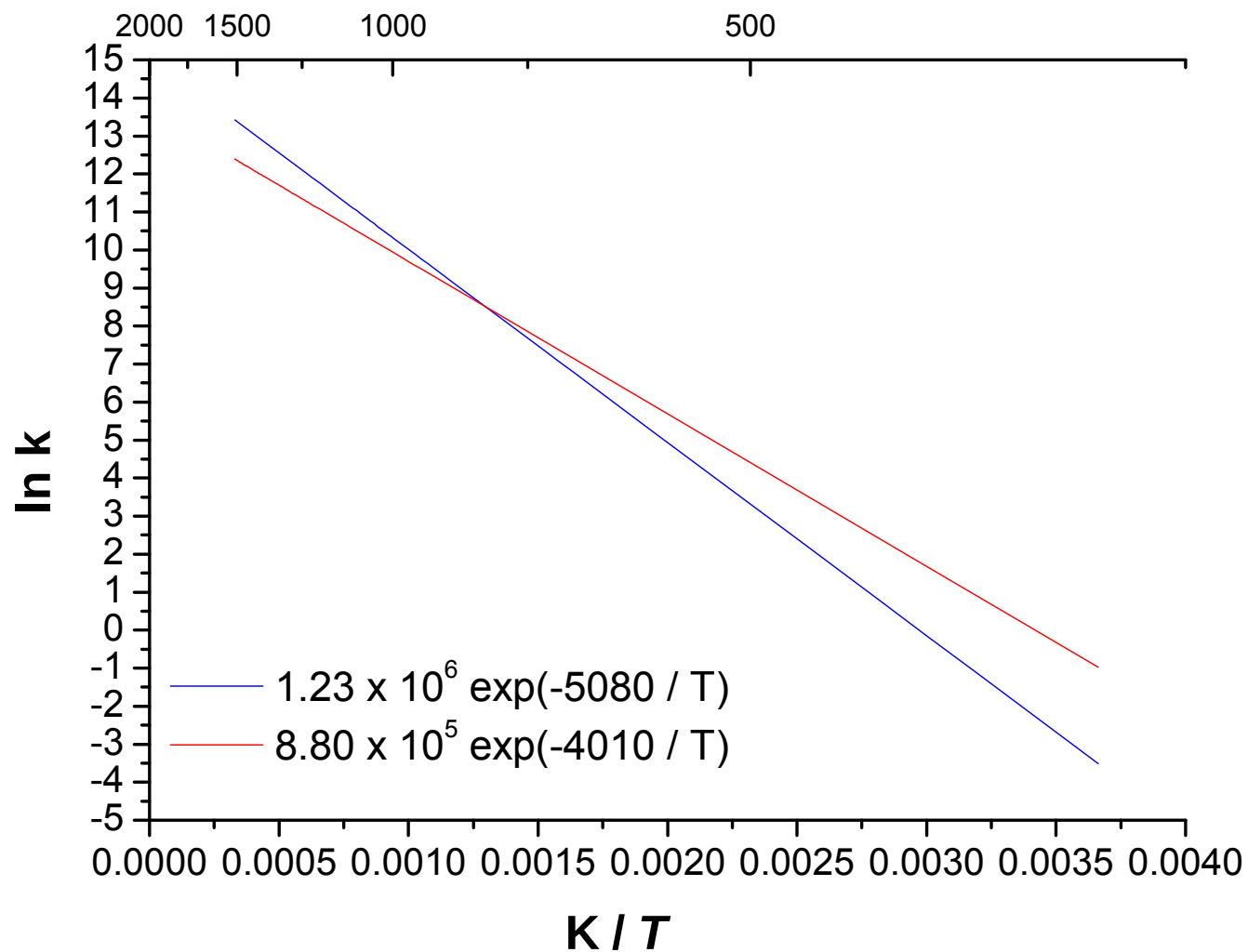
first step: $3.6 \times 10^6 \exp\{-5,080/T\} \text{ s}^{-1}$

second step: $8.8 \times 10^5 \exp\{-4,010/T\} \text{ s}^{-1}$

- Which step is rate determining if the rxn is carried out in *aqueous solution* under *atmospheric pressure*?



Comparison of rate constant expressions





Rate constant expression

What is the activation of a reaction for which the rate constant doubles on going from 20°C to 30°C?

$$\frac{k_1}{k_2} = \frac{A}{A} \exp\left(\frac{\frac{(-E_A)}{RT_1}}{\frac{(-E_A)}{RT_2}}\right)$$

$$\frac{k_1}{k_2} = \exp\left(\frac{-E_A}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{k_1}{k_2}\right) = \left(\frac{-E_A}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$k = A \exp\left(\frac{-E_A}{RT}\right)$$

$$\ln\left(\frac{1}{2}\right) = \left(\frac{-E_A}{8.314}\right)\left(\frac{1}{293.15} - \frac{1}{303.15}\right)$$

$$-0.693 = \left(\frac{-E_A}{8.314}\right)(1.12526 \times 10^{-4})$$

$$-6158.58 = \left(\frac{-E_A}{8.314}\right) \Rightarrow E_A = 51.202 \text{ kJ mol}^{-1}$$



Rxn. at equilibrium: $A \rightleftharpoons B$

forward rate constant k_F , reverse k_R

Kinetics:

- $k_F[A]_e = k_R[B]_e$ so $[B]_e/[A]_e = k_F/k_R = K$
- $k_F = A_F \exp\{-E_F/RT\}$ $k_R = A_R \exp\{-E_R/RT\}$
- $(k_F/k_R) = (A_F/A_R) \exp\{-(E_F - E_R)/RT\}$

Thermodynamics?

- $\Delta G^0 = -RT \ln(K)$ or $K = \exp\{-\Delta G^0/RT\}$
 $\Delta G^0 = \Delta H^0 - T\Delta S^0$
 $K = \exp\{+\Delta S^0/R\} \exp\{-\Delta H^0/RT\}$
- $(A_F/A_R) = \exp\{+\Delta S^0/R\}$ $E_F - E_R = \Delta H^0$



Problem

For the rxn $\text{trans} \rightarrow \text{cis perfluorobut-2-ene}$

- measured $k_F = 3.16 \times 10^{13} \exp\{-31,030/T\} \text{ s}^{-1}$
- Given that $\Delta H^0 = +3.42 \text{ kJ mol}^{-1}$ and
- $\Delta S^0 = -2.03 \text{ J K}^{-1} \text{ mol}^{-1}$
- Calculate k_R at 750 K.

$$(A_F/A_R) = \exp\{+\Delta S^0/R\} \quad \Rightarrow \quad A_R = A_F \exp\{-\Delta S^0/R\}$$

$$E_F - E_R = \Delta H^0 \quad \Rightarrow \quad E_R = E_F - \Delta H^0$$

$$-(E_F/R) = -31,030 \quad \Rightarrow \quad E_F = 8.3143 \times 31,030 \text{ J mol}^{-1}$$

$$E_F = 258.0 \text{ kJ mol}^{-1} \Rightarrow E_R = 254.6 \text{ kJ mol}^{-1}$$



Reaction profile diagram

➤ Y-axis?

- Energy
- common path via TS

➤ X-axis?

Time?

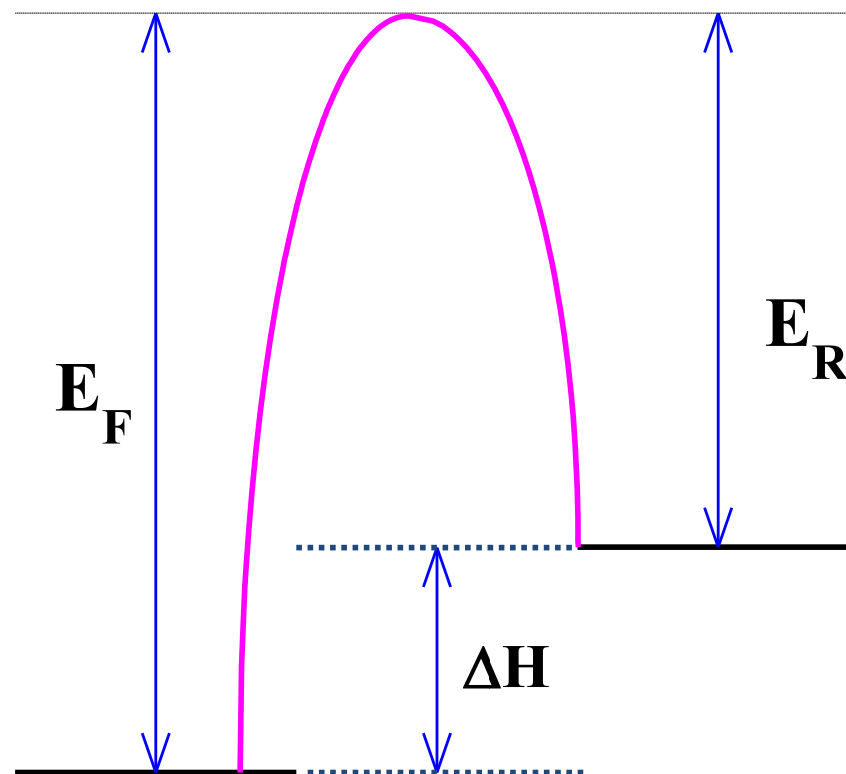
Reactant-product identity

Multi-dimensional

➤ *Reaction co-ordinate*

➤ Schematic diagram

- **Concept of energy barrier to rxn**

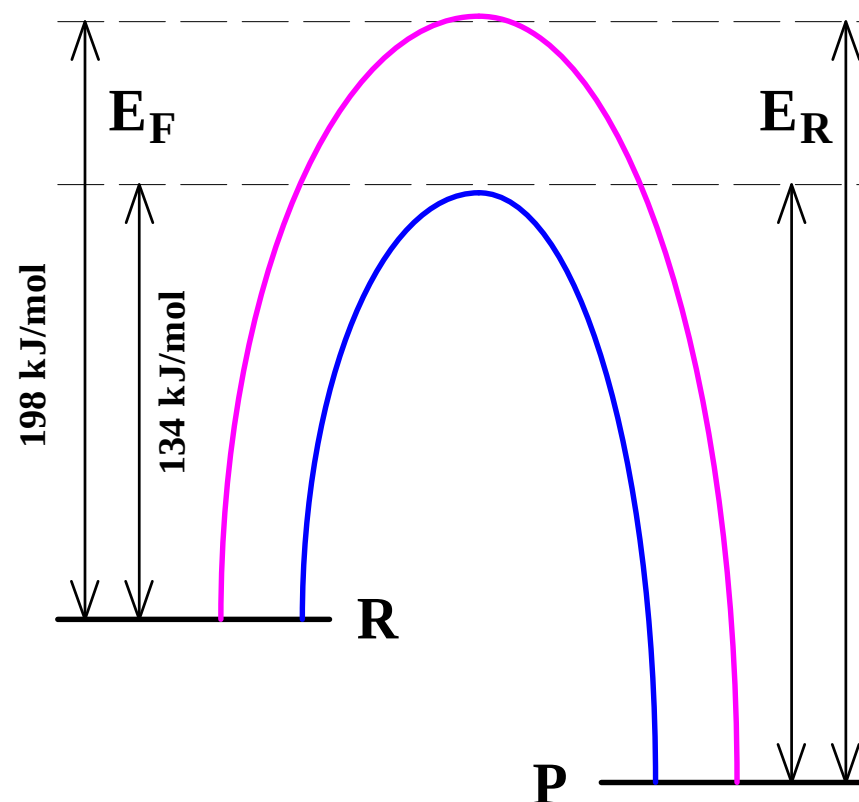




Reaction profile diagram



- $E_F = 198 \text{ kJ/mol}$
- Add some iodine as catalyst
 $E_F = 134 \text{ kJ/mol}$
 - Modest reduction in barrier
 - Massive increase in rate
- At 773 K catalysed rxn is **20,000** times faster
 - $\text{BDE}(\text{C}-\text{C})=340$, $\text{BDE}(\text{C}-\text{H})=420$
 - But $\text{BDE}(\text{I}-\text{I})=153 \text{ kJ/mol}$





Thermochemistry from kinetics



➤ $E_{\text{F}} = 368 \text{ kJ mol}^{-1}$ $E_{\text{R}} = 0 \text{ kJ mol}^{-1}$

$$\Delta H_{\text{RXN}} = E_{\text{F}} - E_{\text{R}} = + 368 \text{ kJ mol}^{-1}$$

$$= 2\Delta H_{\text{f}}(\dot{\text{C}}\text{H}_3) - \Delta H_{\text{f}}(\text{C}_2\text{H}_6)$$

$$\Delta H_{\text{f}}(\dot{\text{C}}\text{H}_3) = [\Delta H_{\text{RXN}} + \Delta H_{\text{f}}(\text{C}_2\text{H}_6)] / 2$$

But $\Delta H_{\text{f}}(\text{C}_2\text{H}_6) = - 85 \text{ kJ mol}^{-1}$

➤ $\Delta H_{\text{f}}(\dot{\text{C}}\text{H}_3) = (368 - 85) / 2 = +141 \text{ kJ mol}^{-1}$

$$\Delta H_{\text{RXN}} = \text{Energy of bond broken} = \Delta(\text{H}_3\text{C}-\text{CH}_3)$$

⇒ *Tables of bond dissociation energies*



Common mathematical functions

Kinetics, Arrhenius

➤ $k = A \exp\{-E/RT\}$

Vapour pressure, Clausius-Clayperon

➤ $p = p_{\infty} \exp\{-\Delta H_v/RT\}$

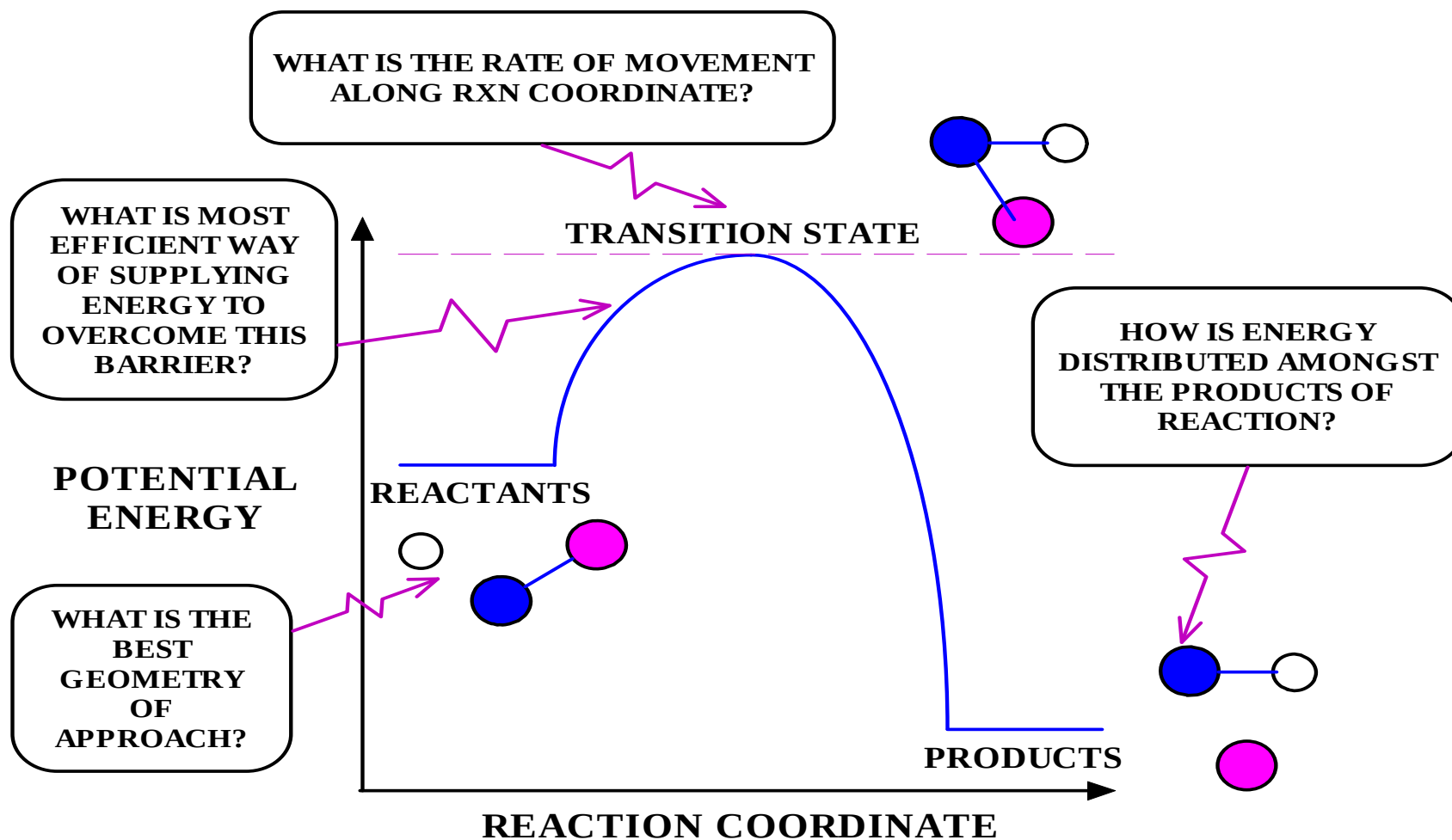
Viscosity, Andrade

➤ $\eta = A \exp\{+E/RT\}$

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

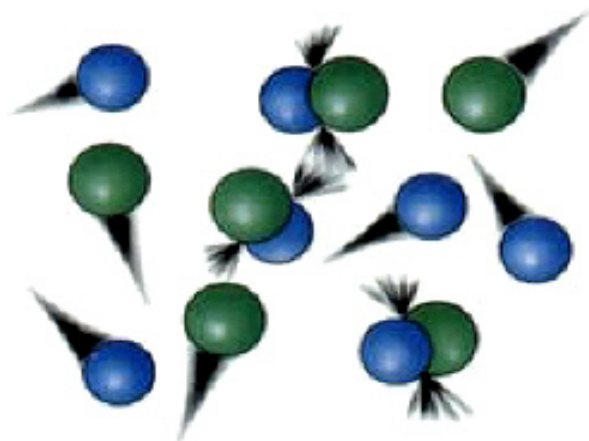


Questions?

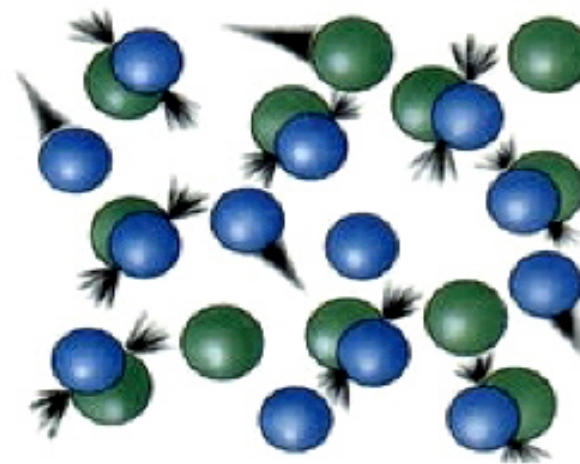




Collision theory



Low concentration = Few collisions



High concentration = More collisions

Assume: Molecules are hard, structure-less spheres like billiard balls

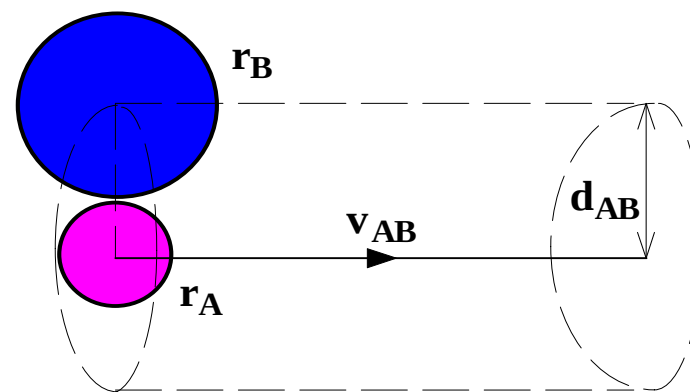
- There are no interactions between them until they come into contact with one another
- They are impenetrable—they maintain their size and shape and they cannot come closer than their radii



Simple collision theory: $A + B \rightarrow \text{products}$

Assumptions?

- molecules hard-spheres
- every collision is reactive



Calculate rate of collision $\Rightarrow$ rate of reaction

➤ In 1 s a typical A travels a distance $d = v_{AB} t$

& will collide with all B's within collision cylinder of

➤ volume = $\pi(r_A + r_B)^2 v_{AB} t$ m³ so $n_B \times \pi(r_A + r_B)^2 v_{AB} t$ collisions per second $\Rightarrow$ collision frequency z_{AB}

➤ Collision rate = $\pi(r_A + r_B)^2 v_{AB} \times n_A n_B$ m⁻³ s⁻¹



SCT

$$\text{Reaction rate} = k_2 n_A n_B$$

$$\text{Collision rate} = \pi(r_A + r_B)^2 v_{AB} \times n_A n_B \quad \text{“collision density”}$$

➤ So $k_2 = \pi(r_A + r_B)^2 v_{AB} = \sigma_{AB} v_{AB}$

where v_{AB} ? Maxwell-Boltzmann distrib. of velocity

$$v_{AB} = (8kT/\pi \mu)^{1/2} \quad \text{where } \mu = (m_A m_B)/(m_A + m_B)$$

$$\text{collision cross-section, } \sigma_{AB} = \pi(r_A + r_B)^2$$

$$\text{Practical units: } v_{AB} = 4.602 \{T (M_A + M_B)/(M_A M_B)\}^{1/2}$$

with M_x in kg mol^{-1} & T in K



Calculation of collision rate

- Calculate the mean time between collisions experienced by a single Ar atom at 300 K & atm pressure. Collision diameter for Ar is 0.29 nm, the RMM is 0.040 kg mol⁻¹.

$$\sigma_{AA} = \pi d^2 = 2.64 \times 10^{-19} \text{ m}^2$$

$$v_{AA} = 563.53 \text{ m s}^{-1} \text{ (NB twice the speed of sound)}$$

$$pV = nRT \quad n_A = n/V = p/(RT) = 101,325 / (8.3143 \times 300)$$

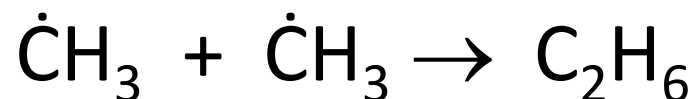
$$n_A = 40.1 \text{ mol m}^{-3} \Rightarrow 2.4 \times 10^{25} \text{ molecules m}^{-3}$$

$$z_{AA} = n_A \sigma_{AA} \times v_{AA} = 3.57 \times 10^9 \text{ molecules s}^{-1} \Rightarrow$$

$$t_c = (1/z_{AA}) = 280 \text{ ps}$$



Test of SCT



M (methyl) = 0.015 kg/mol T = 300 K

d (methyl) $\approx$ 0.308 nm

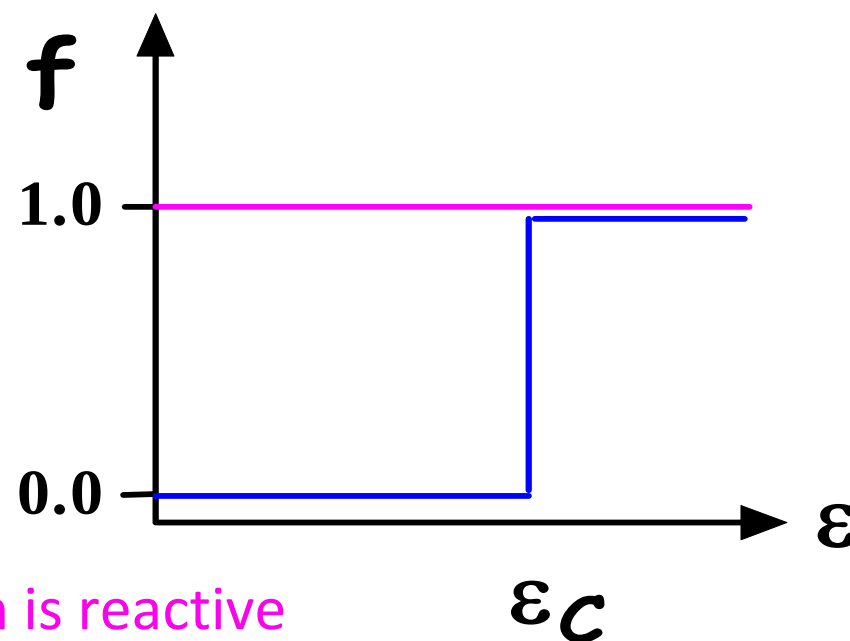
$$\Rightarrow k_2 = \sigma_{AA} v_{AA} = 2.980 \times 10^{-19} \times 920.25 = 2.745 \times 10^{-16} \text{ m}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

convert to cm³ mol⁻¹ s⁻¹

calculated 1.65×10^{14} *experimental* 2.4×10^{13}

- *Unique result; usually calculation >> experiment*
- *T-dependence all wrong anyway*

Improvements?



- Relax assumption that **every collision is reactive**
- If $\epsilon(\text{coll}) \geq \text{critical value } \epsilon_c$ then rxn occurs otherwise not
- What fraction, f , of collisions have $\epsilon \geq \epsilon_c$? M-B

$$f = \exp(-\epsilon_c/kT) = \exp(-E_c/RT)$$

$$k_2 = \sigma_{AB} v_{AB} \exp(-E_c/RT)$$

- Much smaller & T-dependence now OK; but how E_c ?



Comparison with Arrhenius

$$k_2 = A \exp(-E_A/RT) \quad k_2 = \sigma_{AB} (8kT/\pi\mu)^{1/2} \exp(-E_C/RT)$$

➤ Does $E_C = E_A$?

$$d(\ln k)/d(1/T) = -(E_A/R) \quad \text{operational definition}$$

$$k_2 = \sigma_{AB} (8kT/\pi\mu)^{1/2} \exp(-E_C/RT) = Y T^{1/2} \exp(-E_C/RT)$$

$$\ln k = (1/2) \ln T - (E_C/RT) + \ln Y$$

$$\ln k = - (1/2) \ln (1/T) - (E_C/R)(1/T) + \ln Y$$

➤ $d(\ln k)/d(1/T) = - (1/2)T - (E_C/R) = - (E_A/R)$

➤ $E_C = E_A - RT/2$ (NB RT is *small* in cf. with most E_A 's)

$$k_2 = \sigma_{AB} v_{AB} \exp(-E_C/RT) = \sigma_{AB} v_{AB} \exp(-E_A/RT) \times e^{1/2}$$



JSRs and Flow Reactors





Proper rate of reaction

➤ Define as: $(1/v_i)(dn_i/dt) \text{ mol s}^{-1}$

where v_i is a stoichiometric coefficient

+ve for products, – ve for reactants

Example: $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$

➤ $v(\text{H}_2) = -2$, $v(\text{O}_2) = -1$ and $v(\text{H}_2\text{O}) = +2$

➤ At constant volume: $[A] = n/V$ or $n = V \times [A]$

So: $(dn/dt) = V \cdot (d[A]/dt)$

Old rate of reaction (was rxn rate per unit volume)

➤ $(d[A]/dt) = (1/V) (dn_A/dt)$



Flow versus batch reactors $[A]=[A]_0 \exp\{-kt\}$

Stirred flow; perfect mixing

➤ *spherical* shape of volume V

$$[A]_{\text{outlet}} = [A]_{\text{inlet}} / \{ 1 + k (V/v) \}$$

‘Plug’ flow; no mixing at all at all

➤ *cylindrical* shape of volume V

$$[A]_{\text{outlet}} = [A]_{\text{inlet}} \exp\{-k (V/v)\}$$

NB (V/v) has dimensions $(\text{m}^3 / \text{m}^3 \text{ s}^{-1}) = \text{s}$

A ‘residence’ or ‘contact’ time



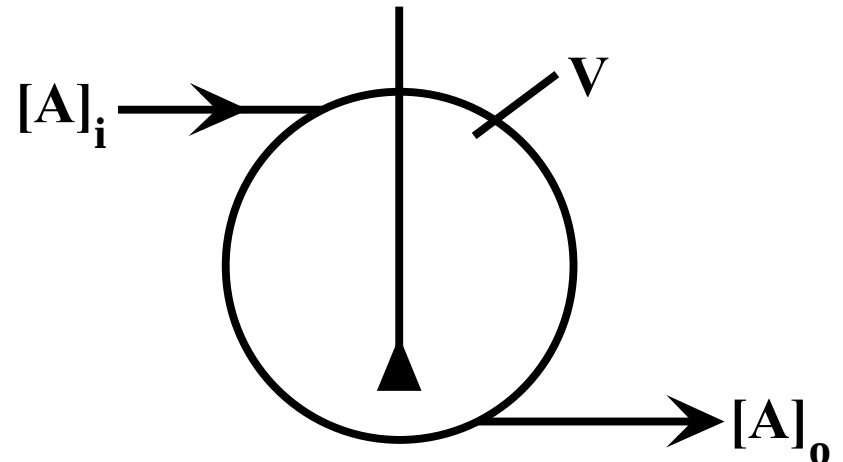
Stirred flow; 1st order

$$-(dn_A/dt) = k n_A = k V [A]$$

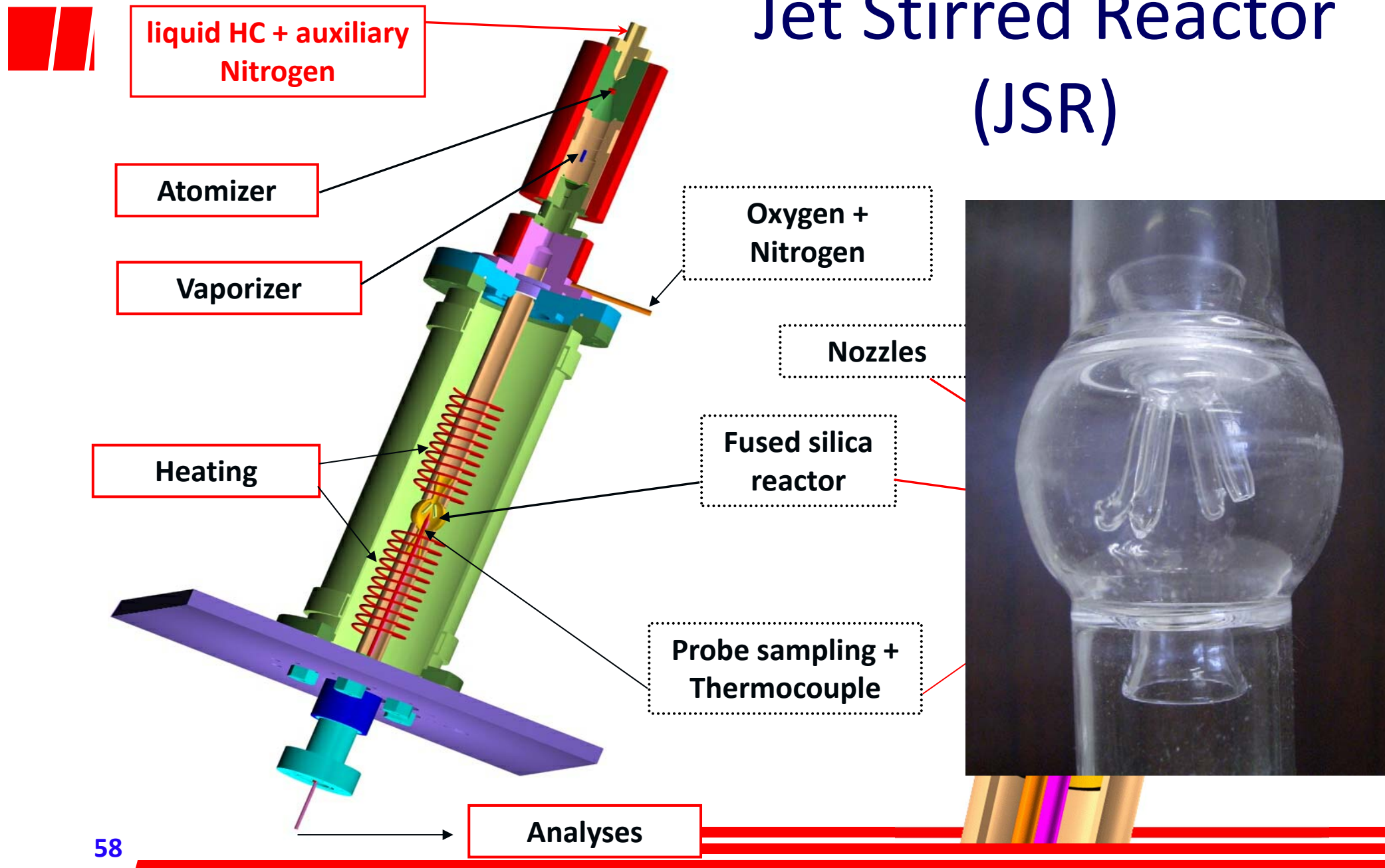
- inflow = outflow + reaction

Assume system at constant volume so that inlet flow rate is equal to outlet flow rate

- $v[A]_i = v[A]_o - (dn_A/dt)$
- $v[A]_i = v[A]_o + k V [A]_o$
- $[A]_i = [A]_o + (k V [A]_o)/v$
- $[A]_i/[A]_o = 1 + k (V/v)$
- $[A]_o = [A]_i / \{1 + k(V/v)\}$ **Test?** vary v , measure $[A]_o$ & $[A]_i$, is k the same?

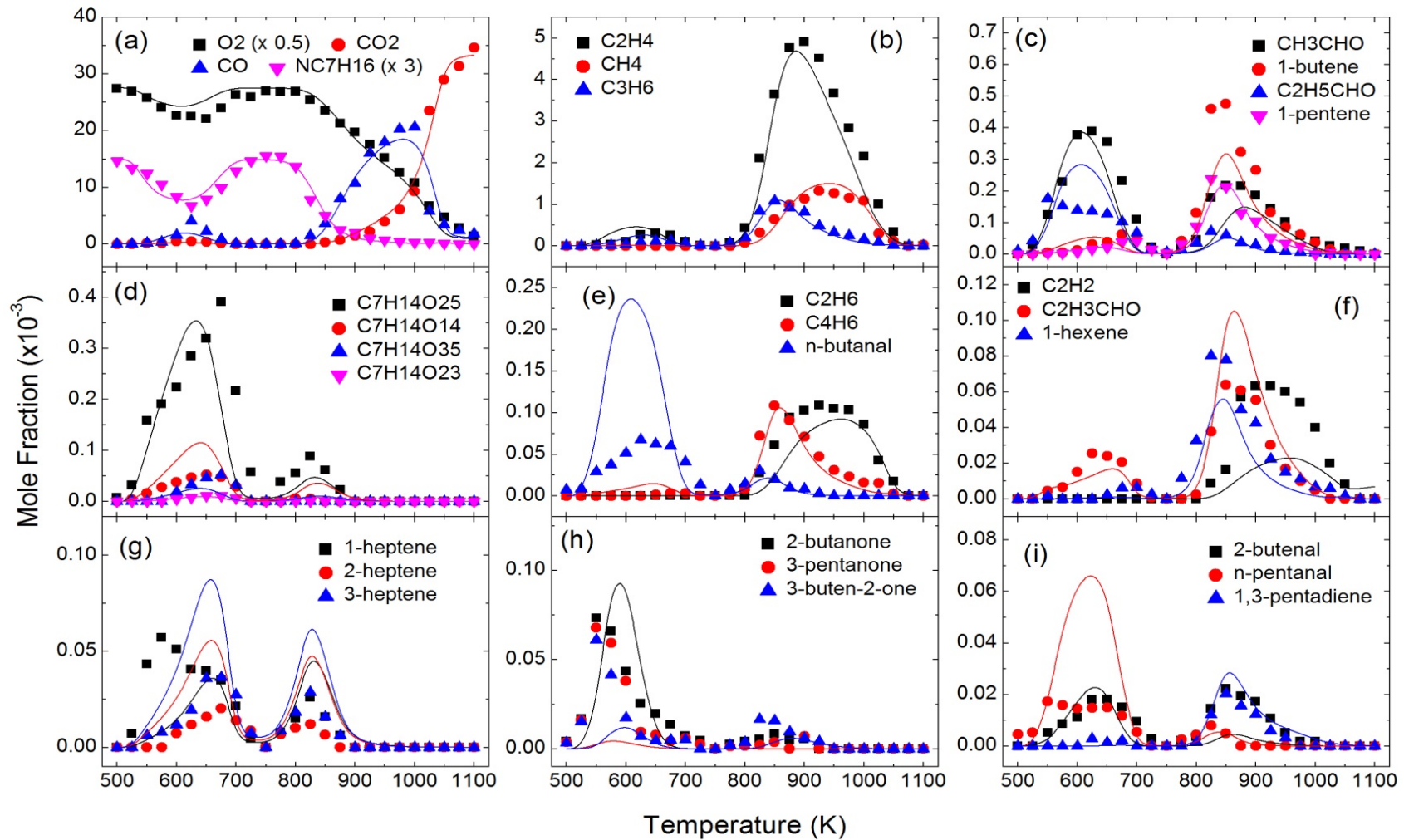


Jet Stirred Reactor (JSR)





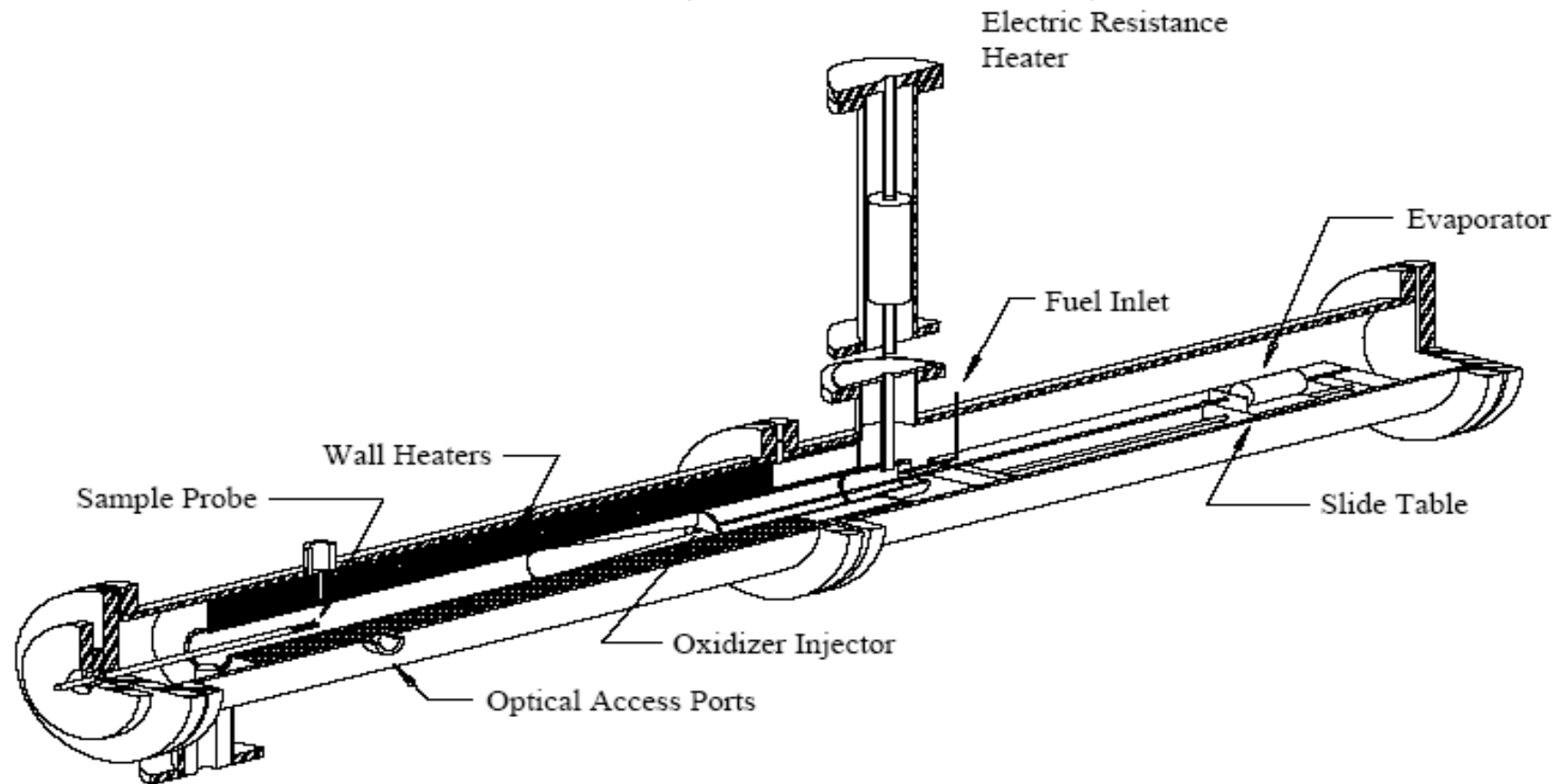
Example data: n-Heptane



$\phi = 1.0$, $\tau = 2.0$ s, 1.06 bar, 0.5% fuel
Herbinet et al., Combust. Flame, 159 (2012), 3455-3471



Variable Pressure Flow reactor (Princeton U.)





Plug flow; 1st order rxn

$$-(dn_A/dt) = k n_A = k V [A]$$

inflow = outflow + reaction

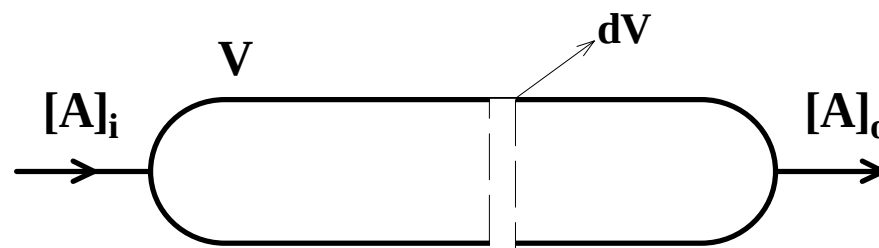
$$v[A] = v([A] + \delta[A]) - (dn_A/dt)$$

$$v[A] = v[A] + v\delta[A] - (dn_A/dt)$$

$$-v\delta[A] = -(dn_A/dt)$$

$$-v\delta[A] = k \delta V [A]$$

$$\int \delta[A]/[A] = -(k/v) \int \delta V$$



At inlet $[A] = [A]_i$; at outlet $[A] = [A]$

$$\int_{[A]_i}^{[A]_o} \frac{\delta[A]}{[A]} = -k/v \int_0^V \delta V$$

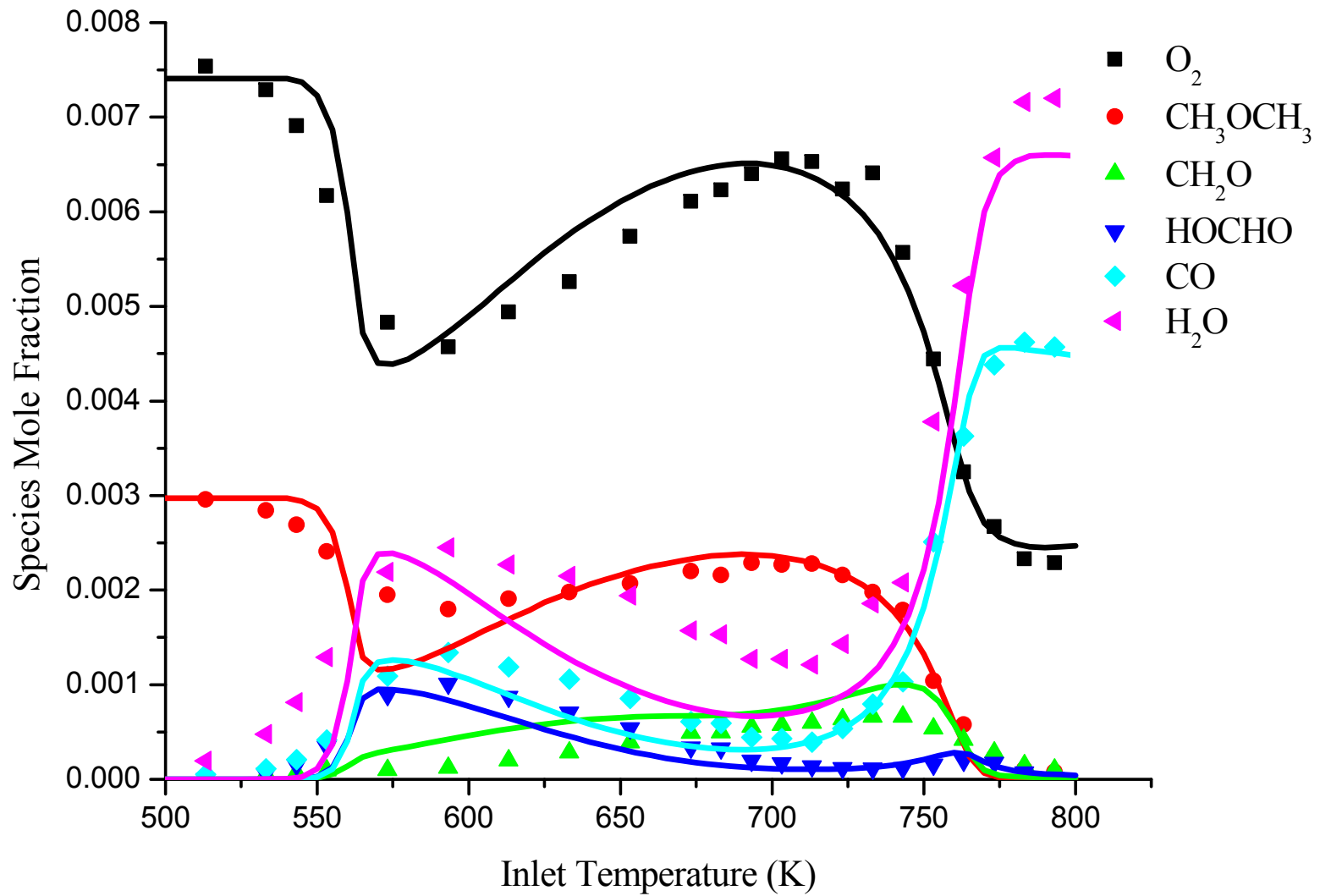
$$\ln[A]_o - \ln[A]_i = -kV/v$$

$$\ln[A]_o = \ln[A]_i - kV/v$$

$$[A]_o = [A]_i \exp(-kV/v)$$



3030 ppm DME, $\phi = 1.19$, $p = 12.5$ atm, $\tau = 1.8$ s.





ST and RCM contribution to mechanism generation and validation





4-Stroke Engine

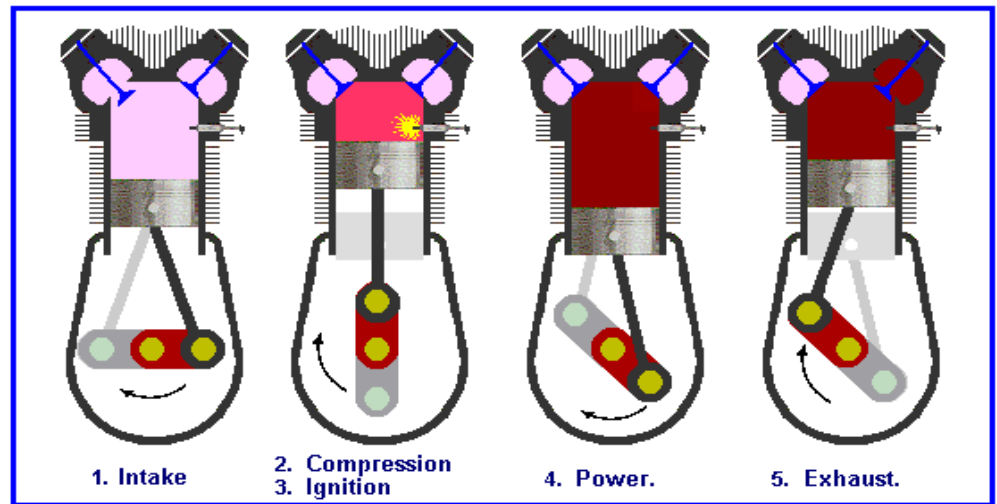
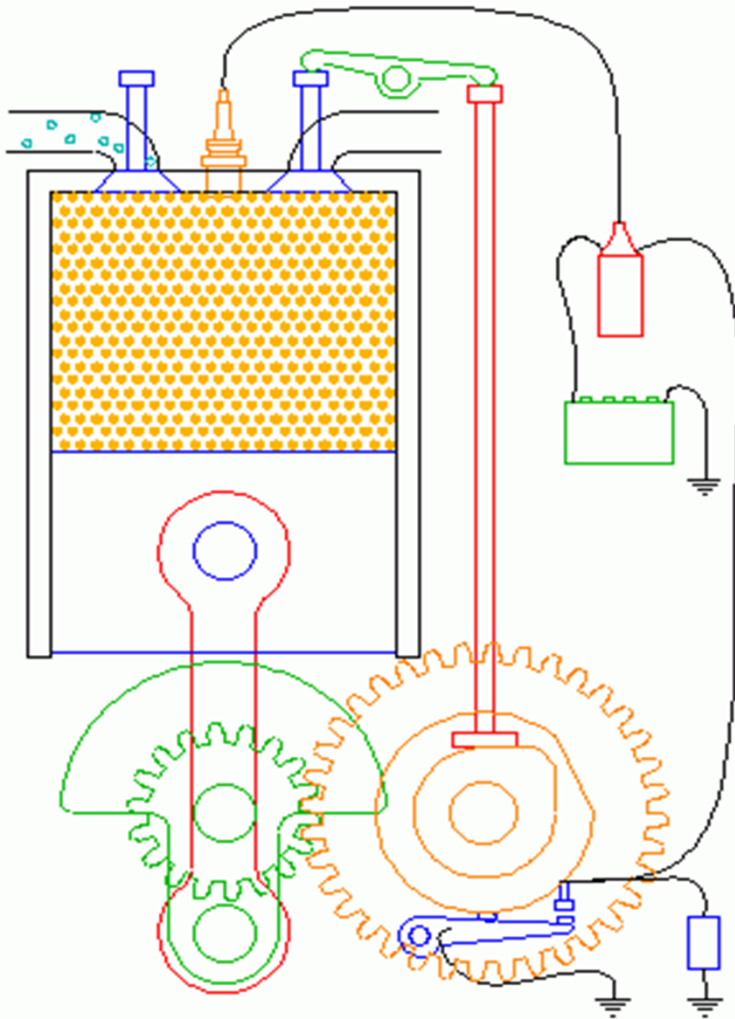
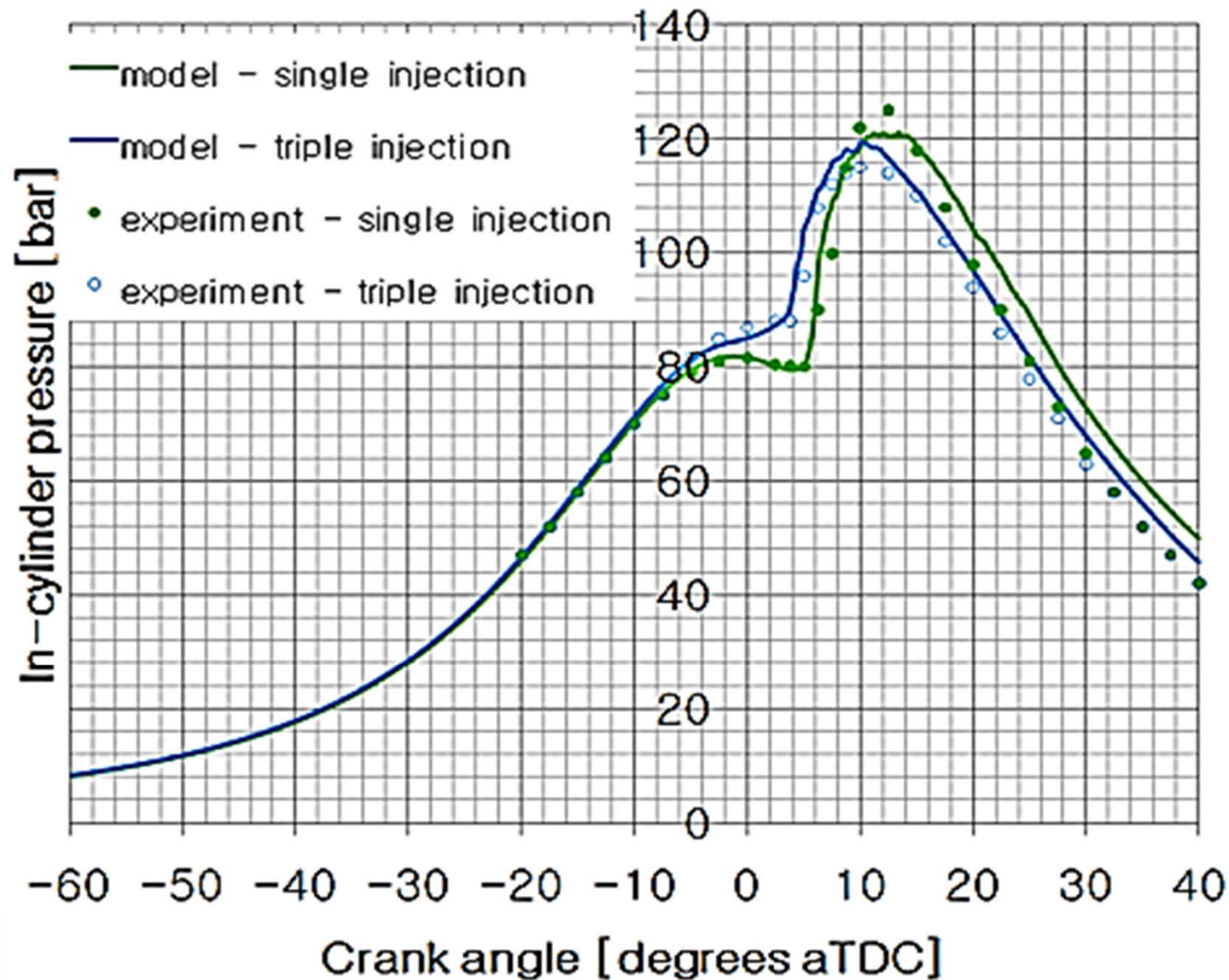


Figure 6-3 Four-stroke five-event cycle.





Pressure vs CAD in an engine





Experimental Studies: Engine Relevant



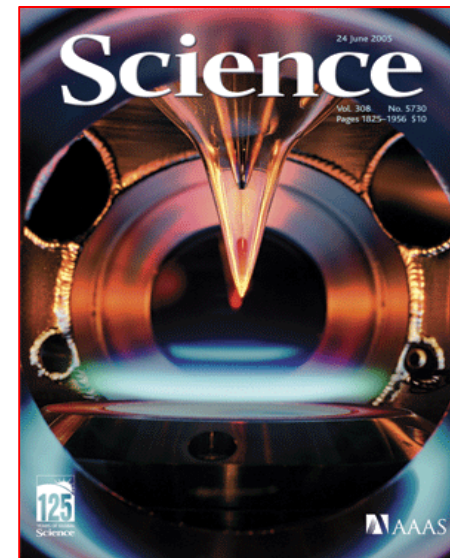
Rapid Compression Machine



Shock Tube



Jet Stirred Reactor



Flat Flame Burner

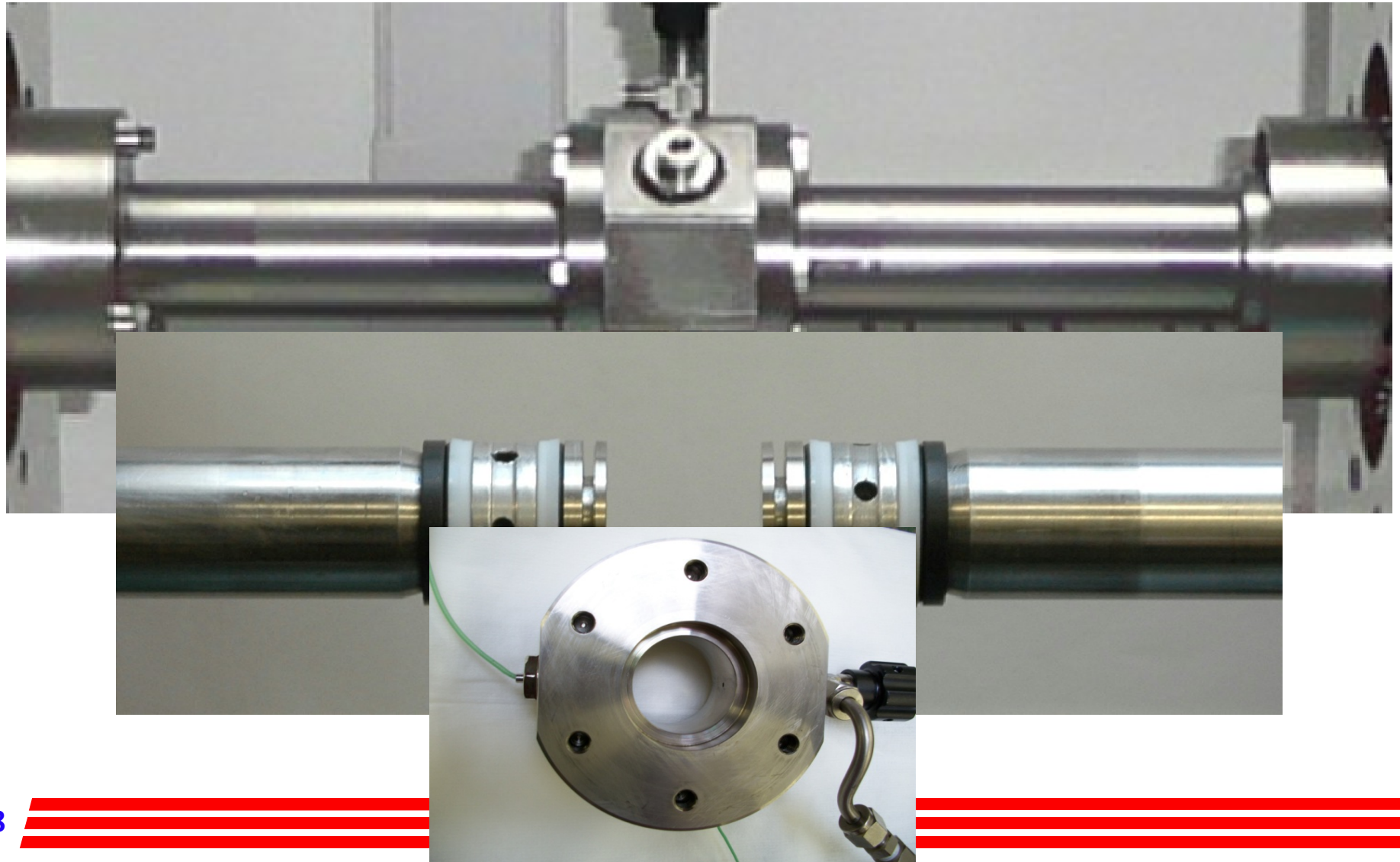


Rapid Compression Machine





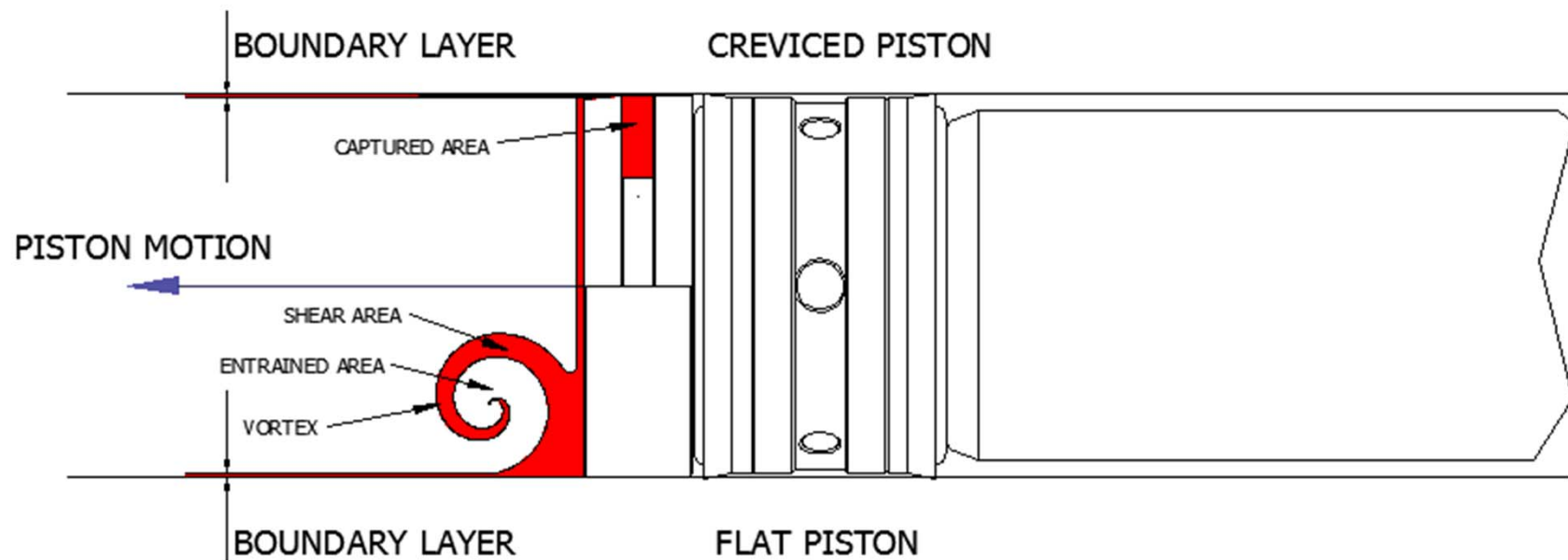
Rapid Compression Machine





Roll up vortex

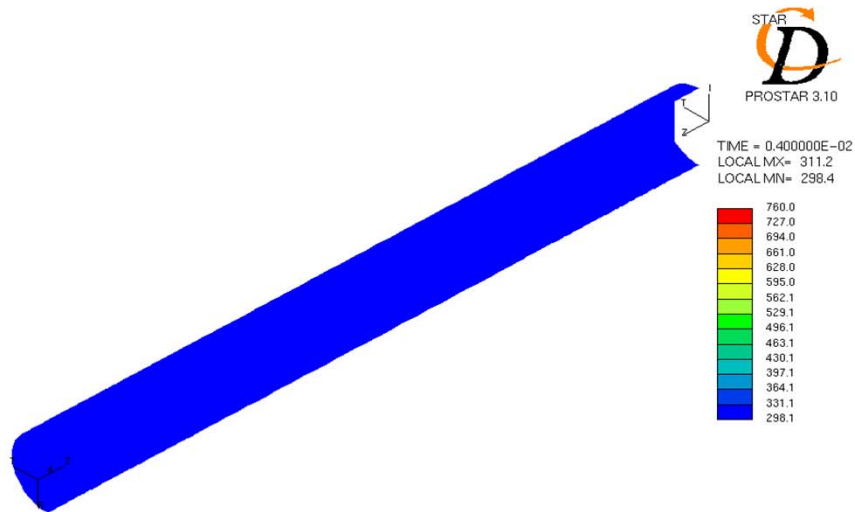
The formation of a vortex on the piston face inside the RCM disrupts the uniformity of the temperature field.



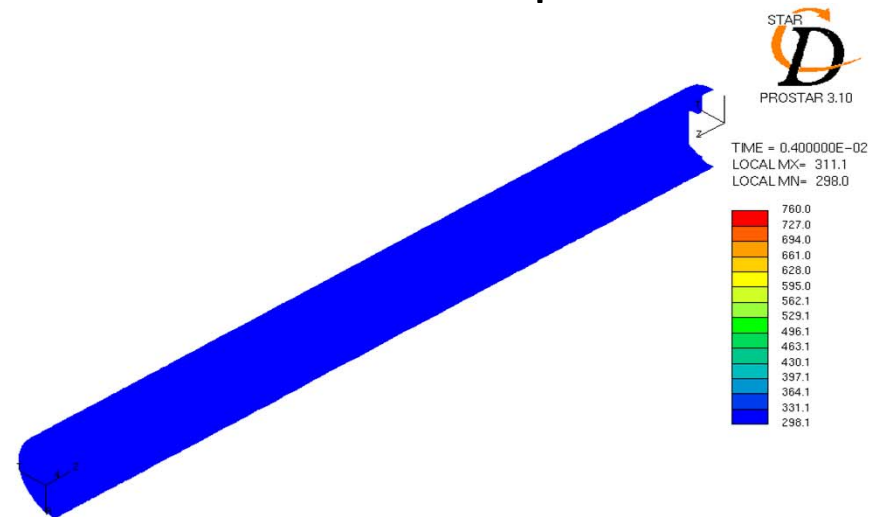


Piston heads: flat versus creviced

Flat piston

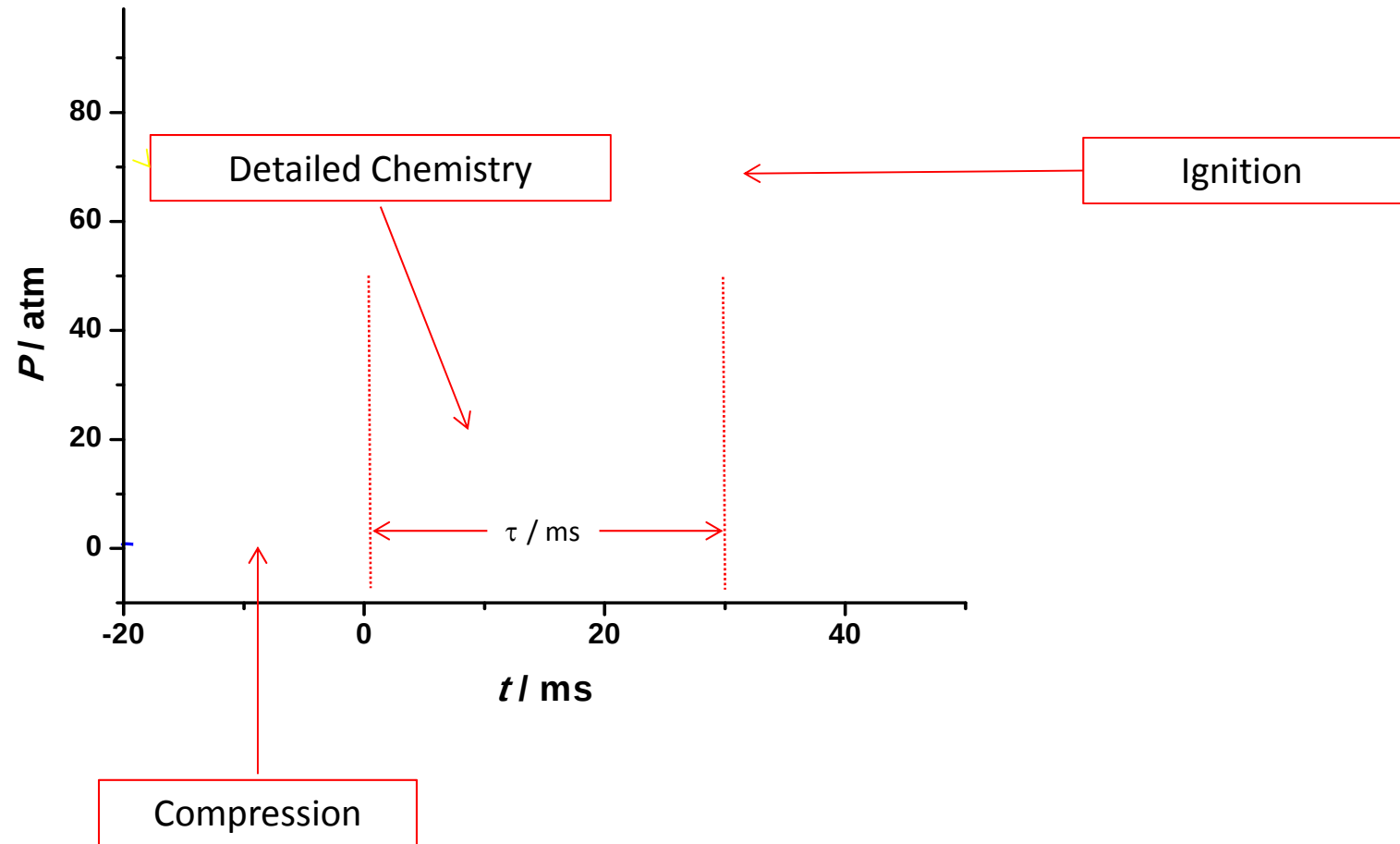


Creviced piston





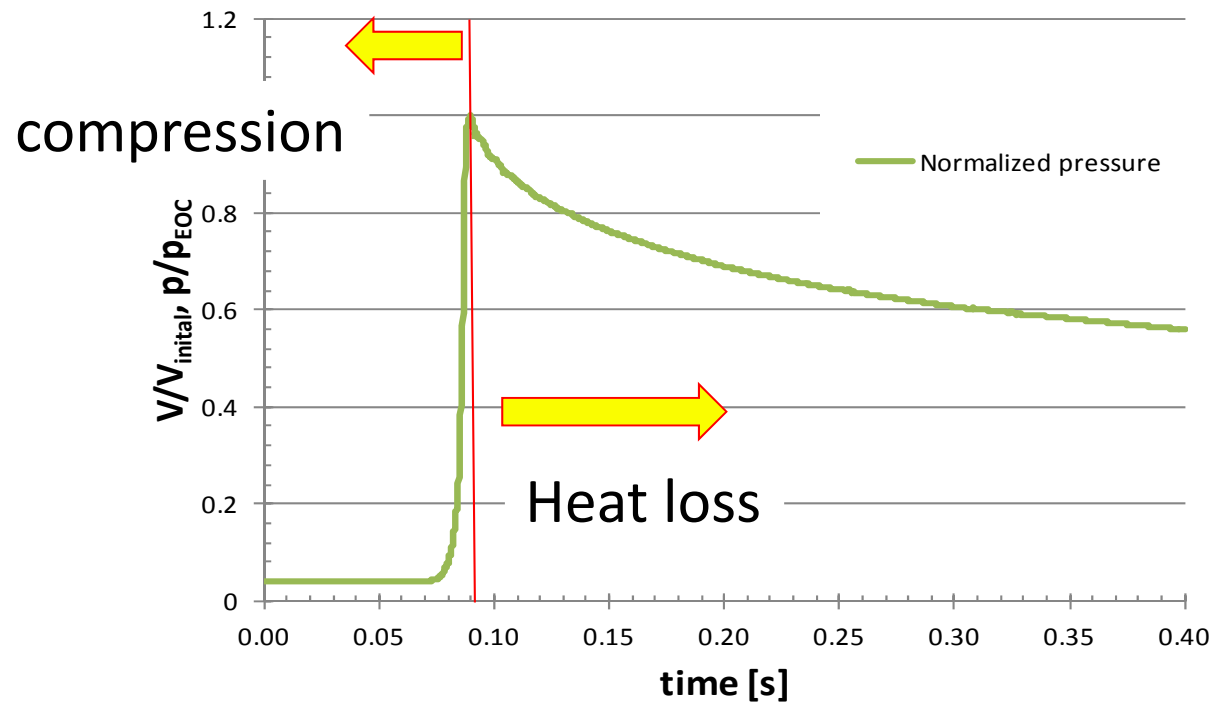
RCM Engine Relevant Studies





Data processing for RCM simulation

Step 1: Non-reactive experiment

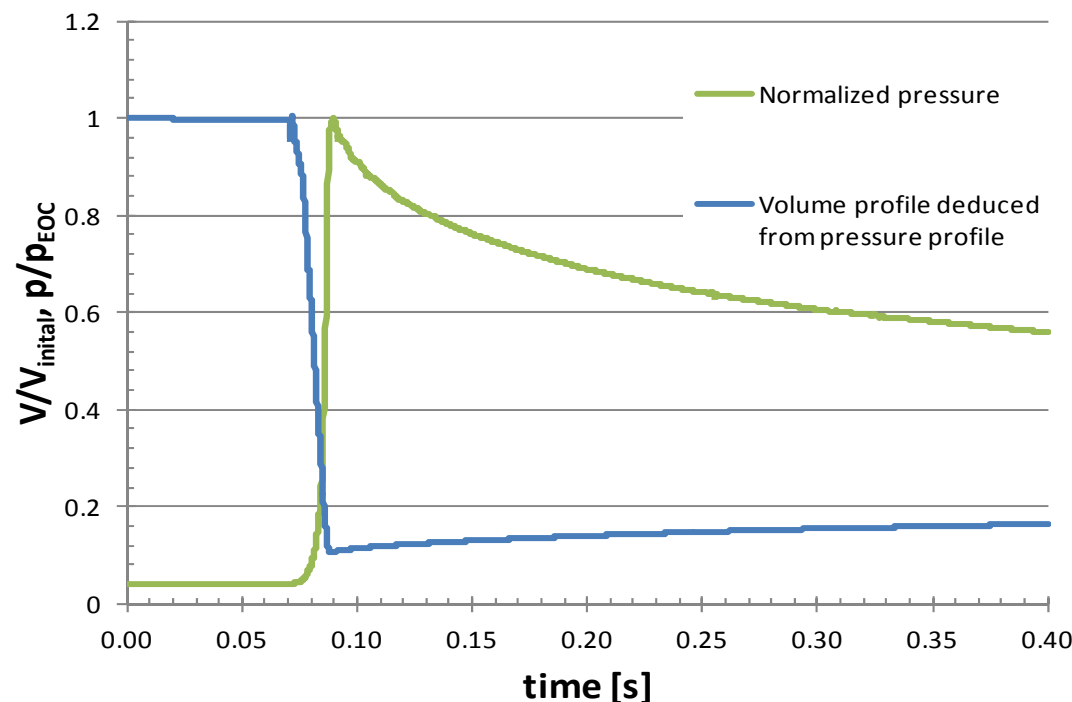


Experiment where O_2 is replaced by N_2 to characterize the compression and heat loss for a specific mixture



Data processing for RCM simulation

Step 2: Volume profile



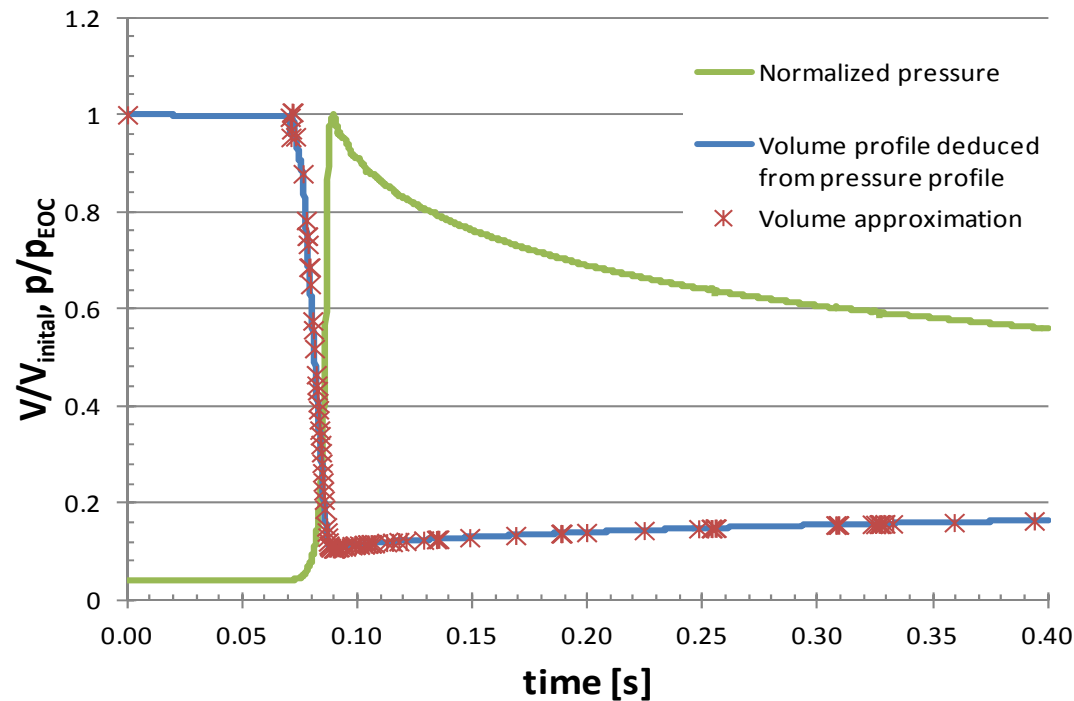
$$\frac{p_2}{p_1} = \left(\frac{V_1}{V_2}\right)^\gamma$$

- A volume profile is deduced from the pressure profile assuming isentropic behaviour (isentropic exponent not constant but temperature dependent).
- Heat loss effects are modelled as change in volume (Assumption of adiabatic core in RCM chamber).



Data processing for RCM simulation

Step 3: Reducing number of data points

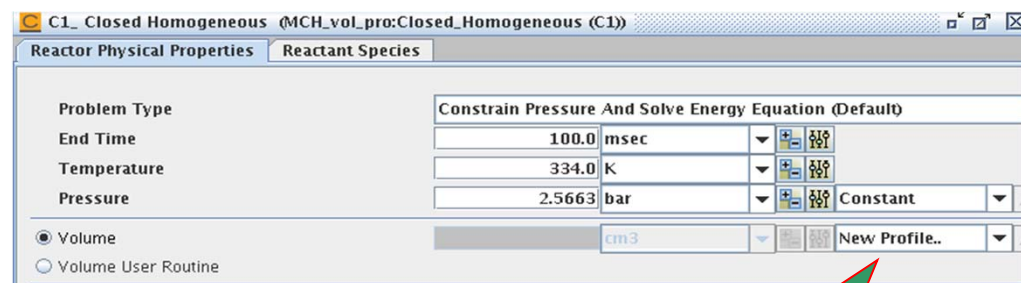


- Reduction in # of data points to reduce simulation time for reactive simulations.
- Non-uniform distribution of data points => accurate reproduction of volume profile.

Data processing for RCM simulation

- Rather than reporting polynomial fit parameters or providing subroutines for modelers to integrate into SENKIN, report the effective volume history in a tabular format
- Advantages:
 - Will not diverge if the maximum time is exceeded
 - Simpler to implement in CHEMKIN-Pro and CHEMKIN-II or III
 - Better agreement with experimental pressure profiles

We want to make the life of modelers easy!



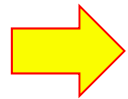
**CHEMKIN-Pro
Volume Profile Input**



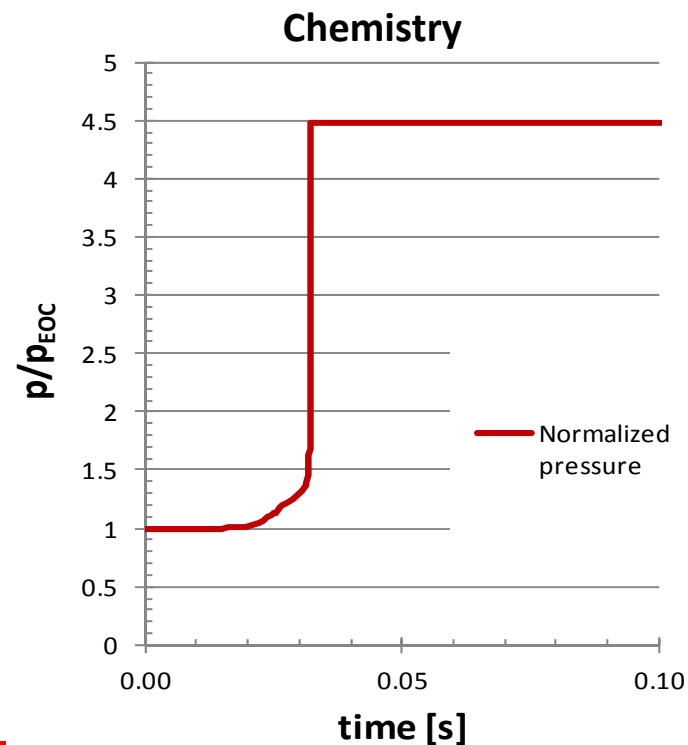
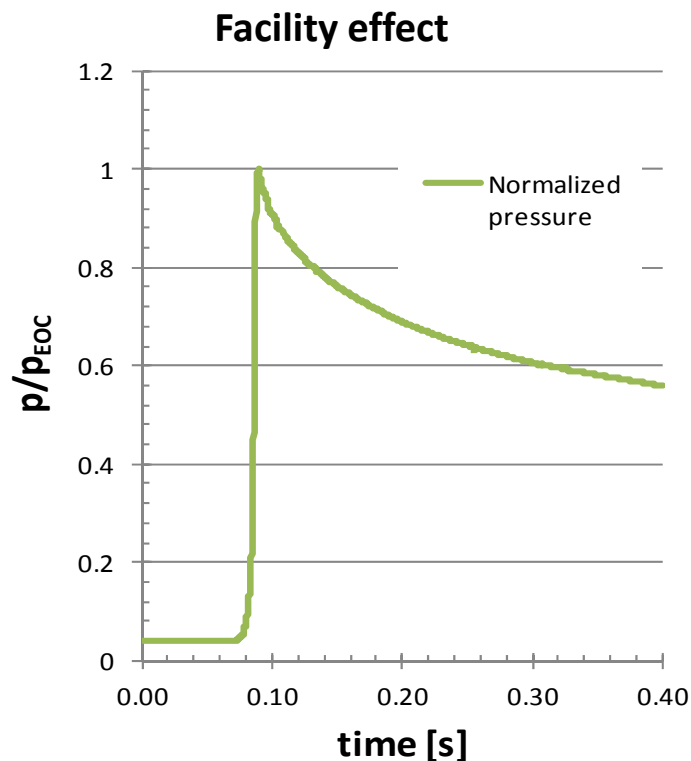
Data processing for RCM simulation

Step 4: Simulating reactive experiment

Input for simulation (CHEMKIN PRO): Volume profile, gas mixture, initial temperature and pressure.



Perturbation of the constant volume reactor by the given volume profile

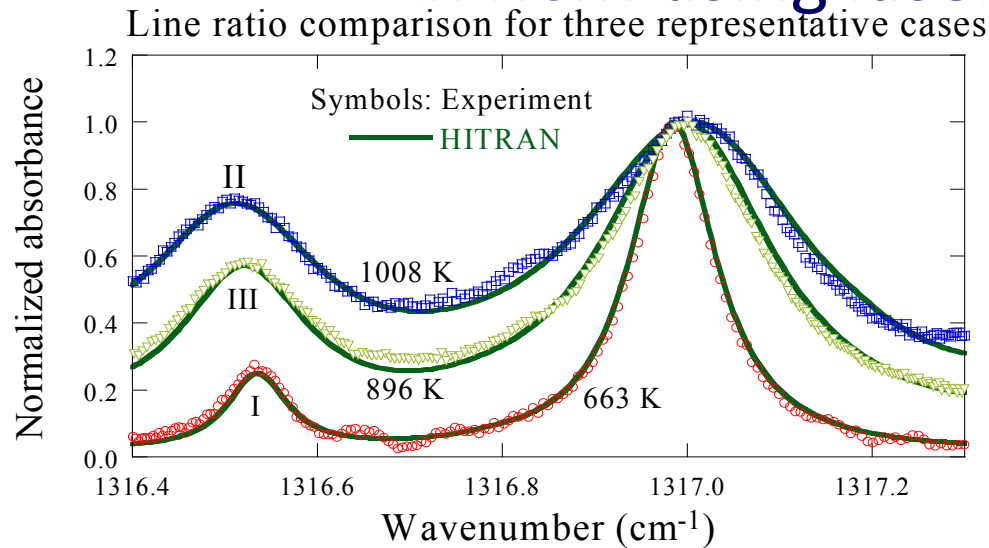


Early pressure rise used to estimate Temp rise

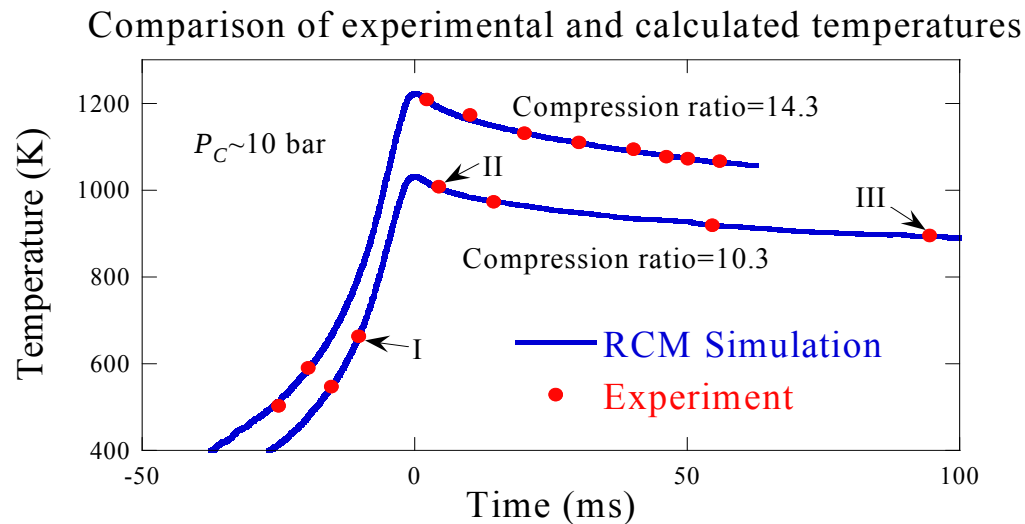
Assume Temperature and Pressure are Related by:

$$\frac{T}{T_i} = \left(\frac{P}{P_i} \right)^{\frac{\gamma-1}{\gamma}}$$

Two-Line Thermometry and H₂O Measurements in RCM using laser absorption at 7.6 μm



Non-Reactive Mixtures

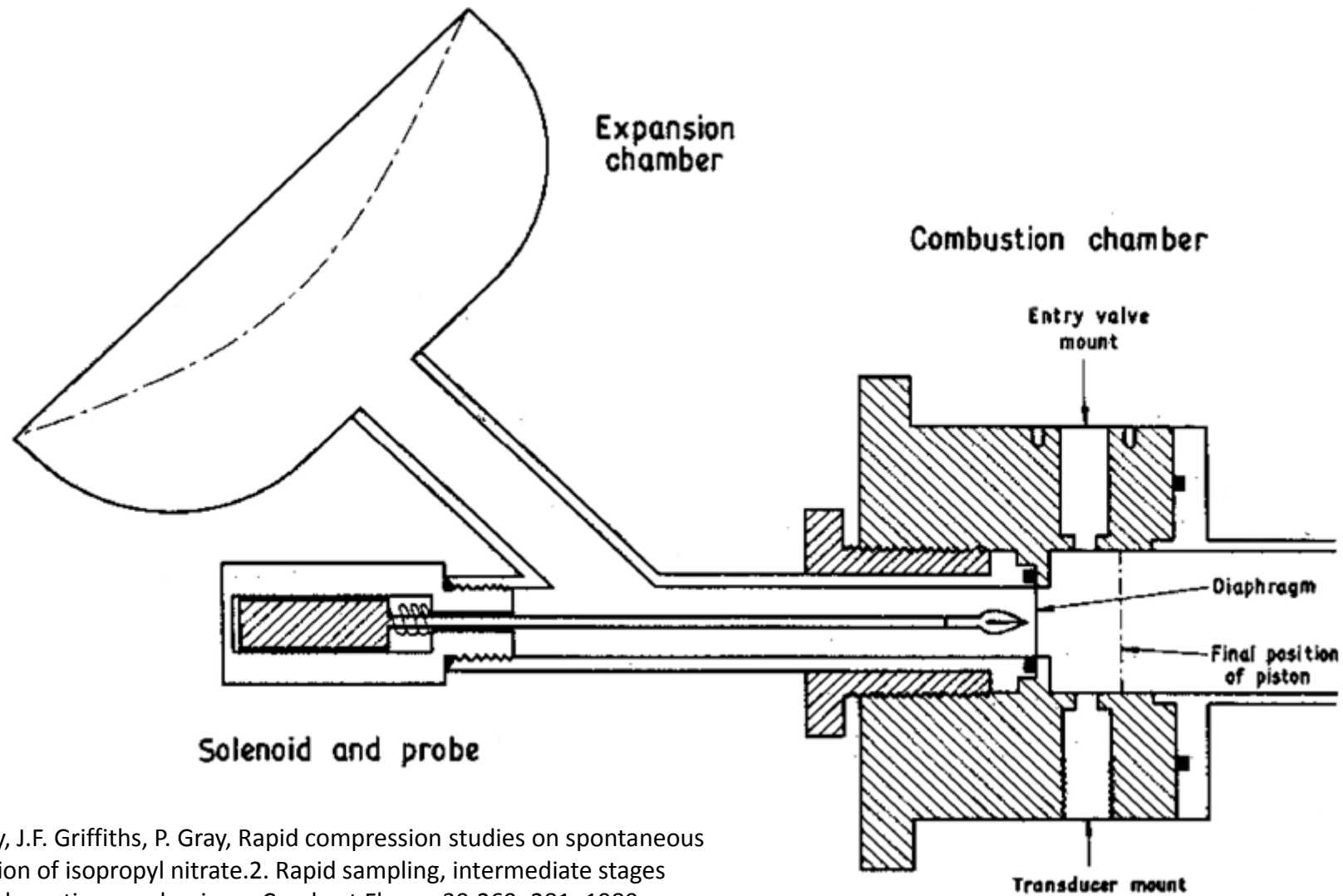


- Mixture of Ar with 2.87% H₂O used in a single pass RCM setup.
 - Experiments at end of compression pressure $P_c = 10$ bar.
 - Compression ratios of 10.3 and 14.3.
 - Comparison of measured temperature was done with simulated temperature evolution (from RCM simulations).
 - Good agreement within ± 5 K.
- Same non-reactive mixture used for higher pressure experiments for compression ratio 10.3 and $P_c = 15$ and 20 bar.
- Good agreement of absorbance profiles for representative conditions (viz. points I, II and III).

A.K. Das, M. Uddi, C-J. Sung
Combust. Flame, 159 (2012) 3493–3501.



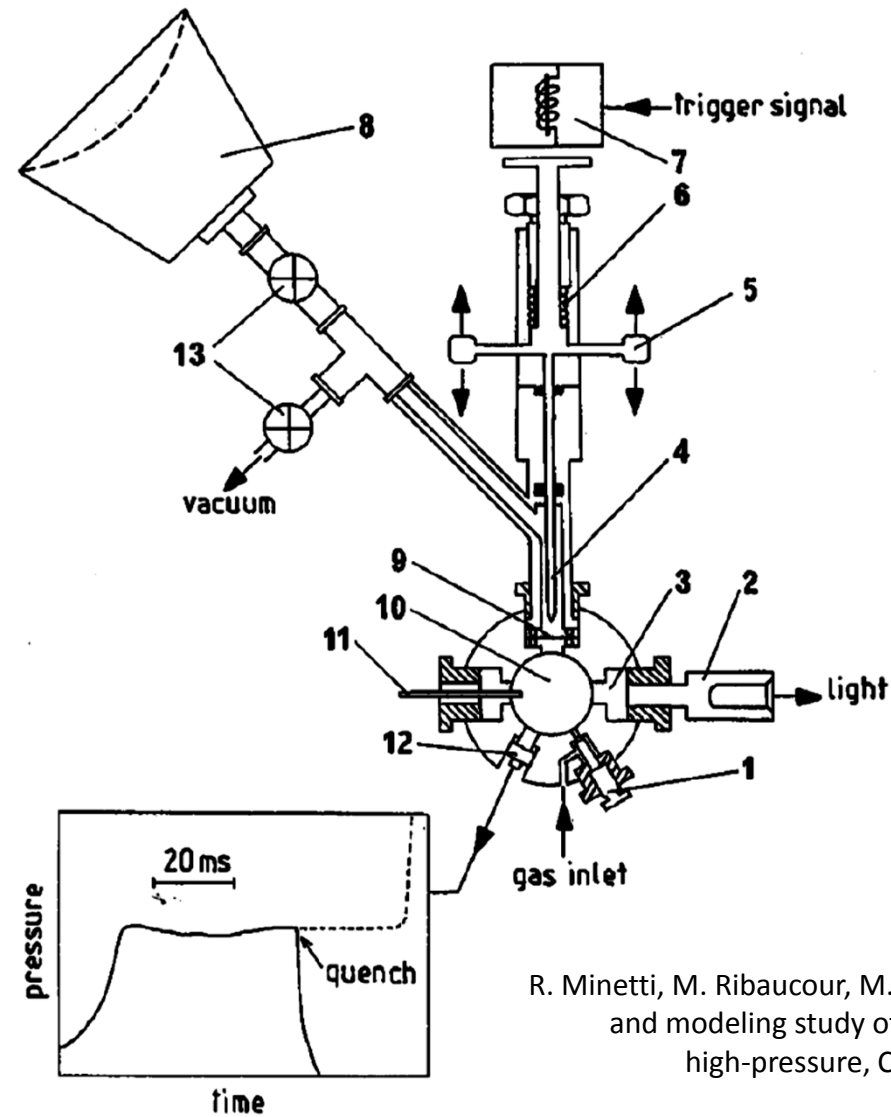
Rapid Sampling in Leeds RCM



P. Beeley, J.F. Griffiths, P. Gray, Rapid compression studies on spontaneous ignition of isopropyl nitrate.2. Rapid sampling, intermediate stages and reaction-mechanisms, *Combust Flame*, 39:269–281, 1980.



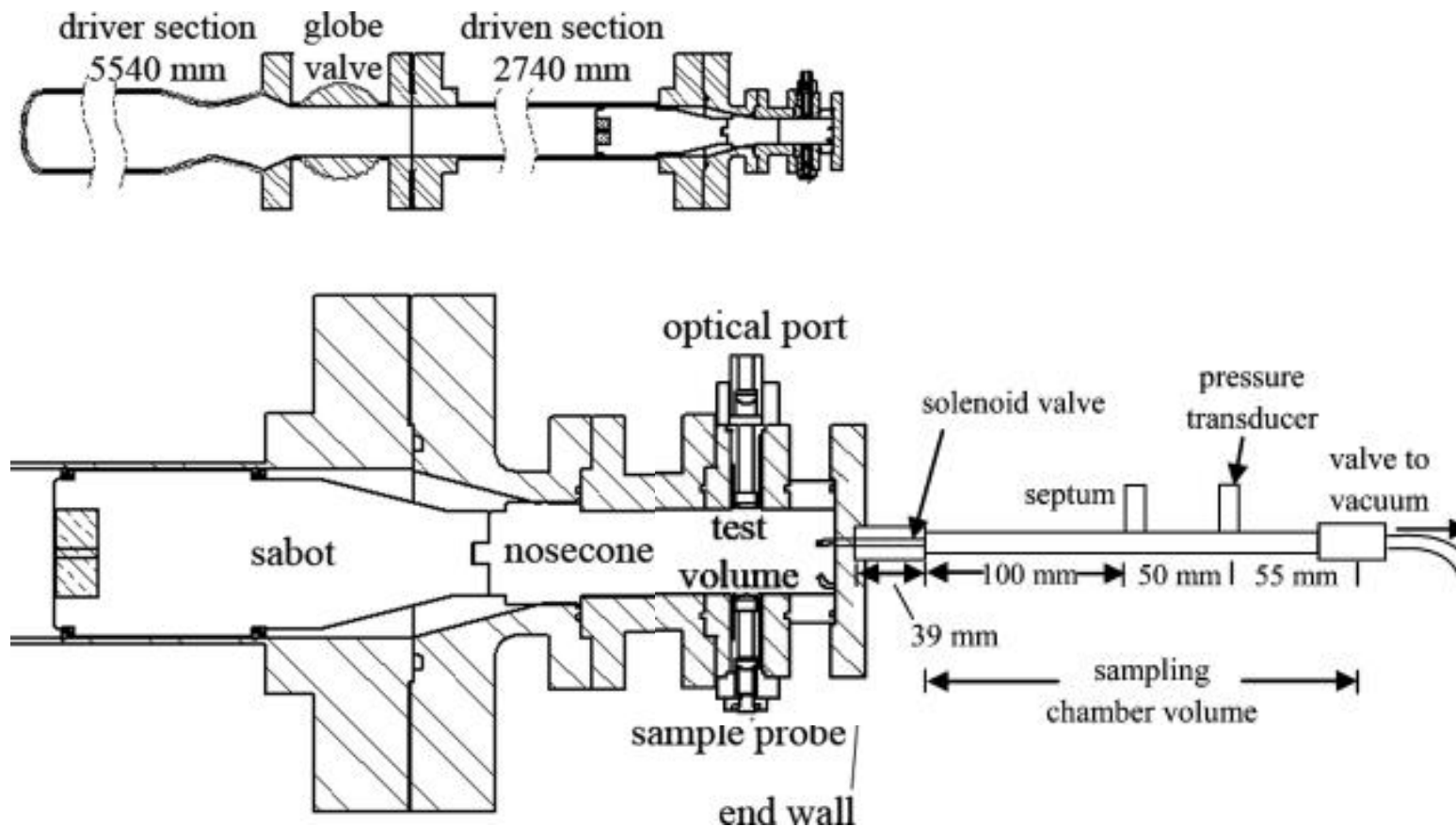
Rapid Sampling in Lille RCM



R. Minetti, M. Ribaucour, M. Carlier, C. Fittschen, L.R. Sochet, Experimental and modeling study of oxidation and autoignition of butane at high-pressure, *Combust Flame*, 96:201–211, 1994.



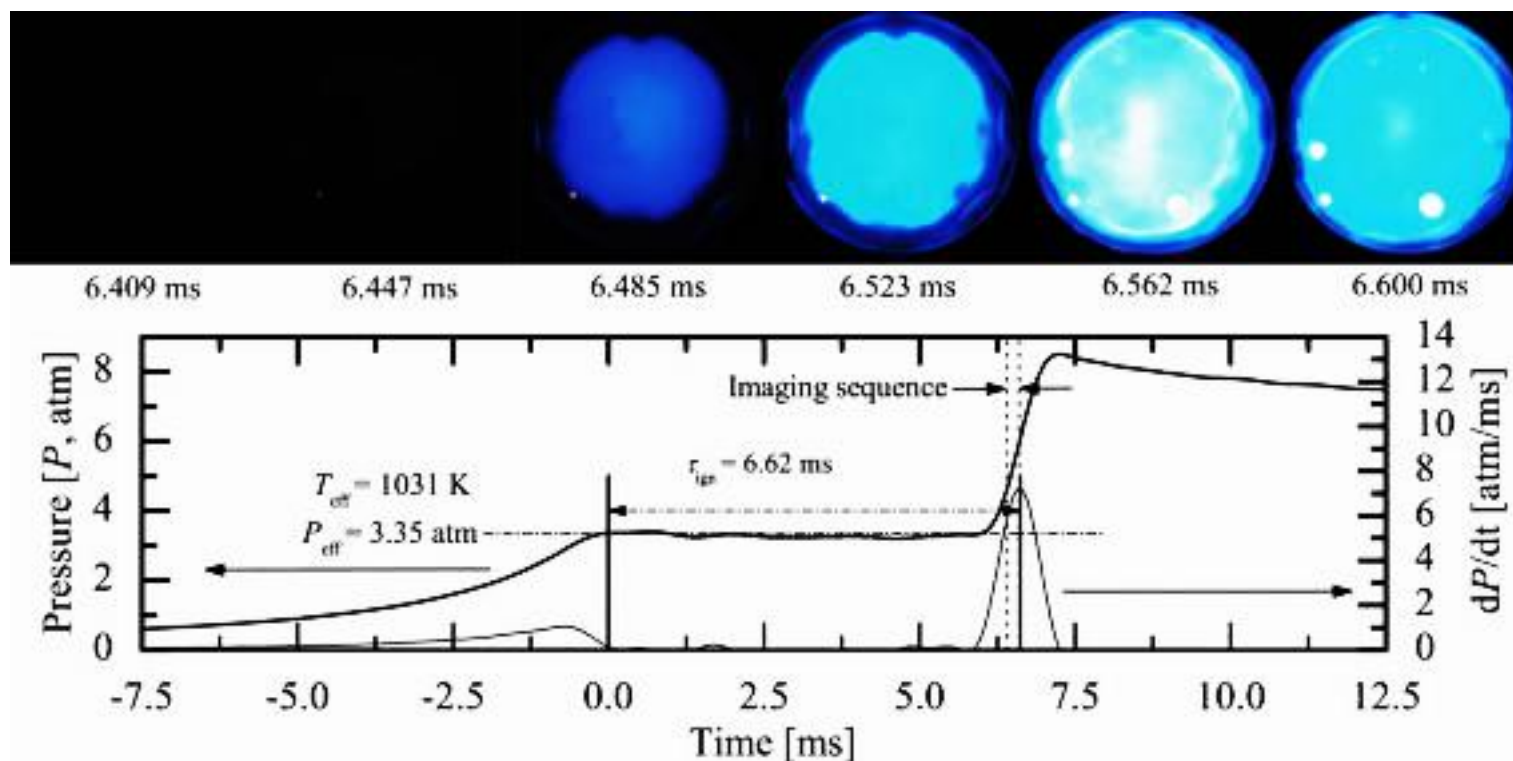
Rapid Sampling in UM RCF



D.M.A. Karwat, S.W. Wagon, P.D. Teini, M.S. Wooldridge
"On the Chemical Kinetics of n-Butanol: Ignition and Speciation Studies"
J. Phys. Chem. A, 115:4909–4921, 2011.



Rapid Sampling in UM RCF



D.M.A. Karwat, S.W. Wagnon, P.D. Teini, M.S. Wooldridge
"On the Chemical Kinetics of n-Butanol: Ignition and Speciation Studies"
J. Phys. Chem. A, 115:4909–4921, 2011.

Experimental Studies: Engine Relevant



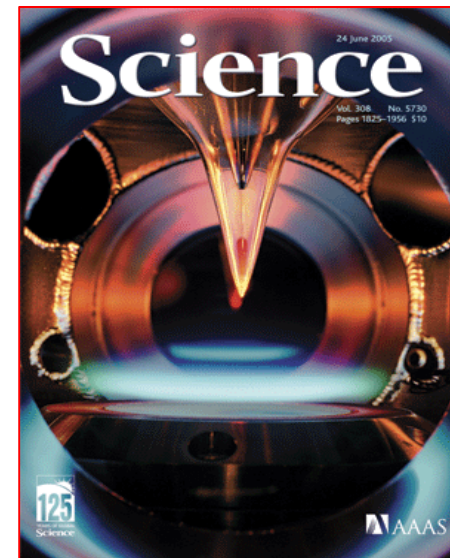
Rapid Compression Machine



Shock Tube



Jet Stirred Reactor



Flat Flame Burner

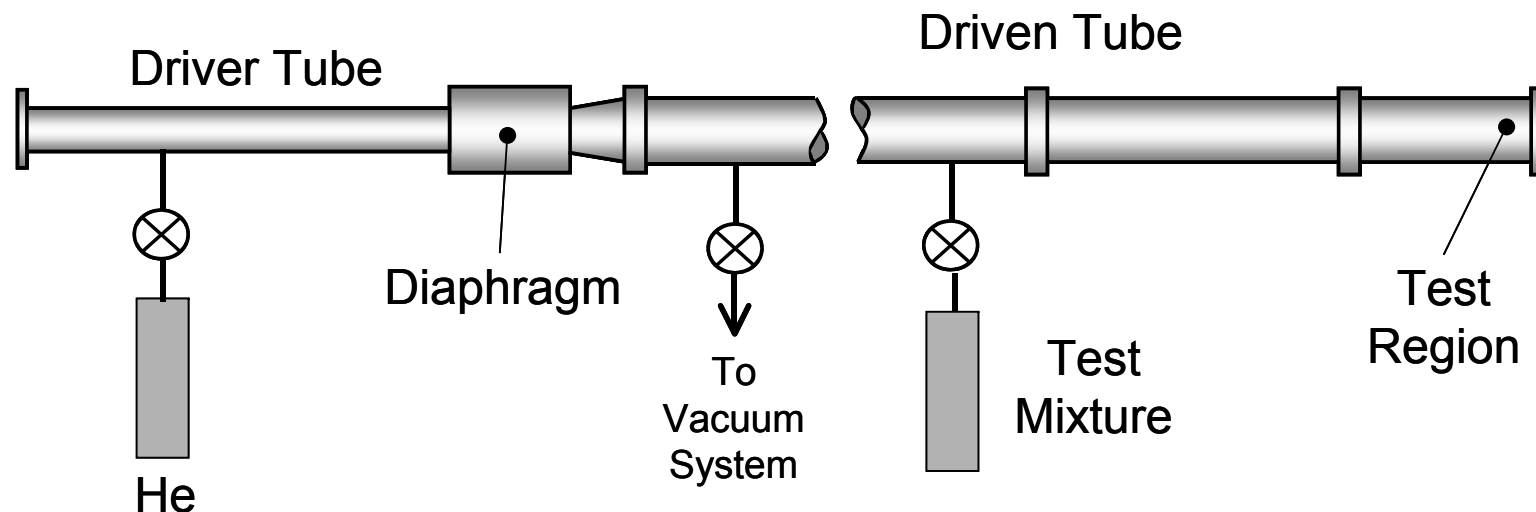


ST and RCM contribution to mechanism generation and validation





Reactions in shock waves

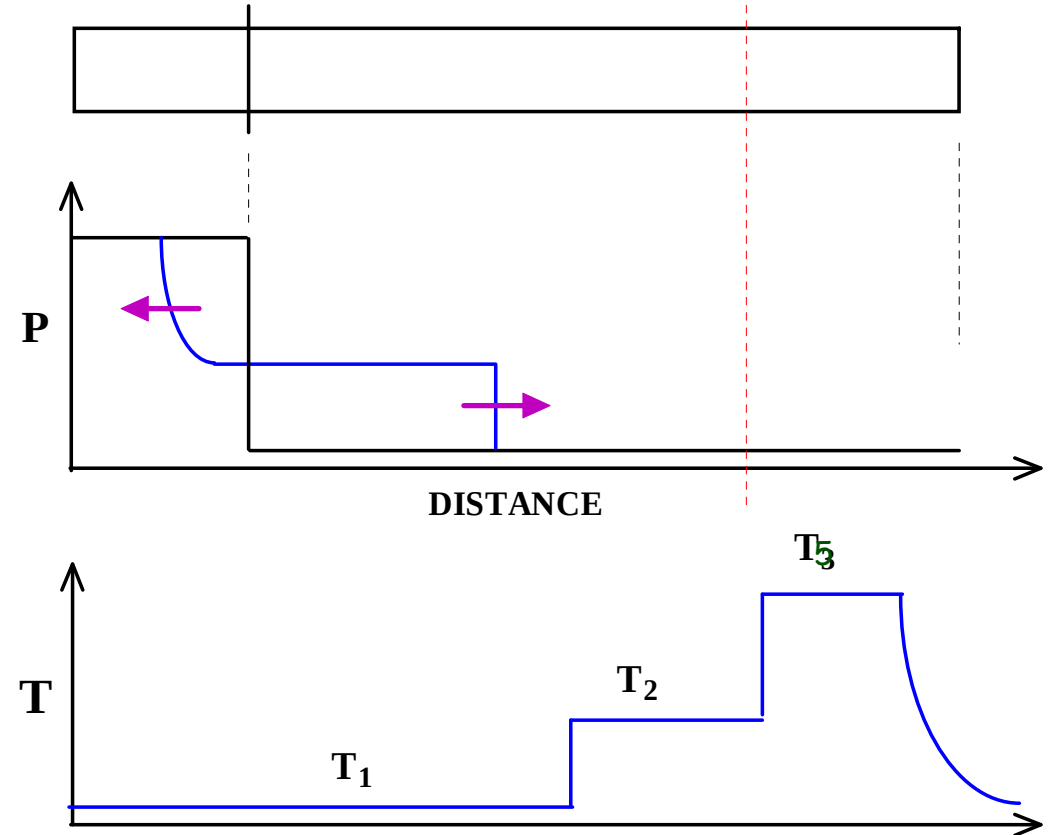


- Wide range of T 's & P 's accessible; 2,000 K, 50 bar routine
- Thermodynamics of high- T species eg Ar up to 5,000 K
- Study birth of compounds: $\text{C}_6\text{H}_5\text{CHO} \rightarrow \text{CO}^* + \text{C}_6\text{H}_6$
- Energy transfer rxns.: $\text{CO}_2 + \text{M} \rightarrow \text{CO}_2^* + \text{M}$
- Relative rates, use standard rxn as “clock”



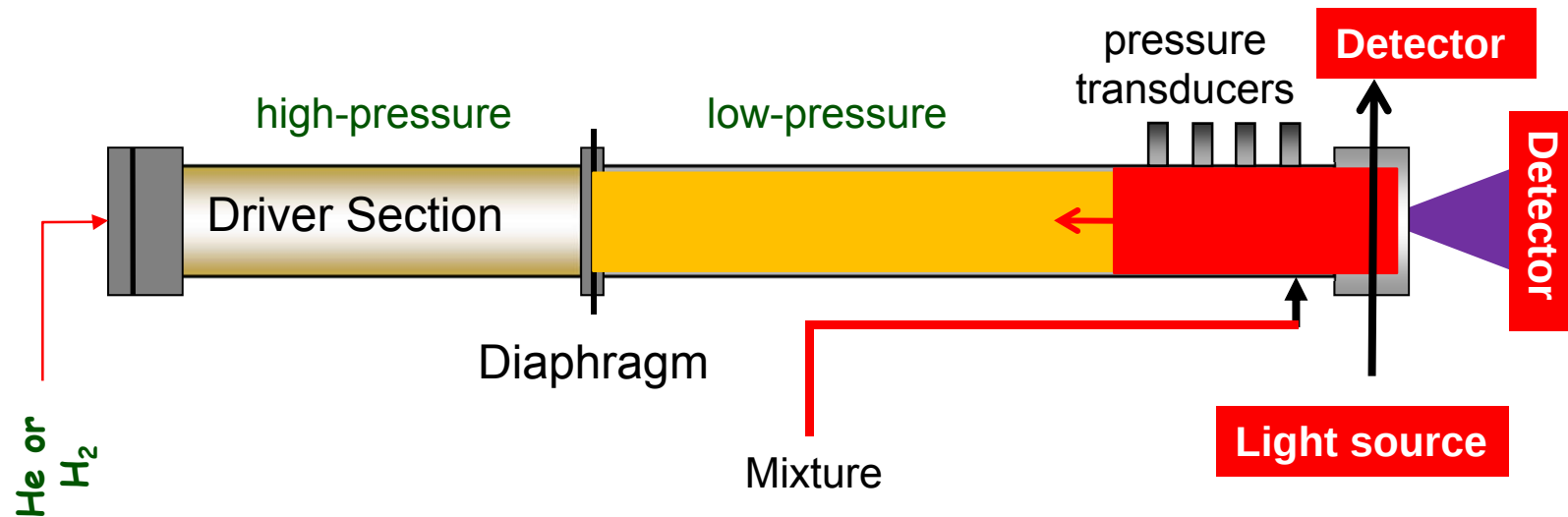
Mode of action of shock tube

- Fast bunsen-burner (ns)
- Shock wave acts as a piston compressing & heating the gas ahead of it
- Study rxns behind incident shock wave or reflected shock wave (ms-ms times)
- Non-invasive techniques
- T & p by computation from measured shock velocity





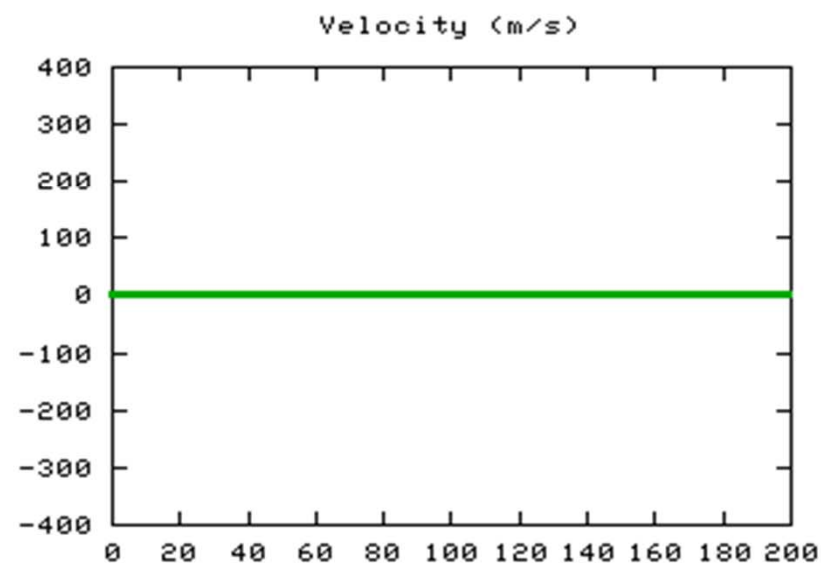
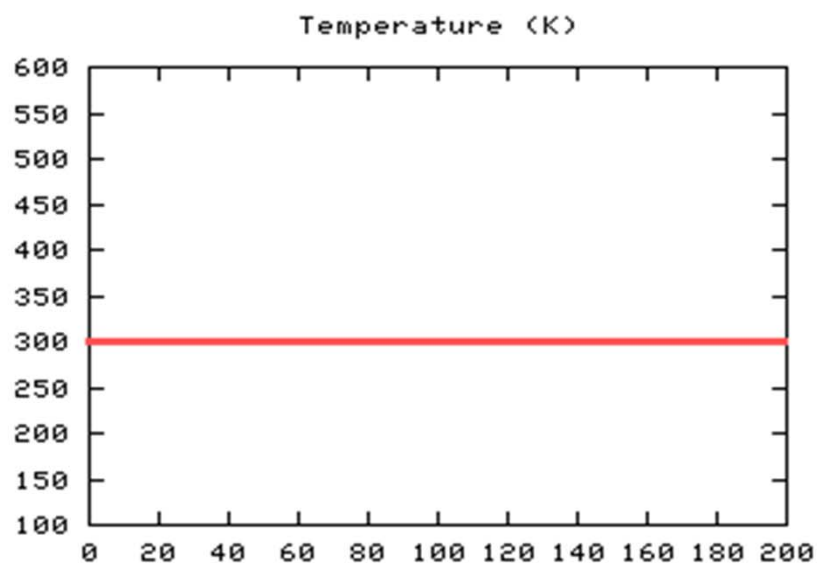
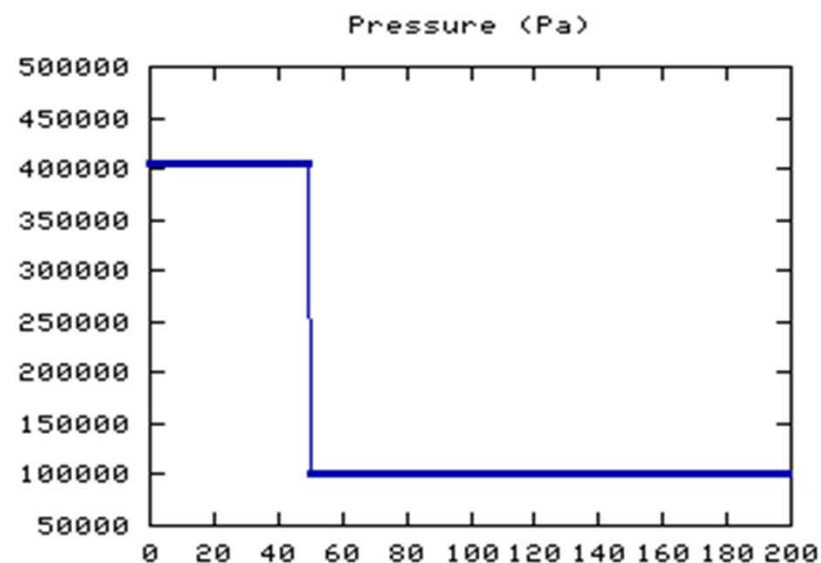
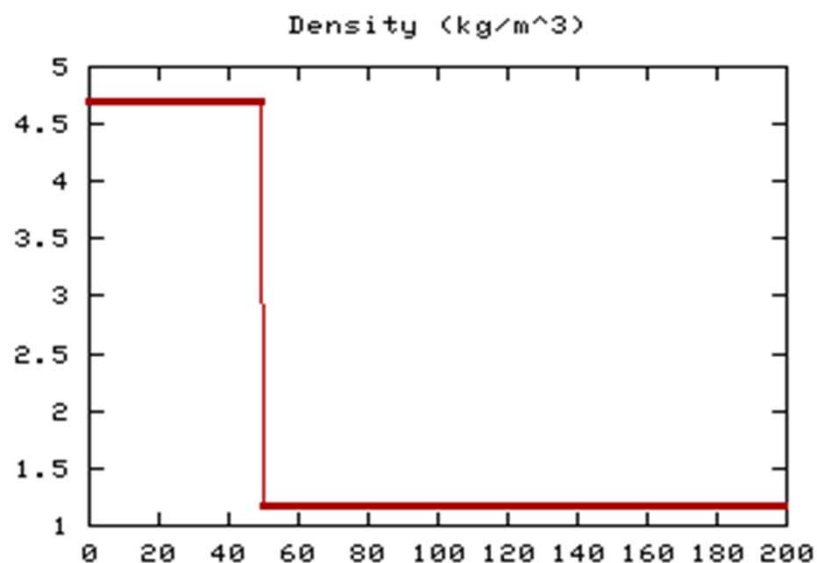
Shock Tube Operation



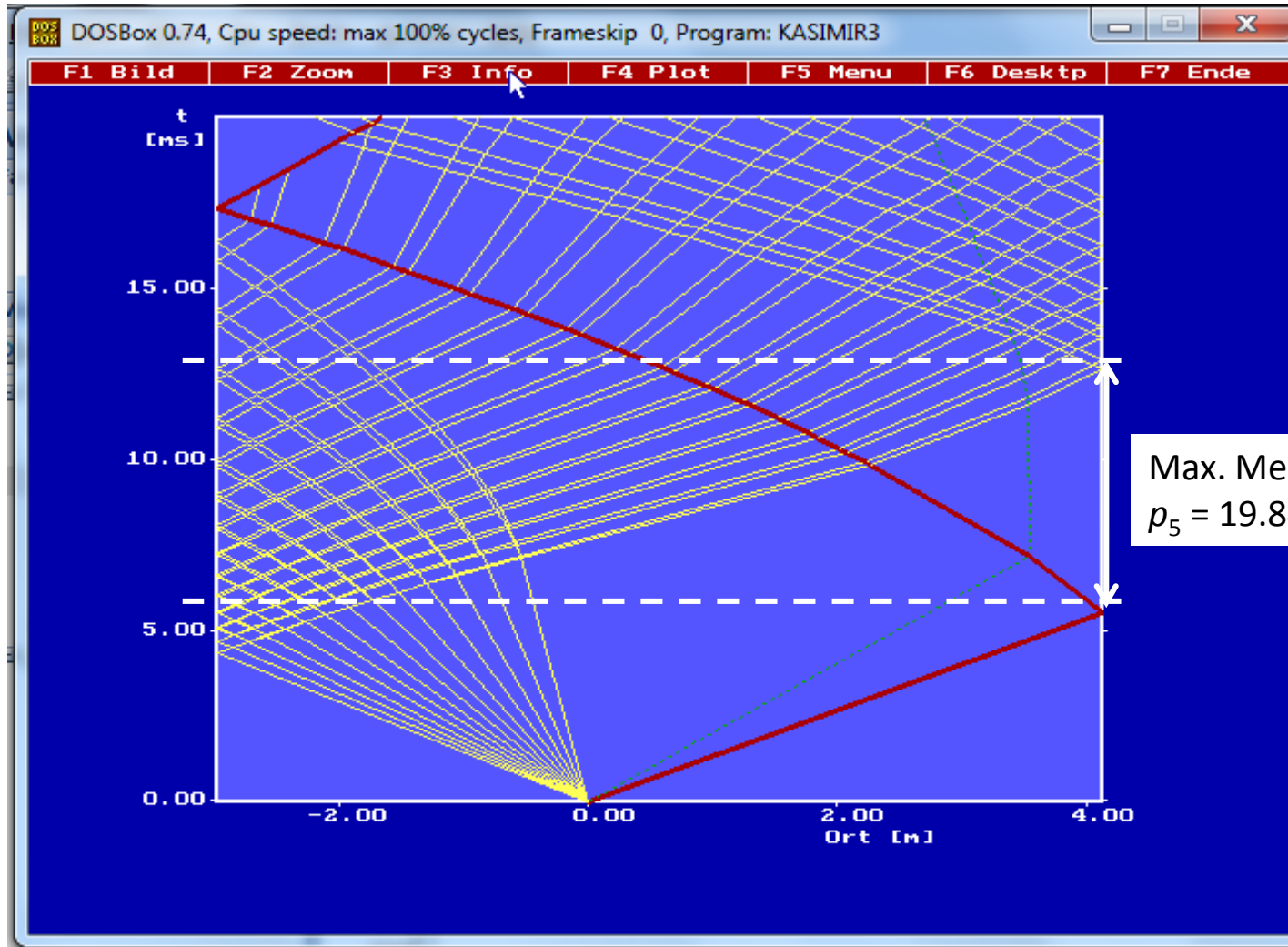
Slide courtesy of: Siavash Zabeti, Stephan Faust, Thomas Dreier, Oliver Welz, Mustapha Fikri, Christof Schulz, University of Duisburg, Essen



Shock Tube Simulation



Time available in ST



Max. Meas. Time ≈ 7 ms
 $p_5 = 19.84$ bar, $T_5 = 806$ K

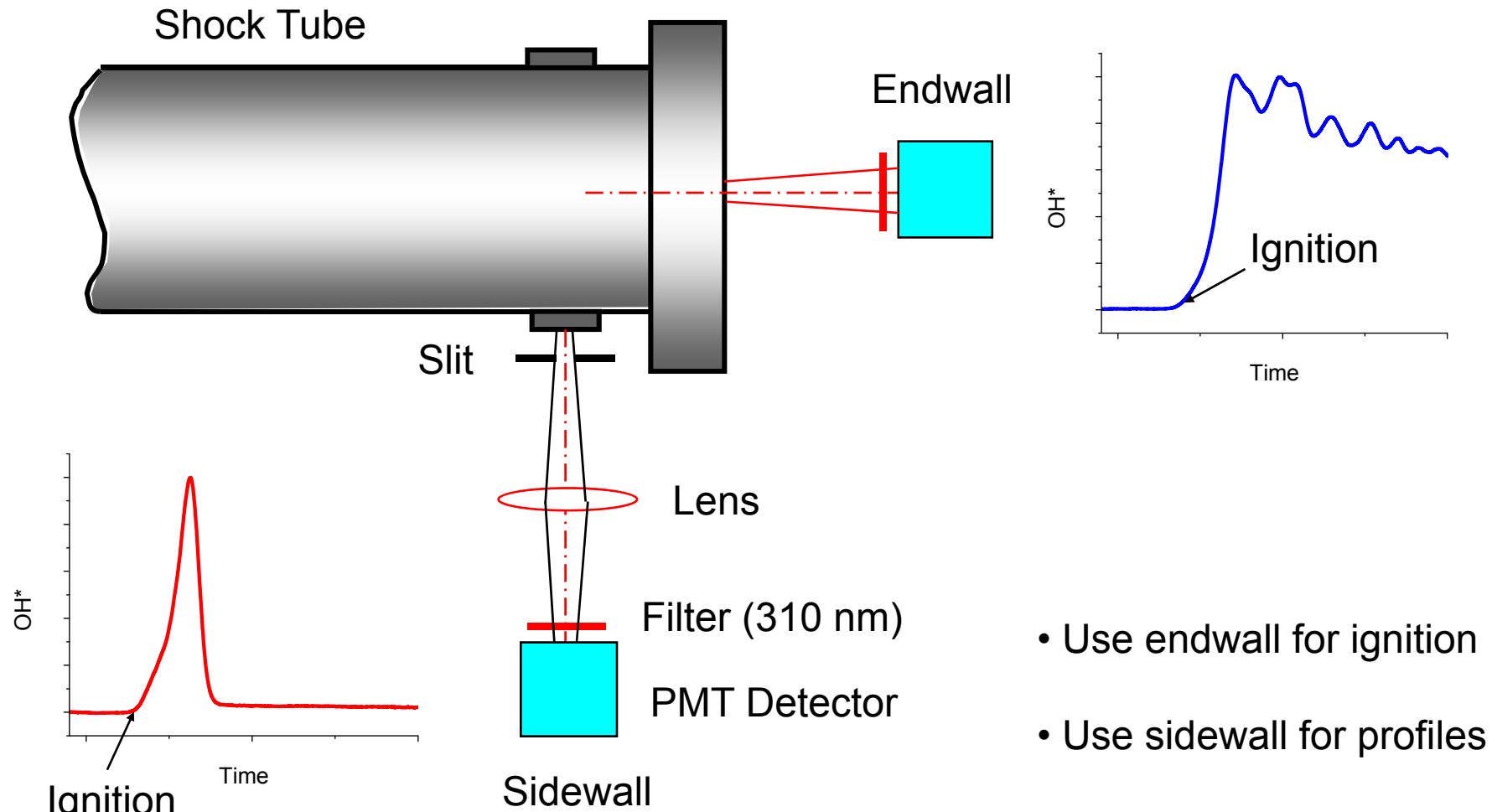
Driver gas: 10% Ar / 90% He Driven gas: air
 $p_4 = 20$ bar, $p_1 = 1$ bar

Real available measuring time
 around 5.3 ms (estimation)



Ignition delay times

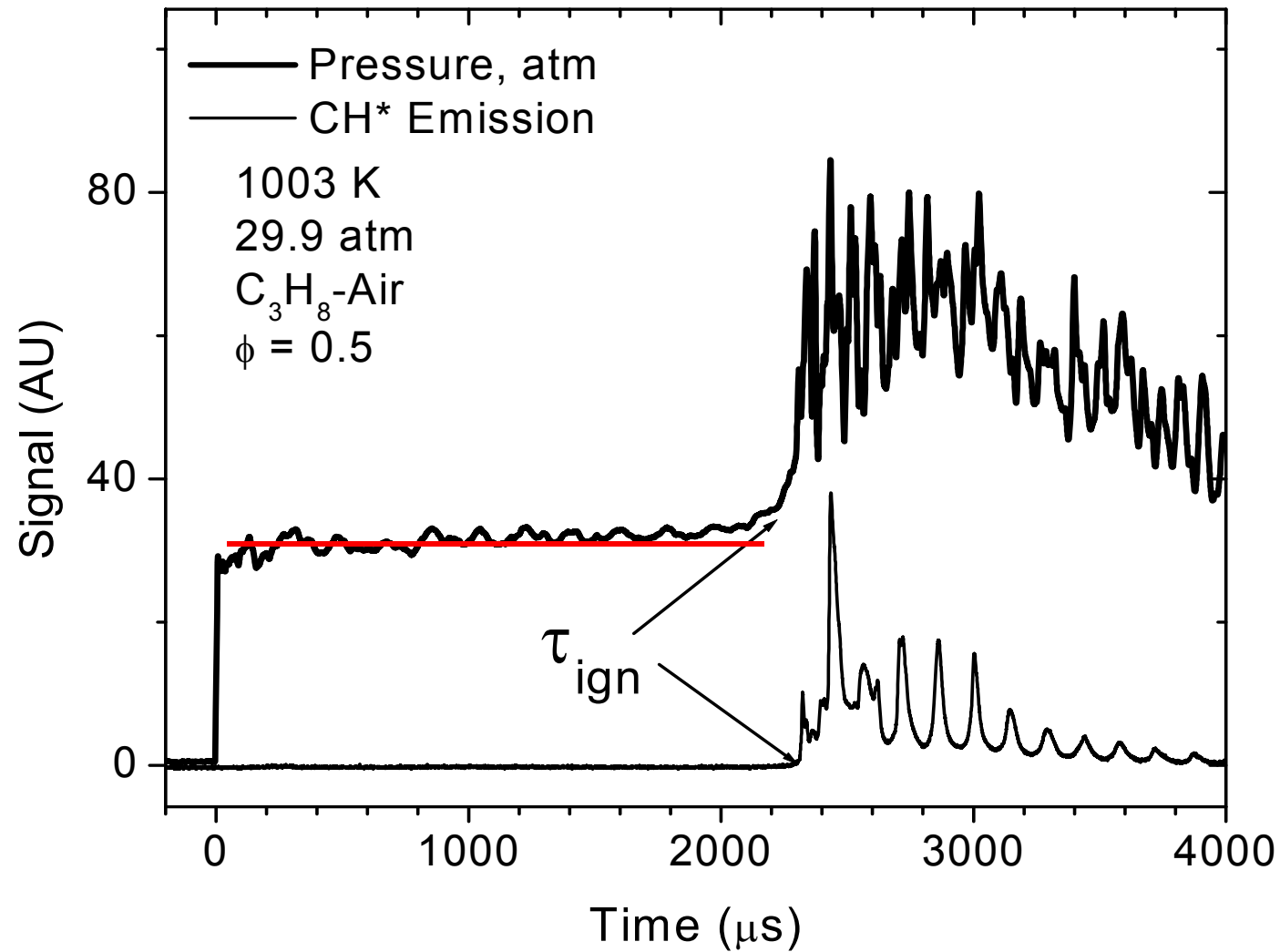
CH Chemiluminescence (431 nm) Detected at Endwall and Sidewall*

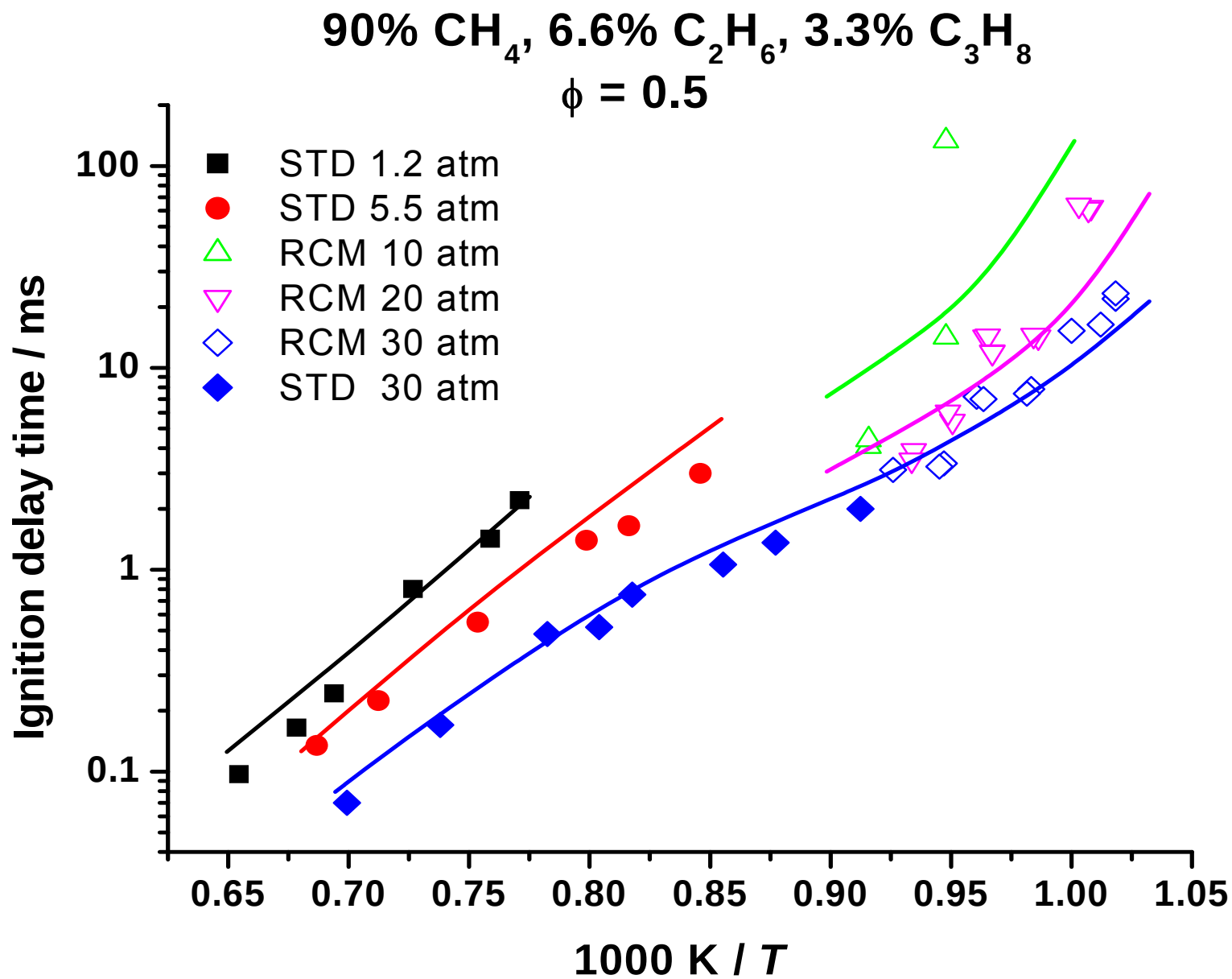


- Use endwall for ignition
- Use sidewall for profiles



Typical ST experimental record







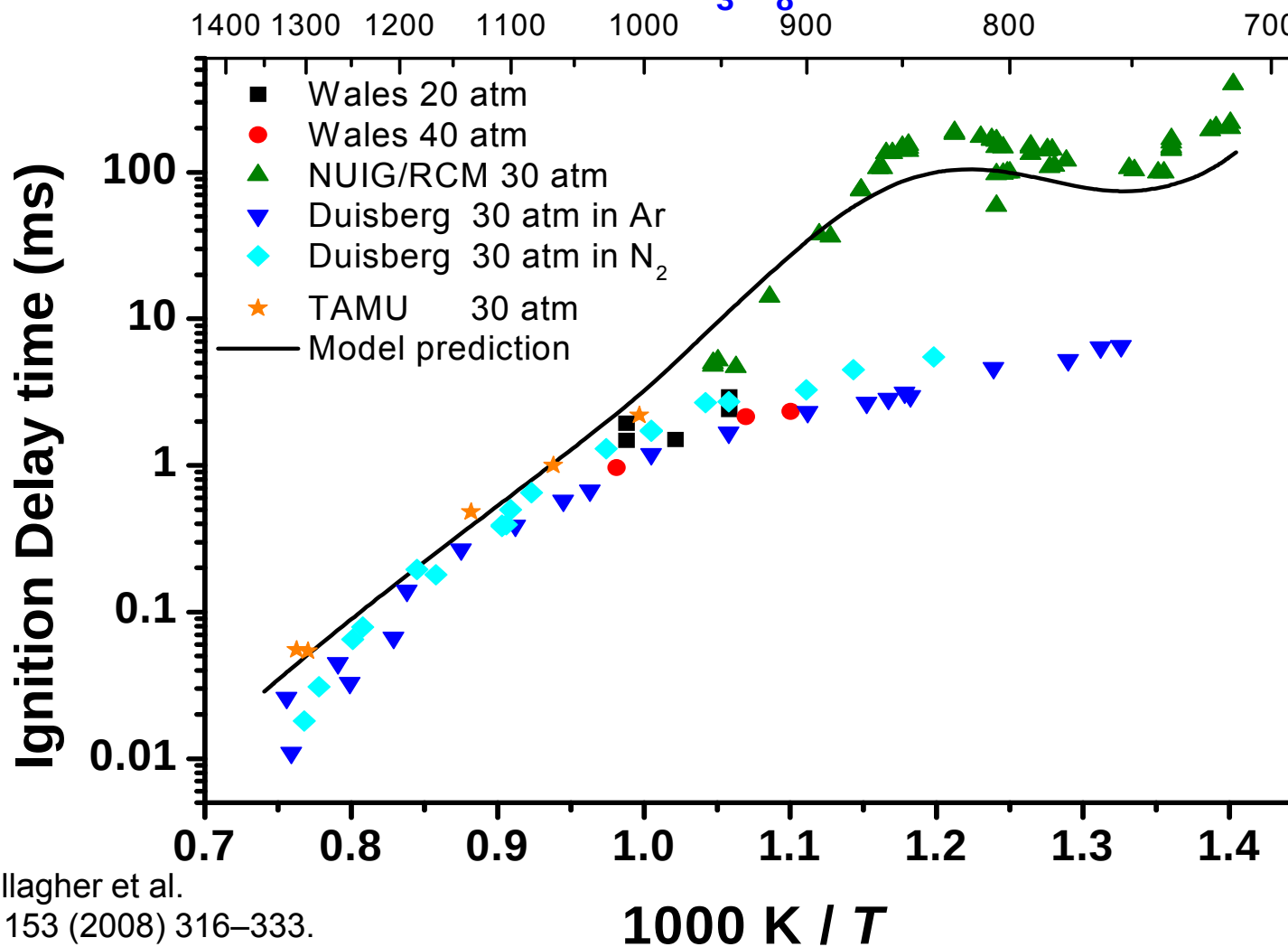
Ignition delay times

- Important indicator of fuel reactivity
 - T, p, ϕ , dilution
 - » RCM: 600—1100 K, ST: 1100—2000 K
 - » based on time available
 - Problems at intermediate T , High p



Propane Results Show Discrepancy between RCM and Shock Tube

2.1% C_3H_8 , $\phi = 0.5$

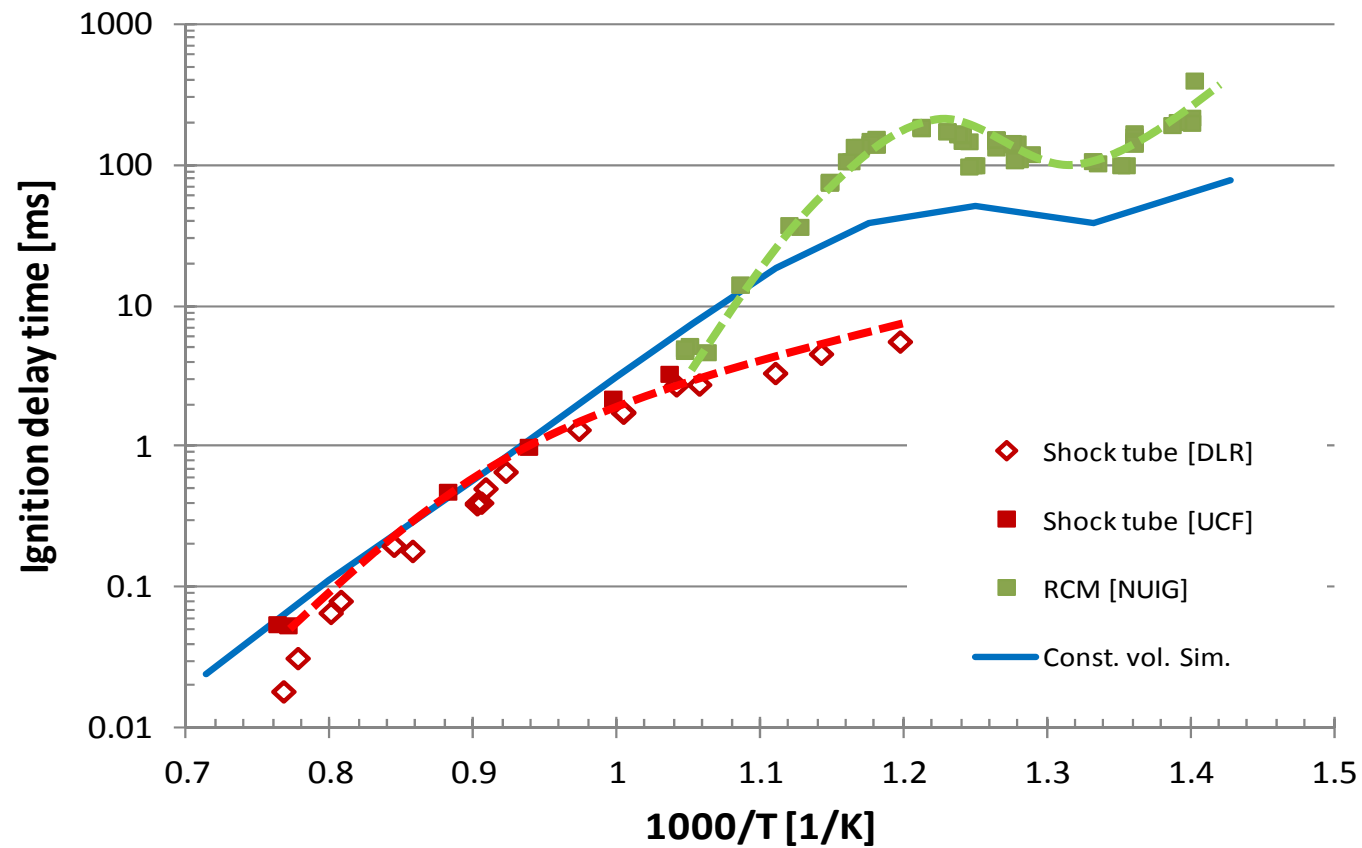


S. M. Gallagher et al.
Combust. Flame, 153 (2008) 316–333.



Typical data

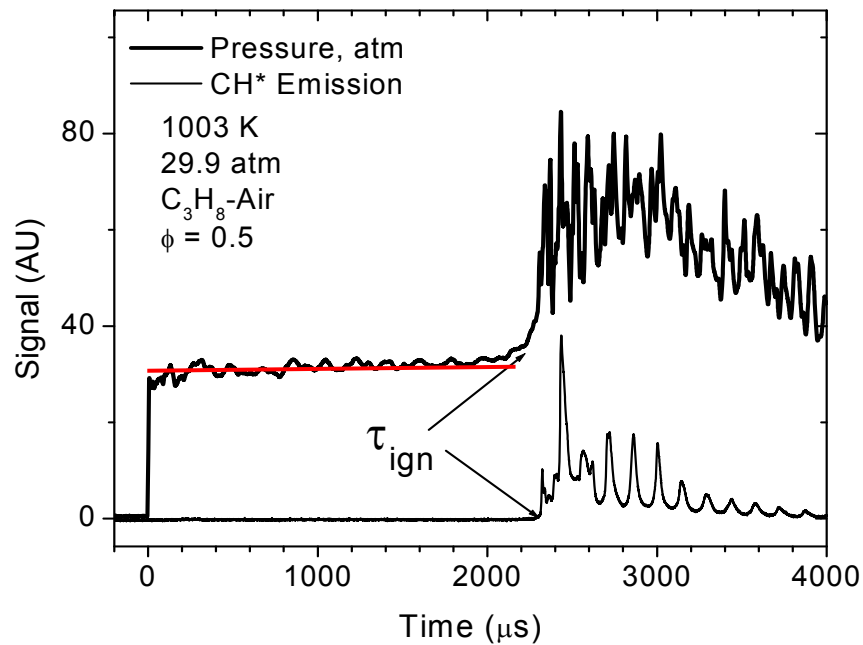
propane in air, 30atm, $\phi=0.5$



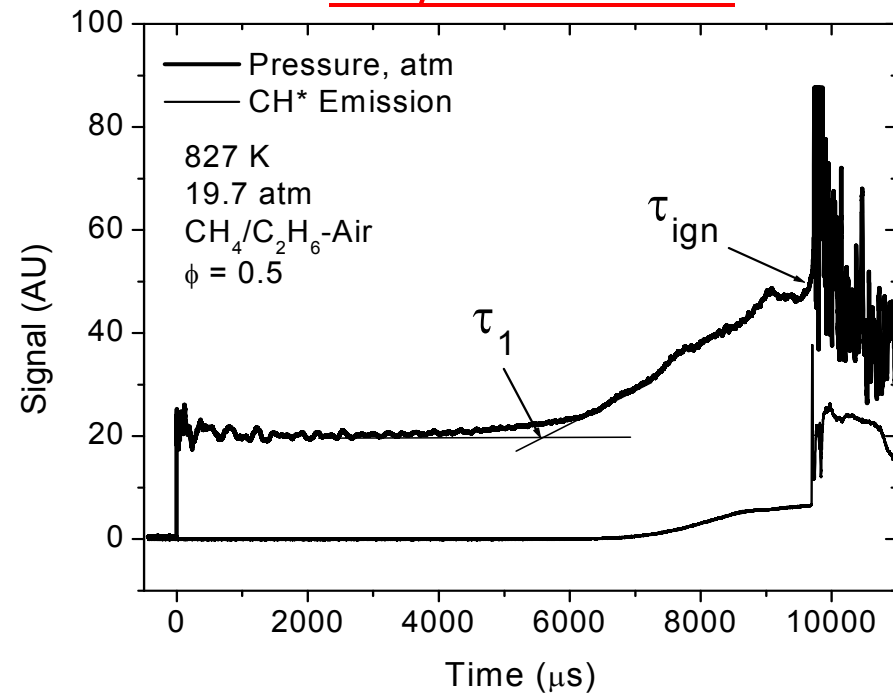


Lower-Temp Runs Exhibit Early Pressure Rise

Standard Ignition

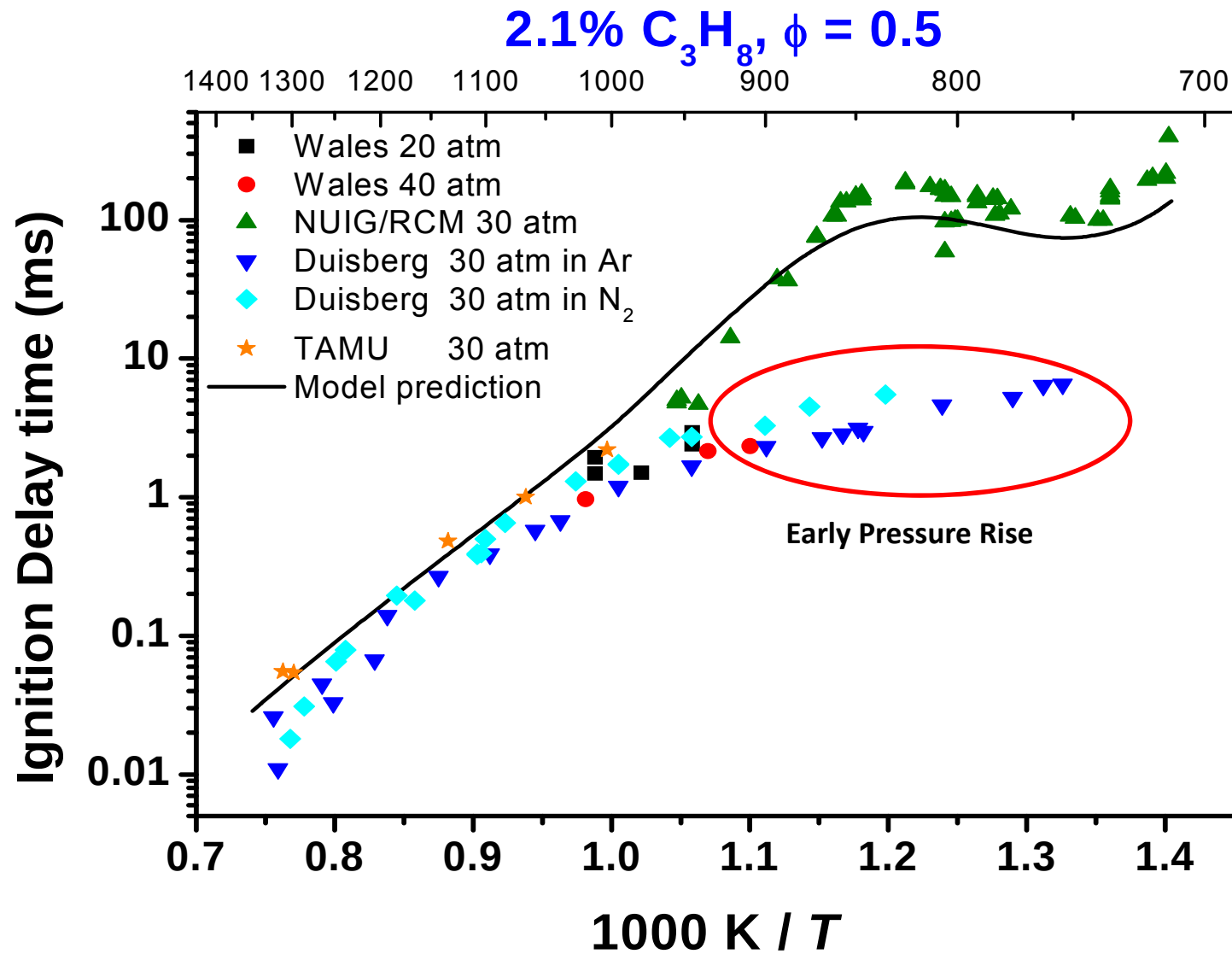


Early Pressure Rise





Lower-Temp Runs Exhibit Early Pressure Rise





H₂ / O₂ in Ar

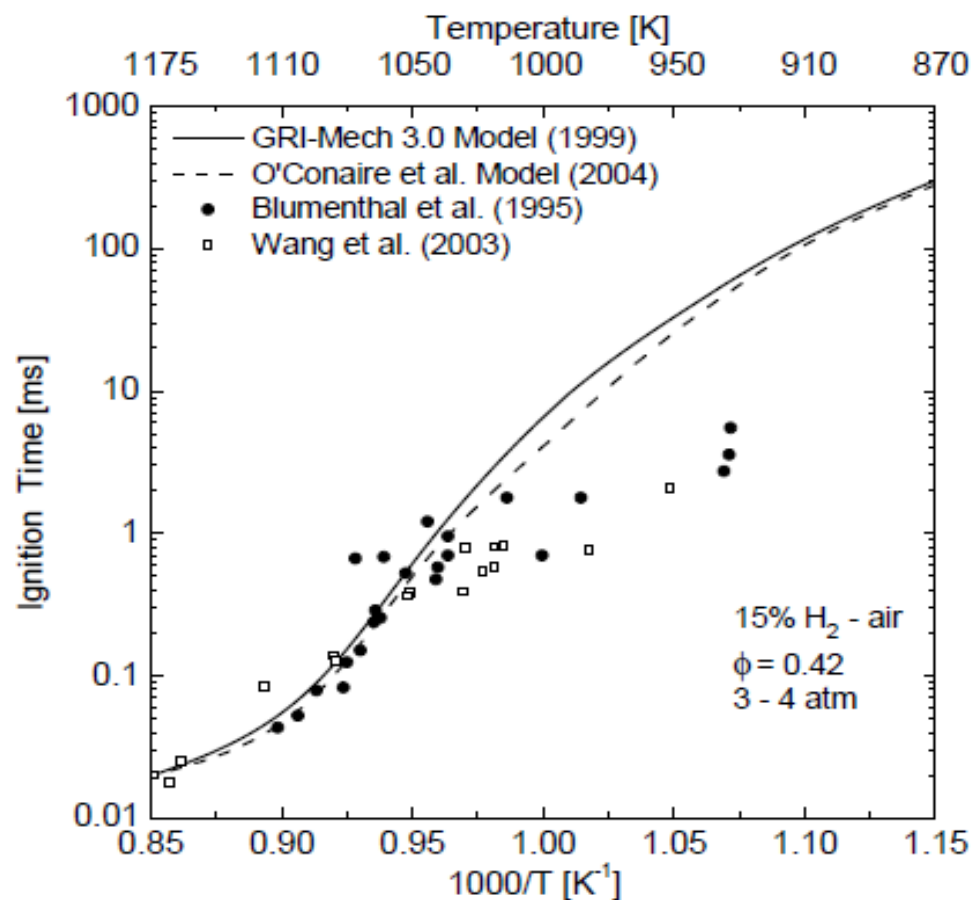


Fig. 1. Reflected-shock ignition delay time data compared to current kinetic models.

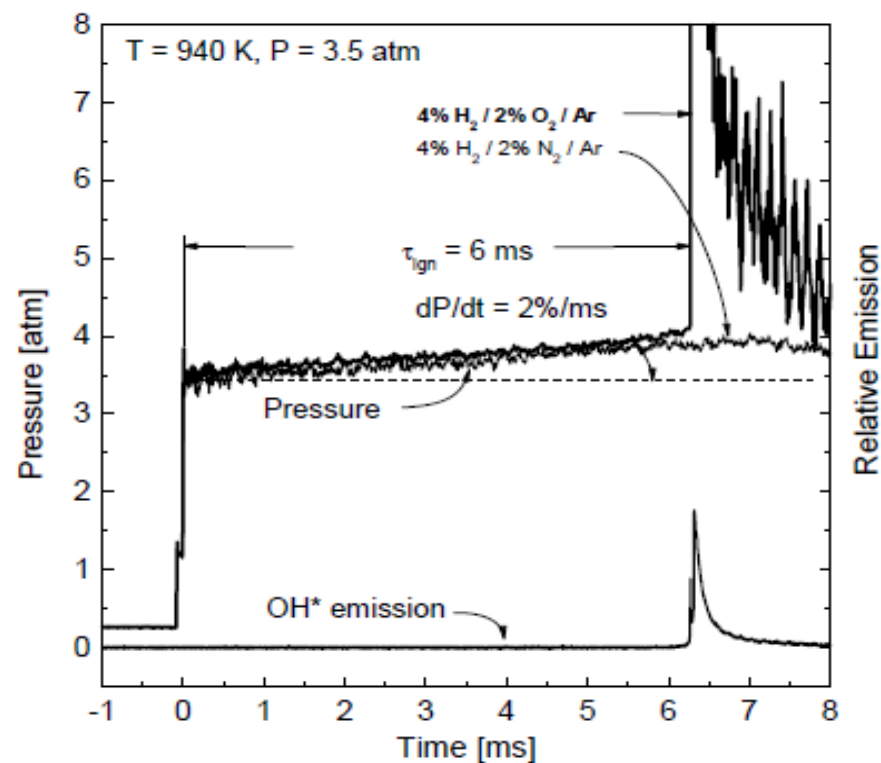


Fig. 2. Experimental data for a 4% H₂/2% O₂/Ar test gas mixture at initial post-shock conditions of 940 K and 3.5 atm for reactive and inert mixtures.

Early pressure rise used to estimate Temp rise

Assume Temperature and Pressure are Related by:

$$\frac{T}{T_i} = \left(\frac{P}{P_i} \right)^{\frac{\gamma-1}{\gamma}}$$

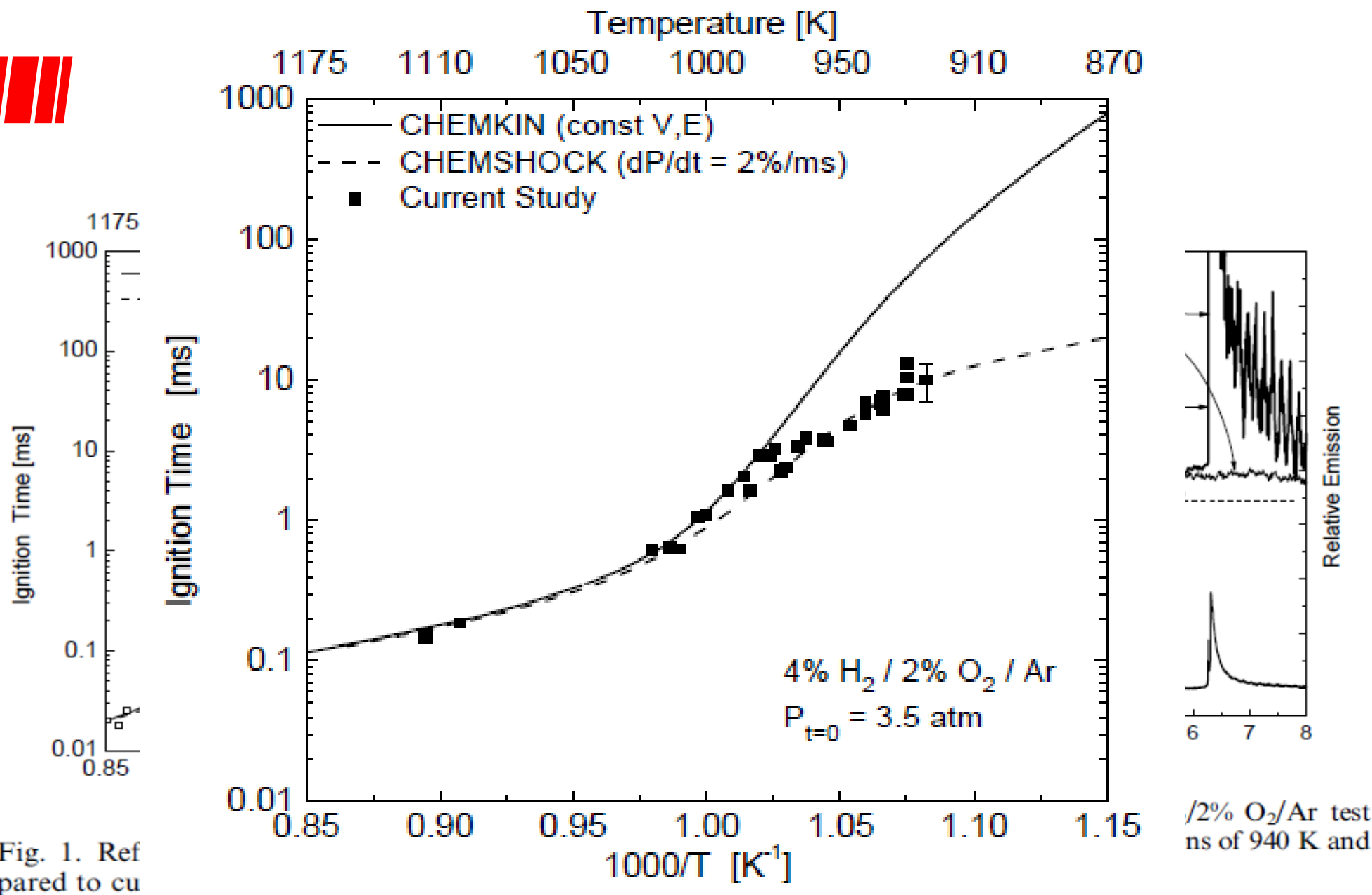


Fig. 1. Ref
pared to cu

100



Fig. 3. Reflected-shock ignition delay times for a 4% H₂/2% O₂/Ar mixture. Experimental data and calculated



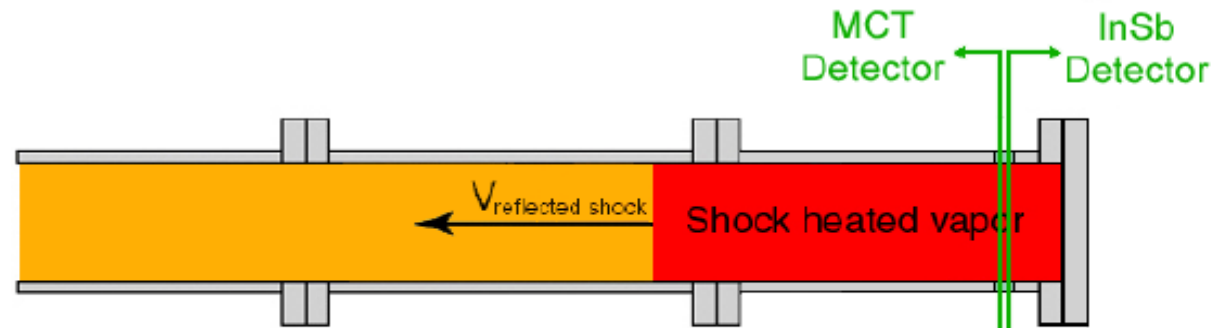


Laser absorption measurements

- OH measurement at 306.7 nm
 - Peak of $R_1(5)$ absorption line in the OH A-X(0,0) band
 - CW laser light at 613.4 nm generated using dye laser
 - Light at 306.7 nm generated by intracavity frequency-doubling, using a temperature-tuned AD*A crystal.
 - OH concentration calculated using Beer's law:

$$I/I_o = \exp(-k_v p_{\text{total}} X_{\text{OH}} L)$$

- ★ I and I_o are the transmitted and incident beam intensities
- ★ k_v is the line-center absorption coefficient at 306.7 nm for OH
- ★ p_{total} total test gas mixture
- ★ X_{OH} is the OH mole fraction
- ★ L is the path length



613.4 nm using
Spectra Physics
380 ring Dye laser

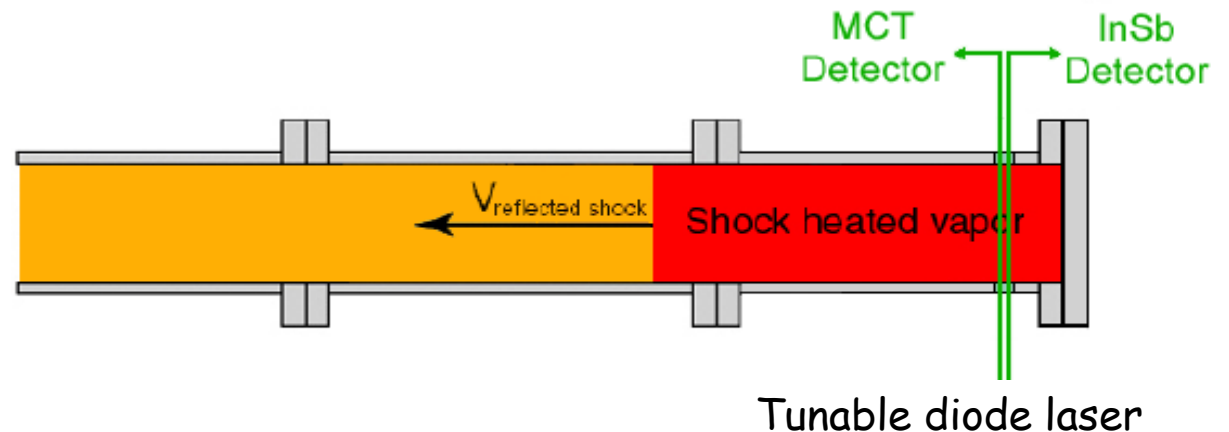


Laser absorption measurements

- CO₂ measured at 2752.5 nm
- H₂O measured at 2550.96 nm
- Concentration calculated using Beer's law:

$$I/I_o = \exp(-k_v p_{\text{total}} X_{\text{species}} L)$$

- ★ I and I_o are the transmitted and incident beam intensities
- ★ k_v is the line-center absorption coefficient at 2752.5 nm for CO₂
- ★ p_{total} total test gas mixture
- ★ X_{CO_2} is the CO₂ mole fraction
- ★ L is the path length





Laser absorption measurements

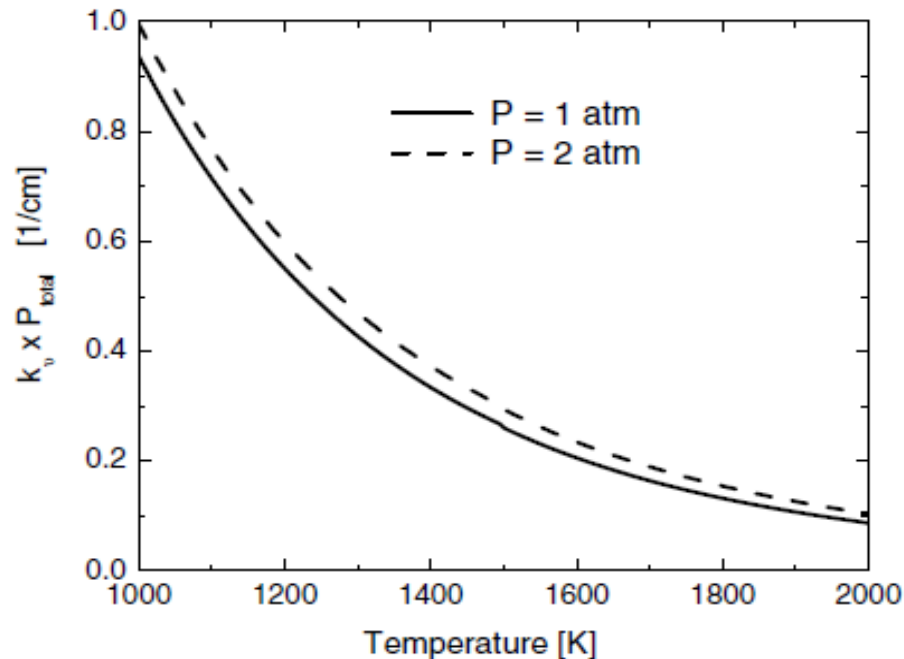


Fig. 1. Absorption coefficient $\times$ pressure product, $k_v \times P_{\text{total}}$ [cm^{-1}] for the R(28) CO_2 transition near 3633.08 cm^{-1} (2752.5 nm) at $P = 1$ and 2 atm .

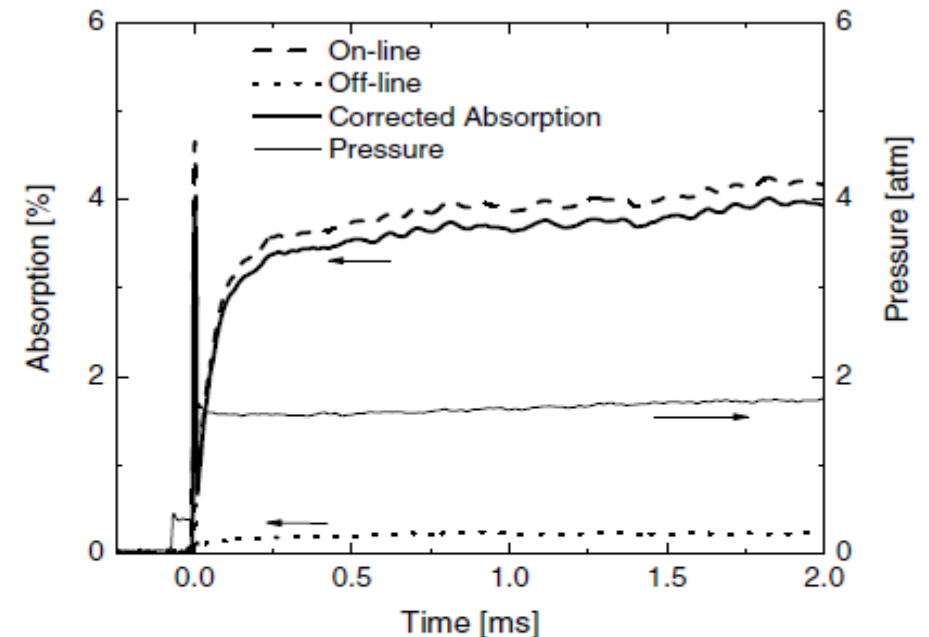


Fig. 2. Example on-line and off-line absorption measurement in 2% MB/Argon. Reflected shock conditions: $T_5 = 1426 \text{ K}$, $P_5 = 1.58 \text{ atm}$. On-line wavenumber = 3633.08 cm^{-1} ; Off-line wavenumber = 3633.25 cm^{-1} .

A. Farooq, D.F. Davidson, R.K. Hanson, L.K. Huynh, A. Violi
Proc. Combust. Inst. 32 (2009) 247–253.



Laser absorption measurements

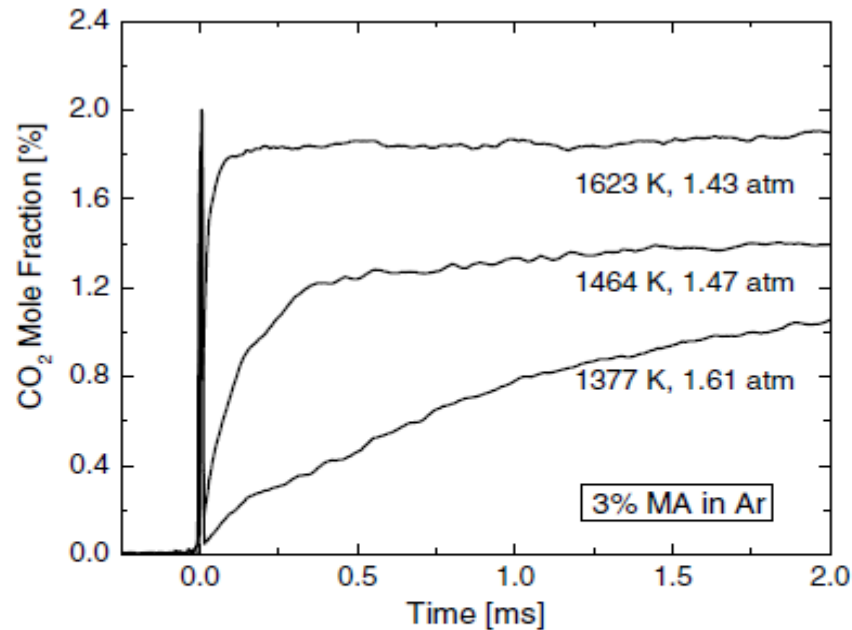


Fig. 3. Measured CO_2 time-histories behind reflected shock waves (T_5 , P_5 shown) for methyl acetate pyrolysis (3% MA in Ar).

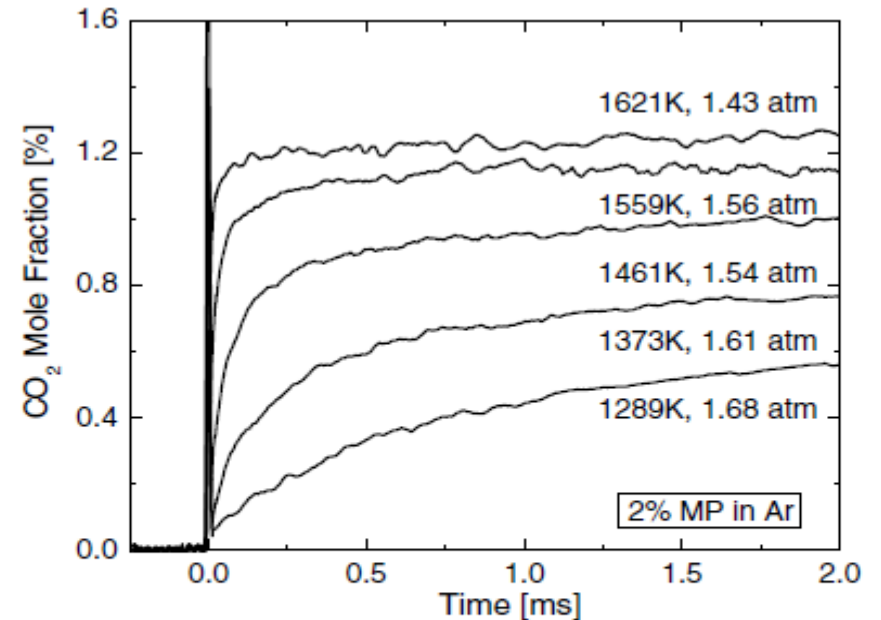


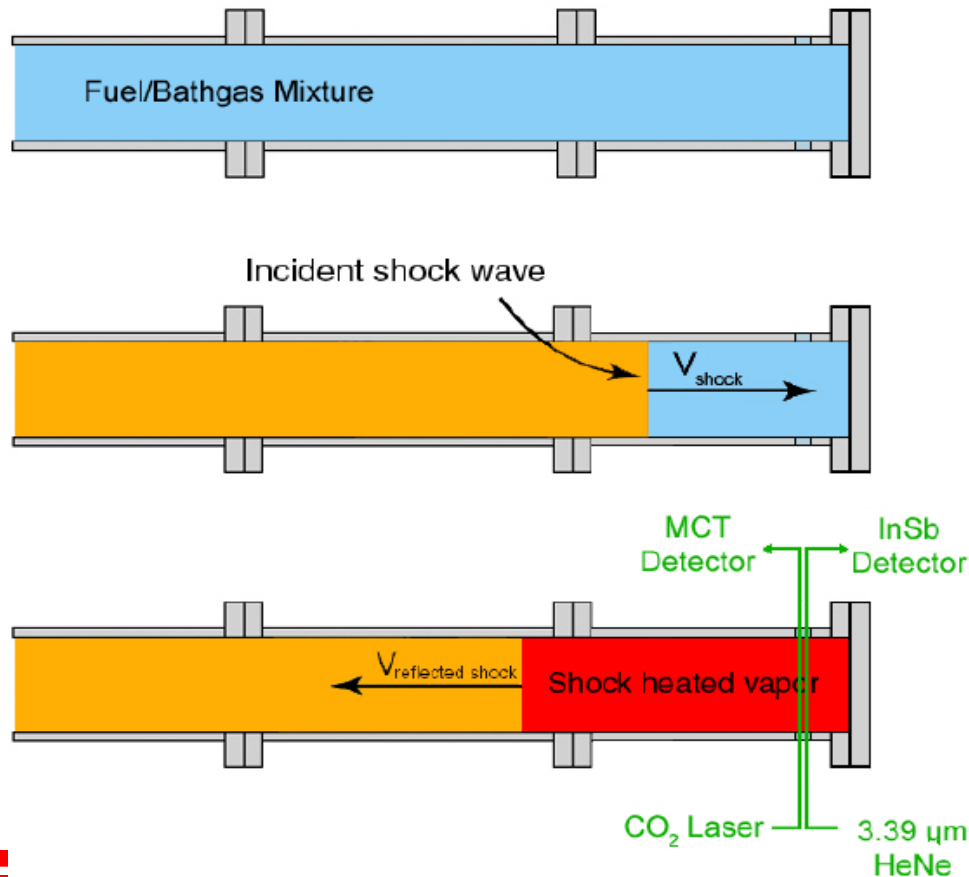
Fig. 4. Measured CO_2 time-histories behind reflected shock waves (T_5 , P_5 shown) for methyl propionate pyrolysis (2% MP in Ar).

A. Farooq, D.F. Davidson, R.K. Hanson, L.K. Huynh, A. Violi
Proc. Combust. Inst. 32 (2009) 247–253.

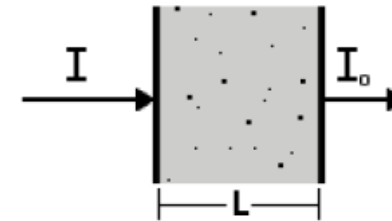


Laser absorption measurements

- Fuel measurement at $3.39\text{ }\mu\text{m}$
- C_2H_4 measurement at $10.5\text{ }\mu\text{m}$



Beer's Law



$$\frac{I}{I_o} = \exp(-\sigma NL)$$

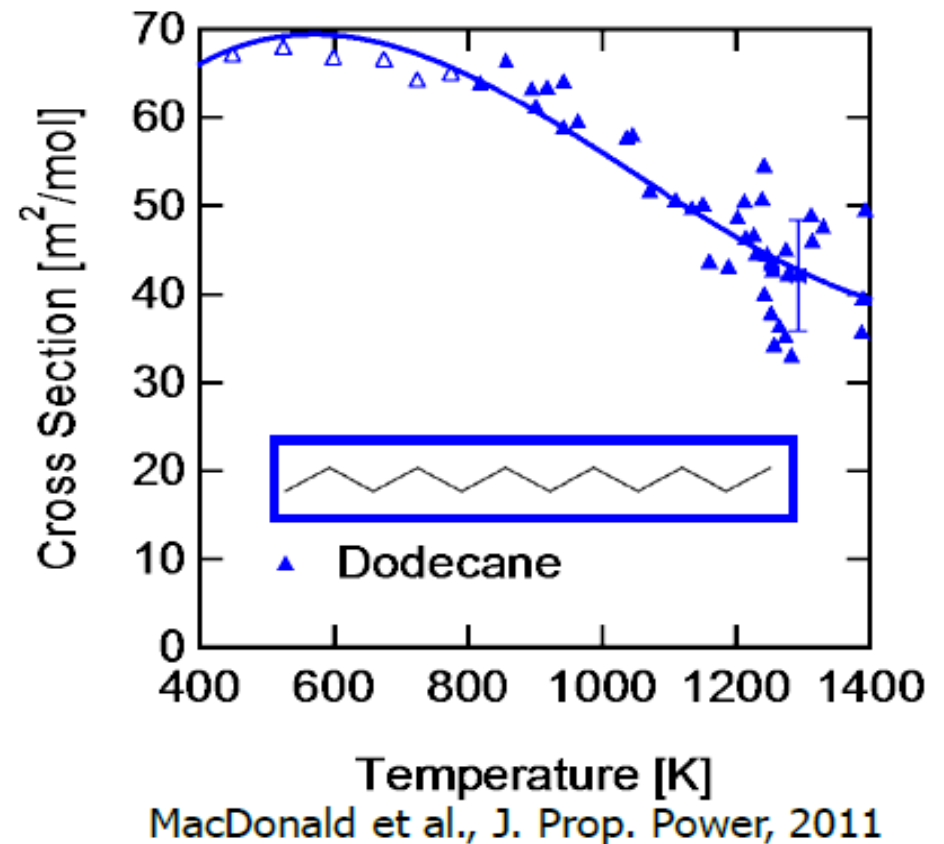
Absorption cross section





IR Fuel Diagnostic ($3.39\ \mu\text{m}$)

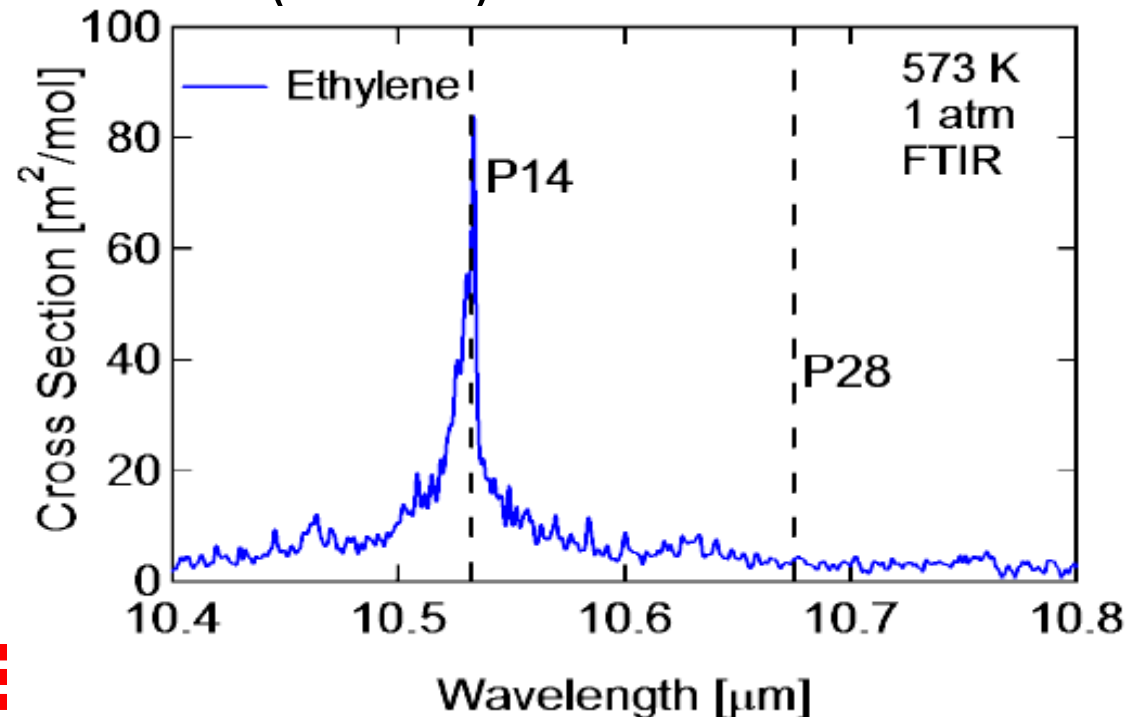
- $3.39\ \mu\text{m}$ strongly absorbed by all HC fuels
- Beer's Law + Absorption cross sections $\rightarrow$ Fuel mole fraction
- **Need fuel cross section at $3.39\ \mu\text{m}$**





IR Ethylene Diagnostic (10.5 μm)

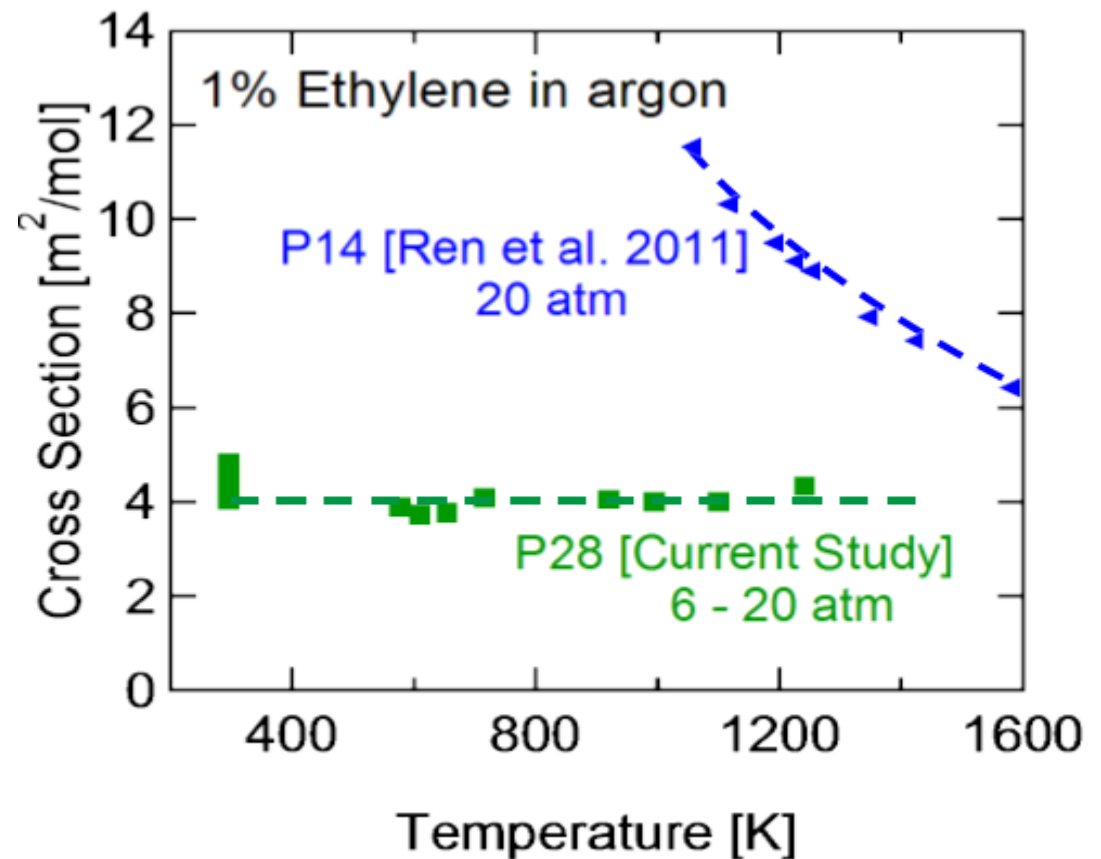
- CO_2 gas laser P14 line is strongly absorbed by C_2H_4
 - but also other alkenes
- Need to measure two wavelengths
 - 10.532 μm P14 line (on-line)
 - 10.675 μm P28 line (off-line)





IR Ethylene Diagnostic (10.5 μm)

- **Need ethylene cross sections at both lines**
- Other alkenes absorb at 10.5 μm
- Interfering species have a constant cross section
- Differential absorption at 2 wavelengths permits isolation of C_2H_4 absorption

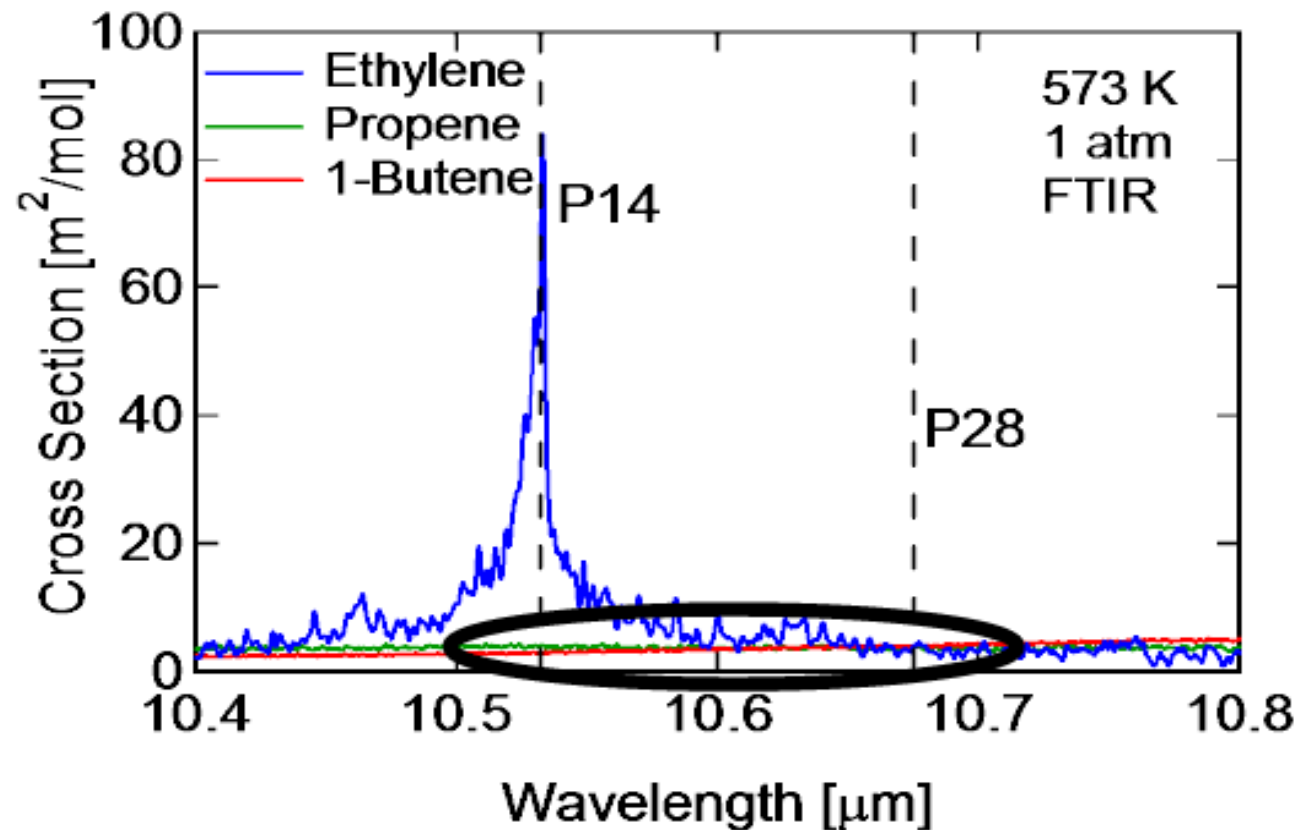


Need to check cross sections of interfering species to ensure they are constant at 10.5 μm



Cross sections of interfering species

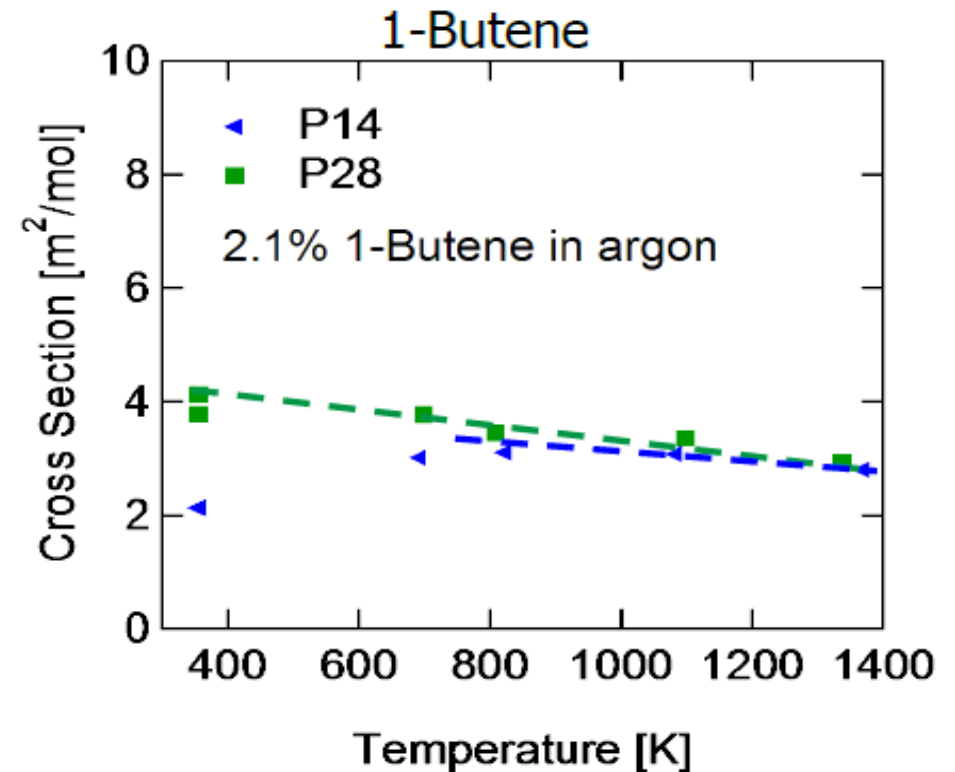
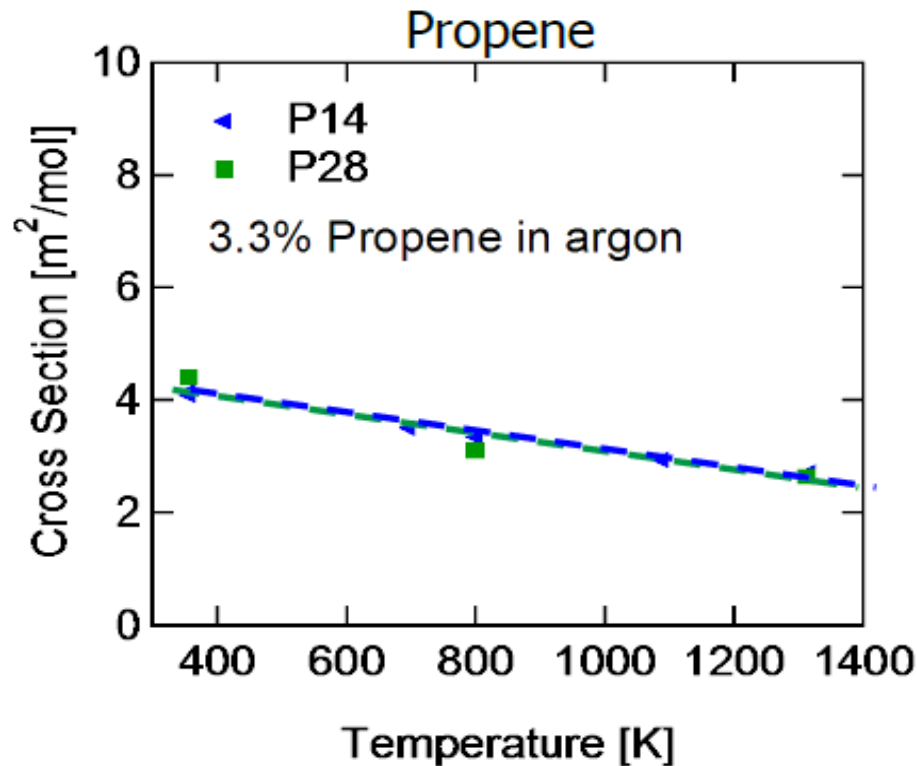
- Small absorption by propene and 1-butene





Cross sections of interfering species

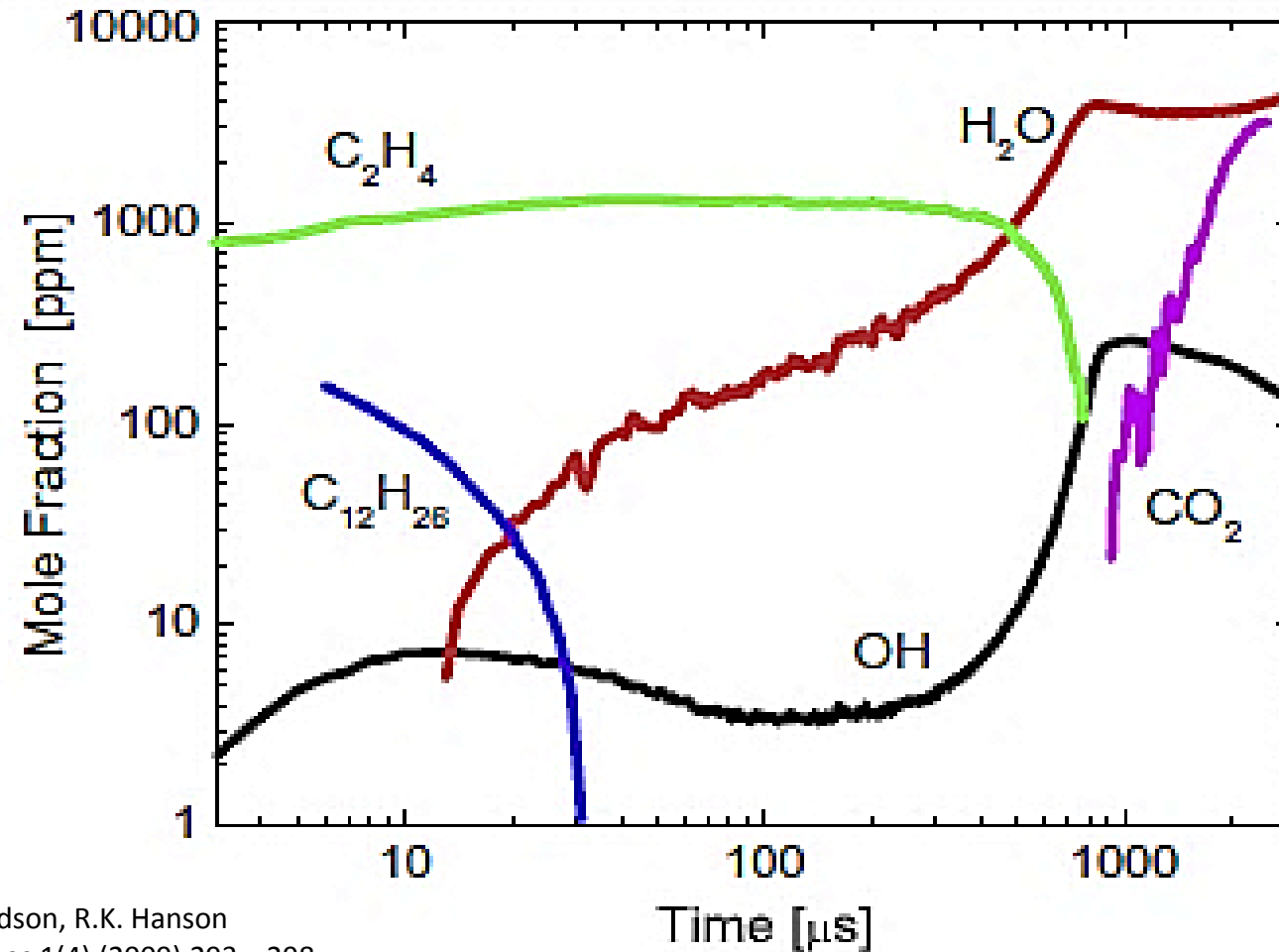
- Small absorption by propene and 1-butene with nearly constant cross-sections at P14 and P28





Species time-history measurements

457 ppm *n*-Dodecane/O₂/Argon
 $\phi = 1.0$, 1410 K, 2.3 atm



S.S. Vasu, D.F. Davidson, R.K. Hanson
26th Intl. Symp. Shock Waves 1(4) (2009) 293–298.

KAUST Laser Sensors Laboratory



Other diagnostics available in our laboratory:

Species	Laser	Wavelength
OH	Ring-Dye w/ external doubling	306 nm
CH ₂ O	Difference-frequency-generation laser	3.6 μm
CO ₂	Quantum-cascade laser (QCL)	4.3 μm
N ₂ O	Quantum-cascade laser (QCL)	4.5 μm
CO	Quantum-cascade laser (QCL)	4.6 μm
H ₂ O	Quantum-cascade laser (QCL)	7.6 μm
H ₂ O ₂	Quantum-cascade laser (QCL)	7.7 μm
CH ₄	Quantum-cascade laser (QCL)	7.7 μm
C ₂ H ₂	Quantum-cascade laser (QCL)	7.8 μm
NH ₃	Quantum-cascade laser (QCL)	9.0 μm
C ₂ H ₄	Quantum-cascade laser (QCL)	10.5 μm
C ₂ H ₂	Quantum-cascade laser (QCL)	13.3 μm



Laser absorption measurements

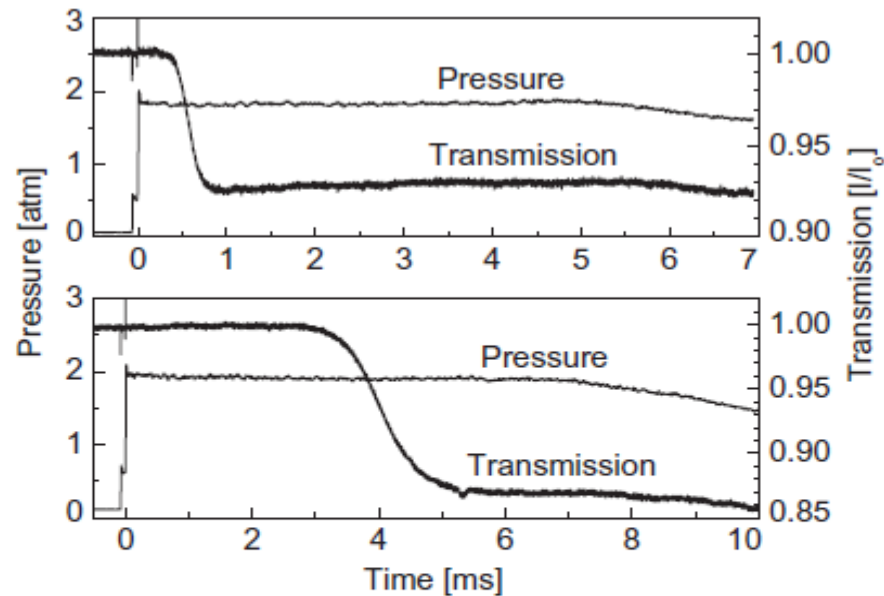


Fig. 1. Typical pressure and laser transmission histories in reflected-shock experiments: (a. upper) 0.1% O₂, 0.9% H₂, 99% Ar, 1472 K, 1.83 atm; (b. lower) 0.1% O₂, 2.9% H₂, 97% Ar, 1100 K, 1.95 atm.

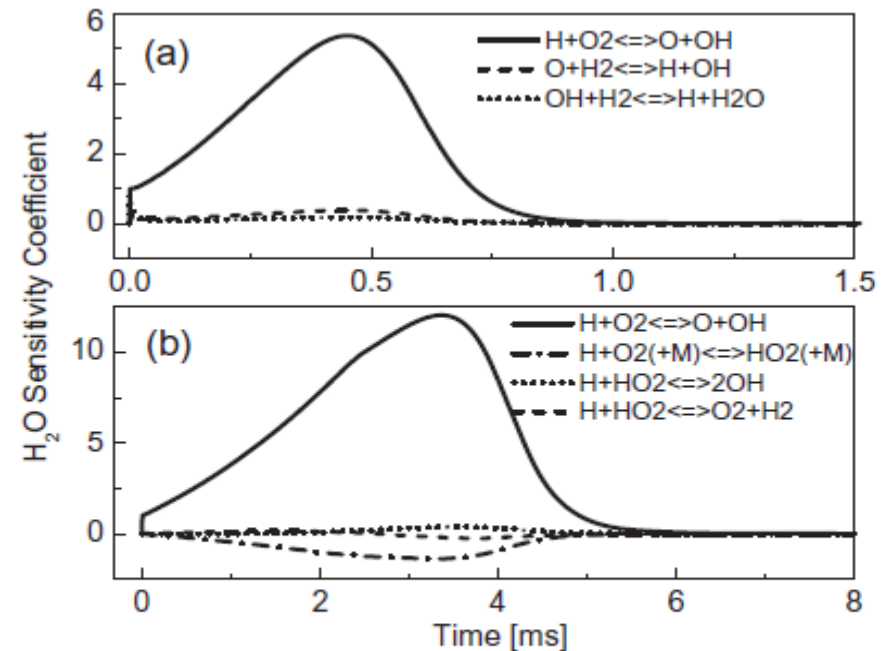


Fig. 2. H₂O sensitivity plot at conditions of the corresponding panels of Fig. 1.

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



Laser absorption measurements

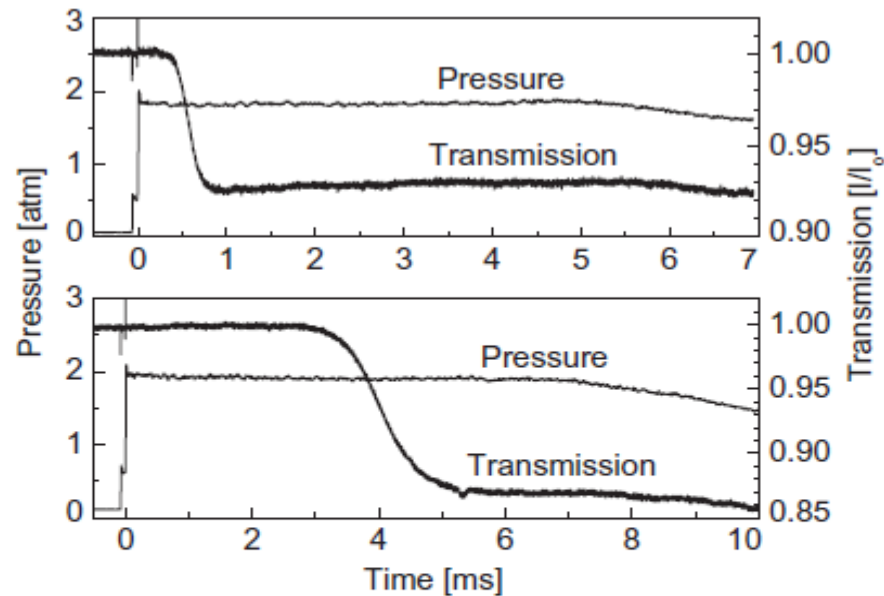


Fig. 1. Typical pressure and laser transmission histories in reflected-shock experiments: (a. upper) 0.1% O₂, 0.9% H₂, 99% Ar, 1472 K, 1.83 atm; (b. lower) 0.1% O₂, 2.9% H₂, 97% Ar, 1100 K, 1.95 atm.

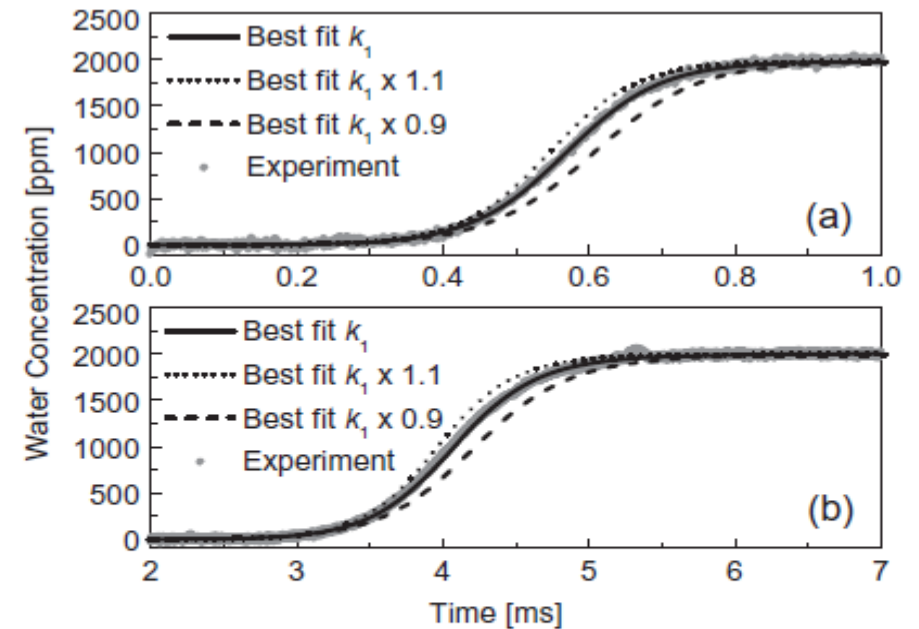
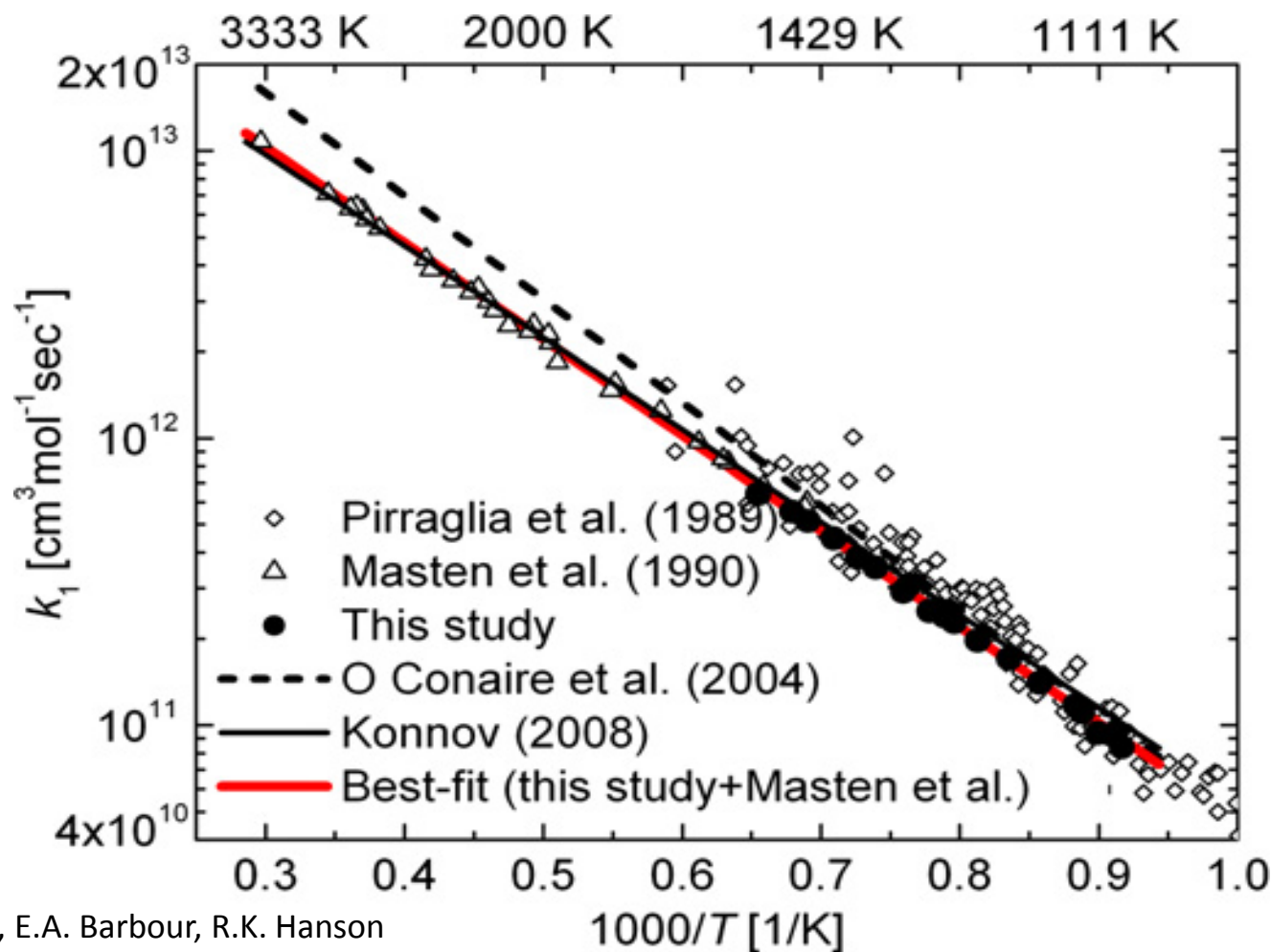
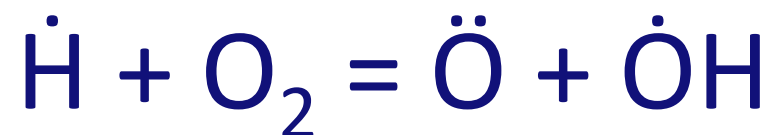


Fig. 3. Comparison of experimental and Senkin calculated H₂O profiles using best-fit k_1 with effect of $\pm 10\%$ variation on k_1 at conditions of the corresponding panels of Fig. 1.

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



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

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



Conclusions

- ST and RCM are complementary
- Understanding the kinetics of fuel oxidation
 - Ignition delay times
 - Speciation data
 - Elementary rate coefficients



Generation of Detailed Chemical Kinetic Models for C_0 – C_2 Hydrocarbon and Oxygenated Fuels



Experimental Studies: Engine Relevant



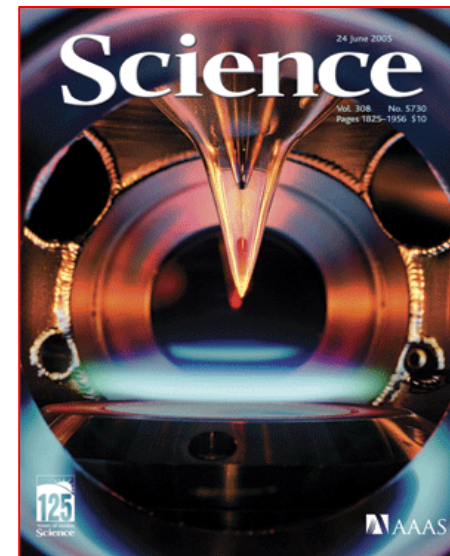
Rapid Compression Machine



Shock Tube



Jet Stirred Reactor

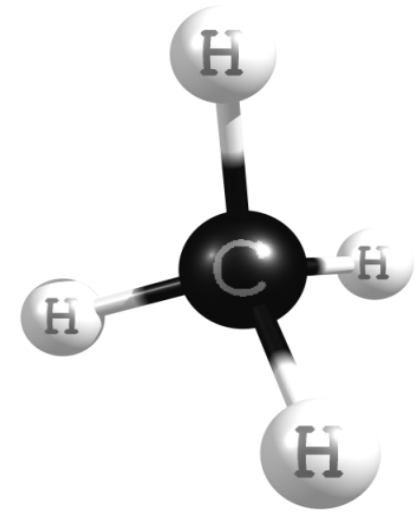


Flat Flame Burner



Chemical Modeling

- Fuel + O₂ -> CO₂ + H₂O + Energy
- Small hydrocarbon fuel (e.g. methane)
 - 200 reactions
 - 30 chemical intermediates
- Chemical mechanism
 - Kinetics
 - Thermodynamics





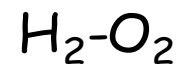
Visualization of fuel consumption





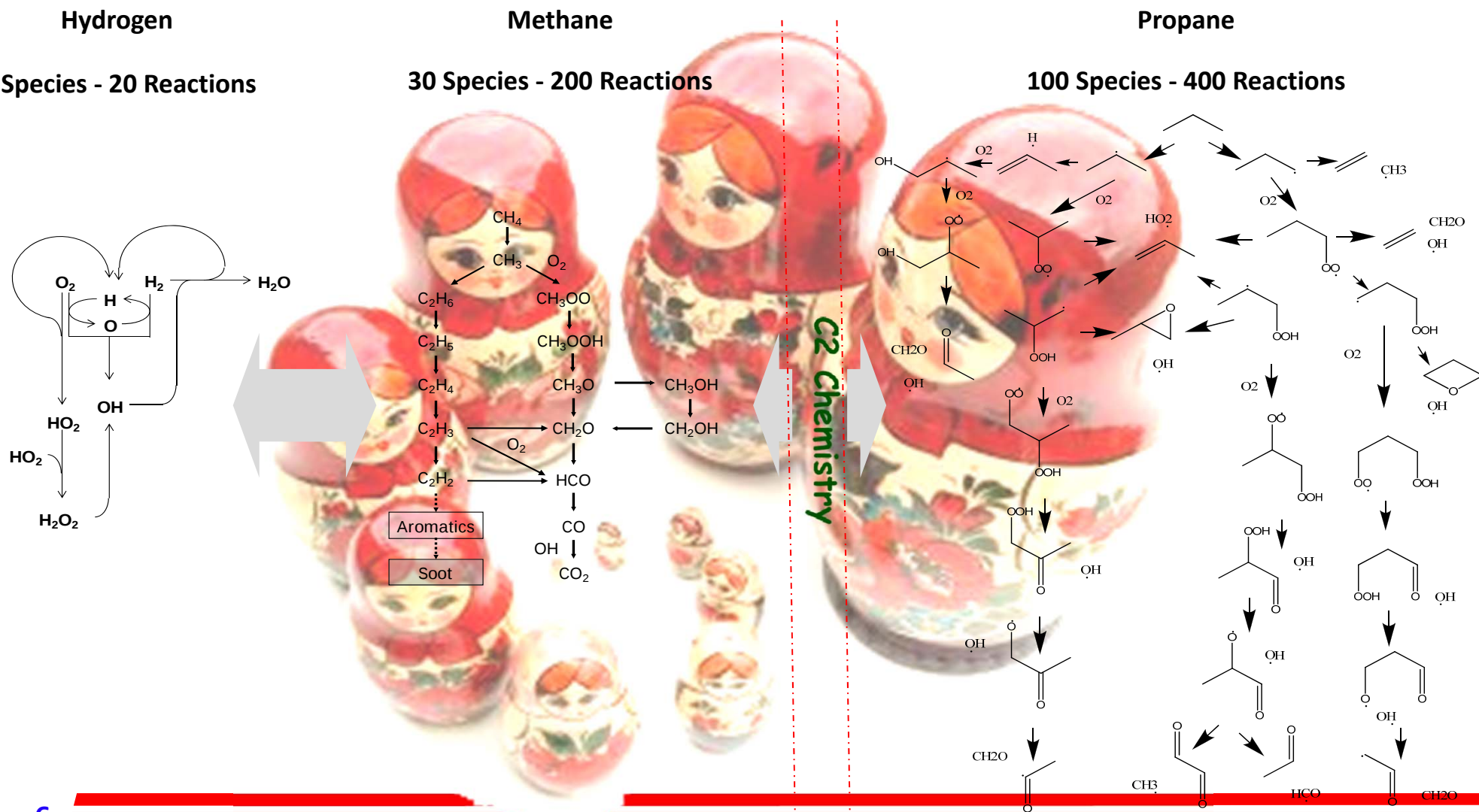
Hierarchical structure

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





What does a mechanism look like?





Mechanism for Syngas Combustion

Combustion and Flame 160 (2013) 995–1011



Contents lists available at SciVerse ScienceDirect

Combustion and Flame

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



An experimental and detailed chemical kinetic modeling study of hydrogen and syngas mixture oxidation at elevated pressures

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^b Case Western Reserve University, Department of Mechanical & Aerospace Engineering, Cleveland, OH 44106, USA

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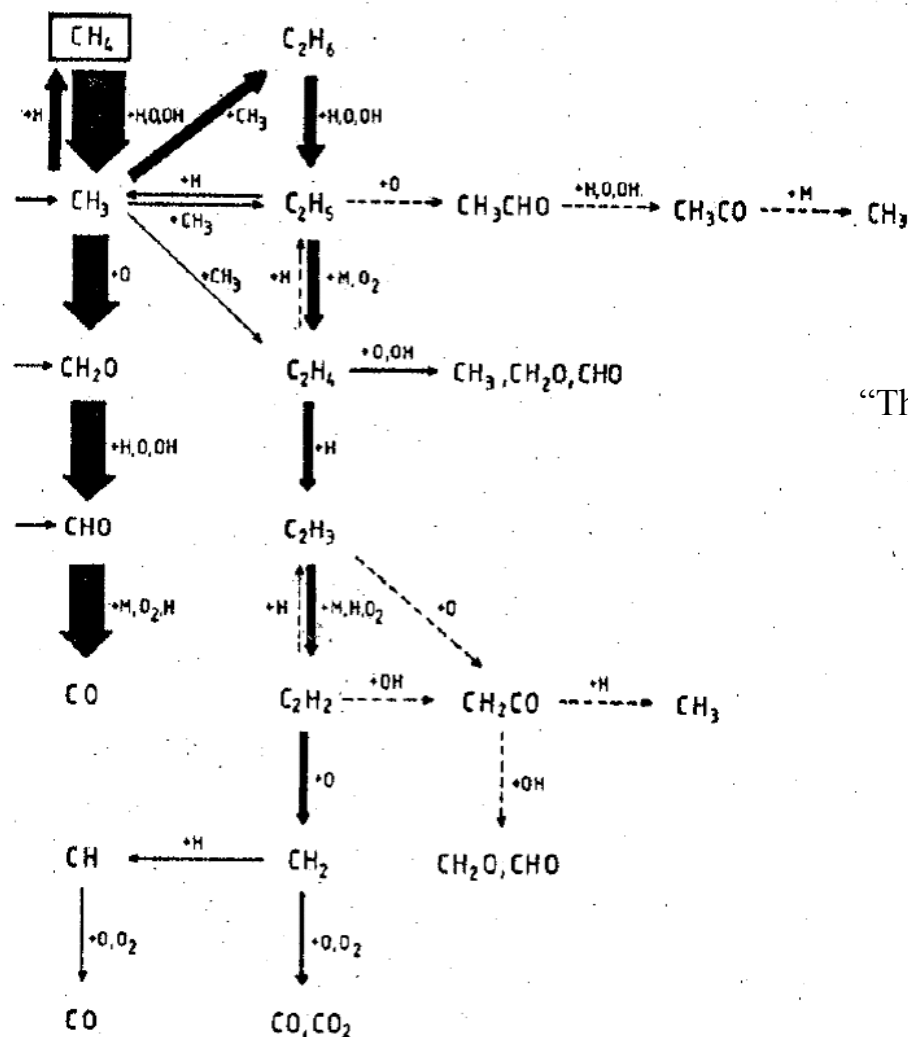
^f Lawrence Livermore National Laboratory, Livermore, CA 94551, USA

Table 1
Detailed H₂-CO reaction mechanism (units: cm³/mol/s/cal).

#	Reaction	A	n	E _A	Ref.
1	H + O ₂ = O + OH	1.040E+14	0.00	1.529E+04	[25]
2	O + H ₂ = H + OH	5.080E+04	2.67	6.292E+03	[90]
3	OH + H ₂ = H + H ₂ O	4.380E+13	0.00	6.990E+03	[47]
4	O + H ₂ O = OH + OH	2.970E+06	2.02	1.340E+04	[91]
5	H ₂ + M = H + H + M ε _{H₂} = 2.5, ε _{H₂O} = 12, ε _{CO} = 1.9, ε _{CO₂} = 3.8, ε _{He} = 0.83	4.577E+19	-1.40	1.044E+05	[36]
6	O + O + M = O ₂ + M ε _{H₂} = 2.5, ε _{H₂O} = 12, ε _{CO} = 1.9, ε _{CO₂} = 3.8, ε _{Ar} = 0.83, ε _{He} = 0.83	6.165E+15	-0.50	0.00	[36]
7	O + H + M = OH + M ε _{H₂} = 2.5, ε _{H₂O} = 12, ε _{CO} = 1.5, ε _{CO₂} = 2.0, ε _{Ar} = 0.75, ε _{He} = 0.75	4.714E+18	-1.00	0.00	[36]
8	H + OH + M = H ₂ O + M ε _{H₂} = 0.73, ε _{H₂O} = 3.65, ε _{Ar} = 0.38, ε _{He} = 0.38, ε _{CO} = 1.9, ε _{CO₂} = 3.8	3.500E+22	-2.00	0.00	[7] × 0.92
9	H + O ₂ (+M) = HO ₂ (+M) ^a Low-pressure limit ε _{H₂} = 1.3, ε _{H₂O} = 10, ε _{CO} = 1.9, ε _{CO₂} = 3.8, ε _{Ar} = 0.0, ε _{He} = 0.0	4.65E+12 1.737E+19	0.44 -1.23	0.00 0.00	[24] [24]
	H + O ₂ (+Ar) = HO ₂ (+Ar) ^b Low-pressure limit	4.65E+12 6.81E+18	0.44 -1.20	0.00 0.0	[24] [26]
	H + O ₂ (+He) = HO ₂ (+He) ^c Low-pressure limit	4.65E+12 9.19E+18	0.44 -1.20	0.00 0.0	[24] [24] × 1.5
10	H ₂ + O ₂ = H + HO ₂	5.176E+05	2.43	5.350E+04	[55] × 0.70
11	HO ₂ + H = OH + OH	7.079E+13	0.00	2.950E+02	[57]
12	HO ₂ + O = OH + O ₂	3.250E+13	0.00	0.0	[52]
13	HO ₂ + OH = H ₂ O + O ₂	2.456E+13	0.00	-4.970E+02	[51] × 0.85
14	HO ₂ + HO ₂ = H ₂ O ₂ + O ₂ HO ₂ + HO ₂ = H ₂ O ₂ + O ₂	1.300E+11 3.658E+14	0.00 0.00	-1.630E+03 1.200E+04	[54] [54] × 0.87
15	H ₂ O ₂ (+M) = OH + OH (+M) ^d Low-pressure limit ε _{H₂} = 3.7, ε _{CO} = 2.8, ε _{CO₂} = 1.6, ε _{N₂} = 1.5, ε _{O₂} = 1.2 ε _{He} = 0.65, ε _{H₂O₂} = 7.7, ε _{H₂O} = 0.0	2.000E+12 2.490E+24	0.90 -2.30	4.875E+04 4.875E+04	[41] [41]
	H ₂ O ₂ (+H ₂ O) = OH + OH (+H ₂ O) ^e Low-pressure limit	2.000E+12 1.865E+25	0.90 -2.30	4.875E+04 4.875E+04	[41] [41]
16	H ₂ O ₂ + H = H ₂ O + OH	2.410E+13	0.00	3.970E+03	[36]
17	H ₂ O ₂ + H = H ₂ + HO ₂	2.150E+10	1.00	6.000E+03	[37]
18	H ₂ O ₂ + O = OH + HO ₂	9.550E+06	2.00	3.970E+03	[36]
19	H ₂ O ₂ + OH = H ₂ O + HO ₂ H ₂ O ₂ + OH = H ₂ O + HO ₂	1.740E+12 7.590E+13	0.00 0.00	3.180E+02 7.269E+03	[40] [40]
20	CO + O (+M) = CO ₂ (+M) Low-pressure limit	1.362E+10 1.173E+24	0.00 -2.79	2.384E+03 4.191E+03	[59] × 0.75 [58] × 0.87

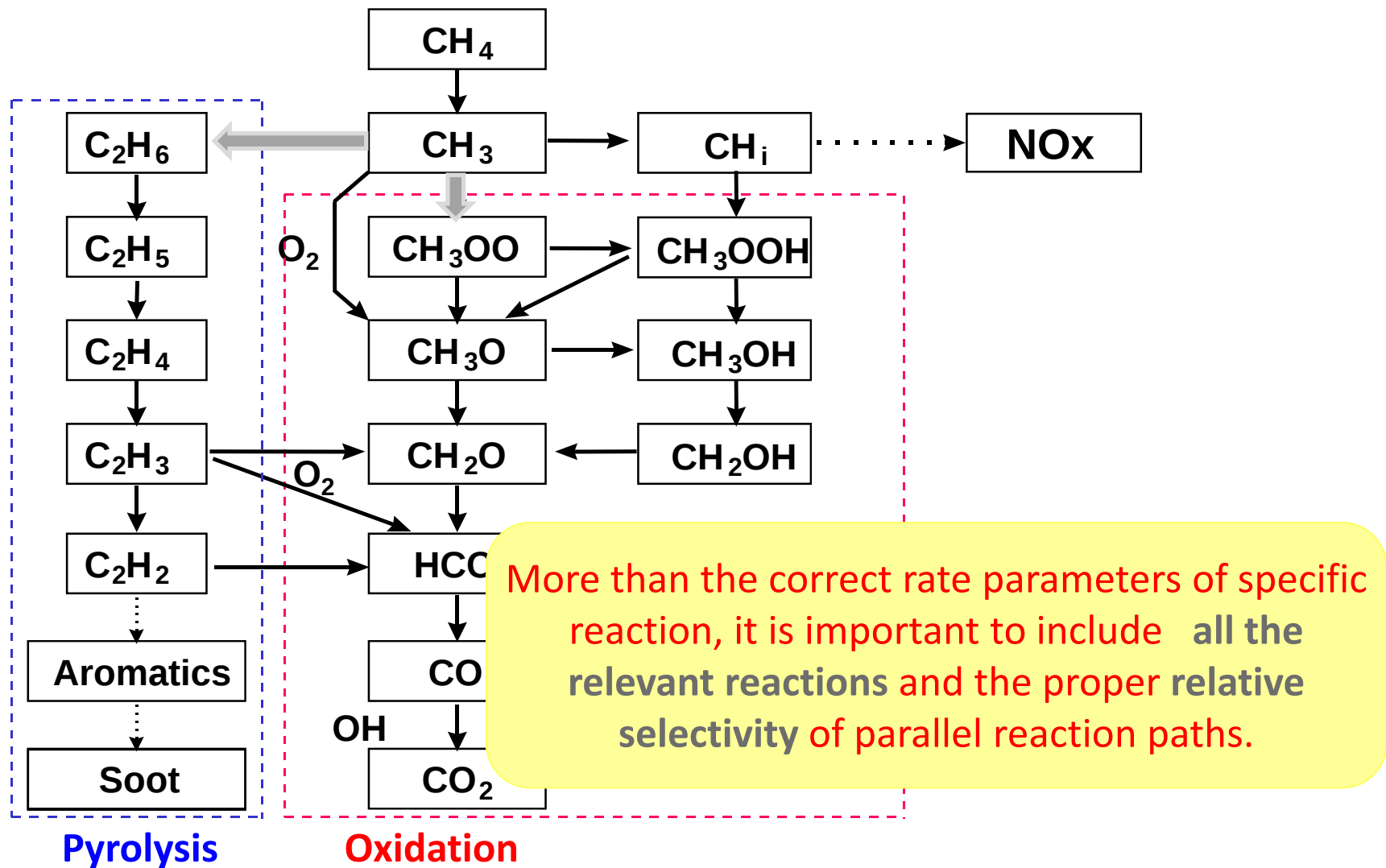


One of the most significant reaction flux diagrams in all of combustion chemistry



Warnatz, J.,
 "The Structure of Laminar Alkane-, Alkene-, and
 Acetylene Flames"
 18th Intl. Symp. Combust. (1981) 369–384.

Detailed Kinetics of Methane Combustion





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:
 - $\dot{\text{H}} + \text{O}_2 = \ddot{\text{O}} + \dot{\text{O}}\text{H}$
 - $\text{CO} + \dot{\text{O}}\text{H} = \text{CO}_2 + \dot{\text{H}}$



Reaction mechanism

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

Reaction			A_f	n_f	E_{a_f}	A_r	n_r	E_{a_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



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)

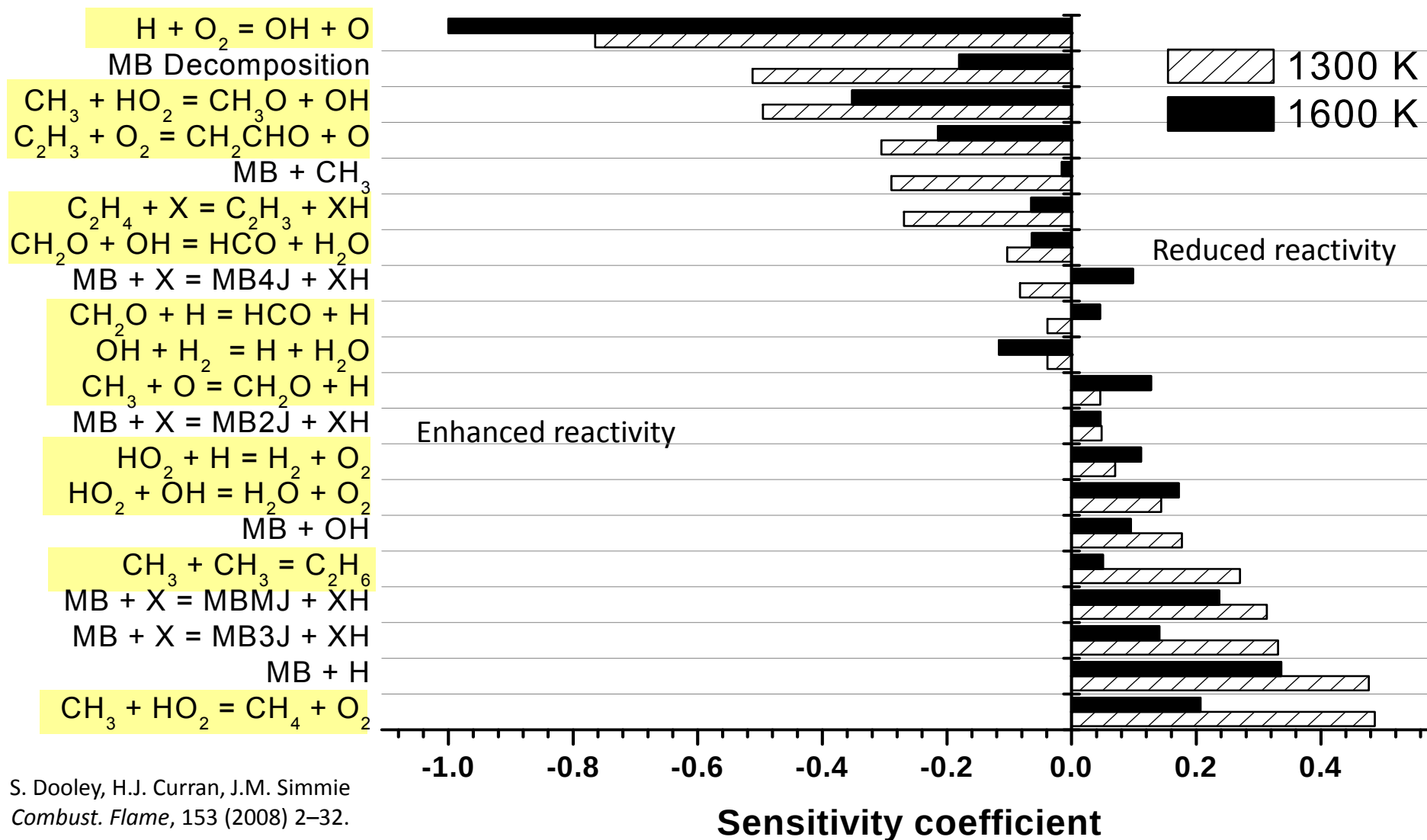
➤ On-line mechanisms:

- 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>



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



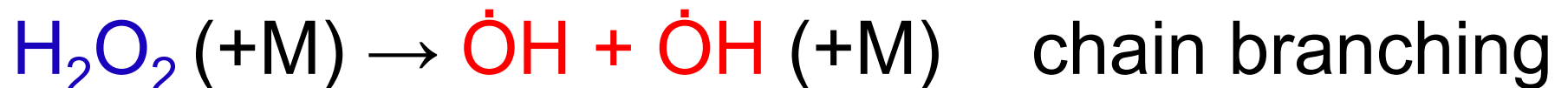
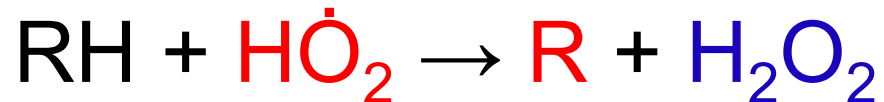
Range of validation

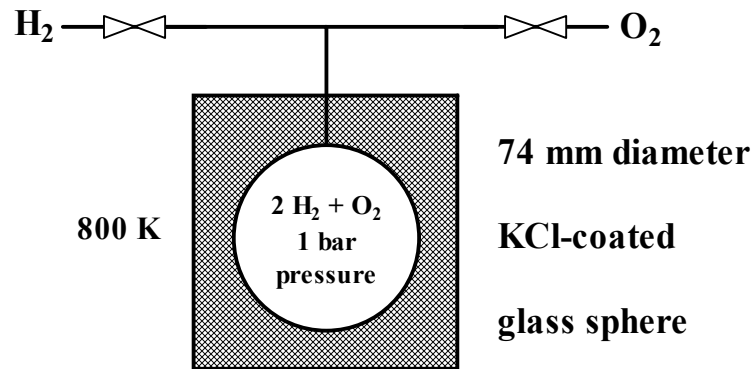
Fuel	Shock Tube	Jet-Stirred Reactor	Flow Reactor	Flame Speed	Flame Speciation
Methane	✓	✓	✓	✓	✓
Ethane	✓	✓		✓	
Ethylene	✓	✓	✓	✓	✓
Acetylene	✓		✓	✓	✓
Formaldehyde			✓		✓
Acetaldehyde	✓		✓		
Methanol	✓		✓	✓	
Ethanol	✓	✓	✓	✓	✓
Temperature / K	833—2500	800—1260	600—1400	295—600	300—2300
Pressure (atm)	0.65—260	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





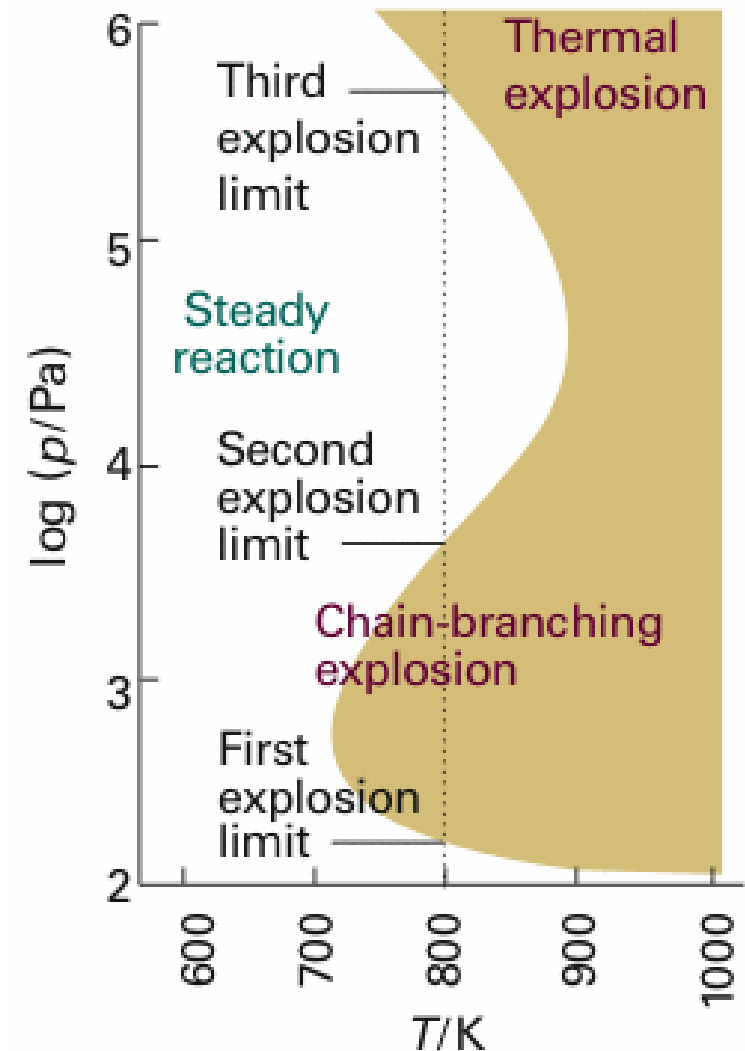
Focus on three distinct chain branching pathways





- $\text{H}_2 + \text{O}_2 \rightarrow \text{HO}_2^\bullet + \text{H}^\bullet$
- $\text{HO}_2^\bullet + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{HO}^\bullet$
- $\text{H}^\bullet + \text{O}_2 + \text{M} \rightarrow \text{HO}_2^\bullet + \text{M}$
- $\text{H}^\bullet + \text{O}_2 \rightarrow \text{HO}^\bullet + \text{O}^\bullet$
- $\text{H}^\bullet \Rightarrow \textit{diffuses to wall}$

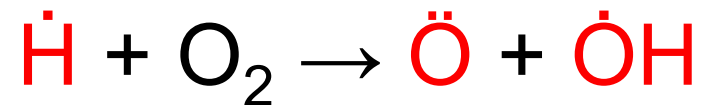
i
p
p
b
t





- **1st limit** (sensitive to surface, vessel shape & added inert gas)
 - Competition between branching and diffusion to wall of $\text{H}^\bullet$
 - **no explosion wall** $\leftarrow \text{H}^\bullet + \text{O}_2 \rightarrow \text{O}^\bullet + \text{OH}^\bullet$ **explosion**
- **2nd limit** (*not*)
 - Competition:
 - $\text{H}^\bullet + \text{O}_2 + \text{M} \rightarrow \text{HO}_2^\bullet + \text{M}$ **no explosion** third order
 - $\text{H}^\bullet + \text{O}_2 \rightarrow \text{O}^\bullet + \text{OH}^\bullet$ **explosion** second order
 - hydroperoxyl radical $\text{HO}_2^\bullet$ much less reactive than $\text{H}^\bullet$, $\text{OH}^\bullet$
- **3rd limit** (sensitive to vessel shape/size)
 - rate very fast, high rate of heat release, faster than can be conducted away $\Rightarrow$ *thermal explosion*
 - added gases have effect $\propto$ to their heat transport properties

Chain Branching at High Temperatures



The most important reaction in combustion

- Activation energy is relatively high (16.44 kcal/mol)
- $\dot{\text{H}}$ atoms produced by thermal decomposition of radicals (e.g. $\text{H}\dot{\text{C}}\text{O}$, $\dot{\text{C}}_2\text{H}_3$, $\dot{\text{C}}_2\text{H}_5$, $i\dot{\text{C}}_3\text{H}_7$ etc.)
activation energy relatively high (~ 30 kcal/mol)
- Therefore this sequence requires High T
- Illustrated best by shock tube experiments



Relative reactivity of fuels

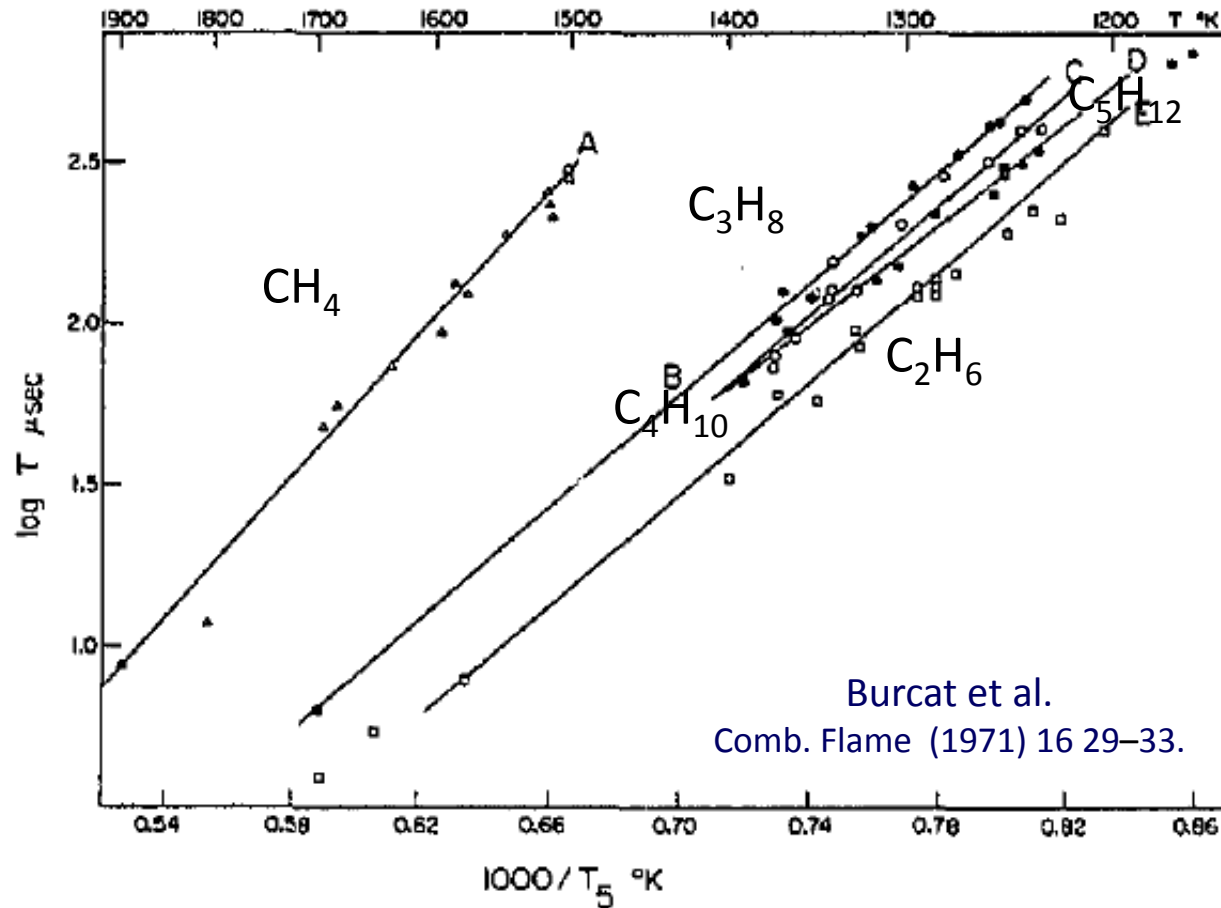
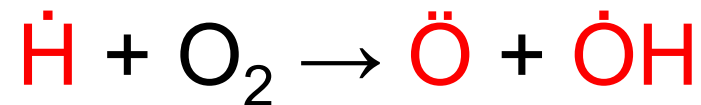


Figure 1. A plot of $\log \tau$ versus $1/T_5$ for five alkane-oxygen-argon mixtures; $p_1 \sim 185 \pm 15$ torr. A. 7.7% CH_4 + 15.4% O_2 ; B. 3.22% C_3H_8 + 16.1% O_2 ; C. 2.5% C_4H_{10} + 16.25% O_2 ; D. 2.04% C_5H_{12} + 16.3% O_2 ; E. 4.54% C_2H_6 + 15.91% O_2 .

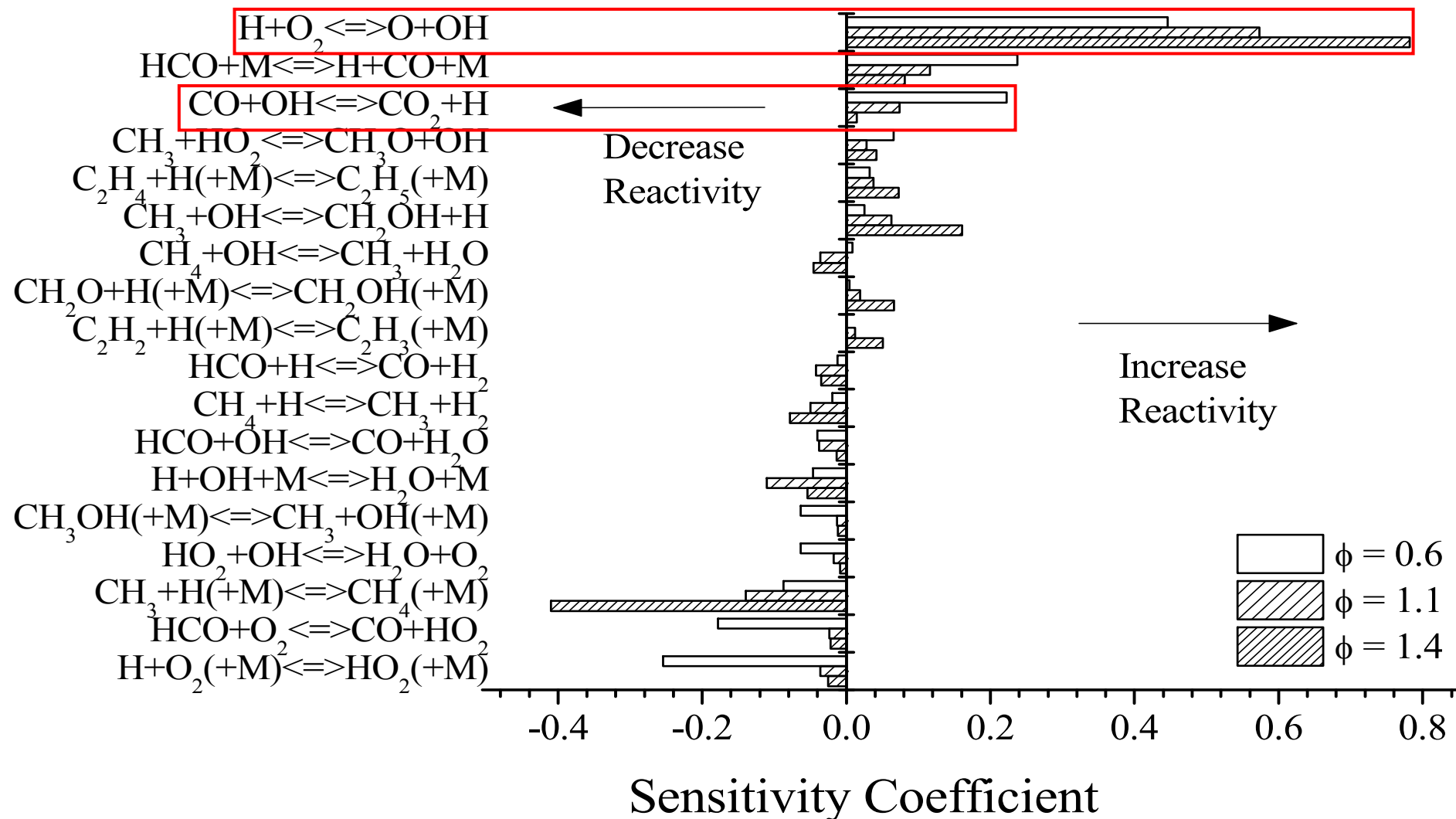
Chain Branching at High Temperatures

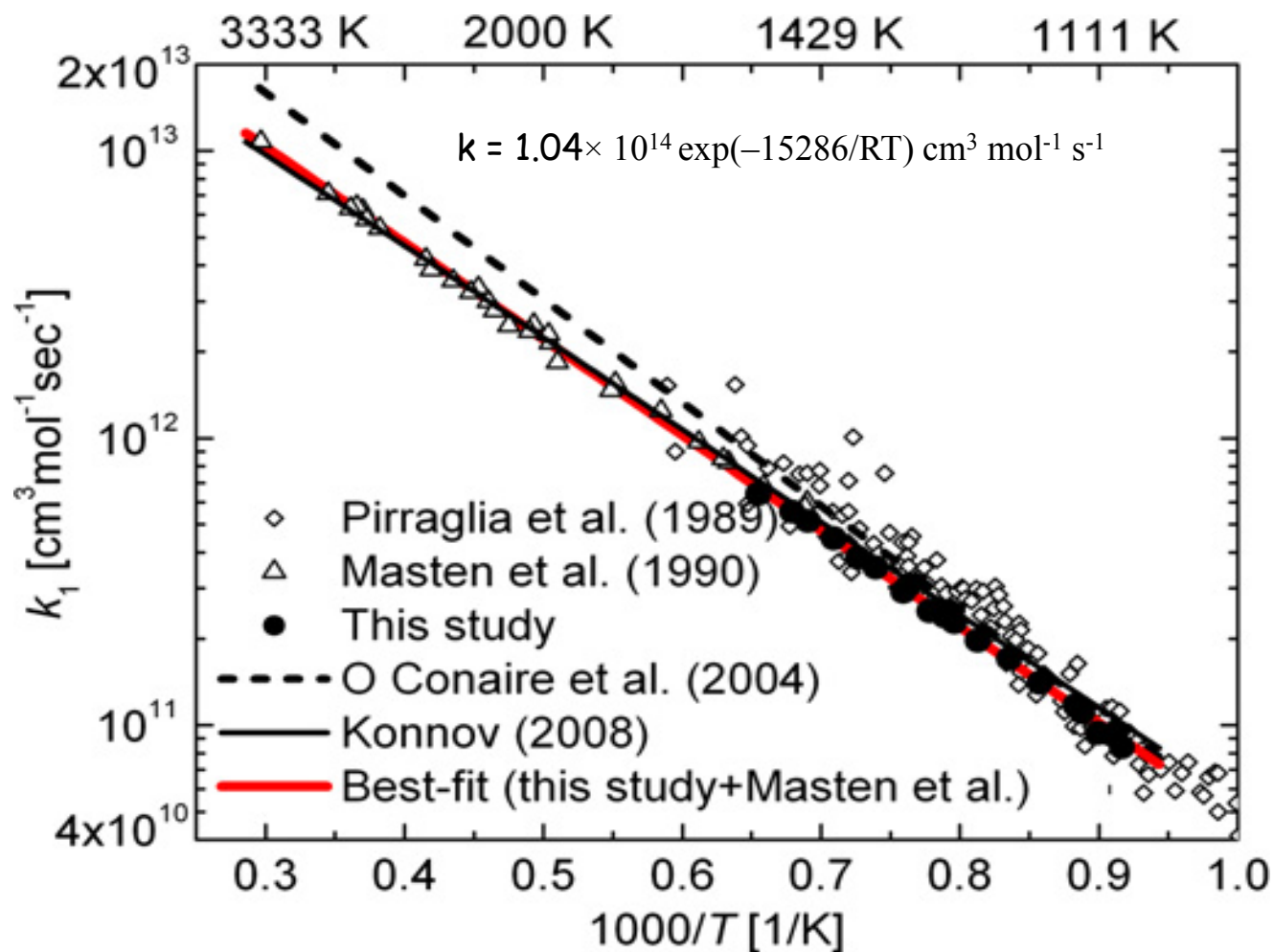
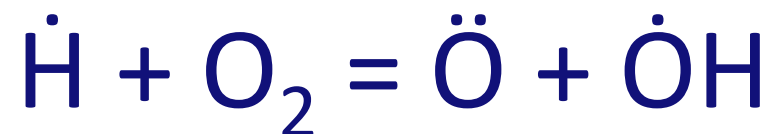


- Chain branching for oxidation, not for pyrolysis
- Lean mixtures ignite faster than rich mixtures
- Different fuels produce $\dot{\text{H}}$ atoms at different rates, their ignition rates vary correspondingly
- Additives that produce $\dot{\text{H}}$ atoms will accelerate ignition, those that remove $\dot{\text{H}}$ atoms slow ignition

Sensitivity Analysis—CH₄ Flame Speed

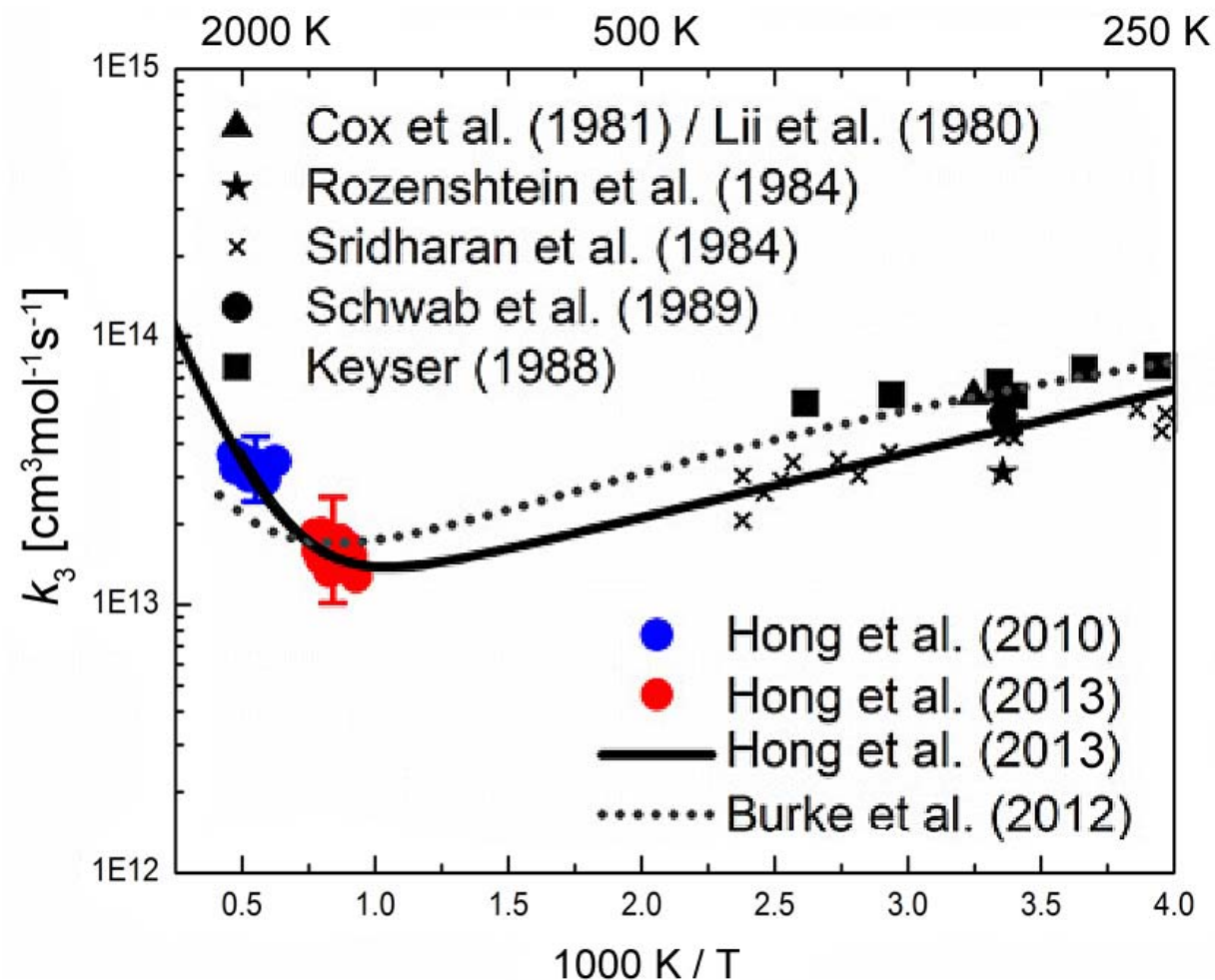
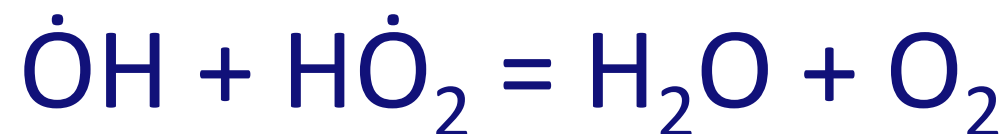
$p = 1.0 \text{ atm}, T_i = 298 \text{ K}$



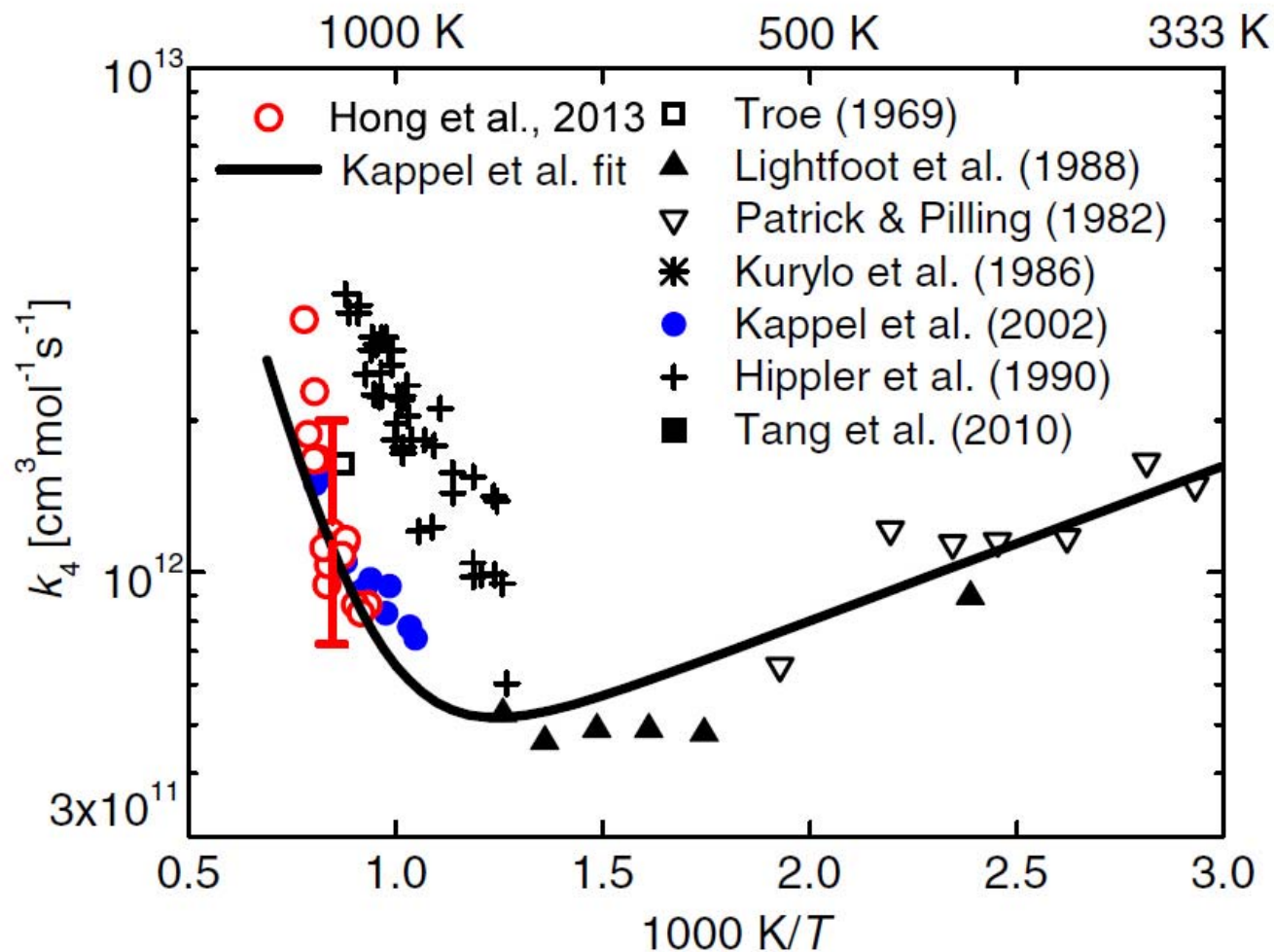
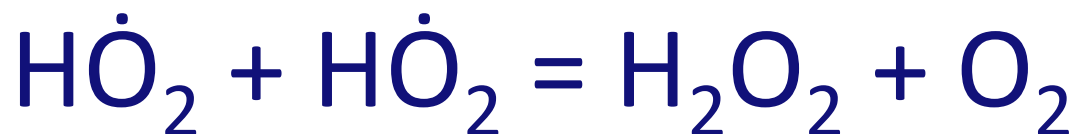


Z. Hong, D.F. Davidson, E.A. Barbour, R.K. Hanson
Proc. Combust. Inst. 33 (2011) 309–316.

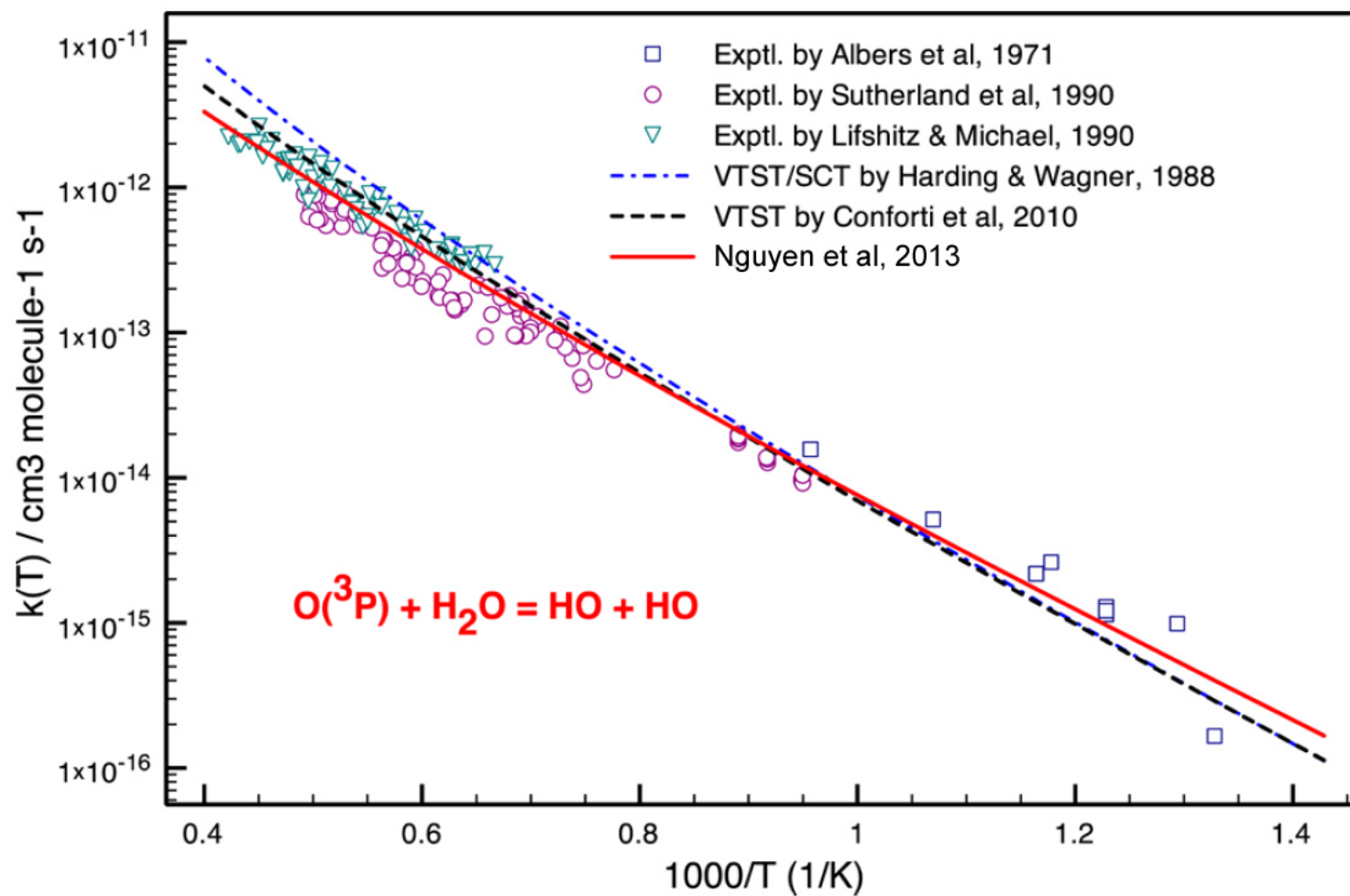
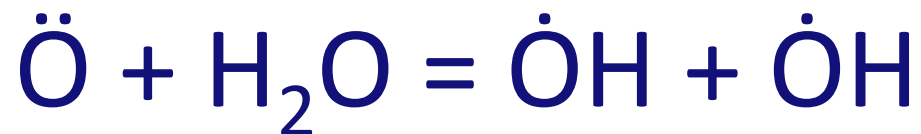




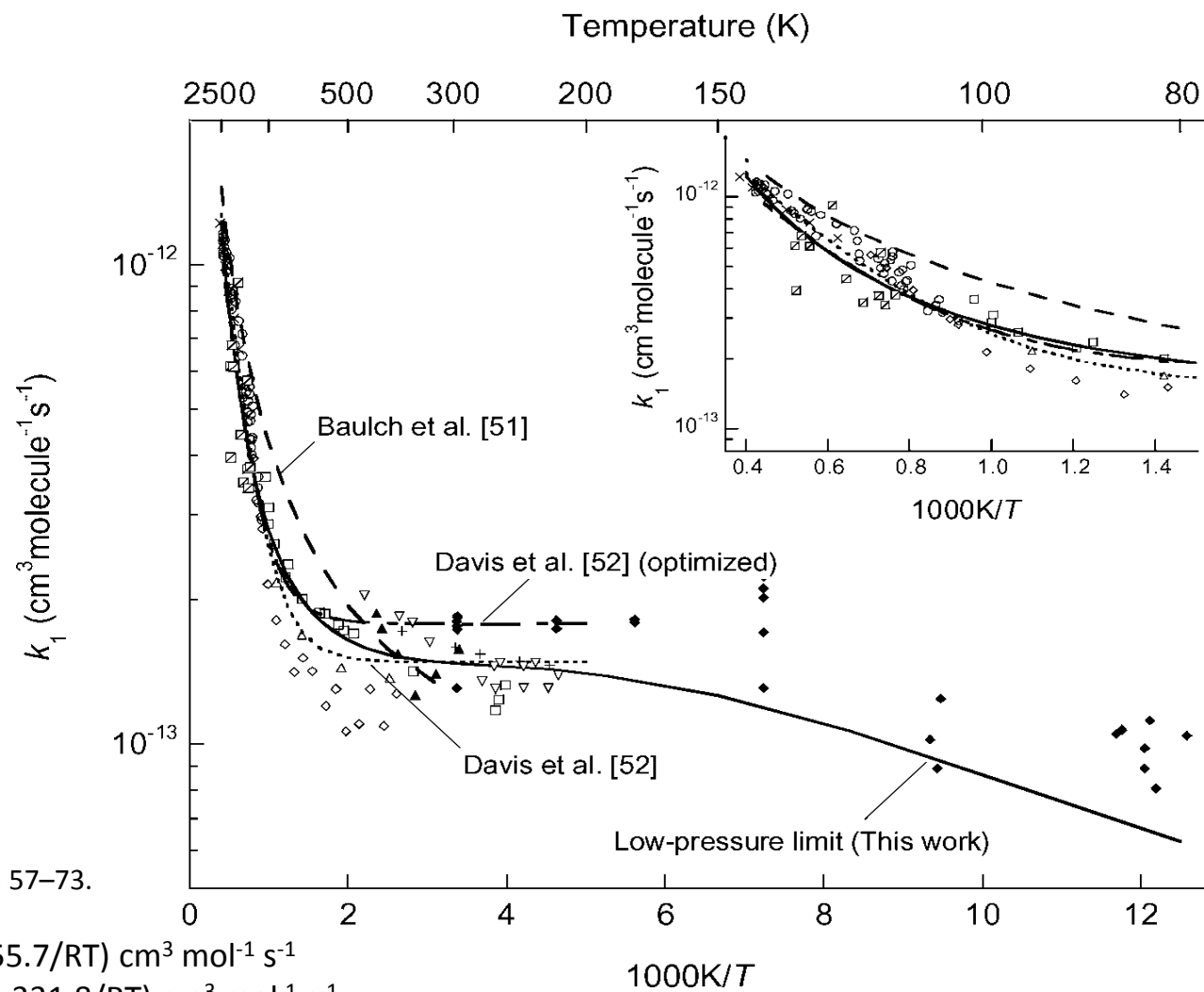
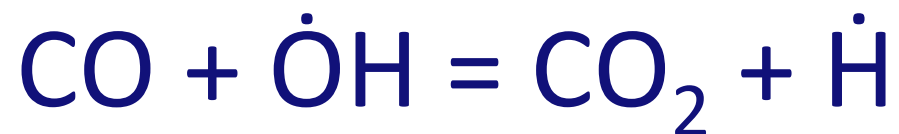
Z. Hong, K.-Y. Lam, R. Sur, S. Wang, D.F. Davidson, R.K. Hanson
Proc. Combust. Inst. 34 (2013) 565–571.



Z. Hong, K.-Y. Lam, R. Sur, S. Wang, D.F. Davidson, R.K. Hanson
 Proc. Combust. Inst. 34 (2013) 565–571.



Thanh Lam Nguyen and John F. Stanton
J. Phys. Chem. A 2013, 117, 2678–2686

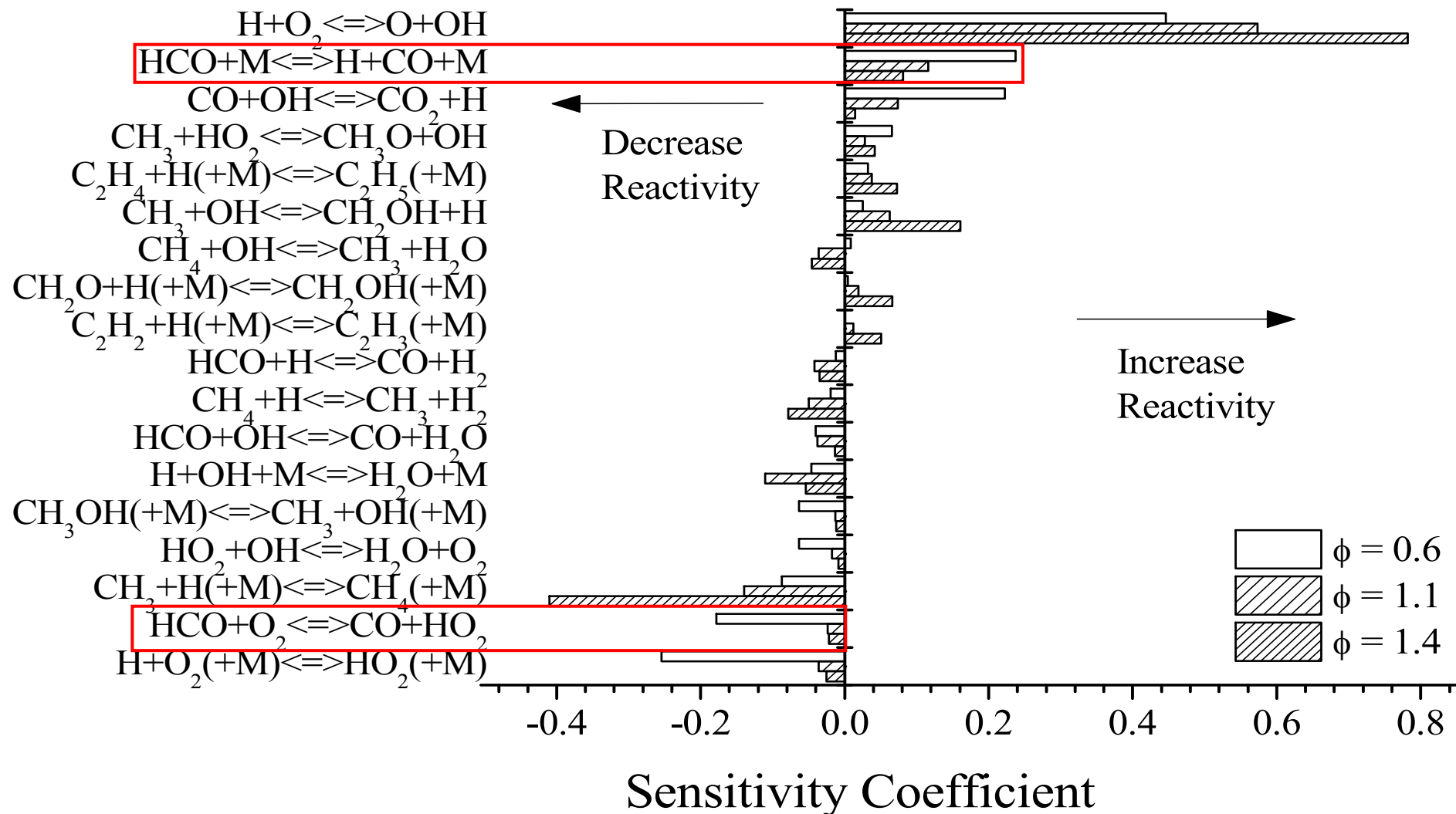


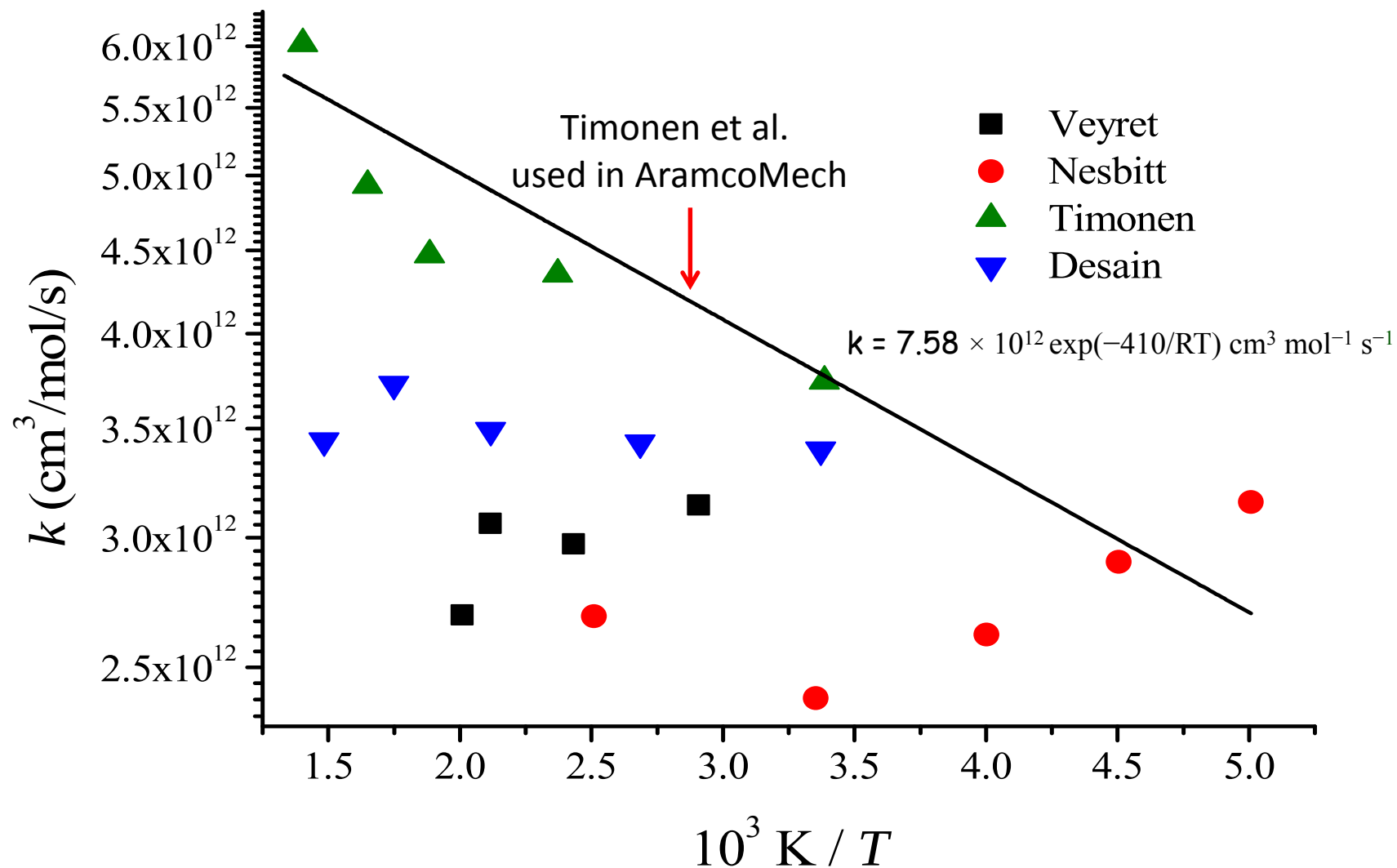
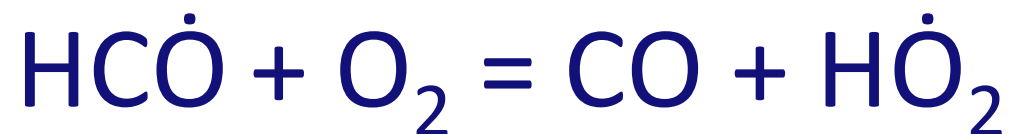
A.V. Joshi, H. Wang
Int. J. Chem. Kinet. 38 (1) (2006) 57–73.

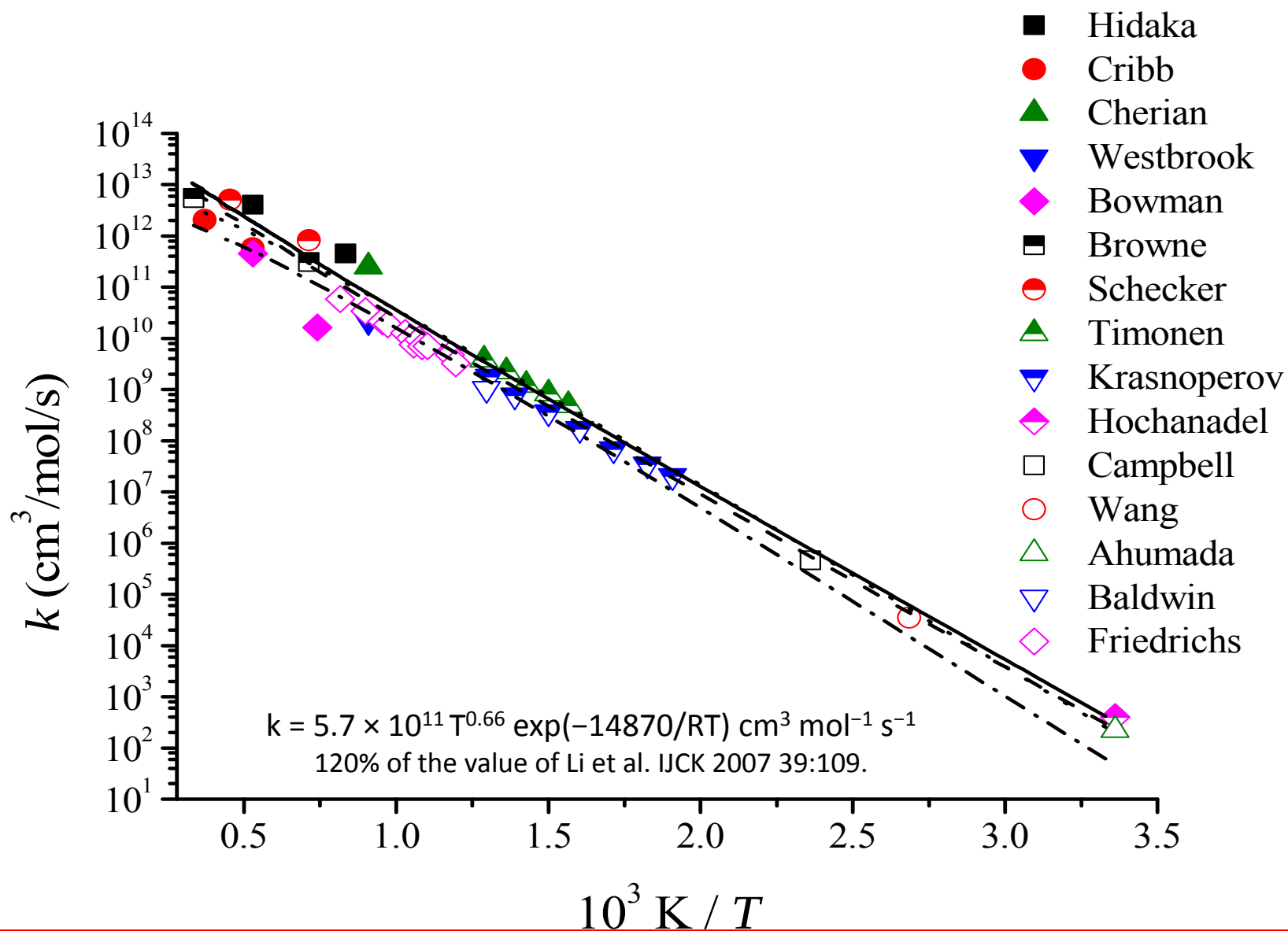
$$k = 7.015 \times 10^{14} T^{2.053} \exp(355.7/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \\ + 5.757 \times 10^{12} T^{-0.664} \exp(-331.8/RT) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Sensitivity Analysis—CH₄ Flame Speed

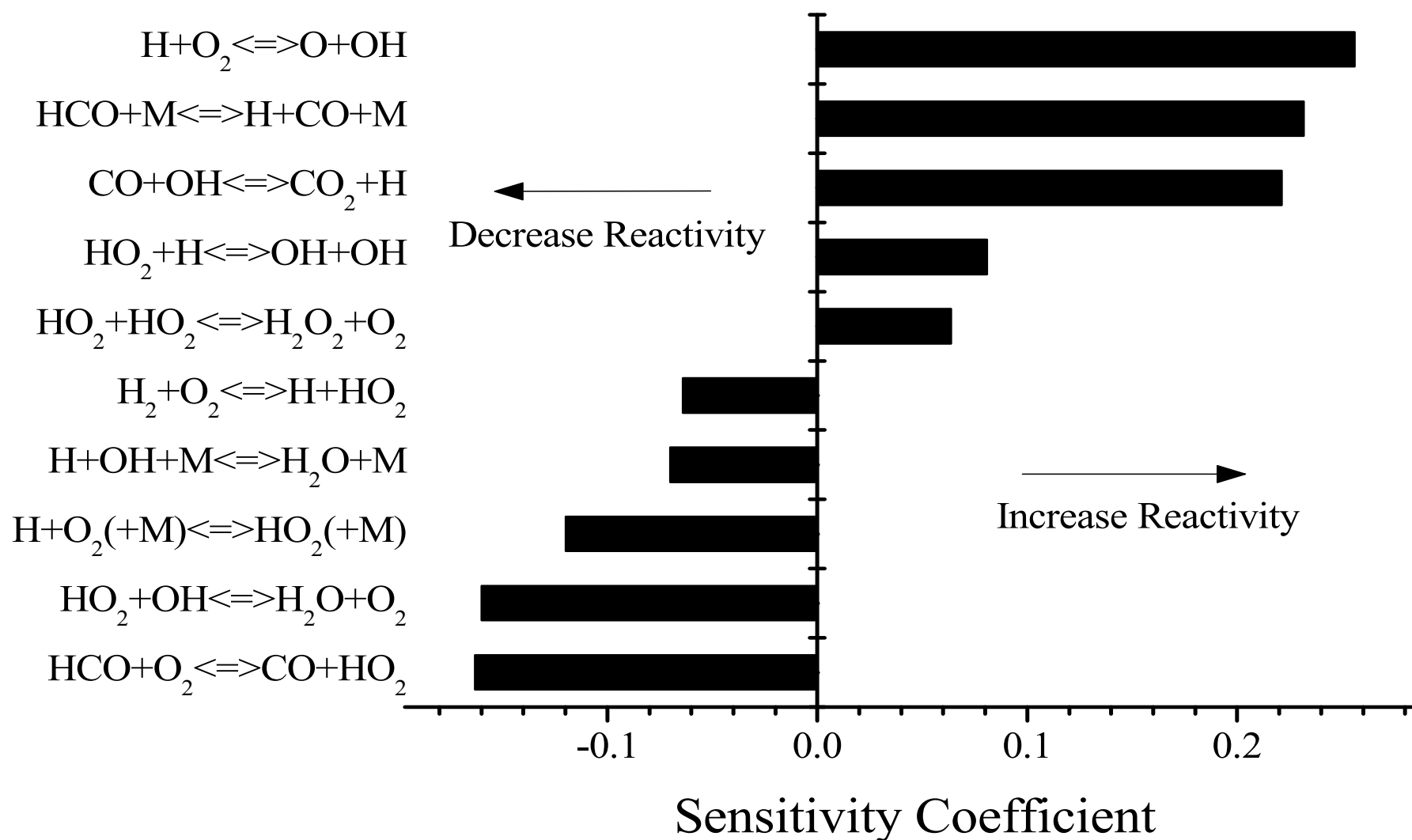
$p = 1.0 \text{ atm}, T_i = 298 \text{ K}$



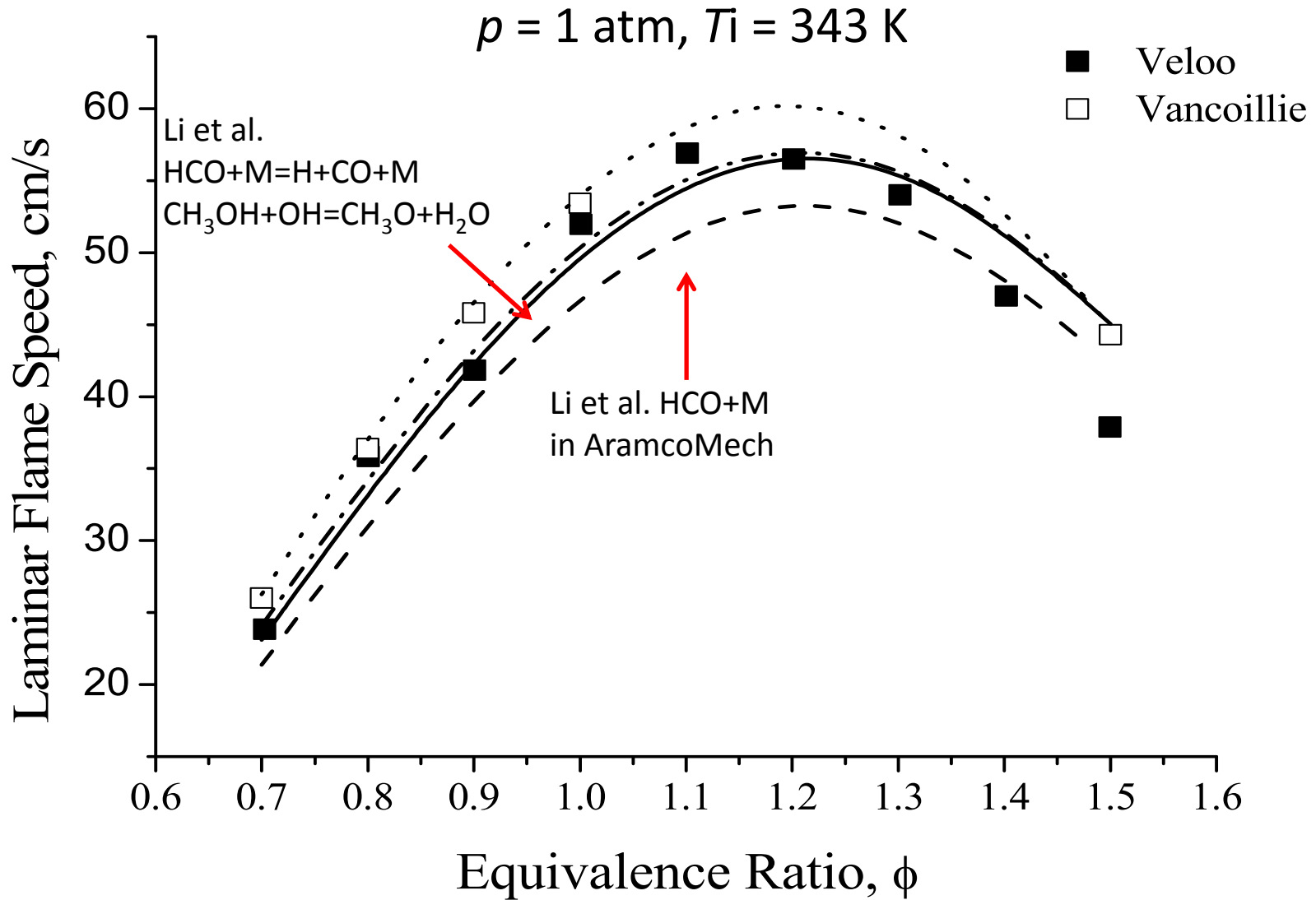


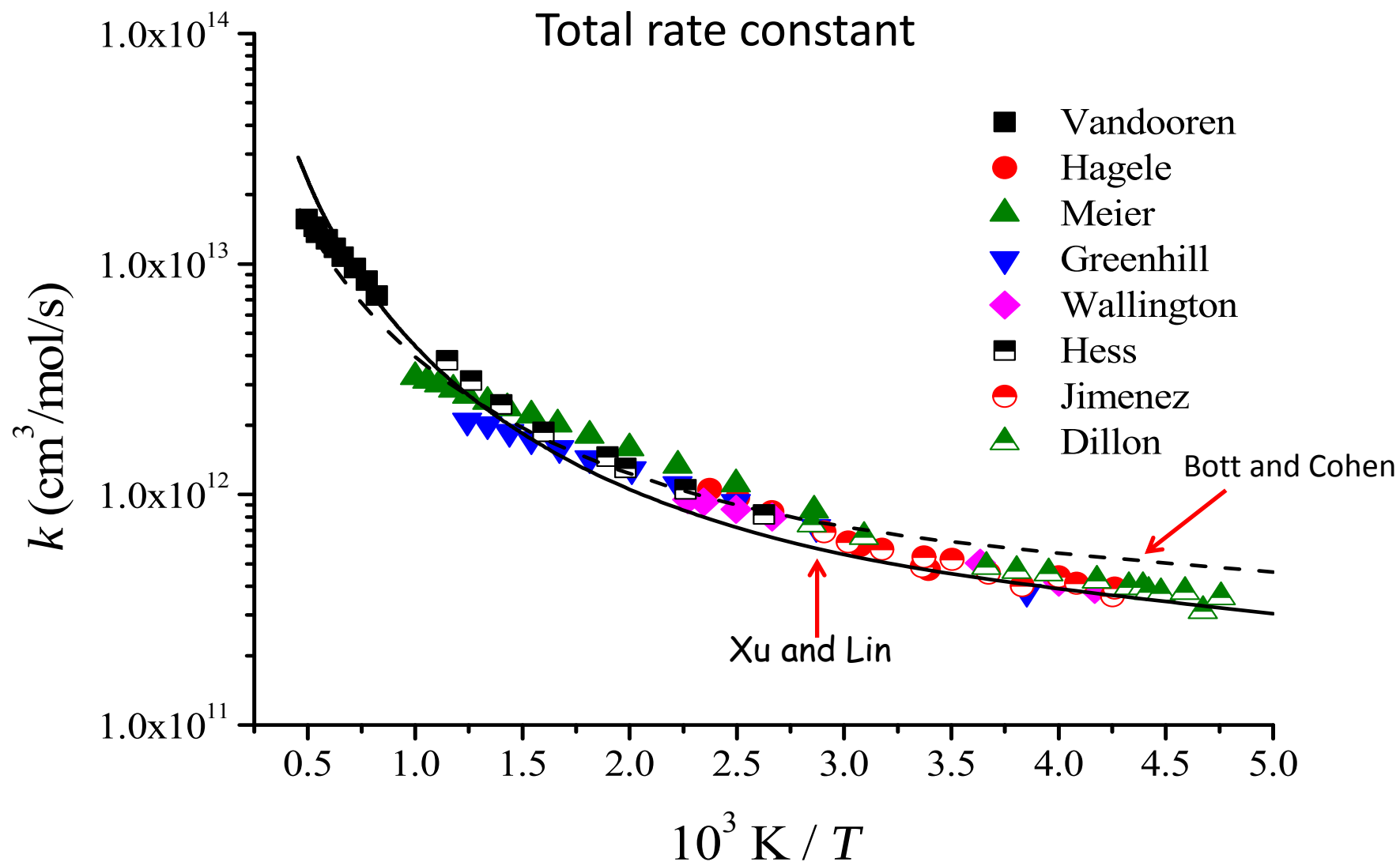


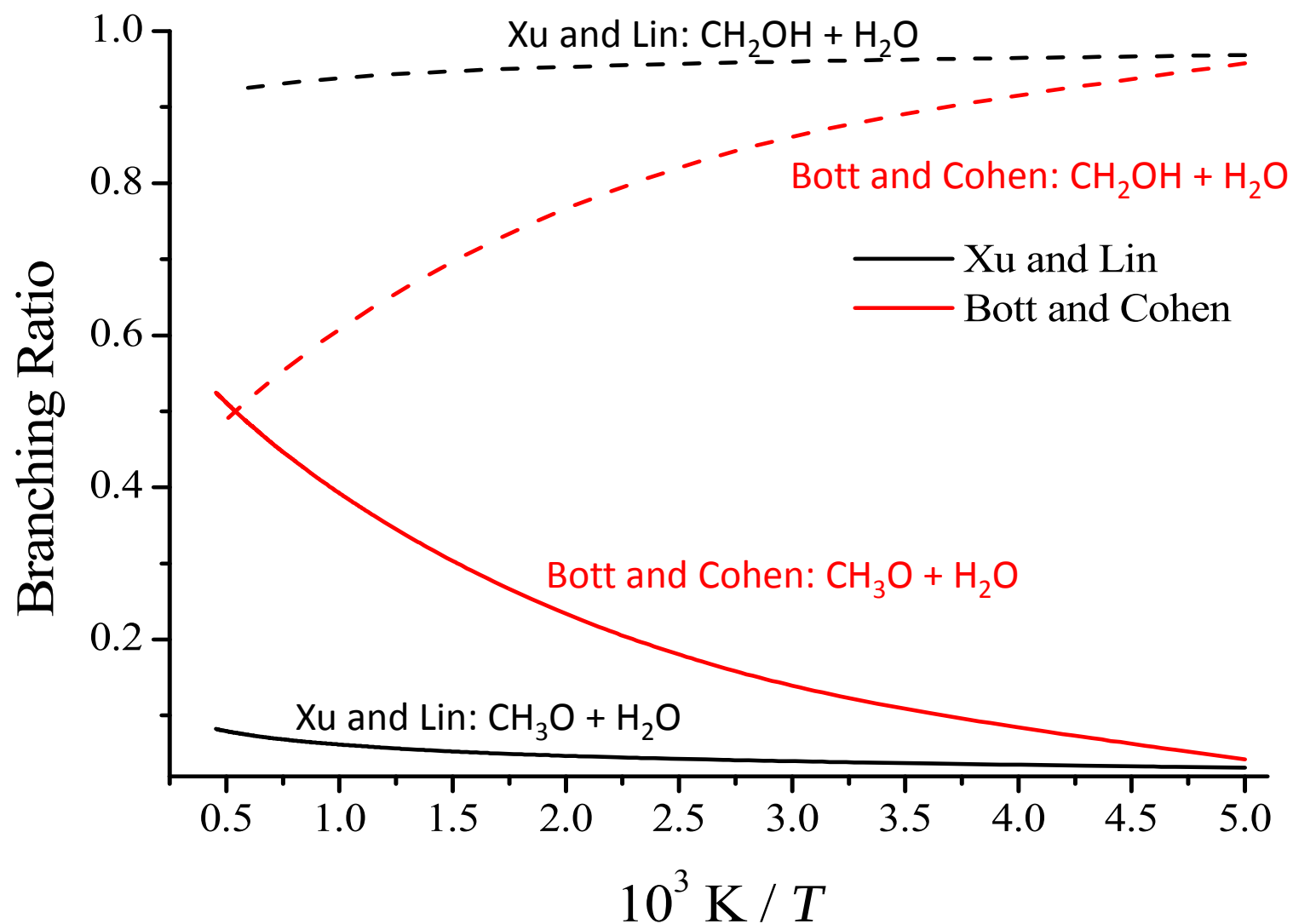
HC $\dot{\text{O}}$ + M: large influence on CH₃OH S_L

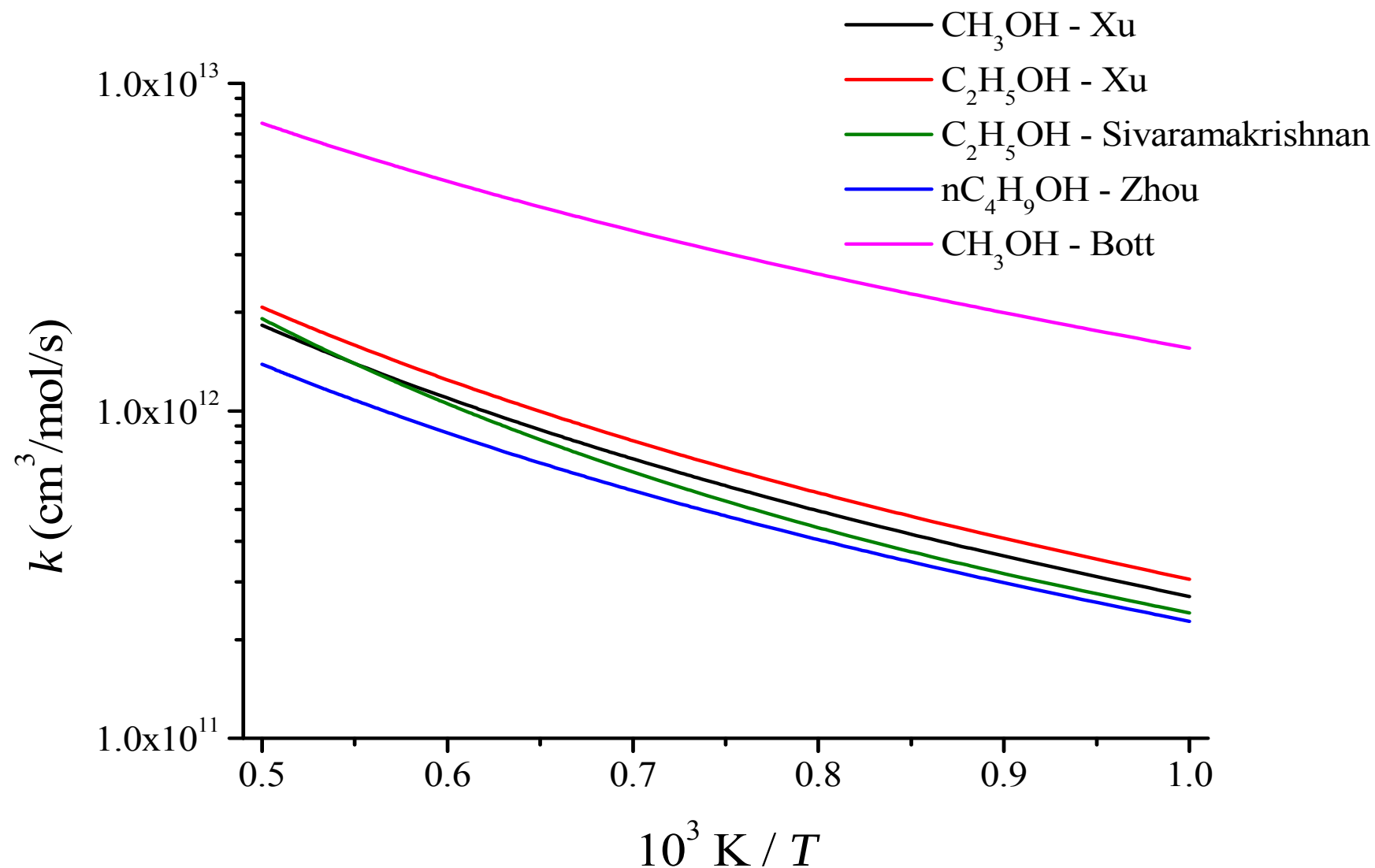


$\text{H}\dot{\text{C}}\text{O} + \text{M}$: large influence on $\text{CH}_3\text{OH } S_L$



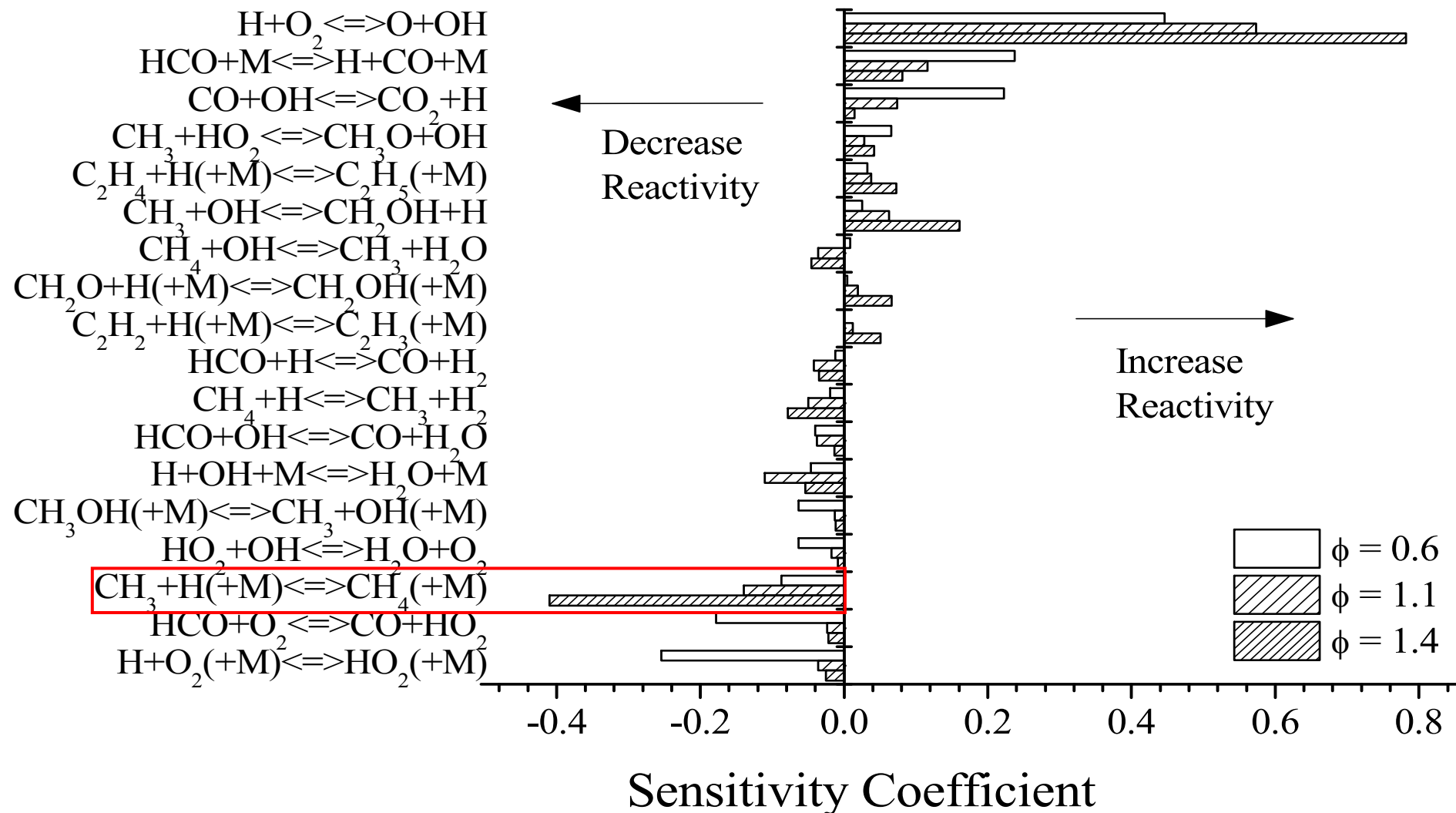






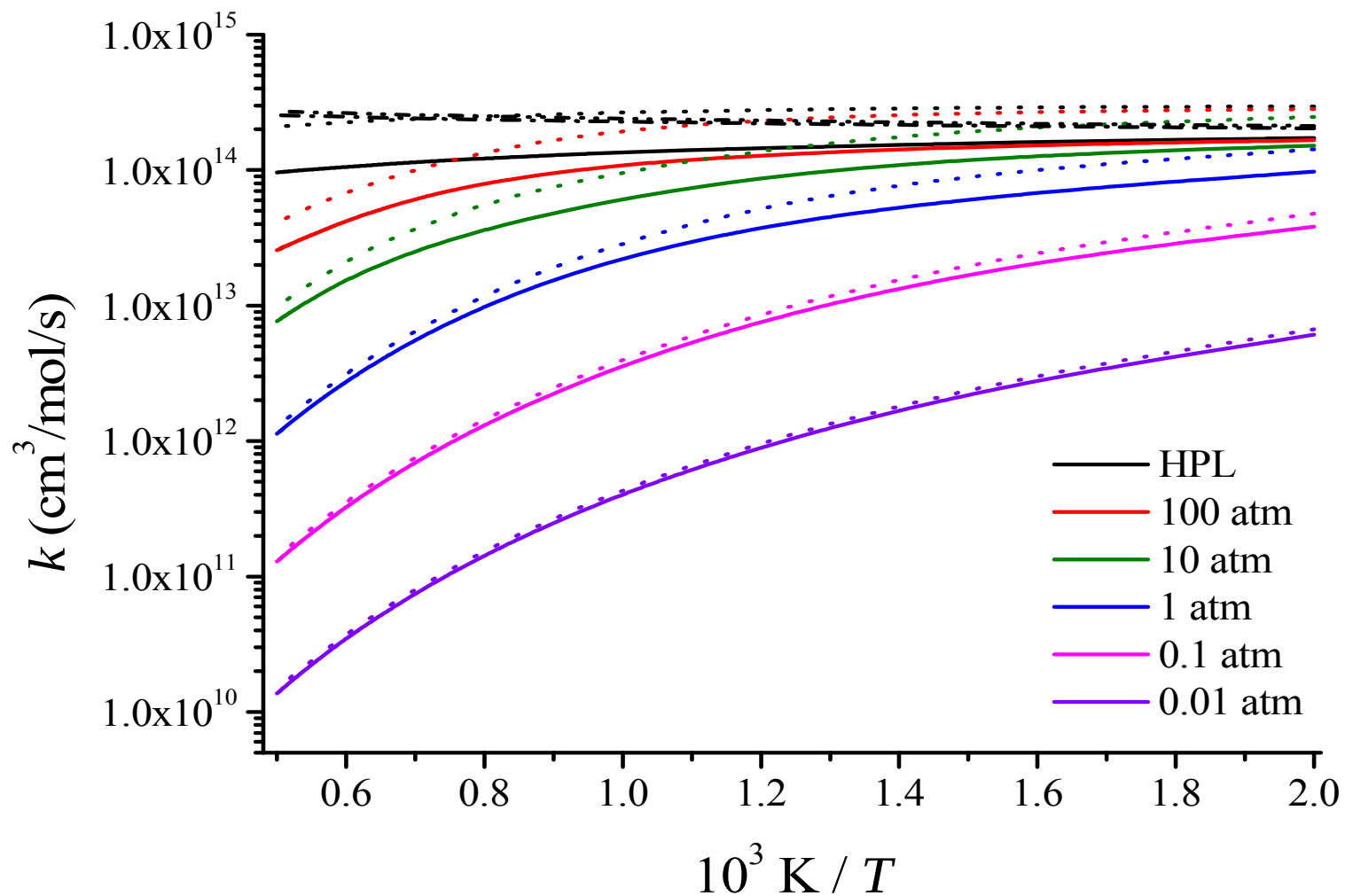
Sensitivity Analysis—CH₄ Flame Speed

$p = 1.0 \text{ atm}, T_i = 298 \text{ K}$



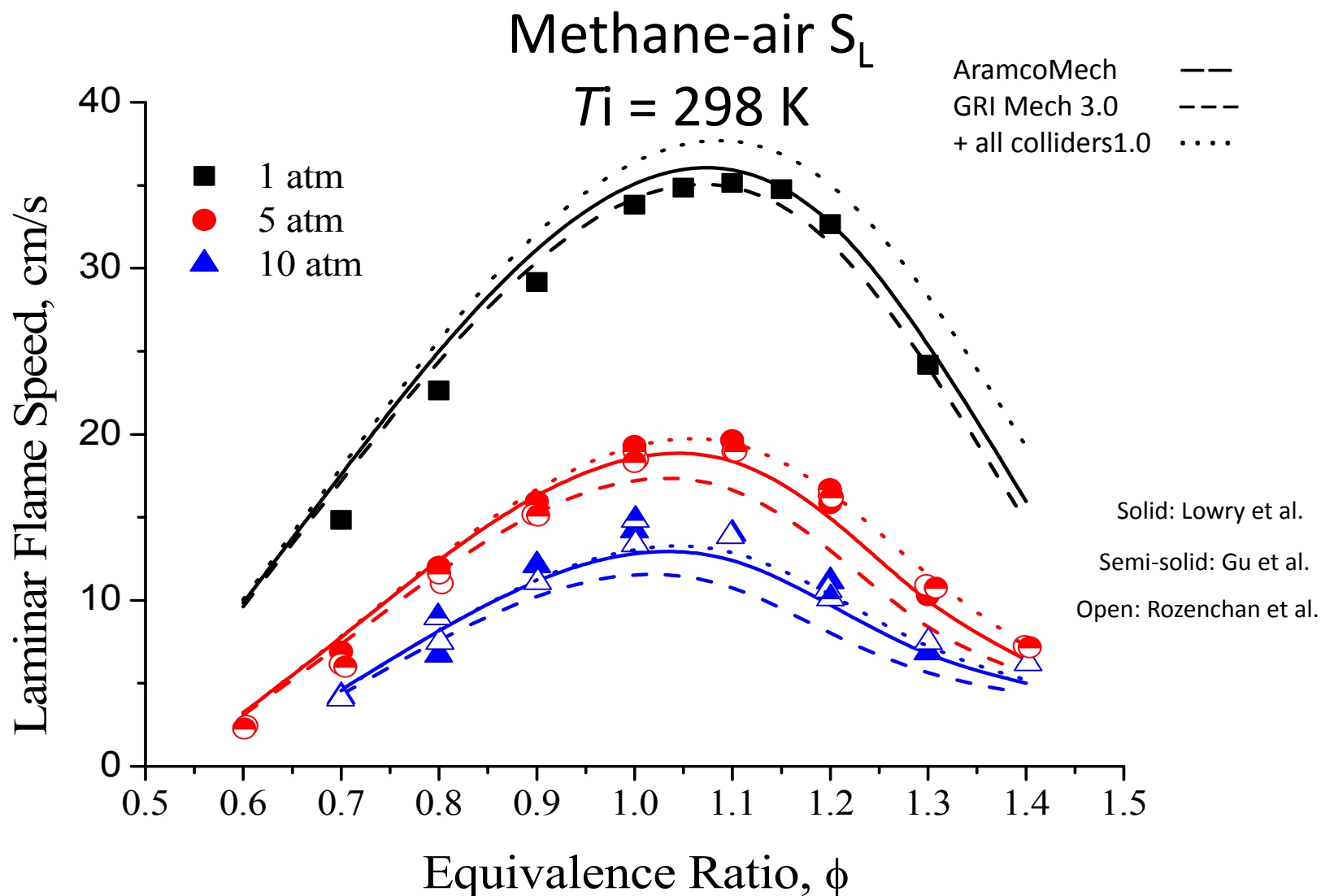


AramcoMech —
USC Mech II —
San Diego Mech —
GRI Mech 3.0 ...
Klippenstein et al. -.-





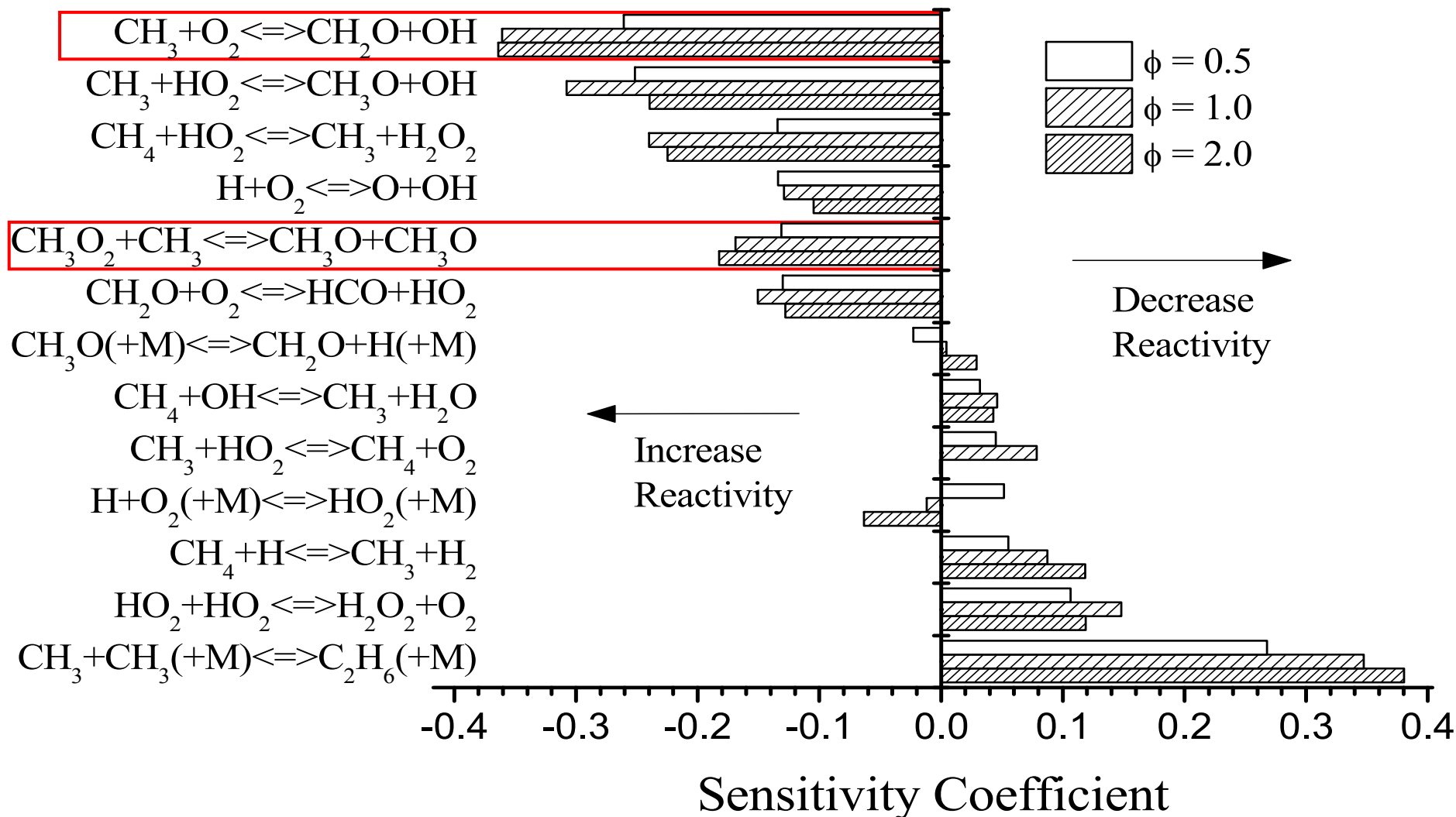
Effect of $\dot{\text{C}}\text{H}_3 + \dot{\text{H}} (+ \text{M}) = \text{CH}_4 (+ \text{M})$

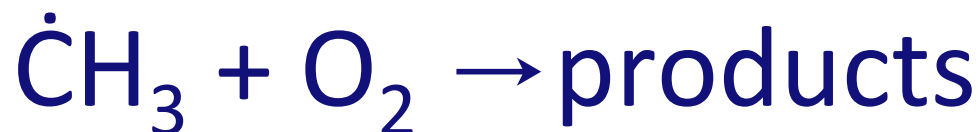




Sensitivity Analysis—CH₄ ST τ

1250 K, 30 atm

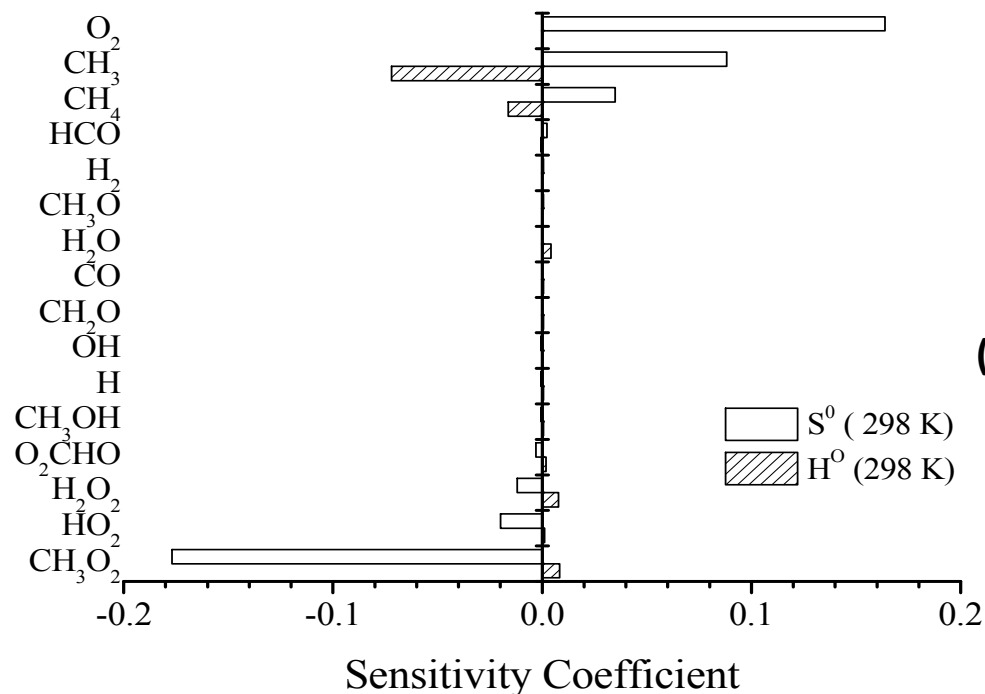




- $\dot{\text{C}}\text{H}_3 + \text{O}_2 (+\text{M}) = \text{CH}_3\dot{\text{O}}_2 (+\text{M})$ (Fernandes et al. JPCA 2006 110:4442)
- $\dot{\text{C}}\text{H}_3 + \text{O}_2 = \text{CH}_2\text{O} + \dot{\text{O}}\text{H}$ (S. Klippenstein, private communication)
- $\dot{\text{C}}\text{H}_3 + \text{O}_2 = \text{CH}_3\dot{\text{O}} + \ddot{\text{O}}$ (Srinivasan et al. 2005 JPCA 2005 109:7902)

Sensitivity of τ to thermochemistry

900 K, 20 atm

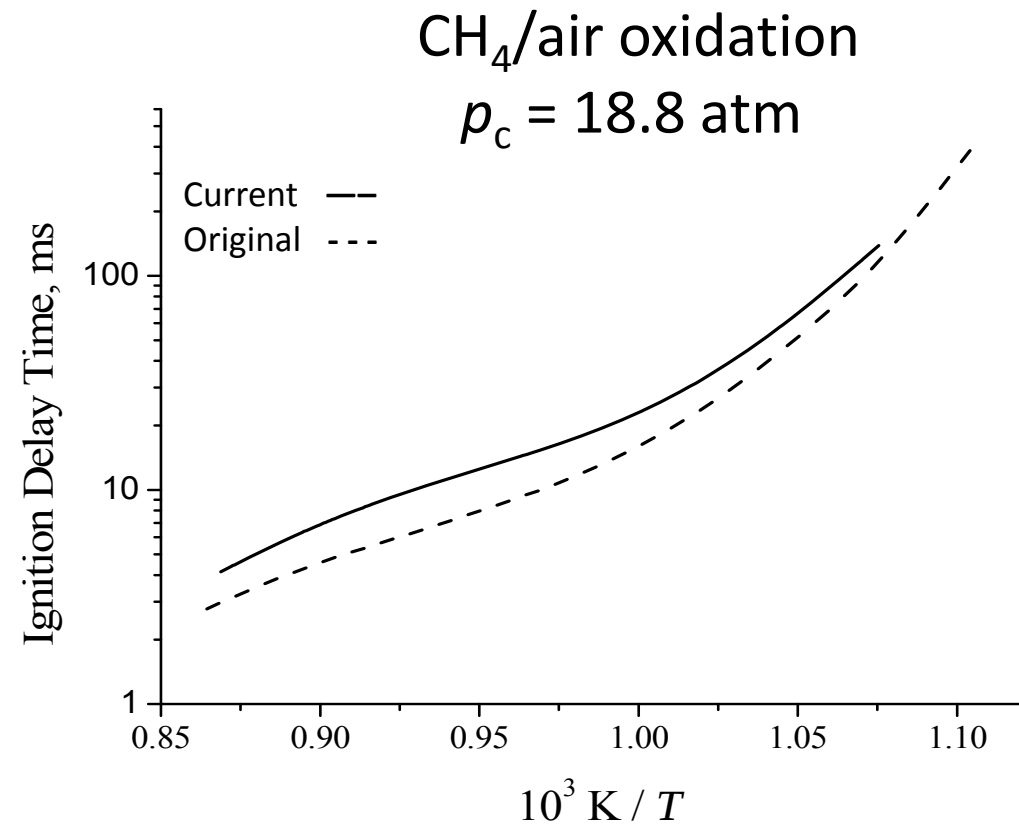
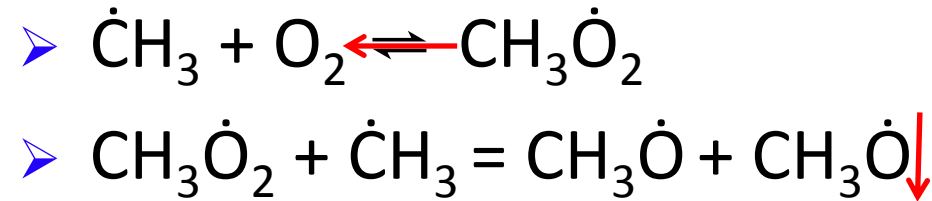


Original
(Simmie et al.)

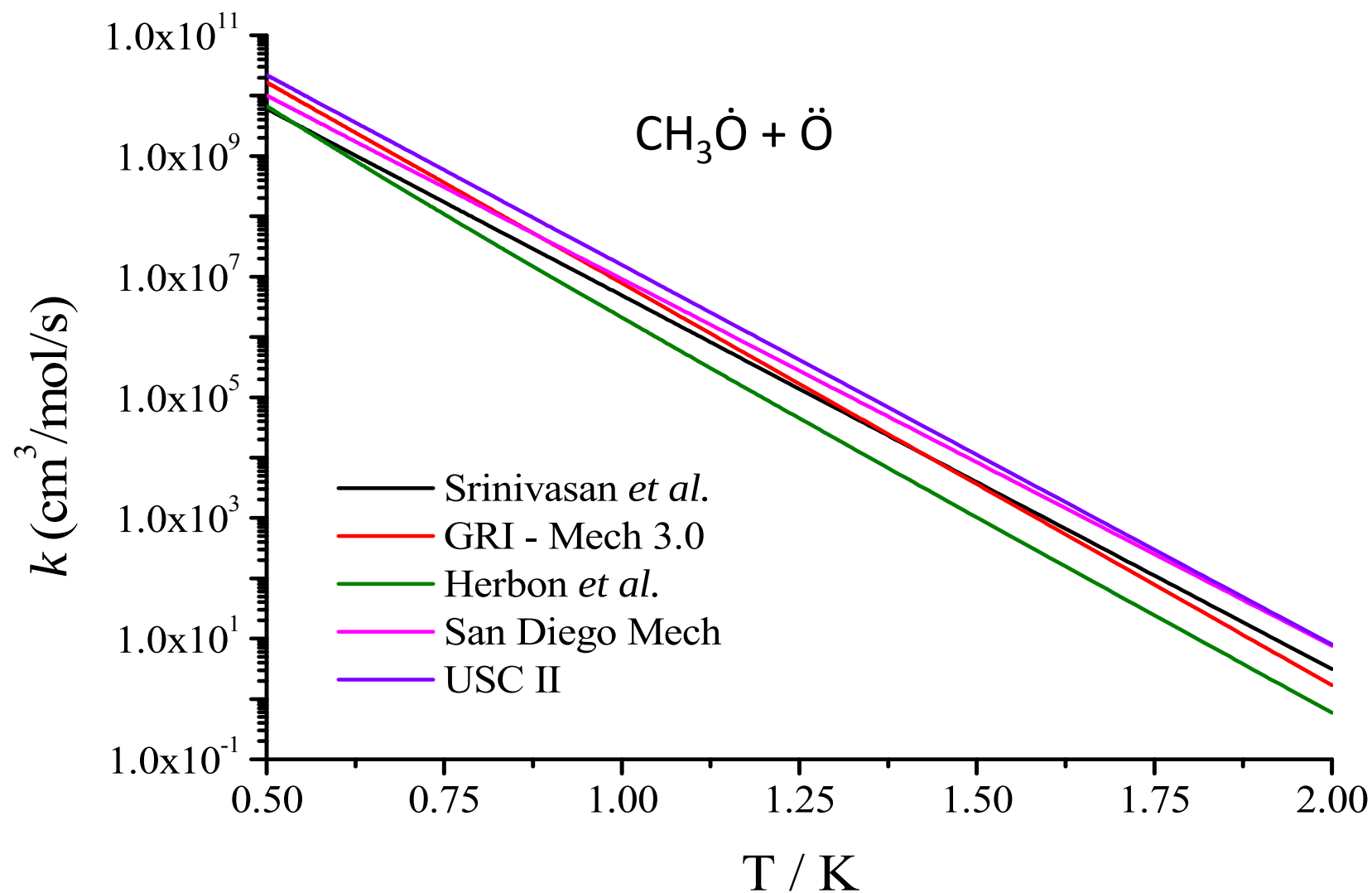
H_f^0 @ 298 K (kcal mol ⁻¹)	S_f^0 @ 298 K (cal K ⁻¹ mol ⁻¹)
2.20	64.36
2.92	64.50



Effect of thermochemistry

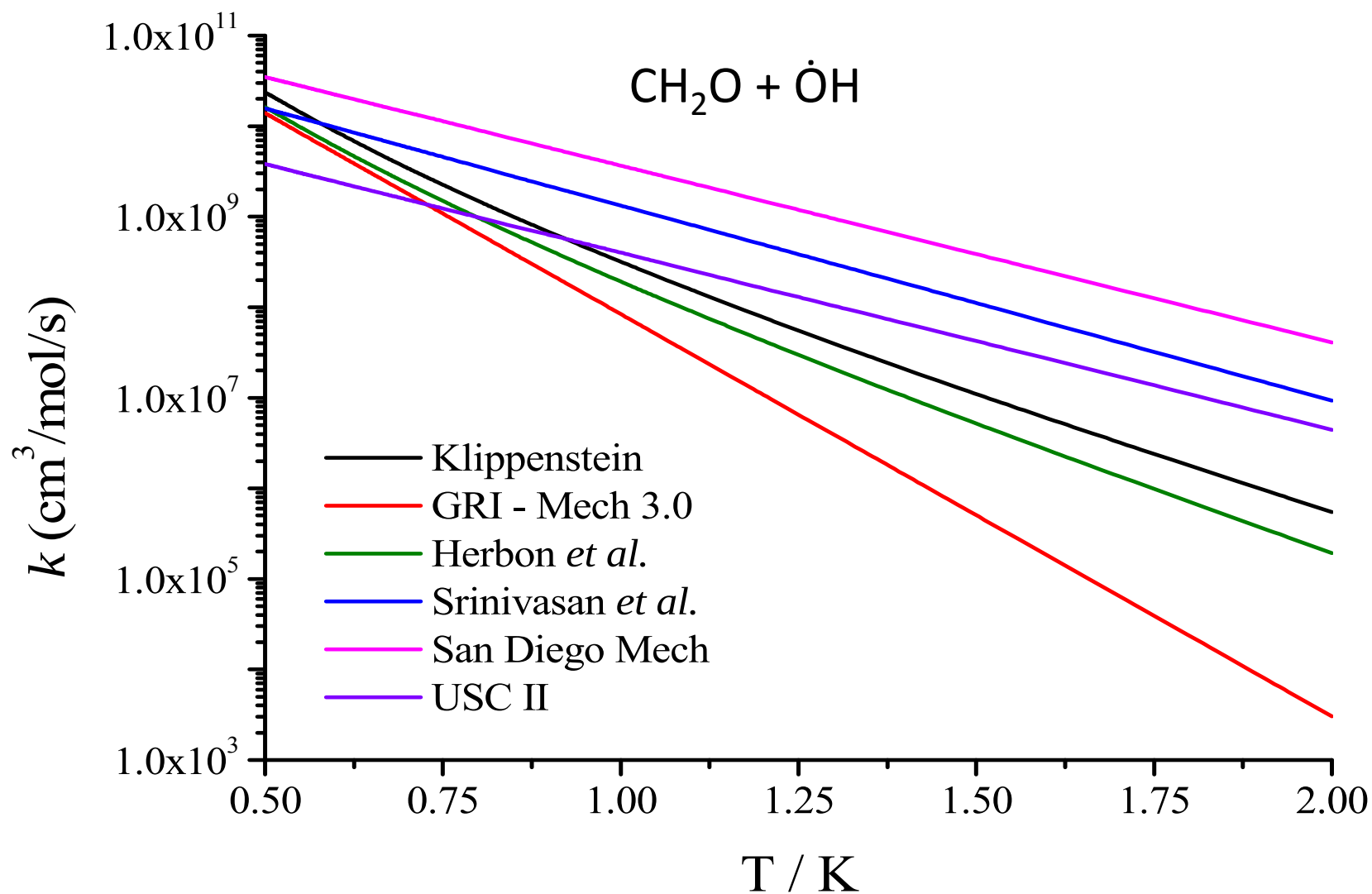


$\dot{\text{C}}\text{H}_3 + \text{O}_2$ reactions



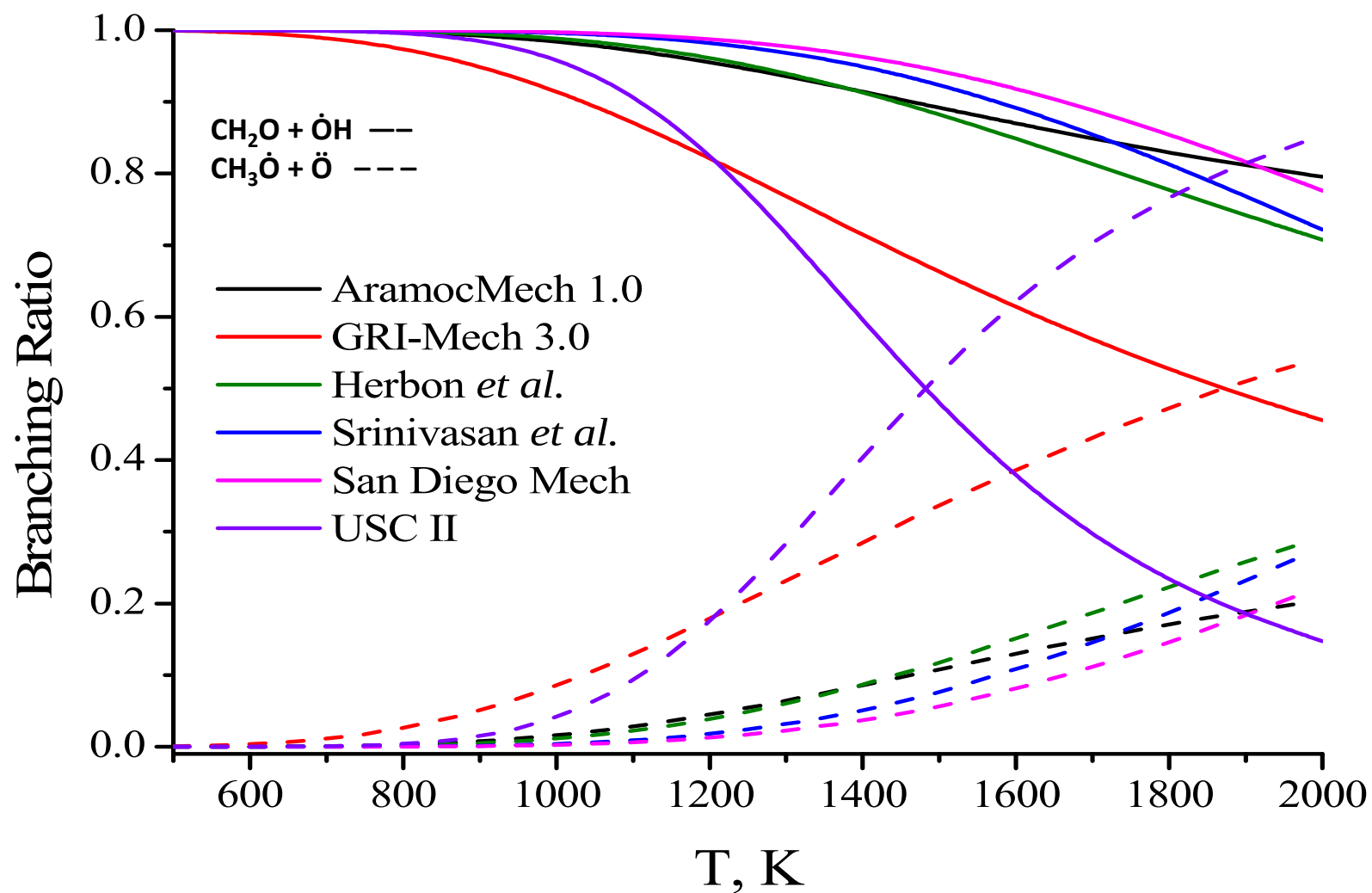


$\dot{\text{C}}\text{H}_3 + \text{O}_2$ reactions



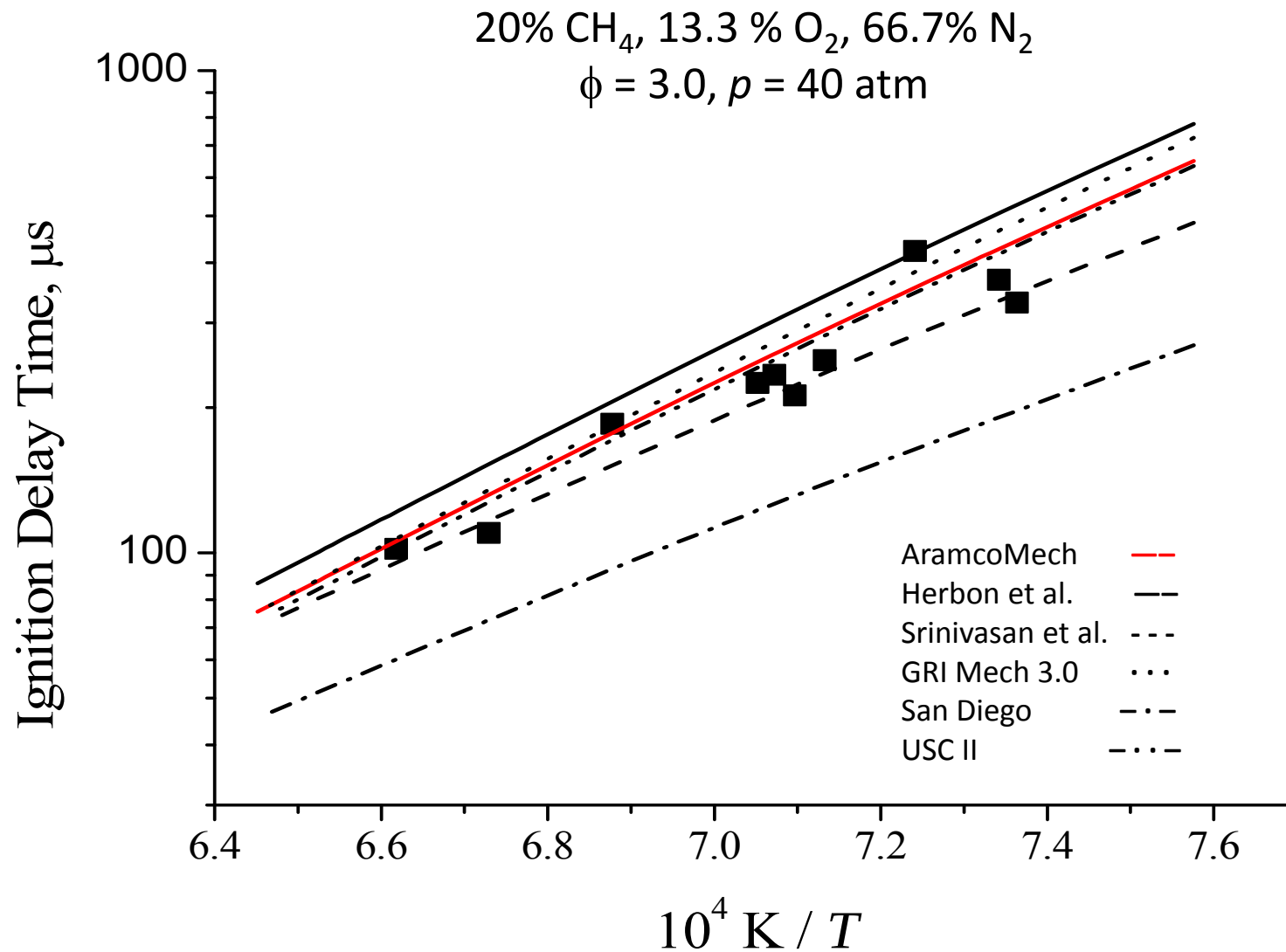


$\dot{\text{C}}\text{H}_3 + \text{O}_2$ reactions





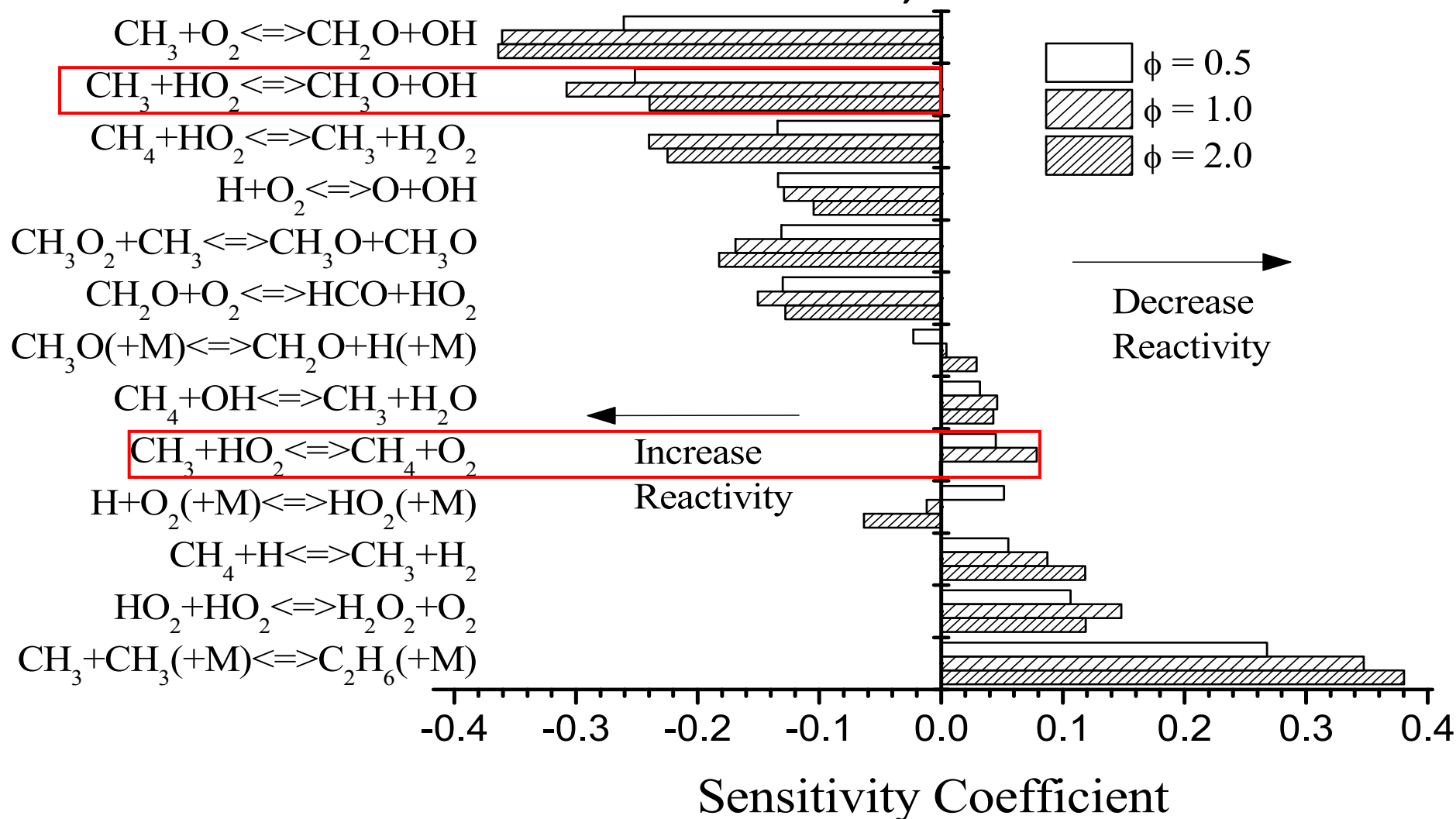
Influence of choice of $\dot{\text{C}}\text{H}_3 + \text{O}_2$ on τ





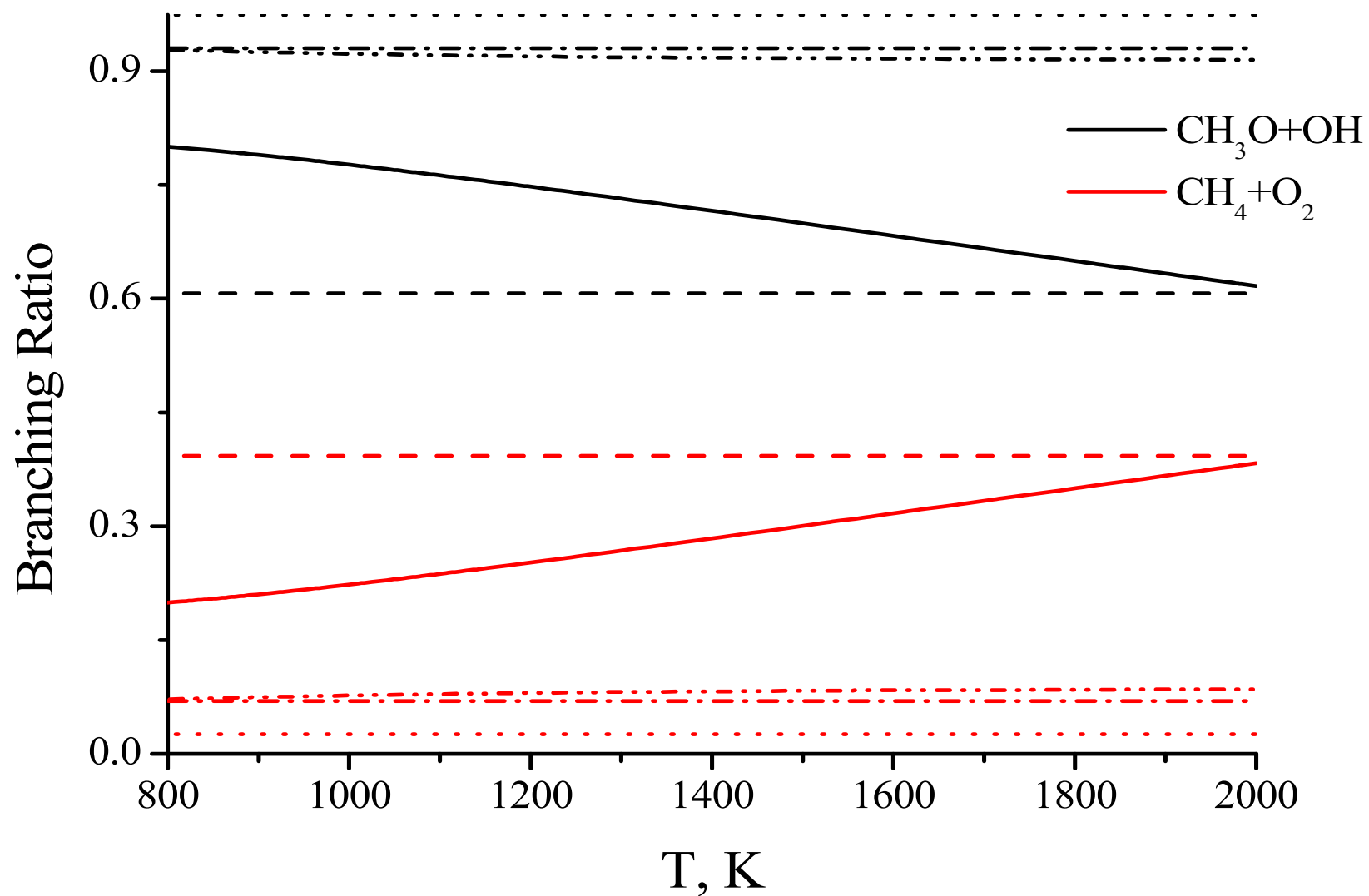
Sensitivity Analysis—CH₄ ST τ

1250 K, 30 atm



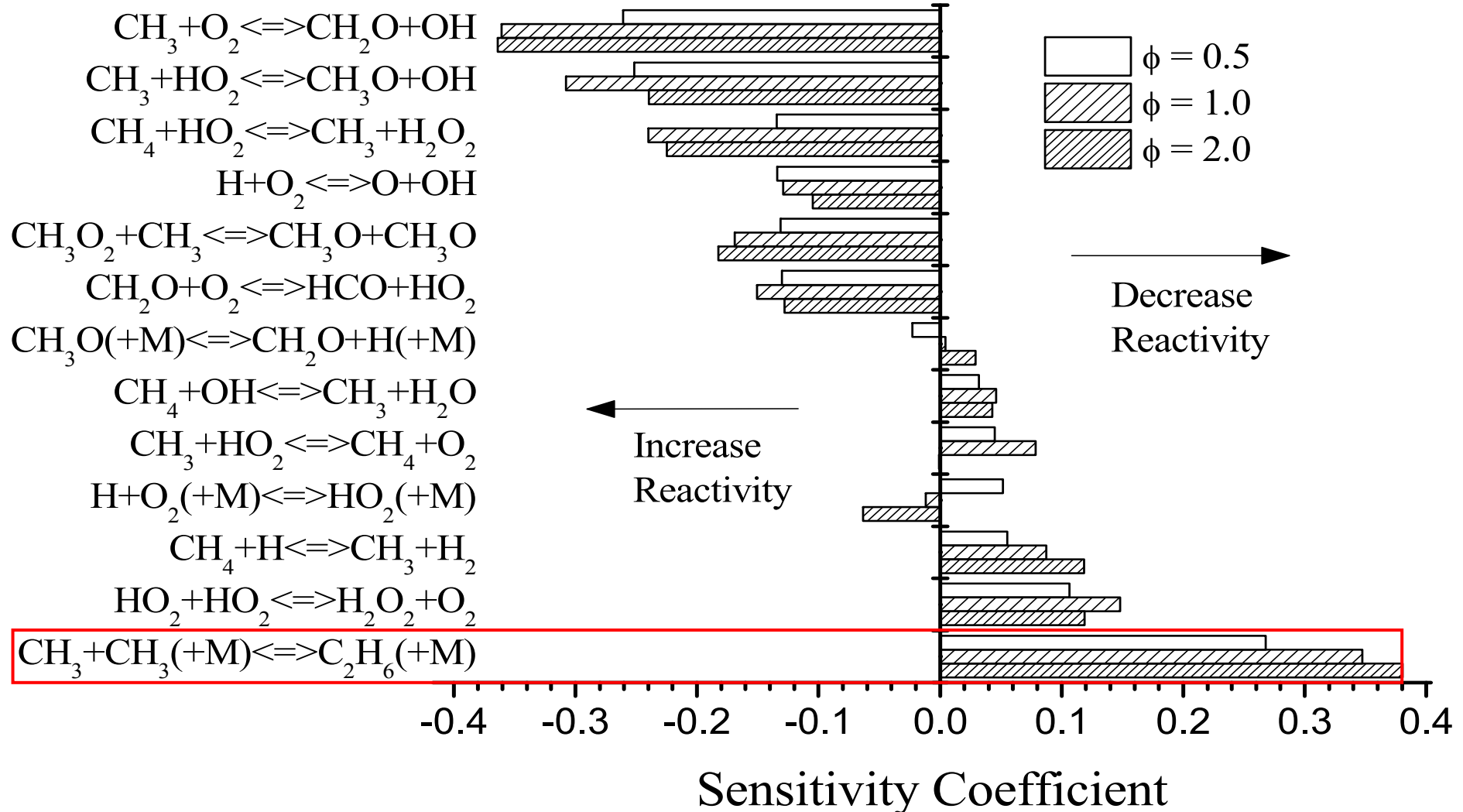


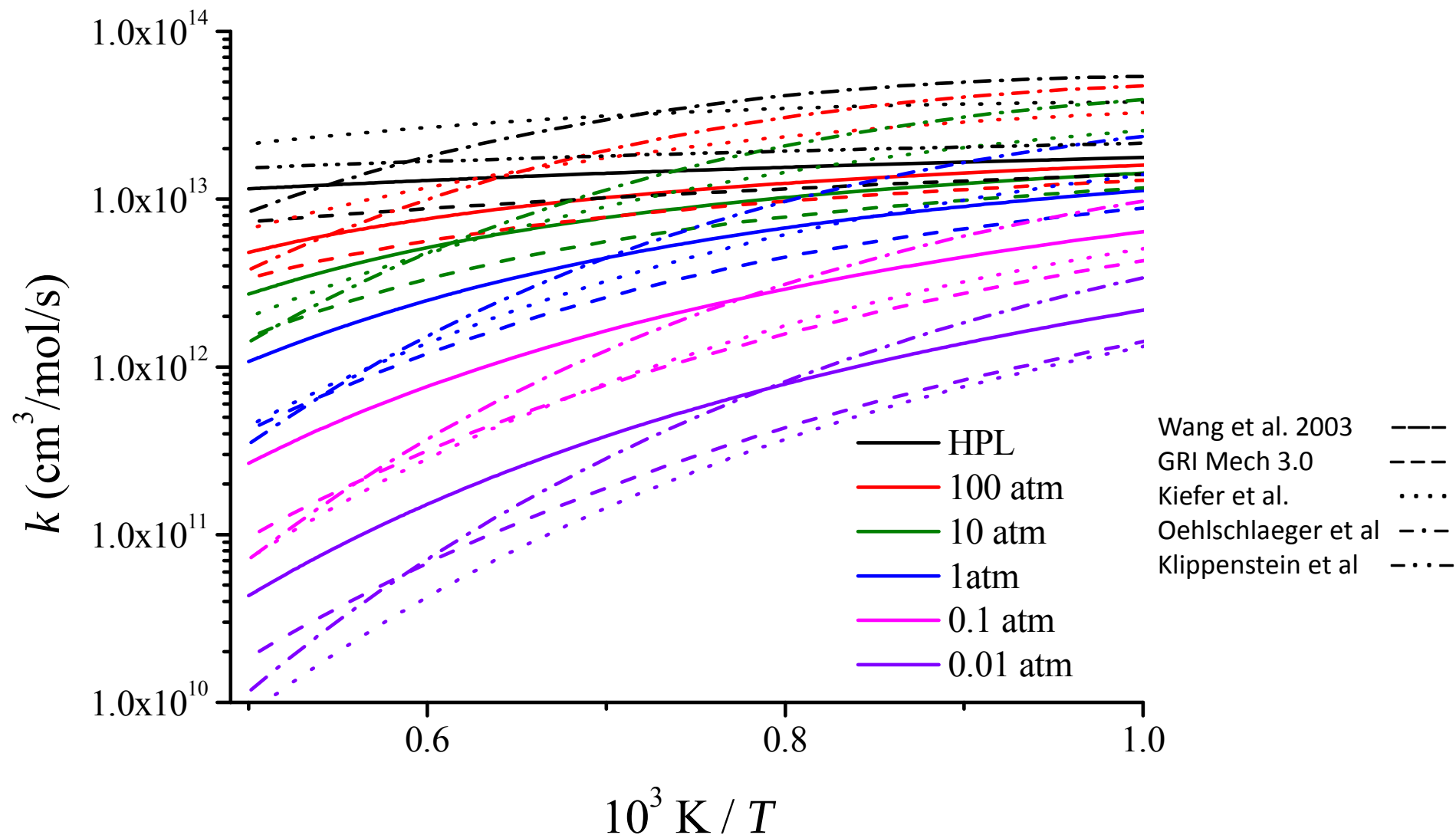
$\dot{\text{C}}\text{H}_3 + \text{H}\dot{\text{O}}_2$ branching ratio

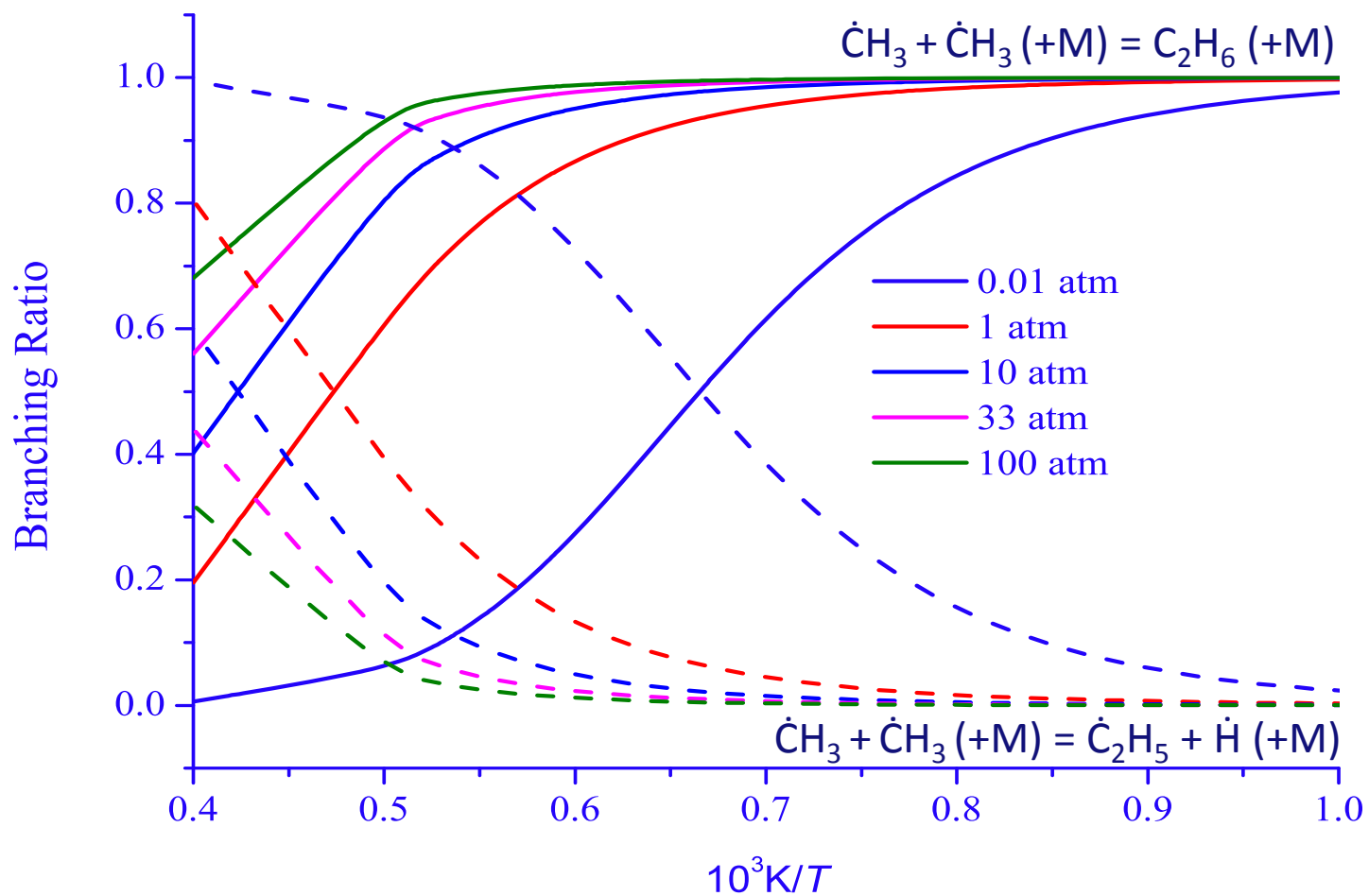
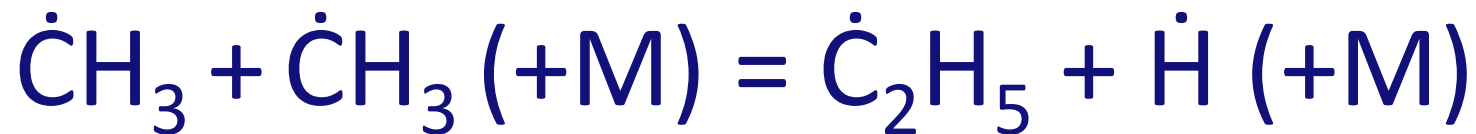


Sensitivity Analysis—ST ignition delay

1250 K, 30 atm





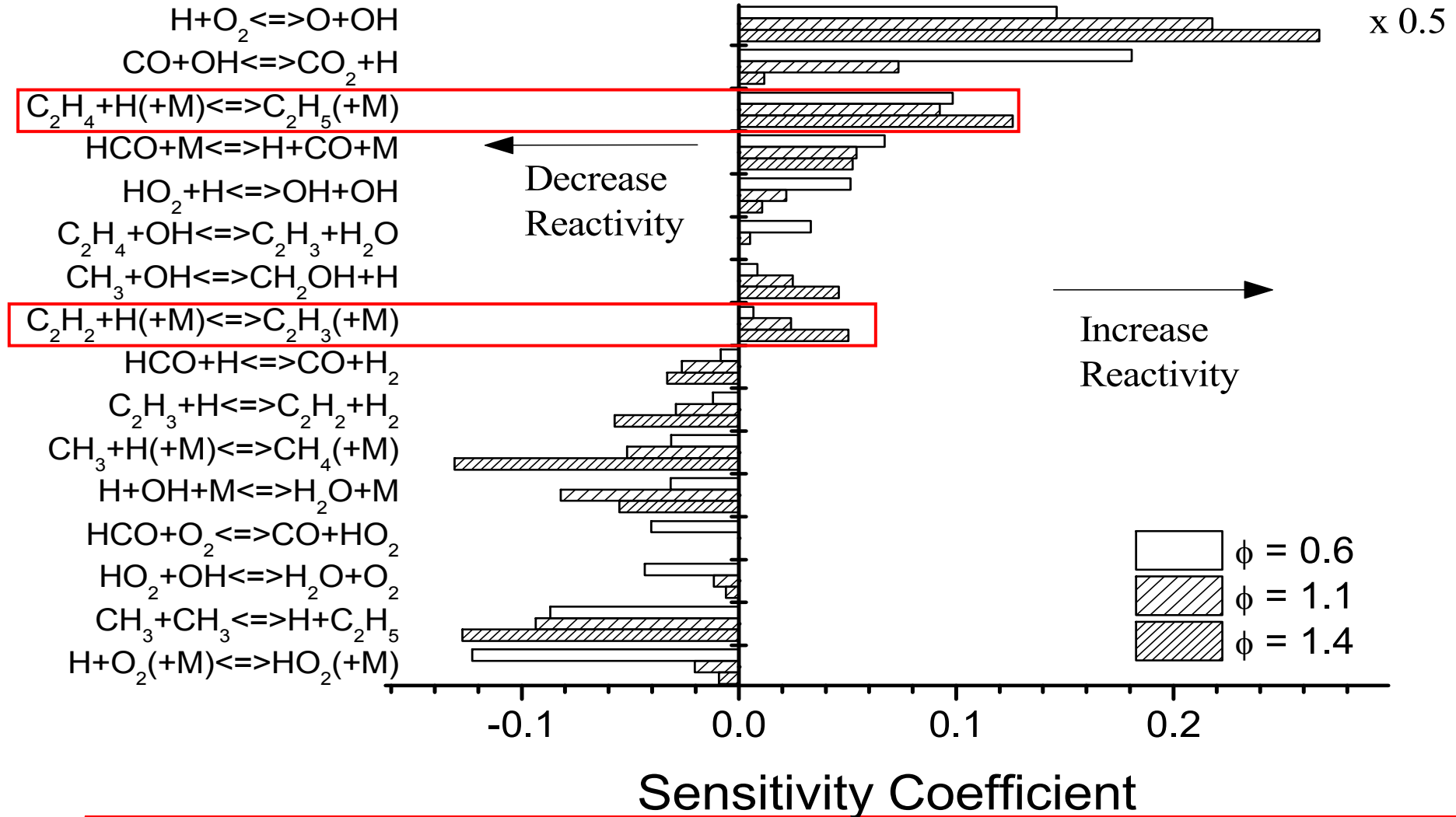


Stewart PH, Larsen
of reactor
 $2\text{CH}_3 =$

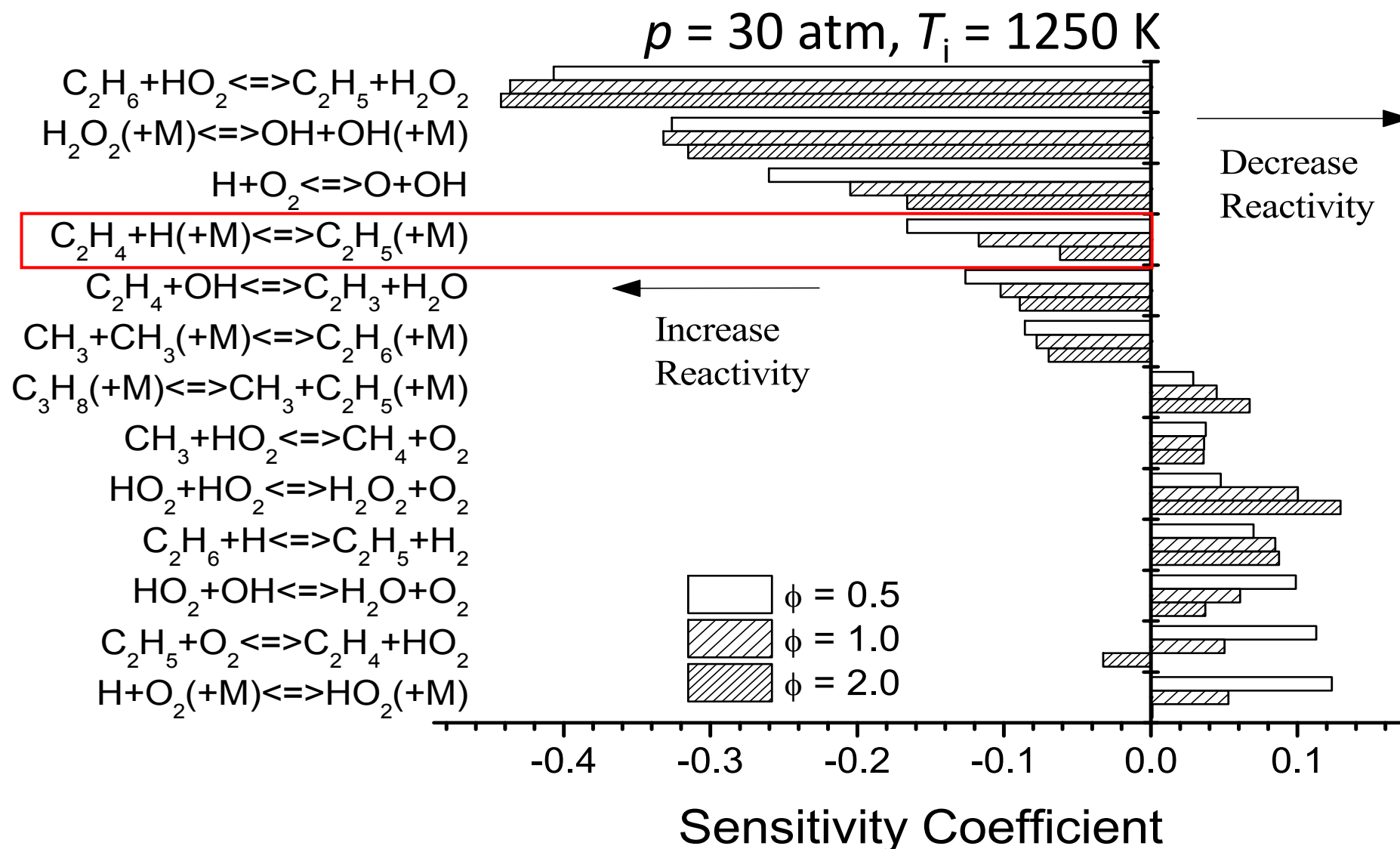


Sensitivity Analysis—C₂H₆ Flame Speed

$p = 1.0 \text{ atm}, T_i = 298 \text{ K}$

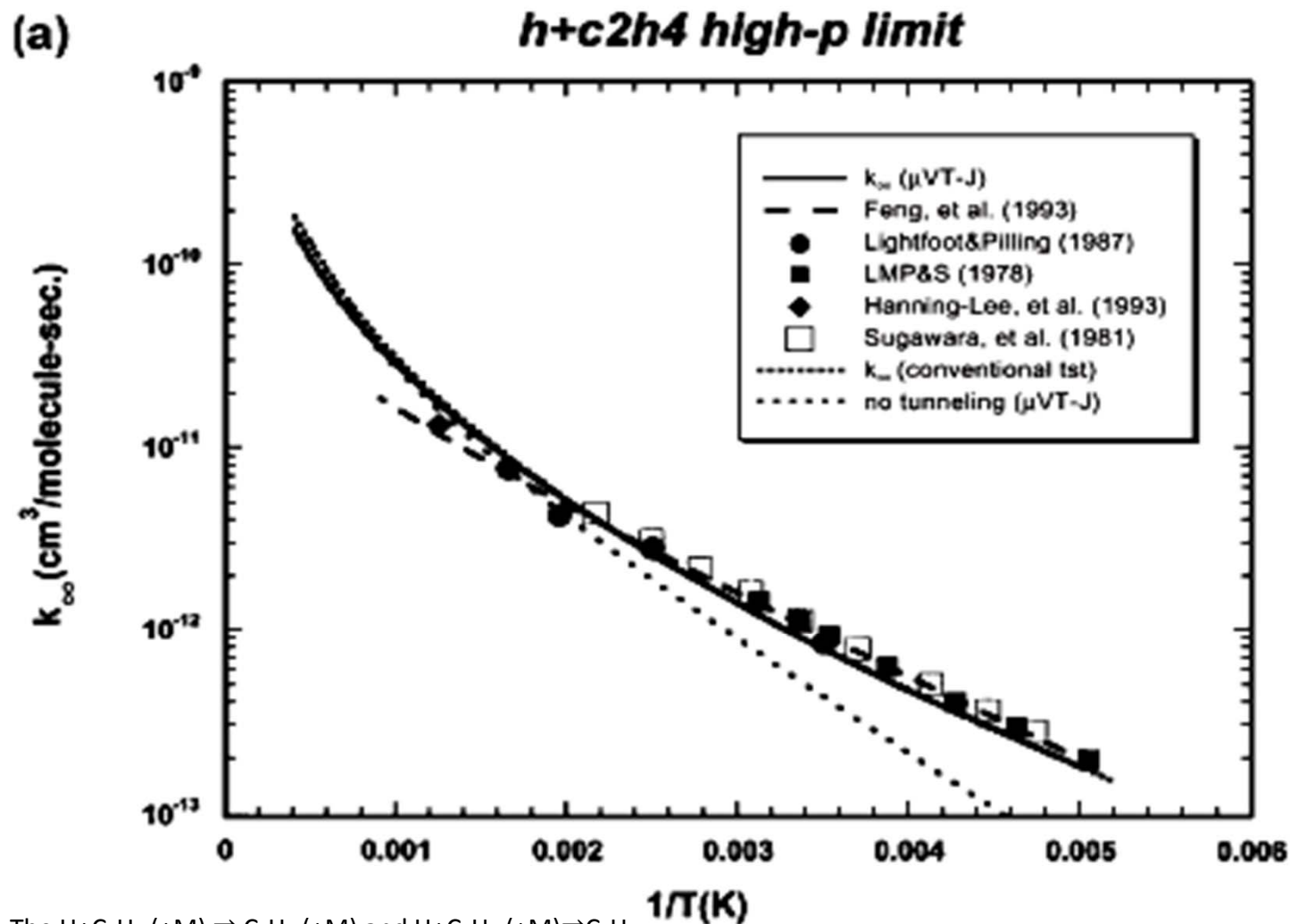


Sensitivity Analysis—C₂H₆ Ignition delay





$\dot{\text{H}} + \text{C}_2\text{H}_4$ high-pressure limit



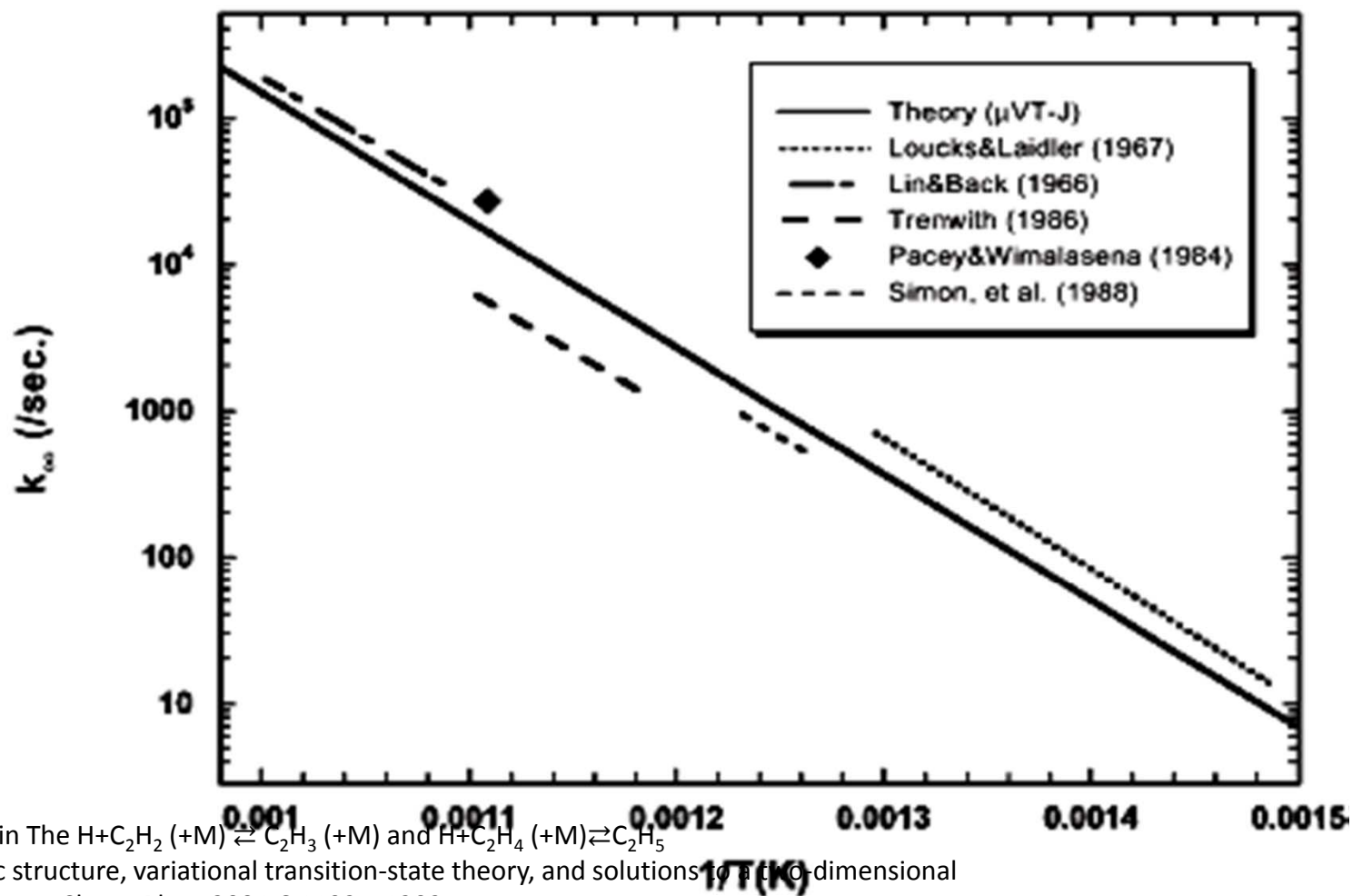
J.A. Miller, S.J. Klippenstein The $\text{H} + \text{C}_2\text{H}_2 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_3 (+\text{M})$ and $\text{H} + \text{C}_2\text{H}_4 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_5 (+\text{M})$ reactions: Electronic structure, variational transition-state theory, 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

(b)

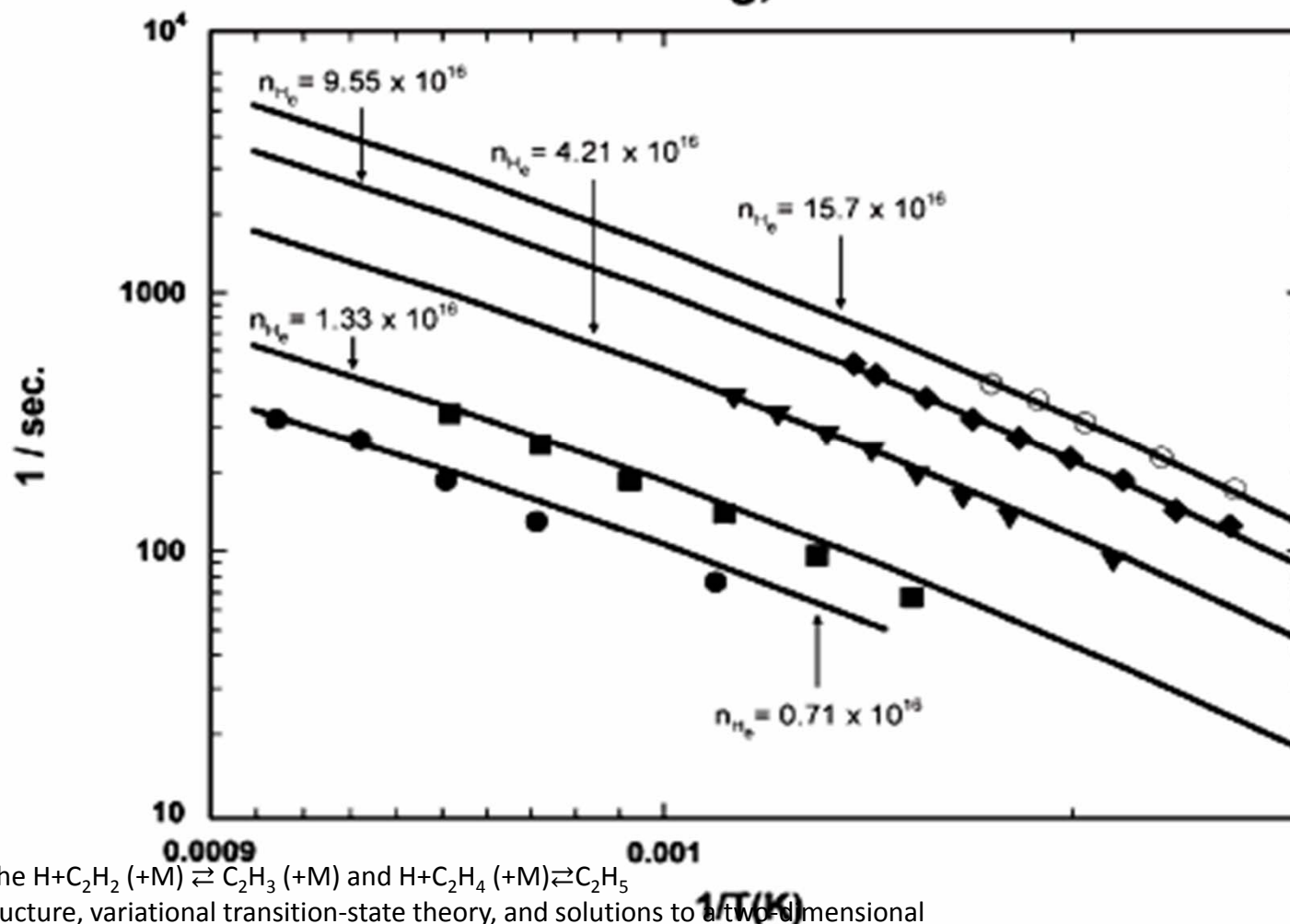
c2h5->c2h4+h high-p limit



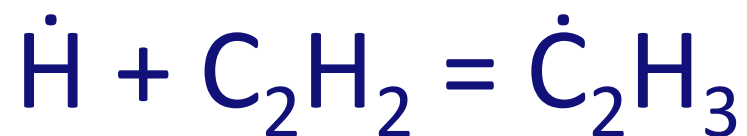
J.A. Miller, S.J. Klippenstein The $H+C_2H_2 (+M) \rightleftharpoons C_2H_3 (+M)$ and $H+C_2H_4 (+M) \rightleftharpoons C_2H_5 (+M)$ reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. Phys. Chem. Chem. Phys. 2004 6 1192—1202.



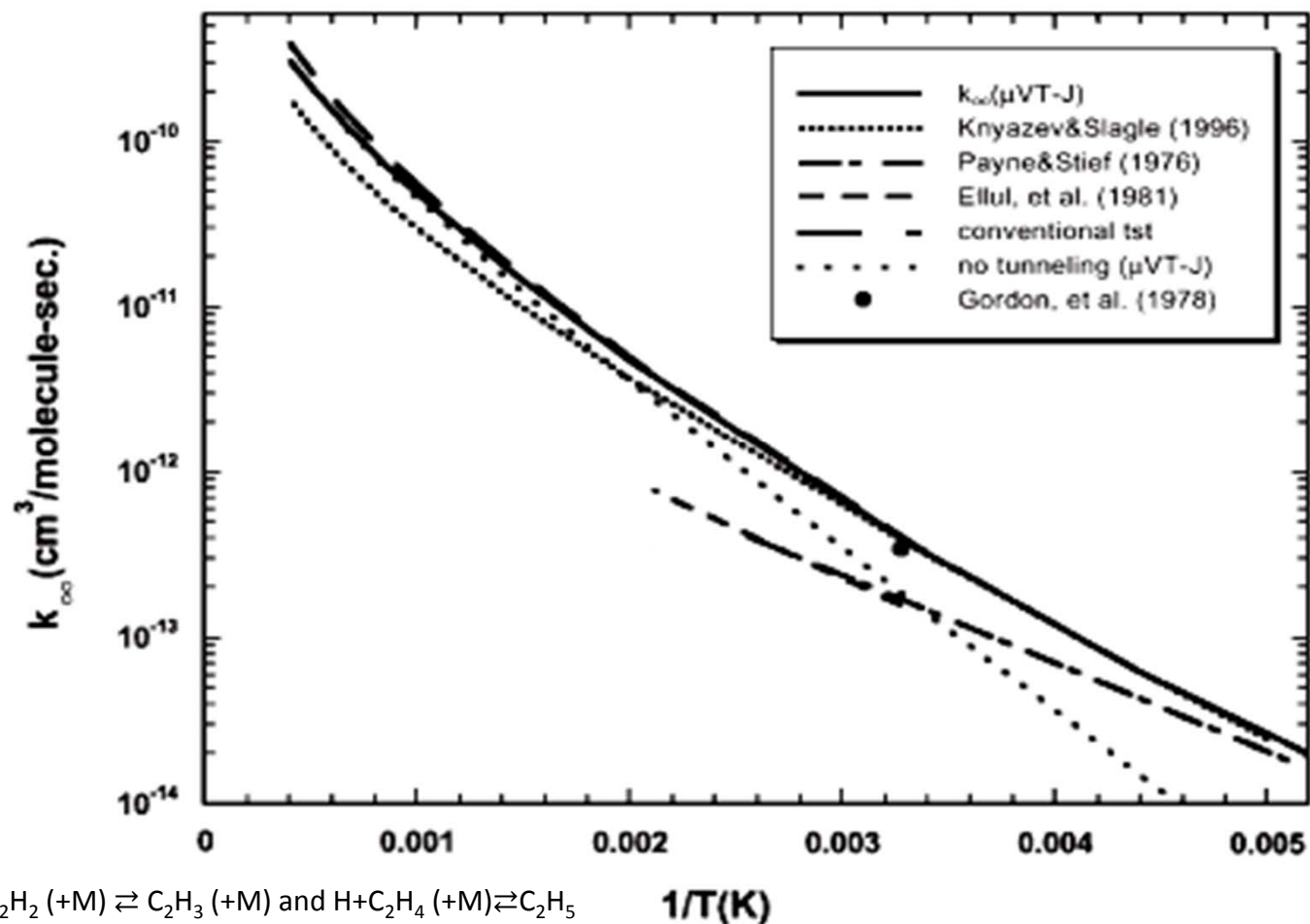
Feng, et al



J.A. Miller, S.J. Klippenstein The $\text{H} + \text{C}_2\text{H}_2 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_3 (+\text{M})$ and $\text{H} + \text{C}_2\text{H}_4 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_5 (+\text{M})$ reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. *Phys. Chem. Chem. Phys.* 2004 6 1192–1202.



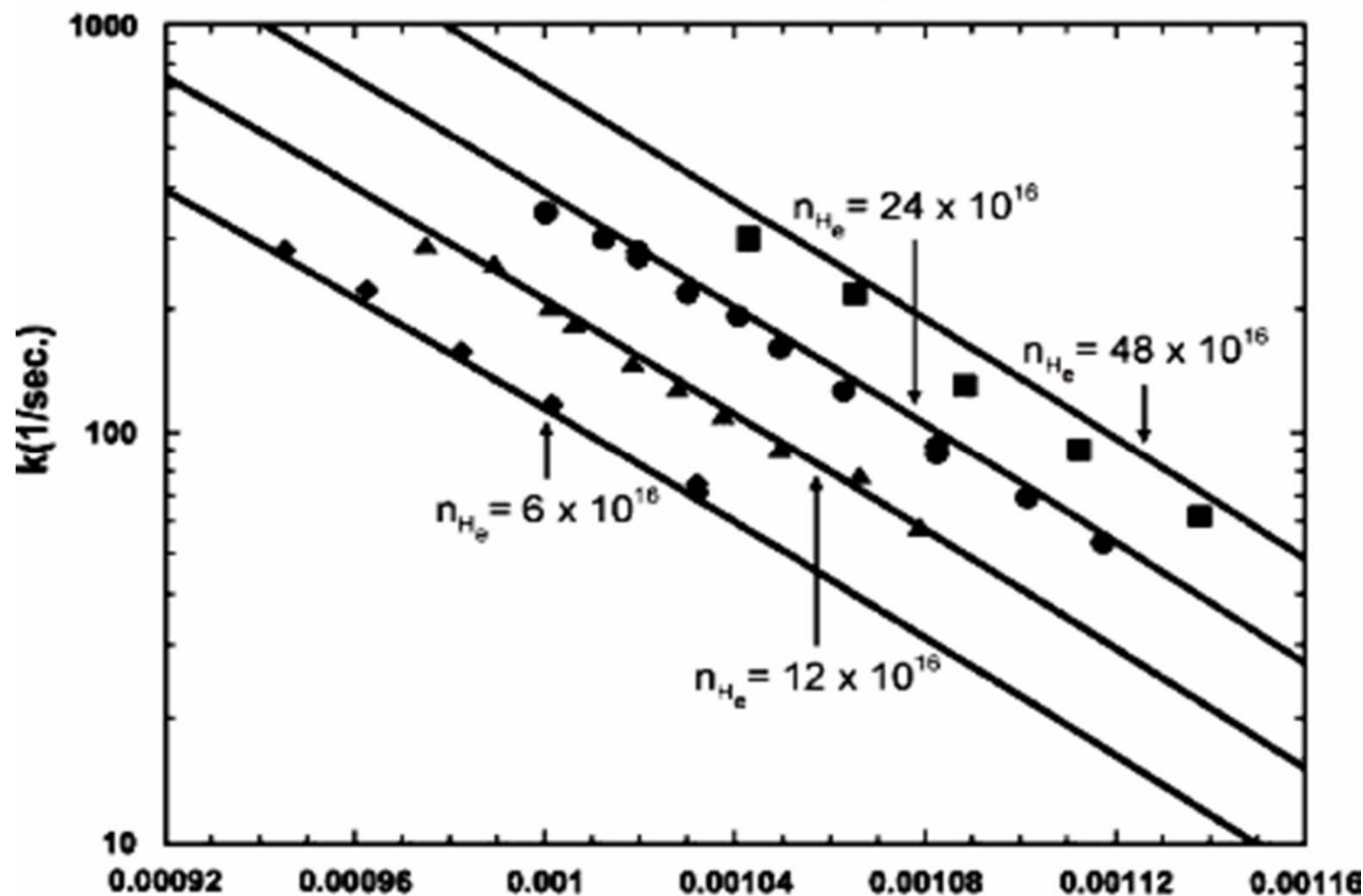
h+c2h2 high-p limit



J.A. Miller, S.J. Klippenstein The $\text{H} + \text{C}_2\text{H}_2 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_3 (+\text{M})$ and $\text{H} + \text{C}_2\text{H}_4 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_5 (+\text{M})$ reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. *Phys. Chem. Chem. Phys.* 2004 6 1192–1202.



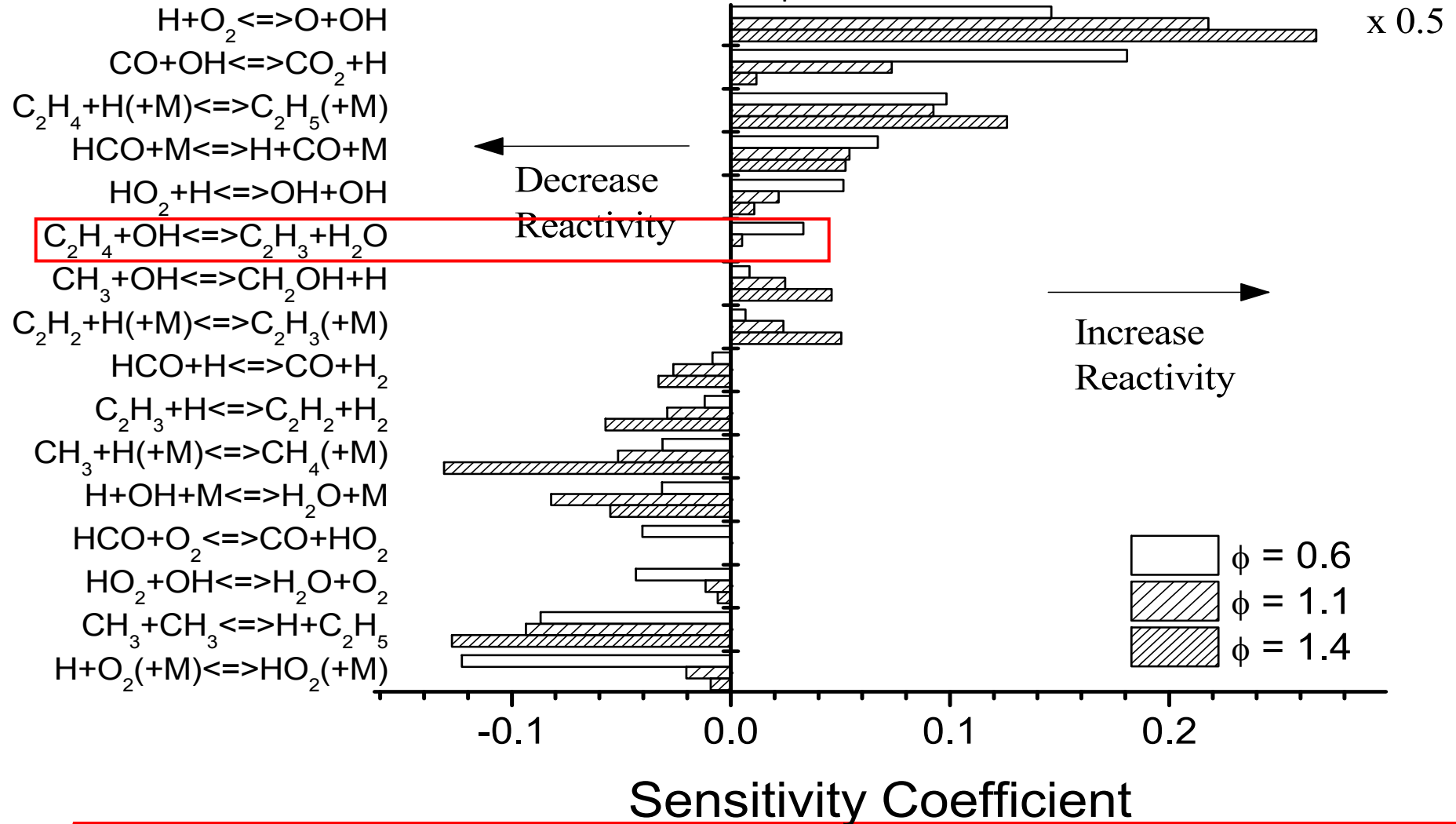
Knyazev&Slagle



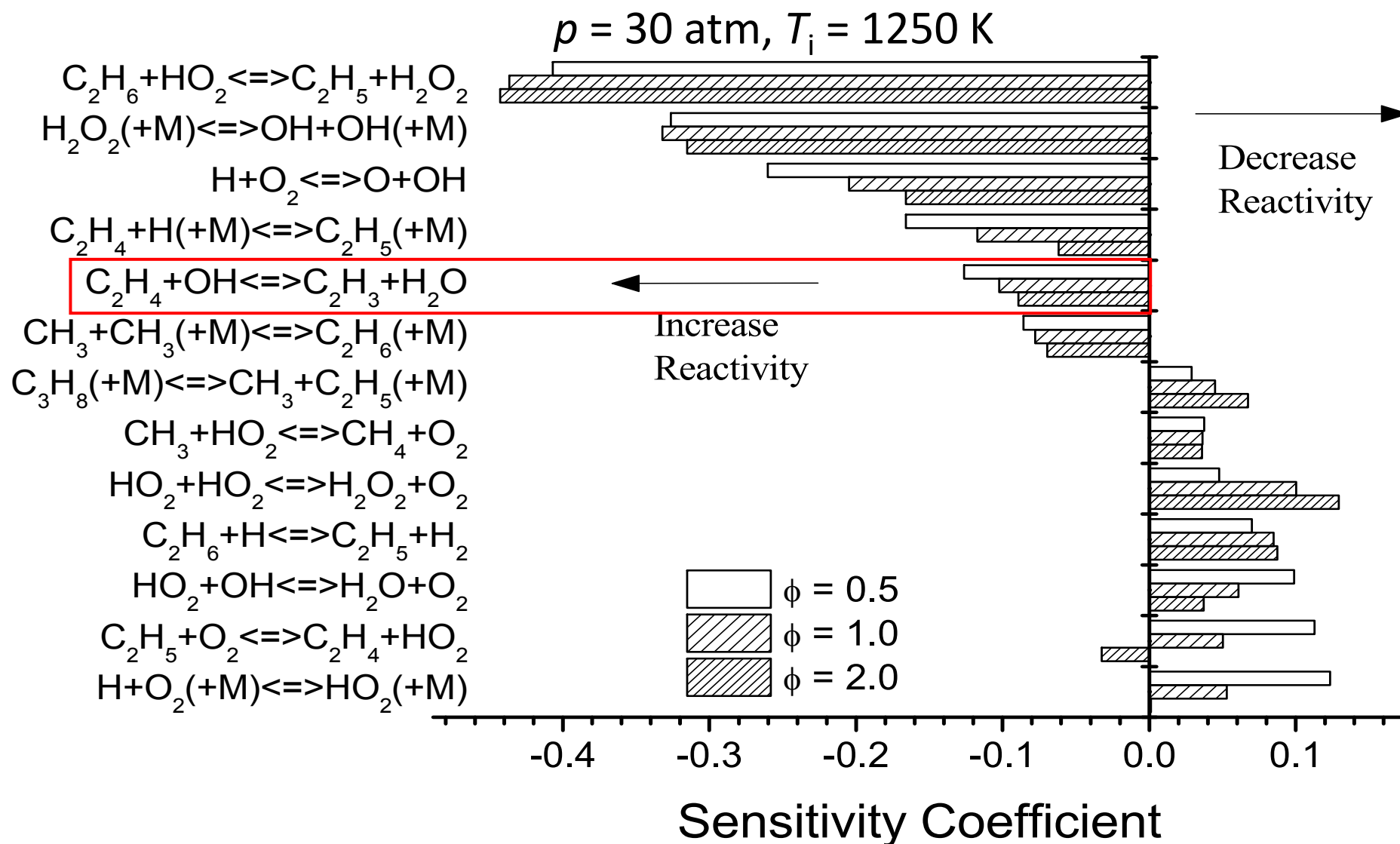
J.A. Miller, S.J. Klippenstein The $\text{H} + \text{C}_2\text{H}_2 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_3 (+\text{M})$ and $\text{H} + \text{C}_2\text{H}_4 (+\text{M}) \rightleftharpoons \text{C}_2\text{H}_5 (+\text{M})$ reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. *Phys. Chem. Chem. Phys.* 2004 6 1192–1202.

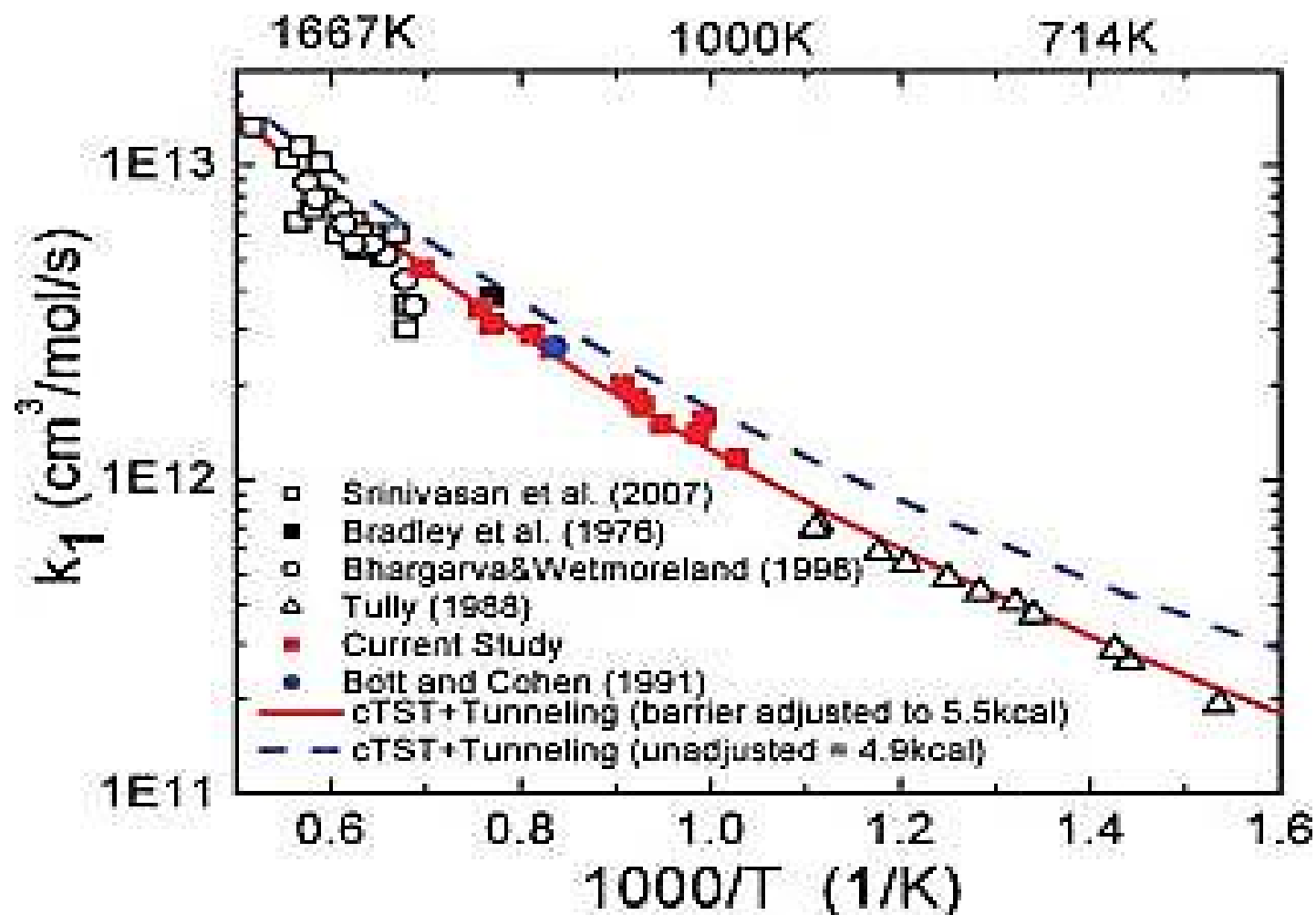
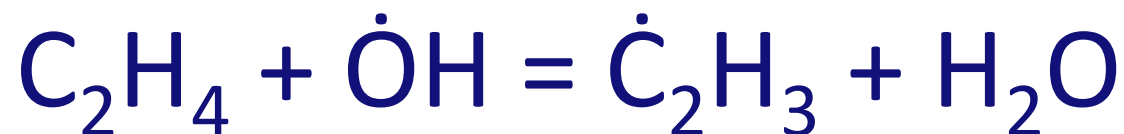
Sensitivity Analysis—C₂H₆ Flame Speed

$p = 1.0 \text{ atm}, T_i = 298 \text{ K}$

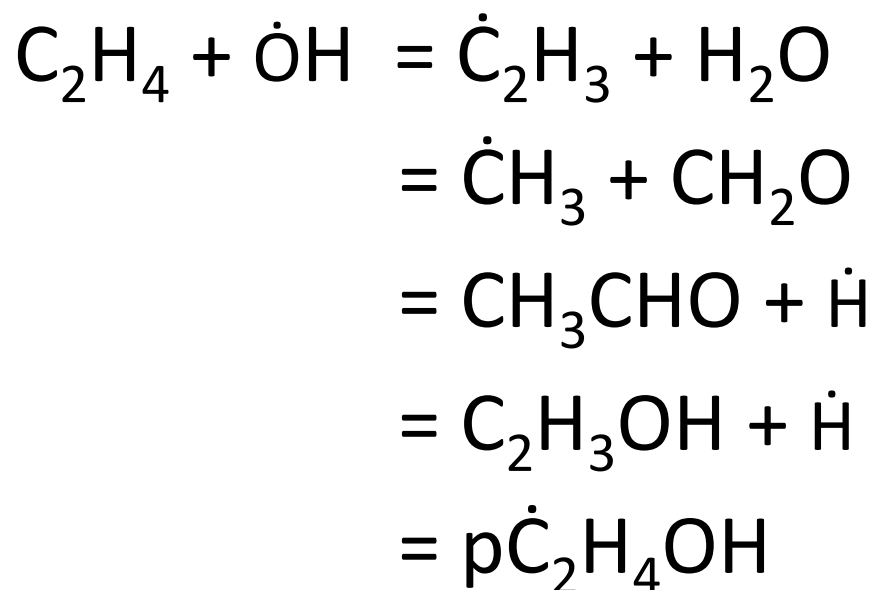


Sensitivity Analysis—C₂H₆ Ignition delay



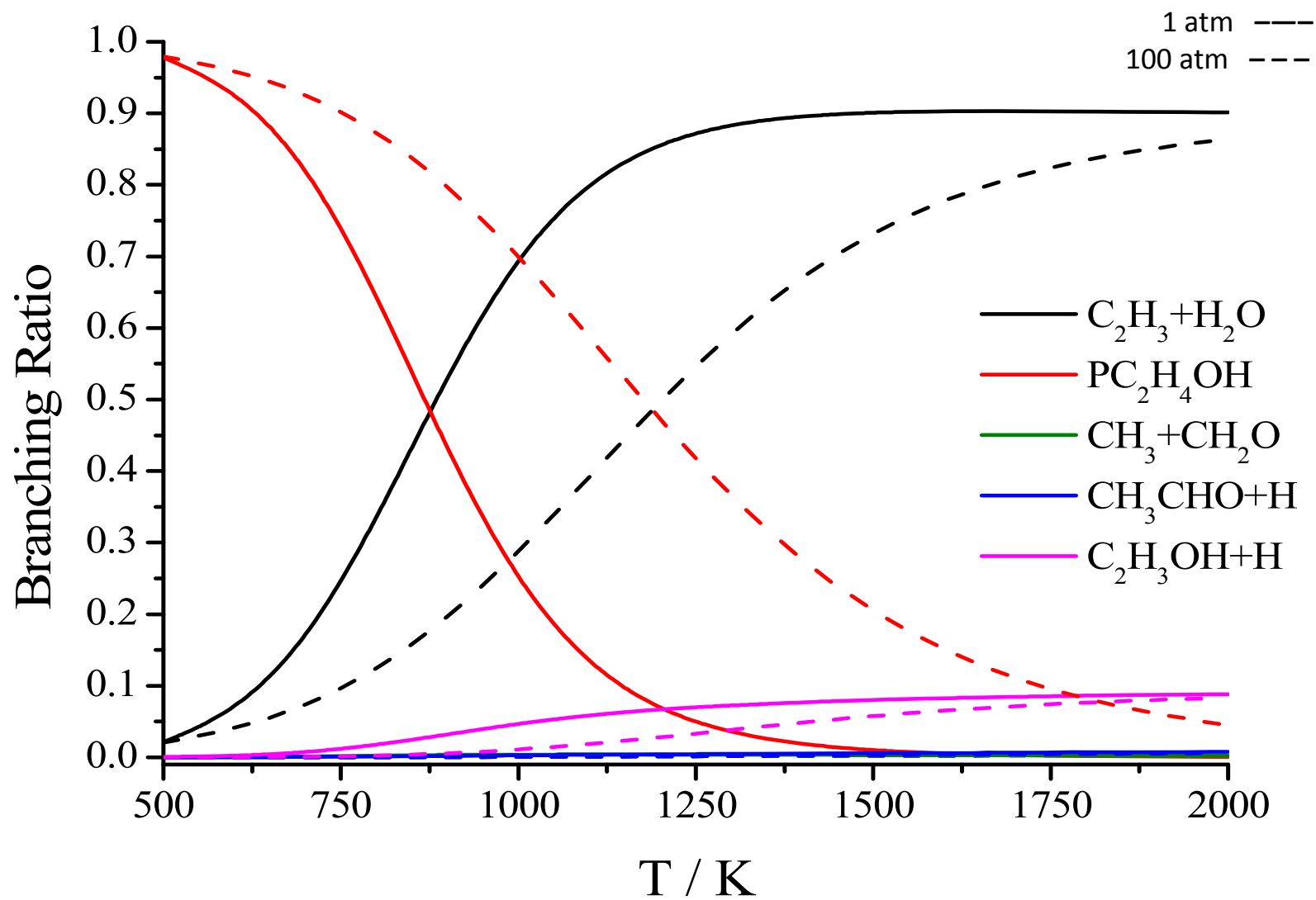


SS Vasu, Z. Hong, DF Davidson, RK Hanson, DM Golden, Shock Tube/Laser Absorption Measurements of the Reaction Rates of OH with Ethylene and Propene. Journal of Physical Chemistry A 2010;114:11529–11537.



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.





Developing a kinetic mechanism for propene oxidation



Why C₃H₆?

- Significant component of LPG
- Important intermediate in combustion
 - Product of larger alkyl radical decomposition
$$e.g. s\dot{C}_4H_9 \rightleftharpoons C_3H_6 + \dot{C}H_3$$
- Literature data limited
 - High-temperature, low-pressure, disagreement
 - Few studies investigate propene rate constants
- Difficult to validate mechanism



Literature data

Reactor Type	Temperature Range, K	Pressure Range, atm	ϕ Range	Dilution
<i>Ignition Delay</i>				
Shock tube	1274–1870	2.19–7.04	0.5–2.0	84–97%
Shock tube	1200–1800	≈ 2.65	–	> 95%
Shock tube	1270–1820	0.95–4.7	0.5–2.0	> 90%
<i>Speciation</i>				

Further data required

Flow reactor	1180–1210	1	0.5–2.0	> 95%
Flat flame	≈ 500 –2200	0.05	2.33	$\approx 25\%$
<i>Flame Speed</i>				
Counterflow	298	1	0.5–2.0	in ‘air’
Outwardly propagating	298	1–5	0.5–2.0	in ‘air’
Spherical bomb	293 and 425	0.5–3.5	0.8–1.6	in ‘air’



New experiments

Experimental data obtained for propene during this study

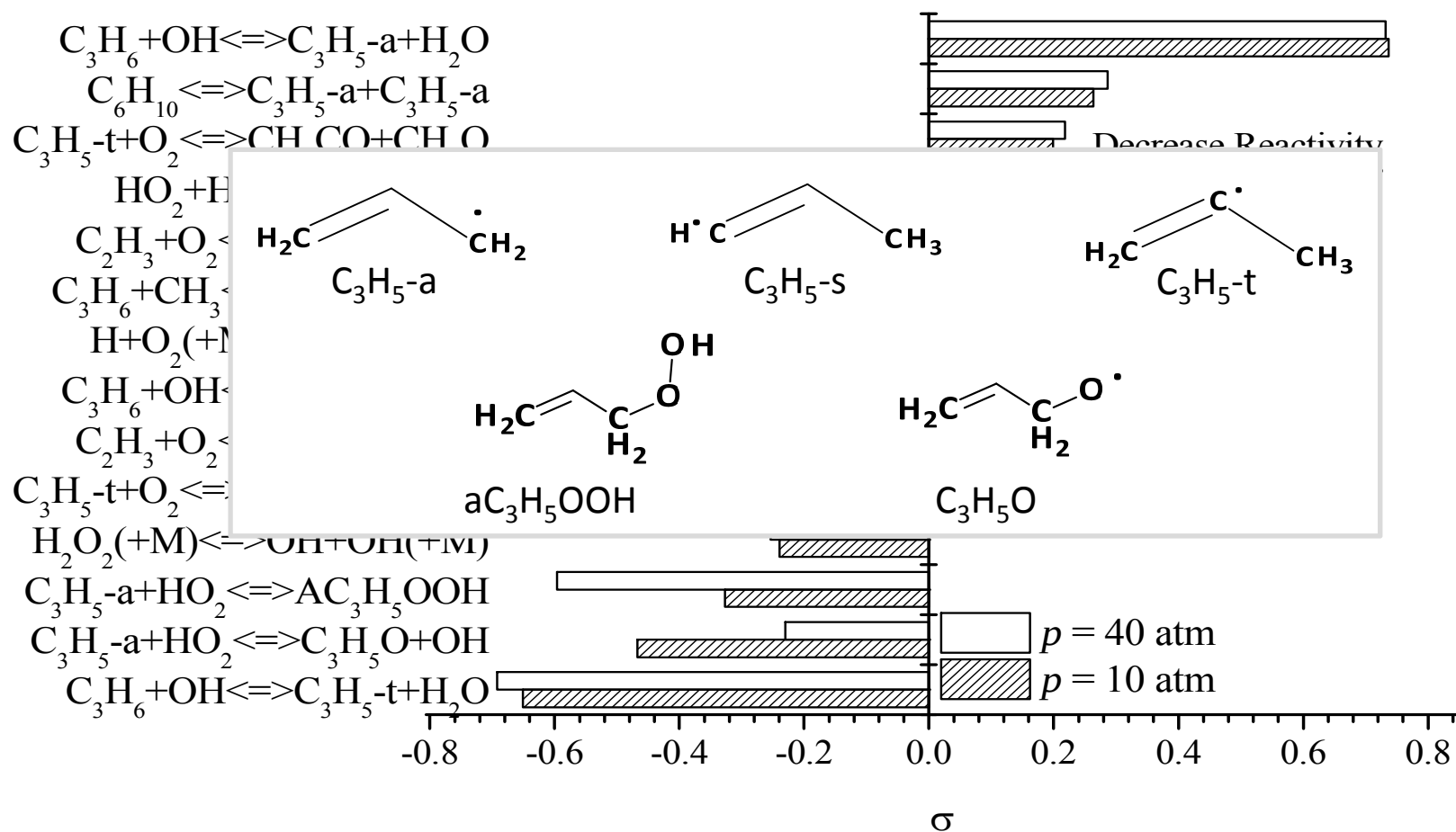
Reactor		Temperature K	Pressure Range, atm	ϕ Range	Dilution
	NUI Galway				
	TAMU				
Shock tube	RPI	50	2.0–40.0	0.5–2.0	72.25–95.55%
RCM	Stanford	10	10.0–40.0	0.5–2.0	75.47–95.11%
JSR	Nancy (STSM)		1.0	0.64–2.19	86.75–95.28%
Flow reactor	Princeton		15.0	0.35–1.25	> 90%
Flow reactor			6–12.5	0.70–1.31	> 97%
Heat flux method	Princeton				
Outwardly propagating	TAMU		1	0.7–1.5	$\approx$ 70.00–80.00%
Spherical bomb	VUB		1	0.7–1.6	in 'air'
			1	0.8–1.6	in 'air'

Validation matrix extended via collaboration with 8 other groups



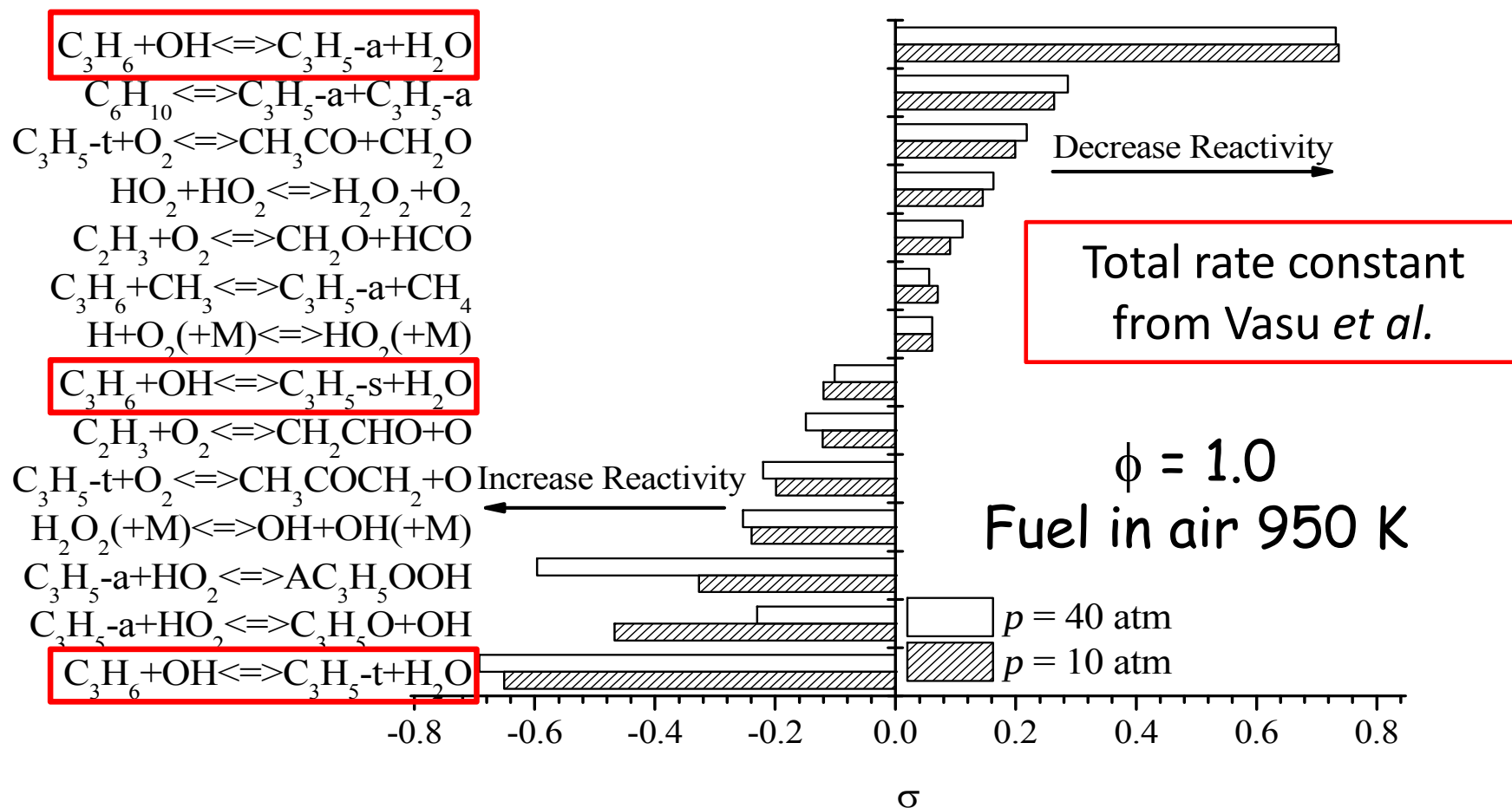
Mechanism Development

Sensitivity to τ at 10 and 40 atm





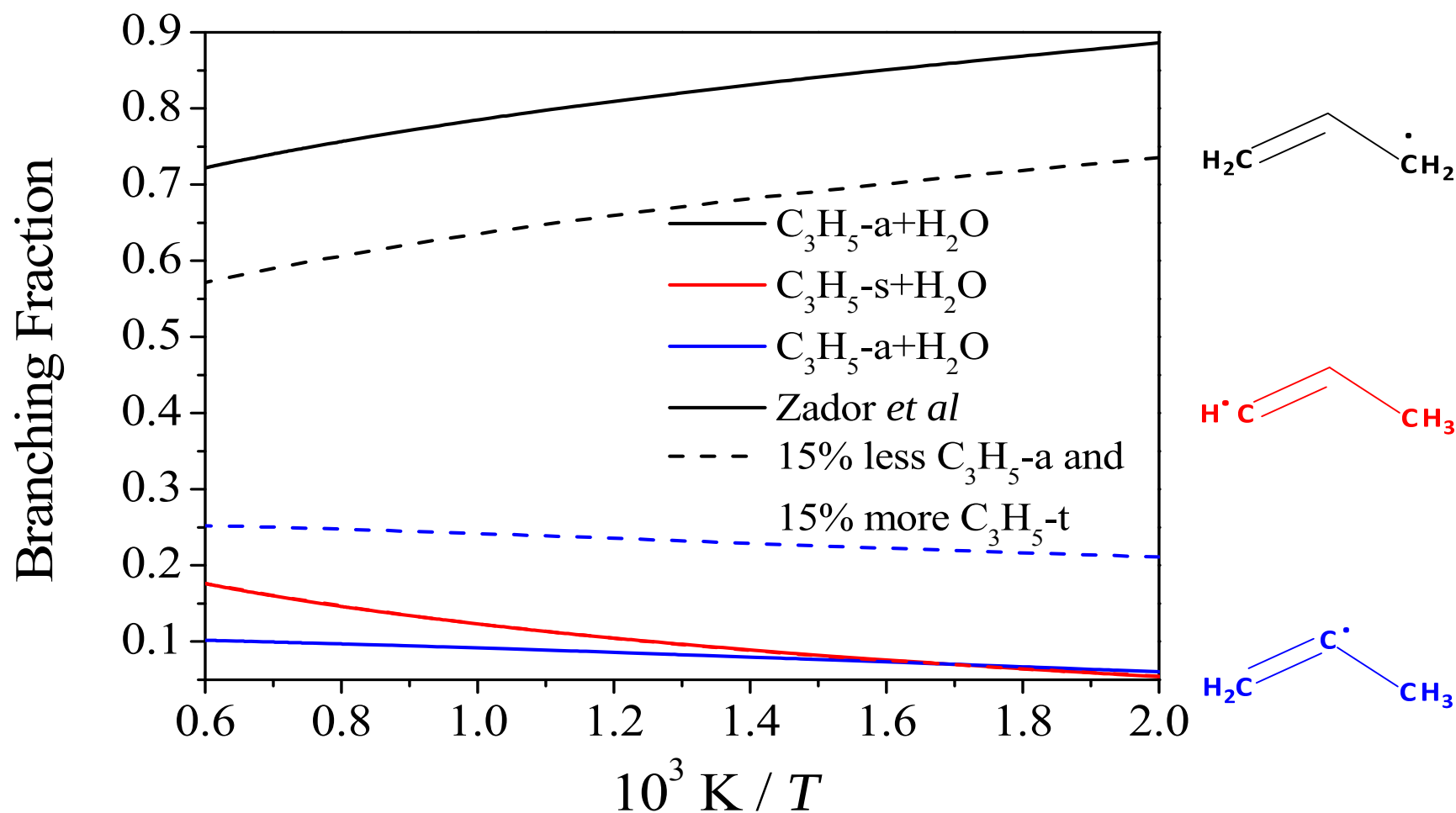
Mechanism Development



S. S. Vasu, Z. Hong, D. F. Davidson, R. K. Hanson, D. M. Golden, J.
Phys. Chem. A 114 (2010) 11529–11537.

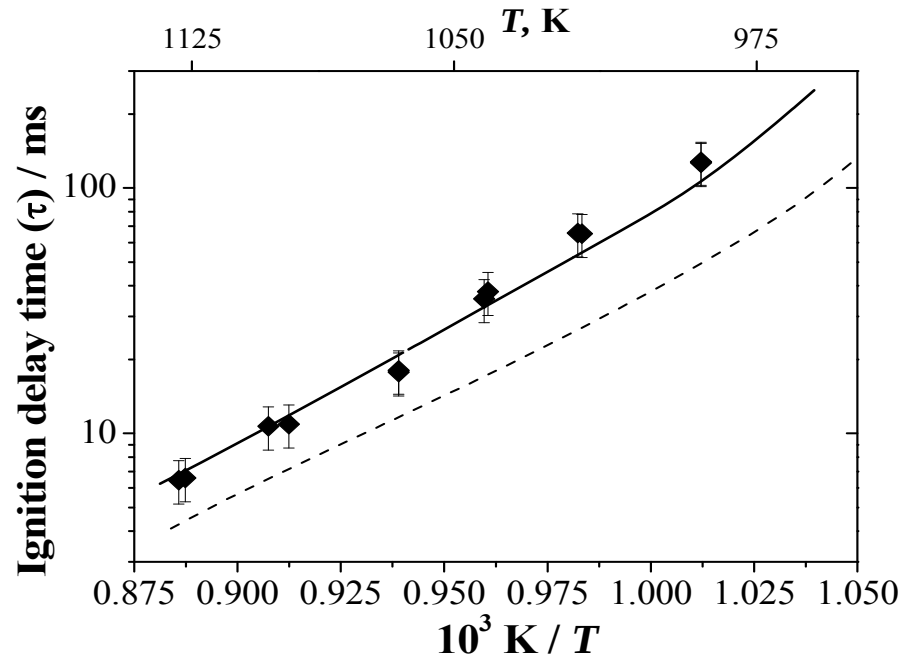


Mechanism Development

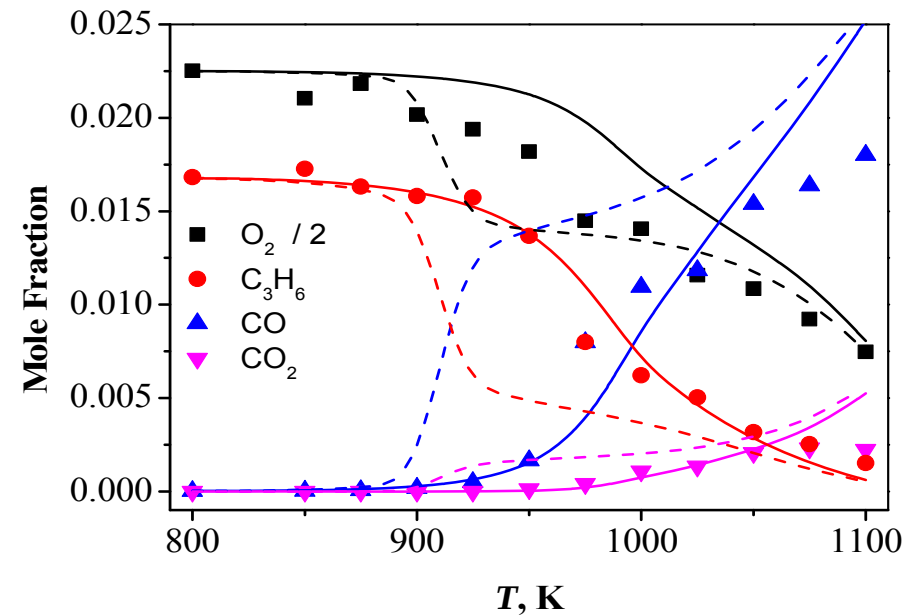


J. Zádor, A. W. Jasper, and J. A. Miller,
Phys. Chem. Chem. Phys. 11 (2009) 11040–11053.

Effect of changing $C_3H_6 + \dot{O}H$ branching ratio



RCM: 10 atm 12% O_2 , $\phi = 1.0$

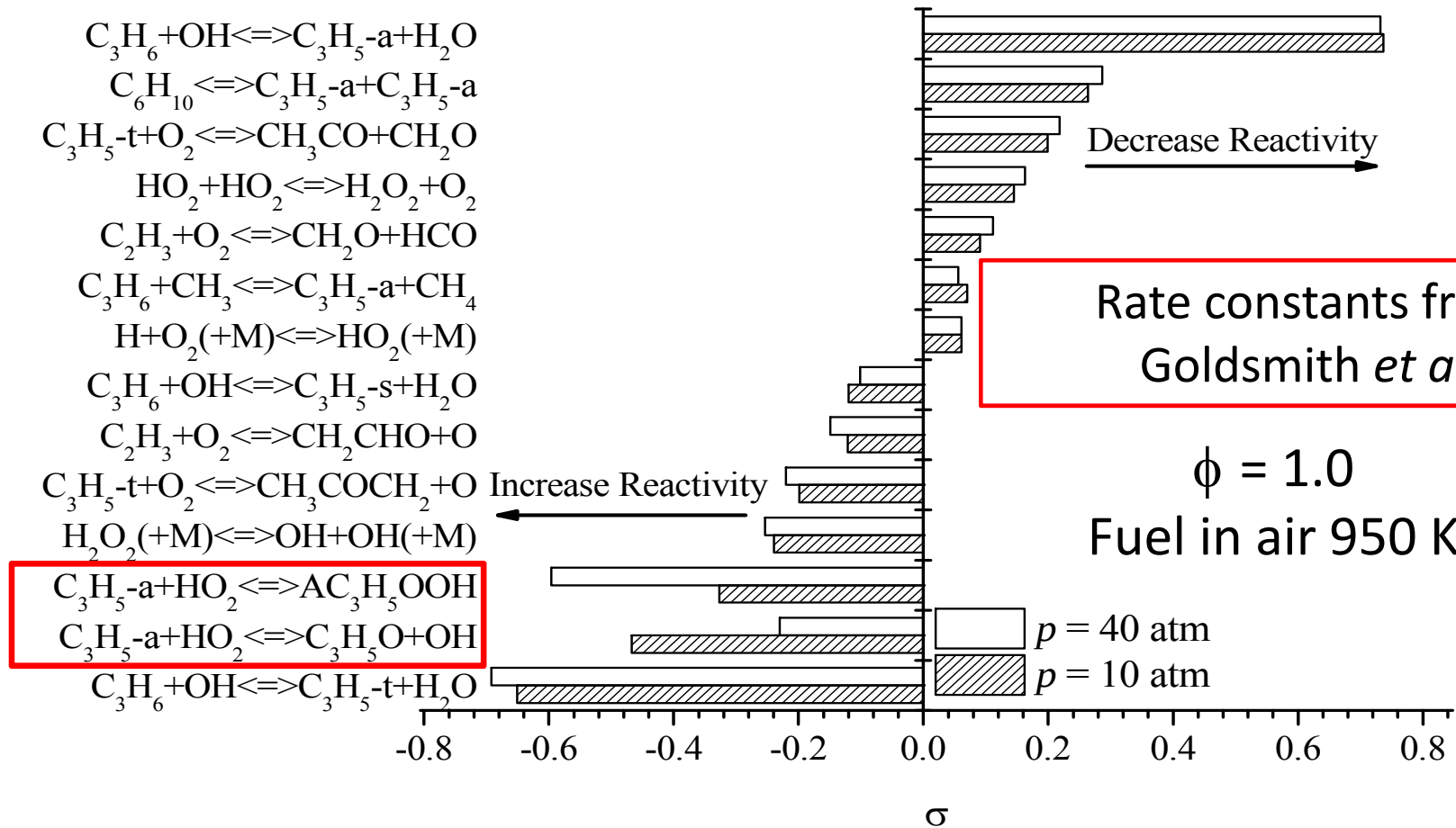


JSR: $\phi = 1.68$

— Current
 --- Branching ratio changed by 15%



Mechanism Development

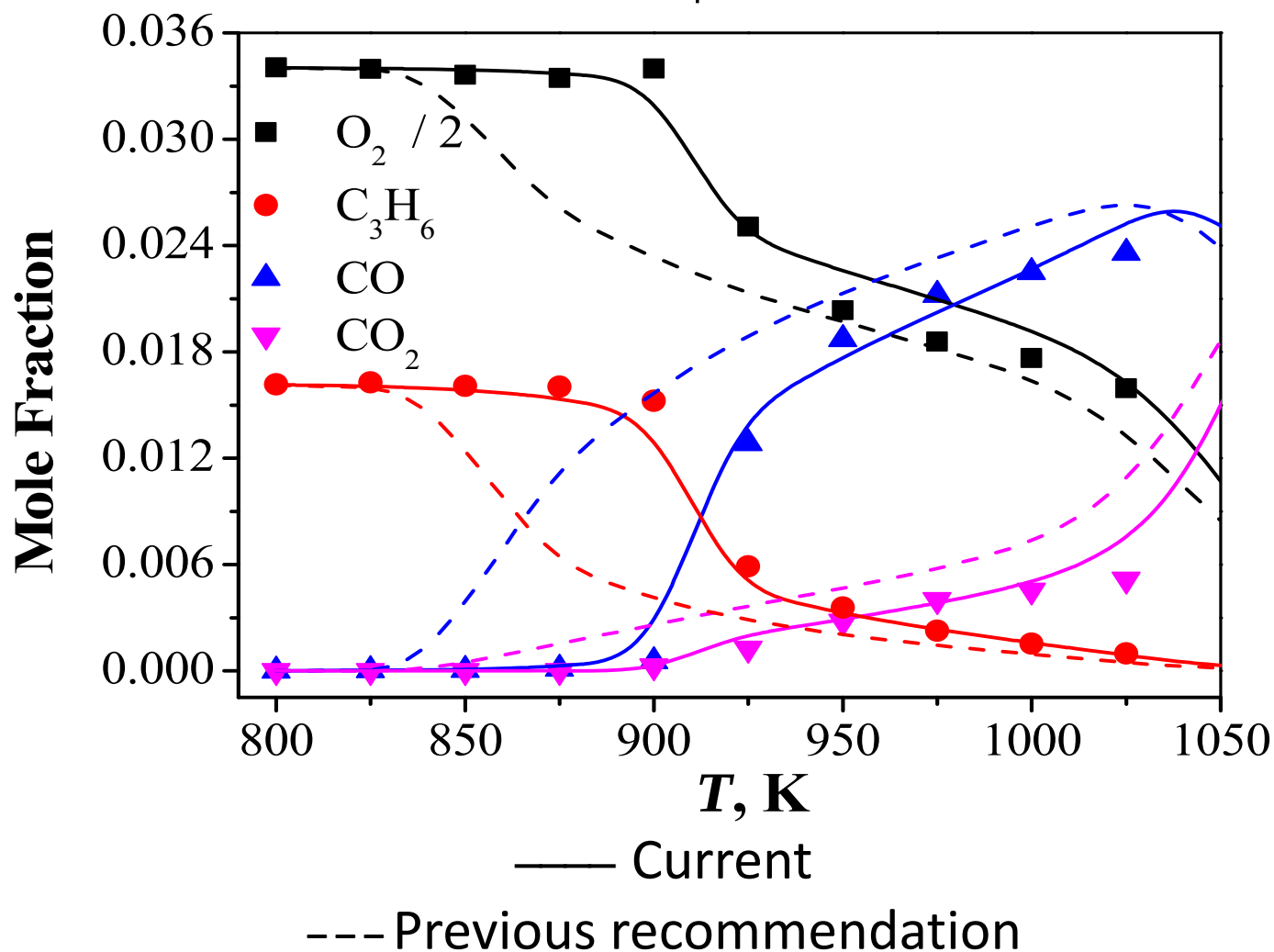


C. F. Goldsmith, S. J. Klippenstein, W. H. Green,
Proc. Combust. Inst. 33 (2011) 273–282.



Effect of $\dot{C}_3H_5\text{-a} + H\dot{O}_2$

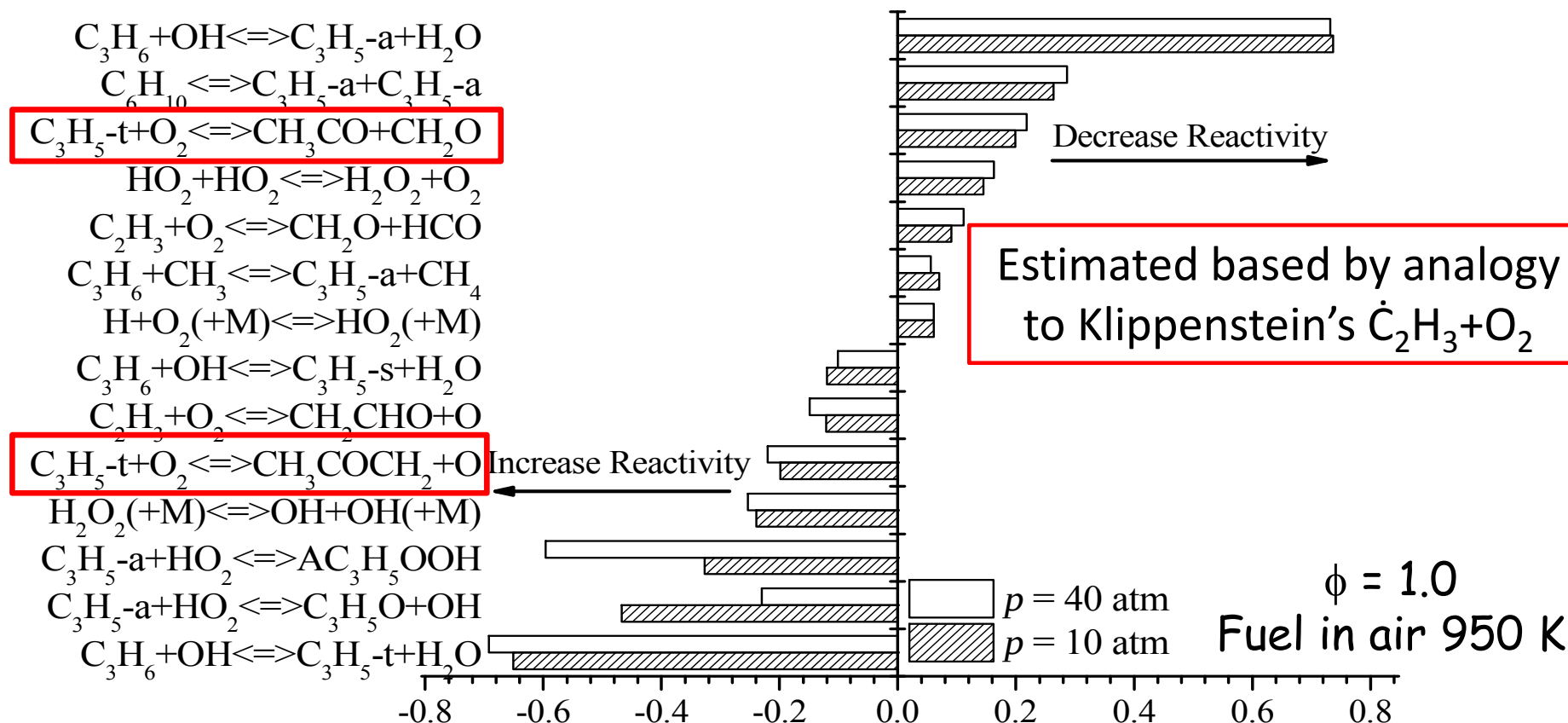
JSR at $\phi = 1.07$





Mechanism Development

Effect of $\dot{C}_3H_5-t + O_2$

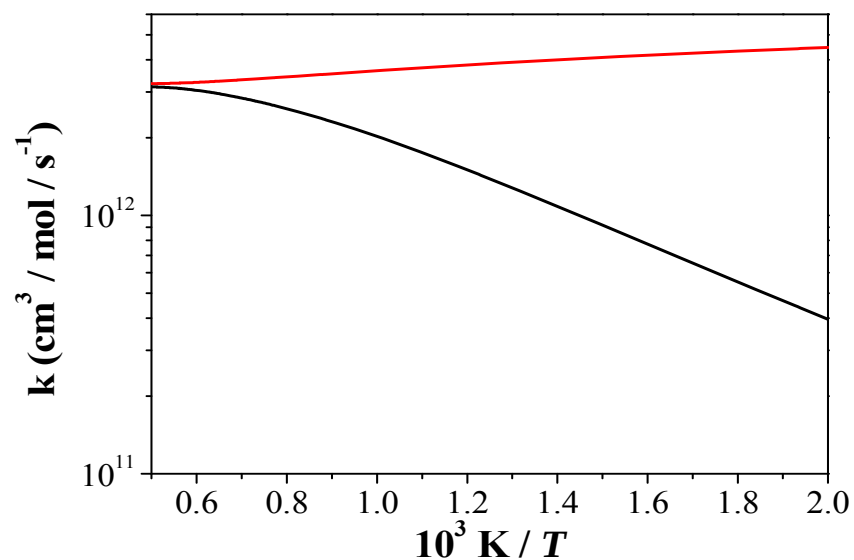


S. J. Klippenstein, Y. Georgievskii, J. A. Miller, J. A. Nummela, B. K. Carpenter, P. R. Westmoreland In Proceedings of the Third Joint Meeting of the U. S. Sections of The

Combustion Institute, 2003.

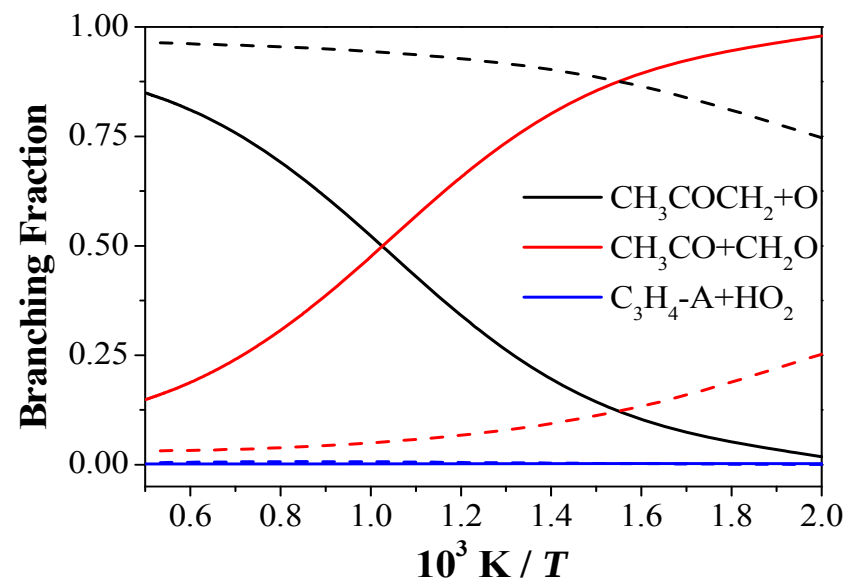


Total rate constant



— Current
— Previous recommendation

Branching ratio

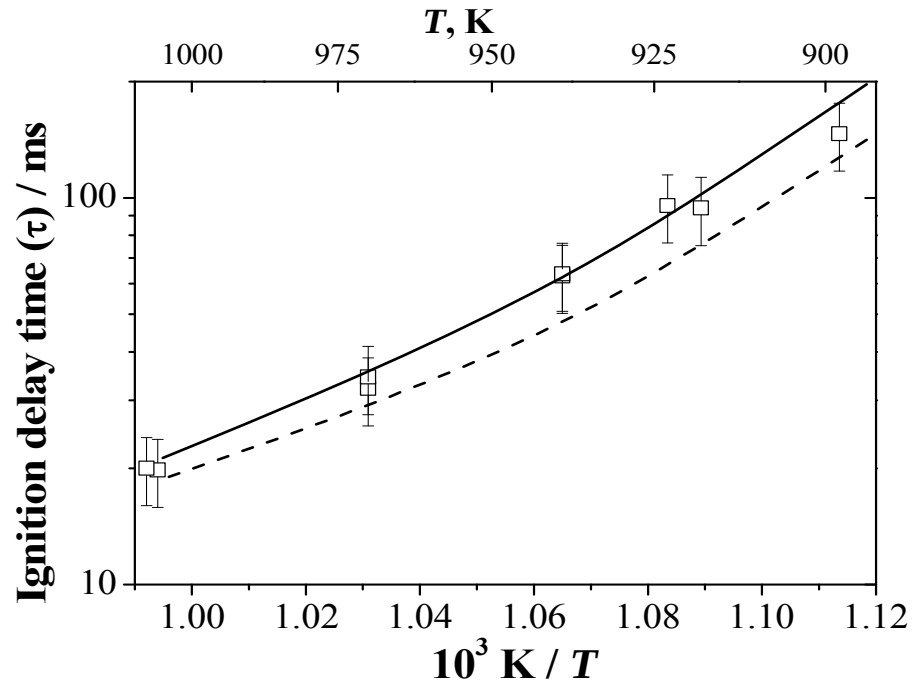


— Current
- - - Previous recommendation

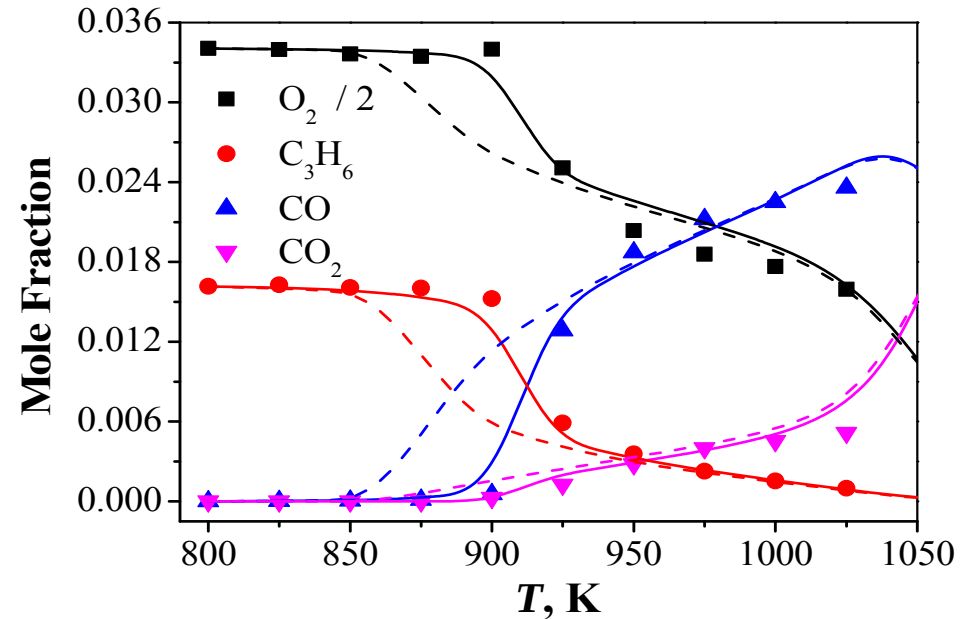




Effect of $\dot{C}_3H_5$ -t and $\dot{C}_3H_5$ -s + O_2



RCM: fuel/4% O_2 , $\phi = 1.0$, $p = 40$ atm



JSR: $\phi = 1.07$, $p = 1$ atm

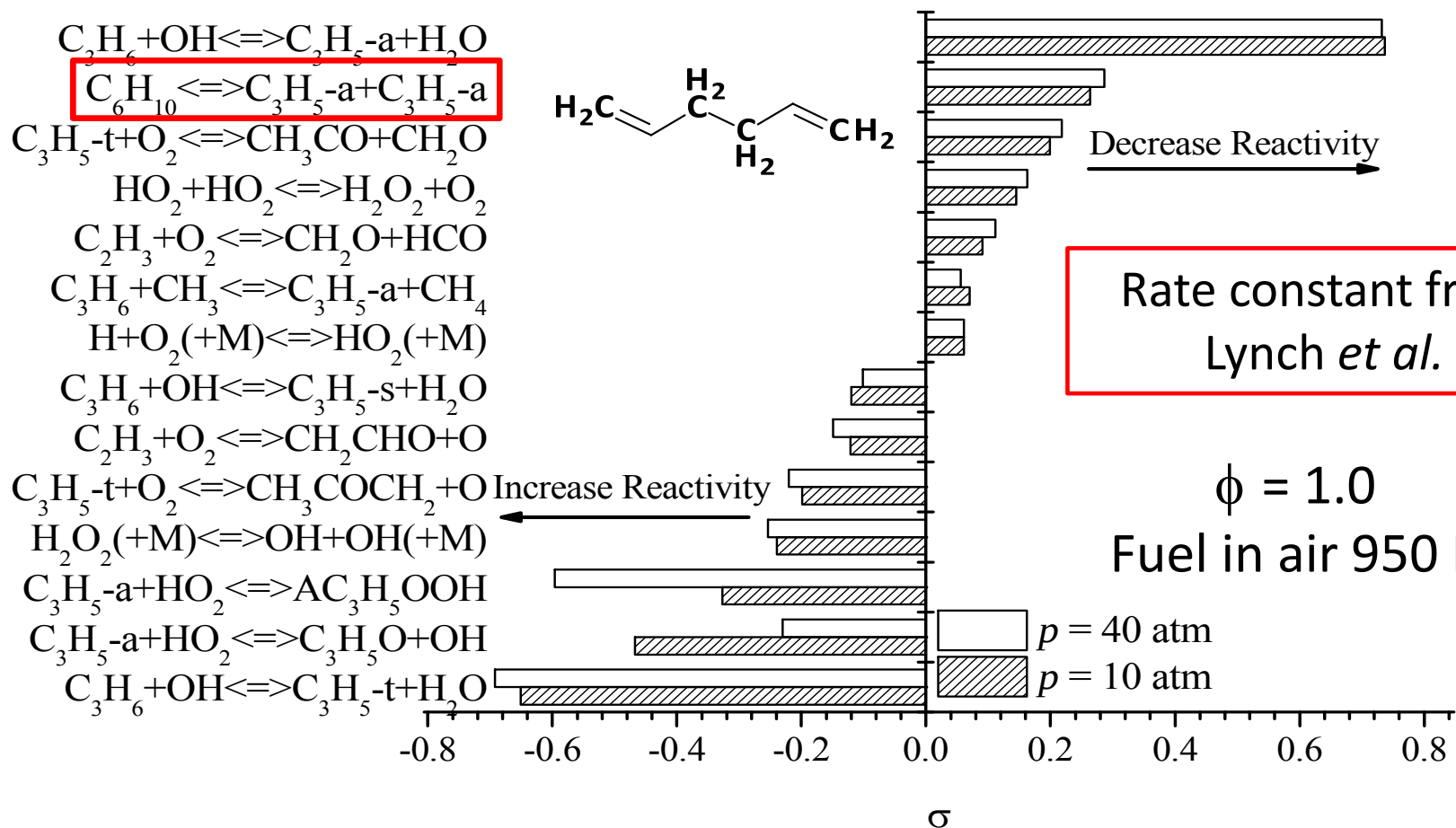
— Current

--- Previous recommendation





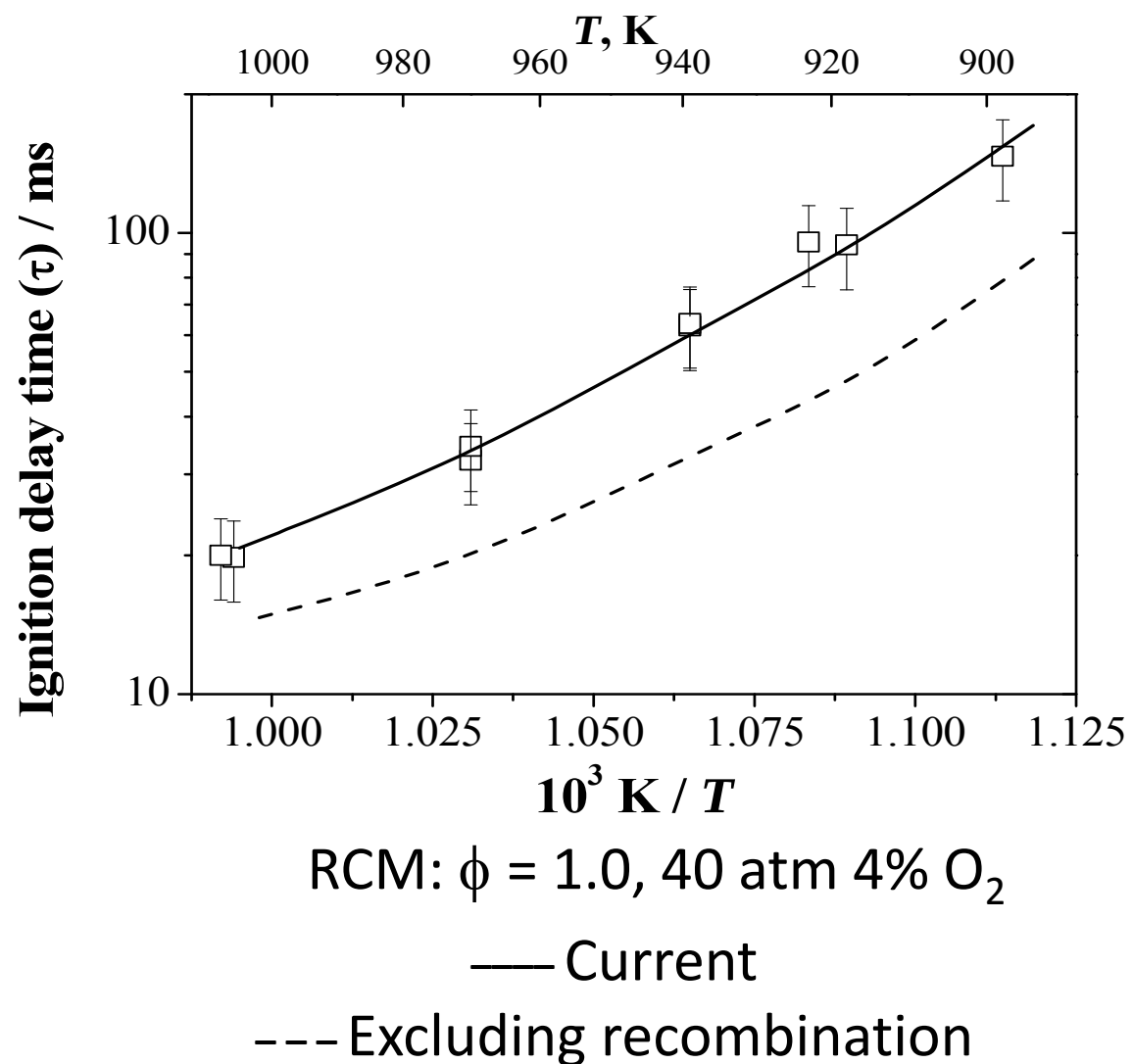
Mechanism Development



P. T. Lynch, C. J. Annesley, C. J. Aul, X. Yang, R. S. Tranter,
J. Phys. Chem. A 117 (2013) 4750-4761.

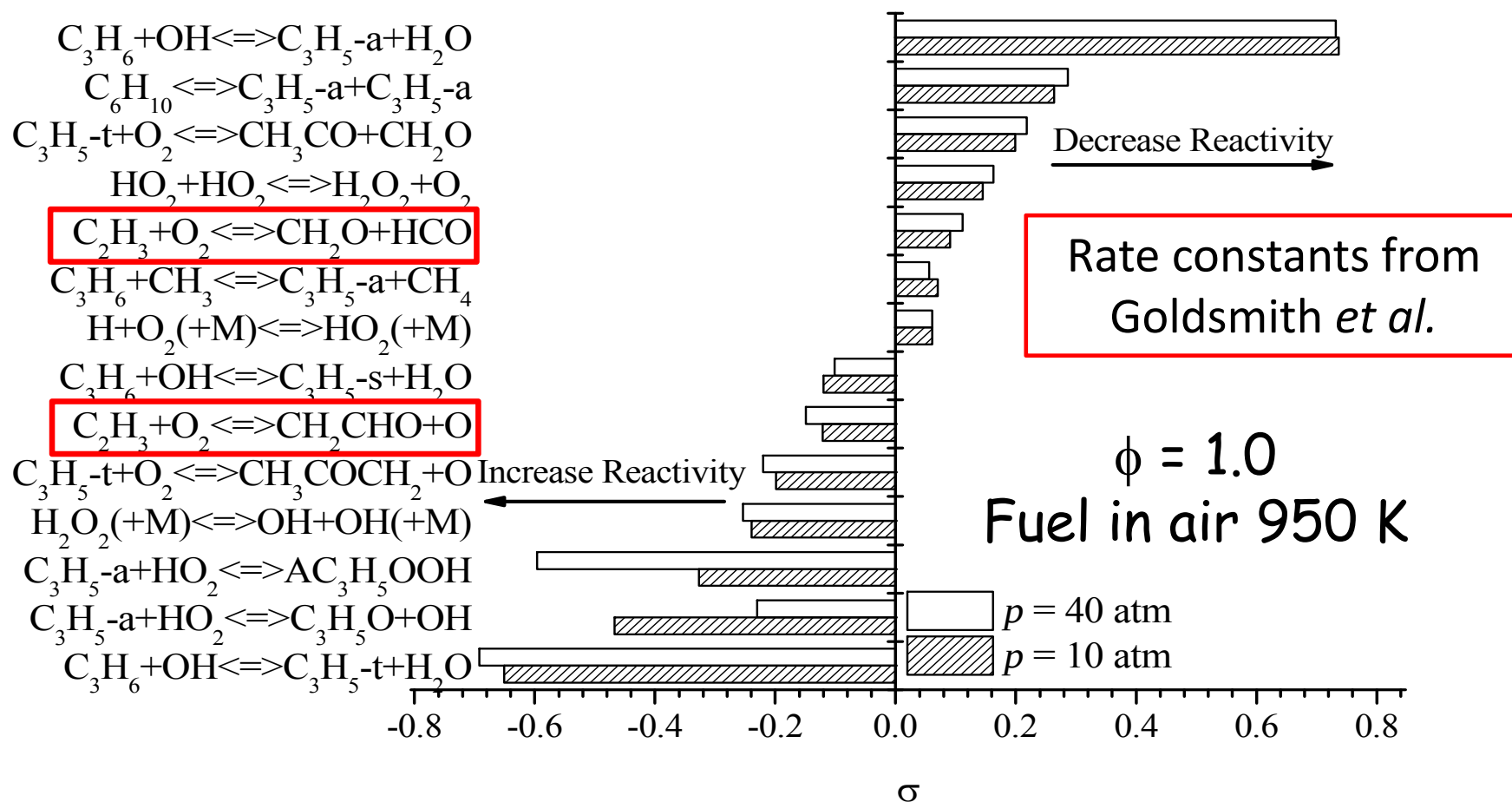


Effect of $\dot{C}_3H_5$ -a + $\dot{C}_3H_5$ -a





Mechanism Development



C. F. Goldsmith, L. B. Harding, Y. Georgievskii, J. A. Miller, S. J. Klippenstein
J. Phys. Chem. A 2015, in press.



Mechanism Development

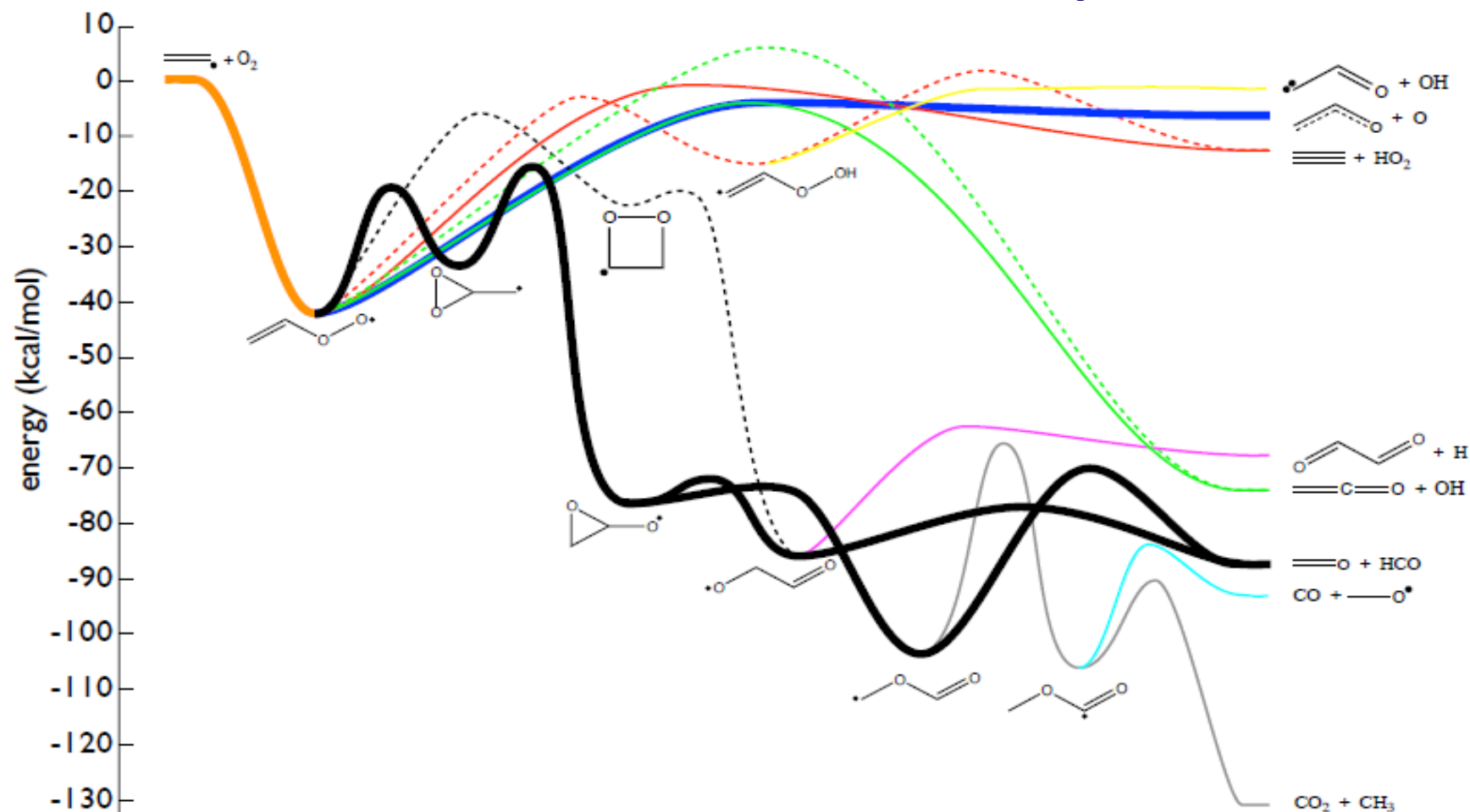
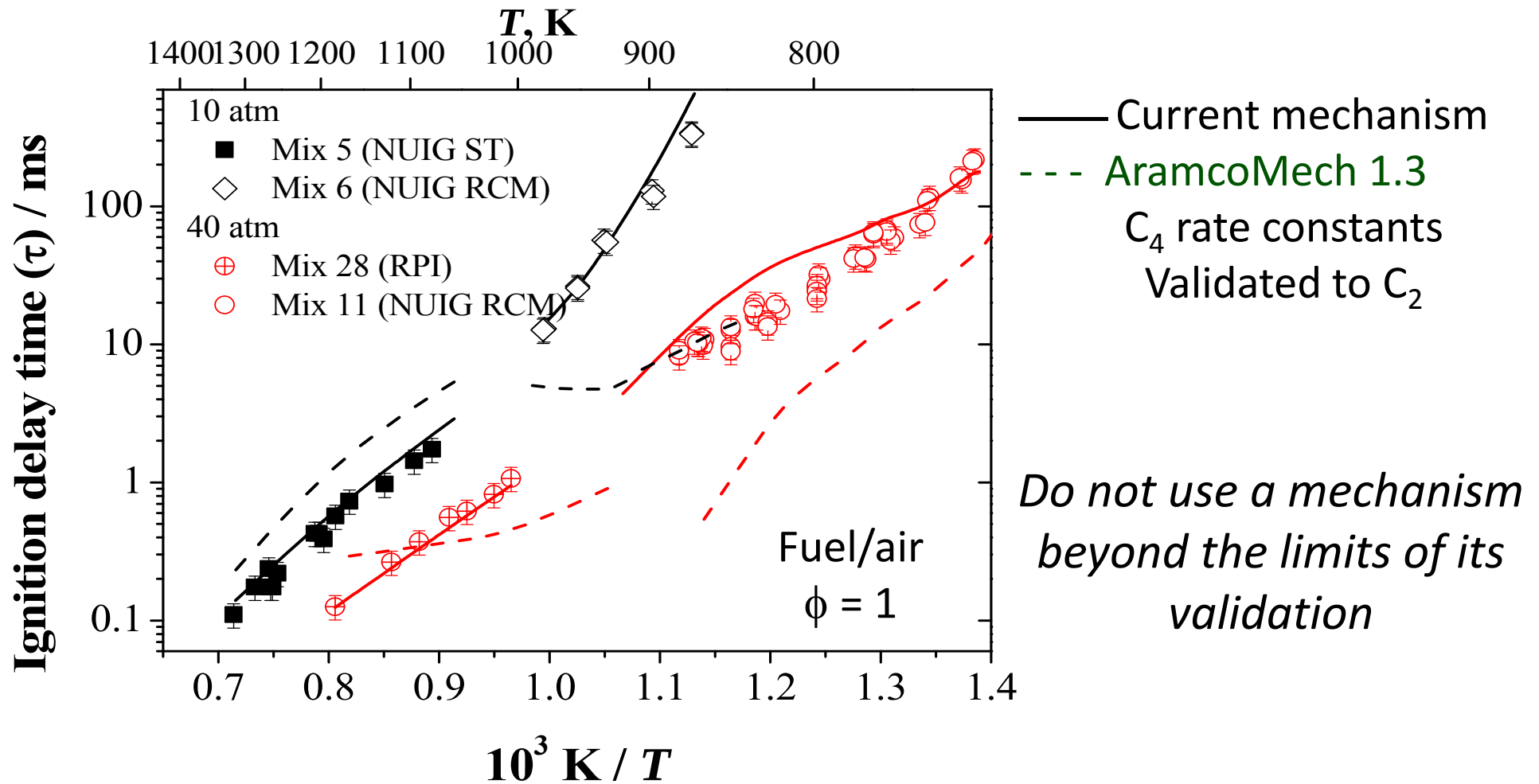


Figure 1: $\text{C}_2\text{H}_3\text{O}_2$ potential energy surface. The pathways to the main product channel at lower temperatures, $\text{CH}_2\text{O} + \text{HCO}$, is shown in black; the pathway to the main product channel at higher temperatures, $\text{CH}_2\text{CHO} + \text{O}$, is shown in blue.



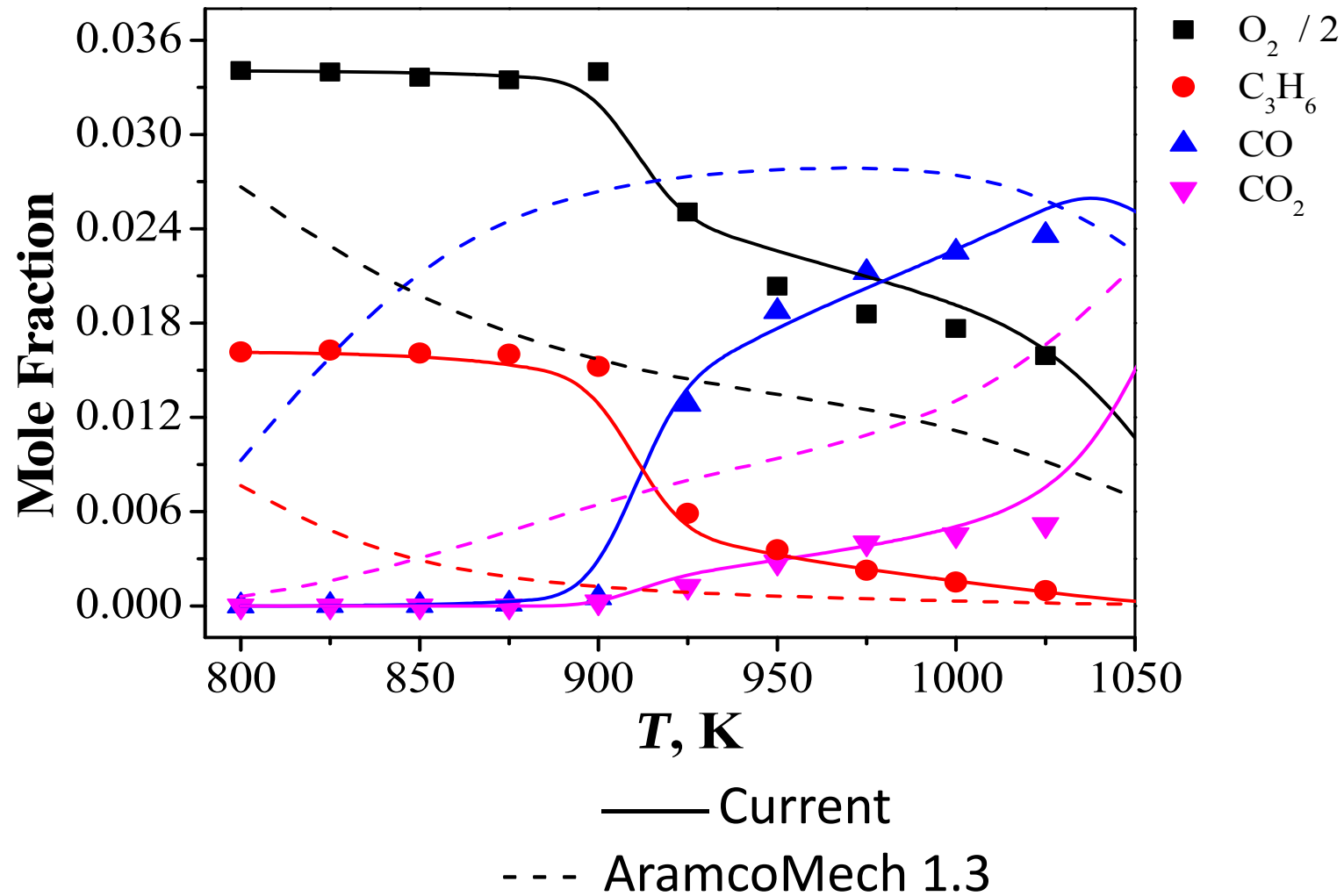
Previous and Current Performance





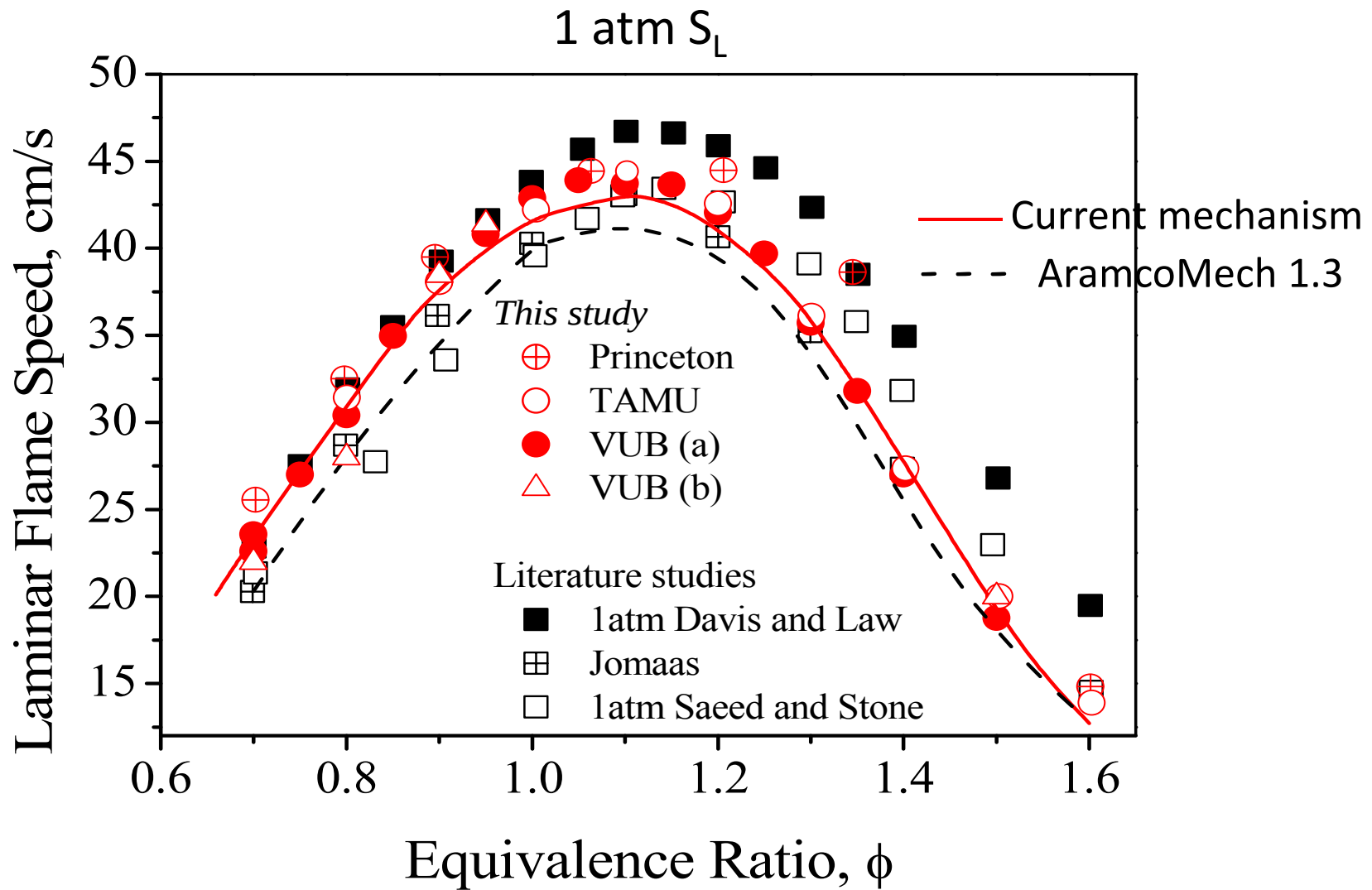
Previous and Current Performance

JSR $\phi = 1.07$





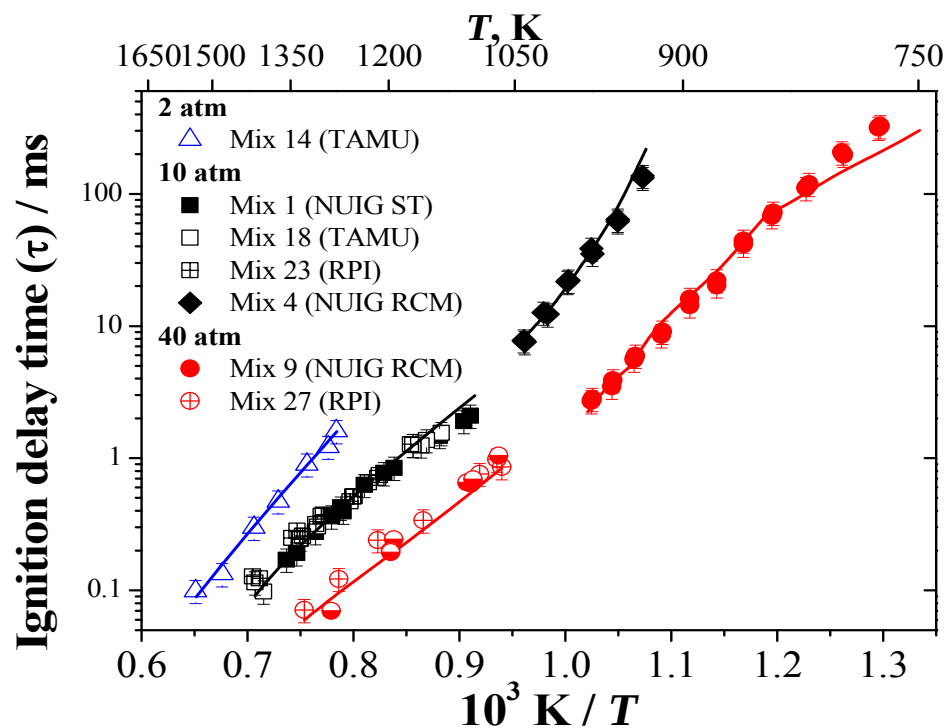
Previous and Current Performance



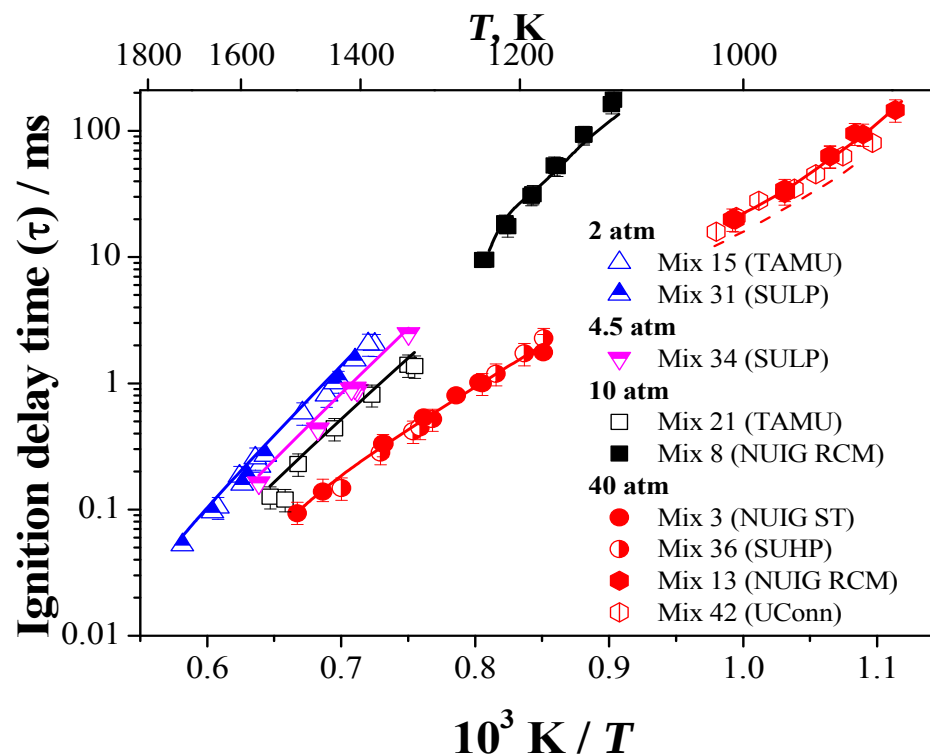


Effect of pressure on ignition delay times

$\phi = 0.5$, fuel/air



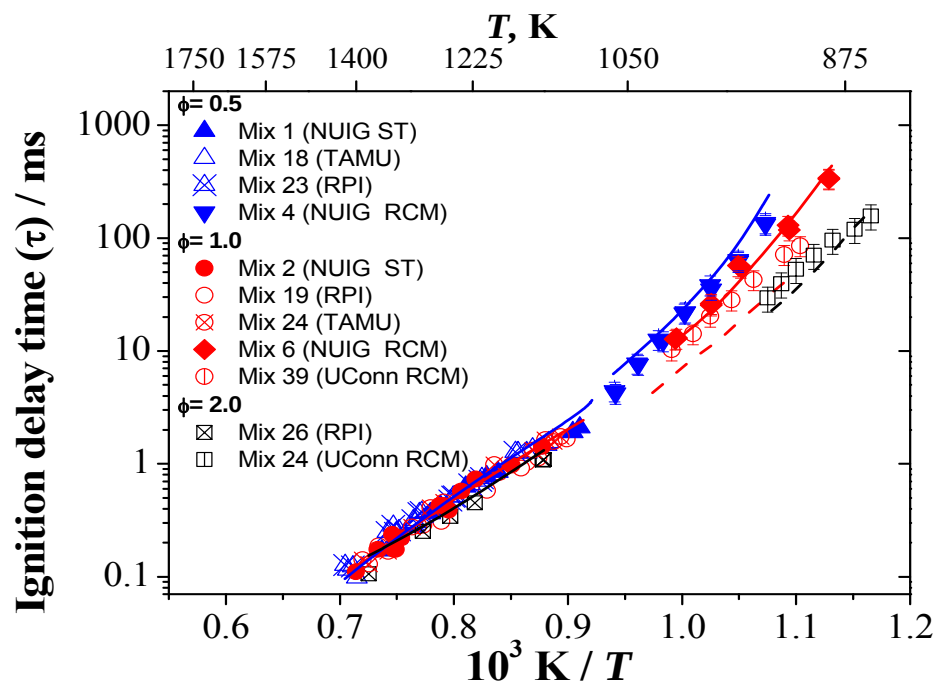
$\phi = 1.0$, 4% O_2



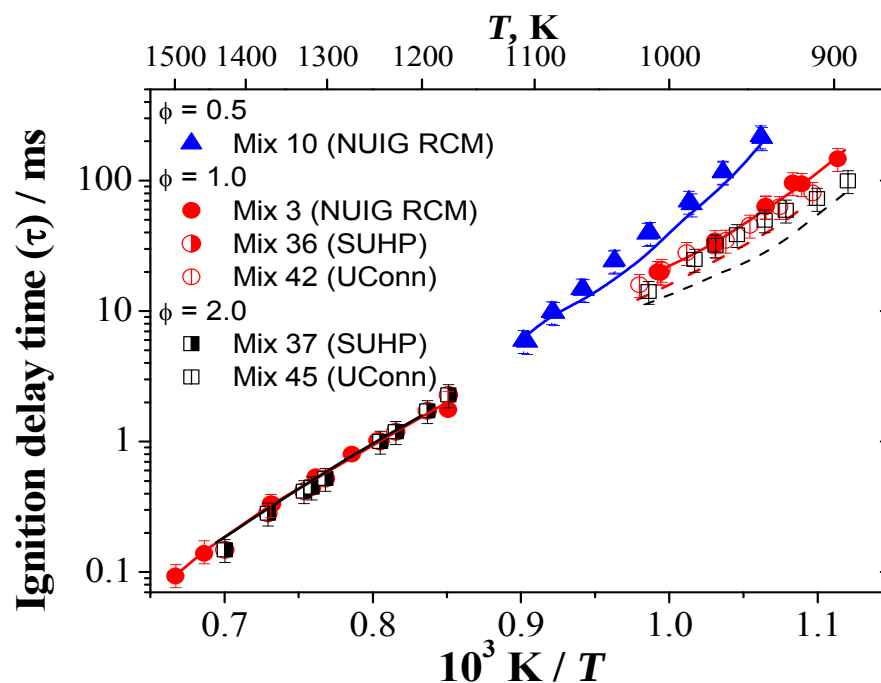


Effect of Φ on ignition delay times

$p = 10 \text{ atm, fuel/air}$

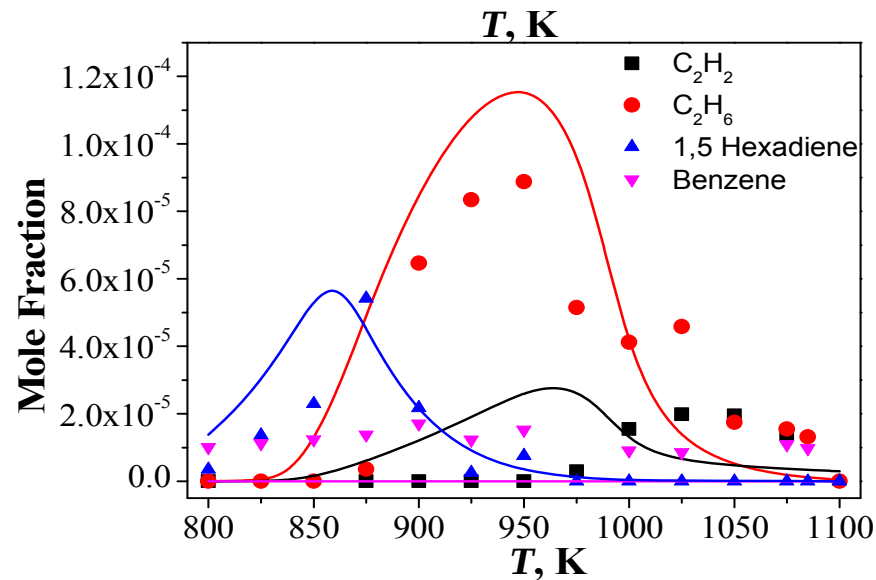
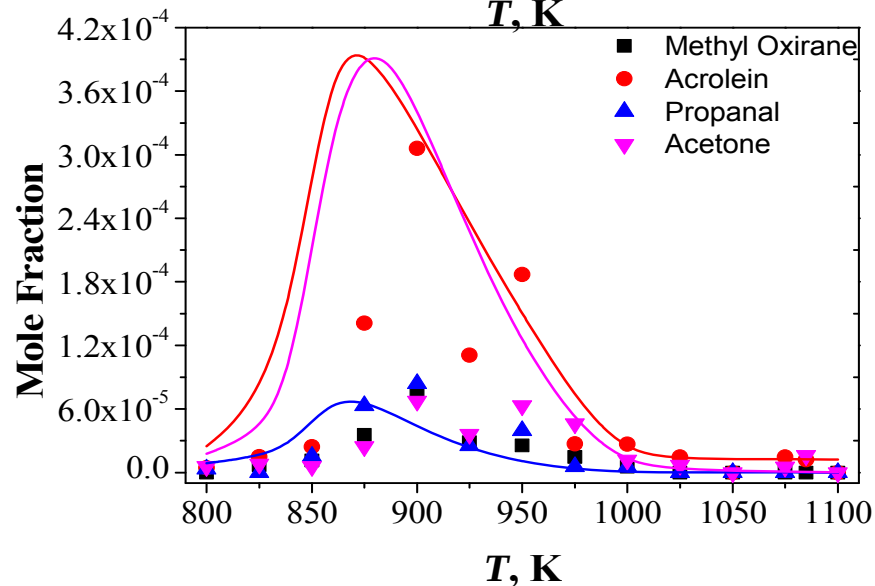
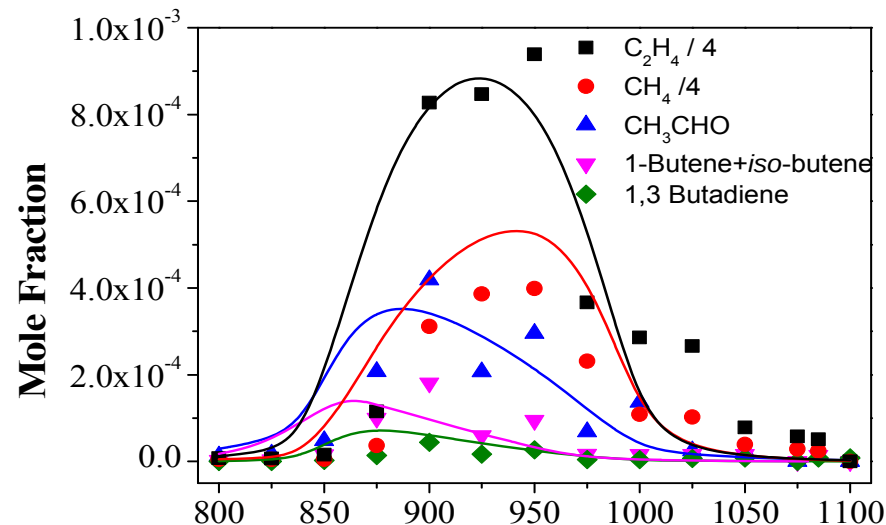
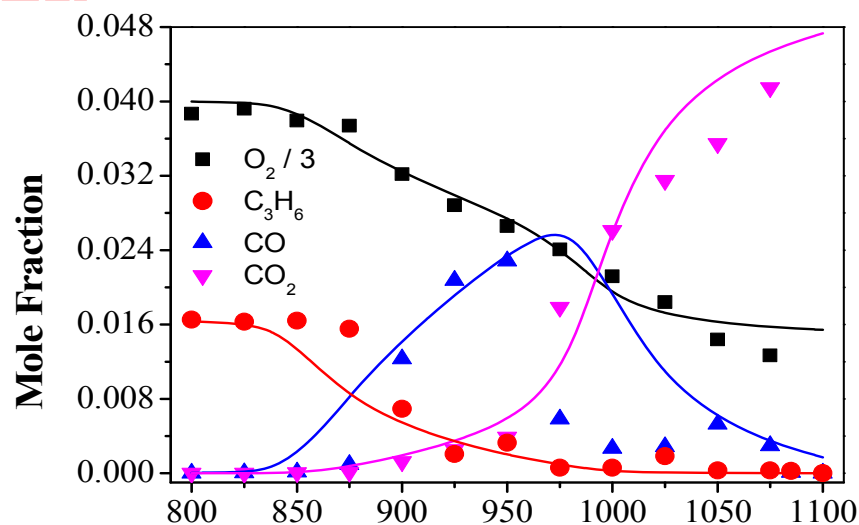


$p = 40 \text{ atm, 4\% O}_2$



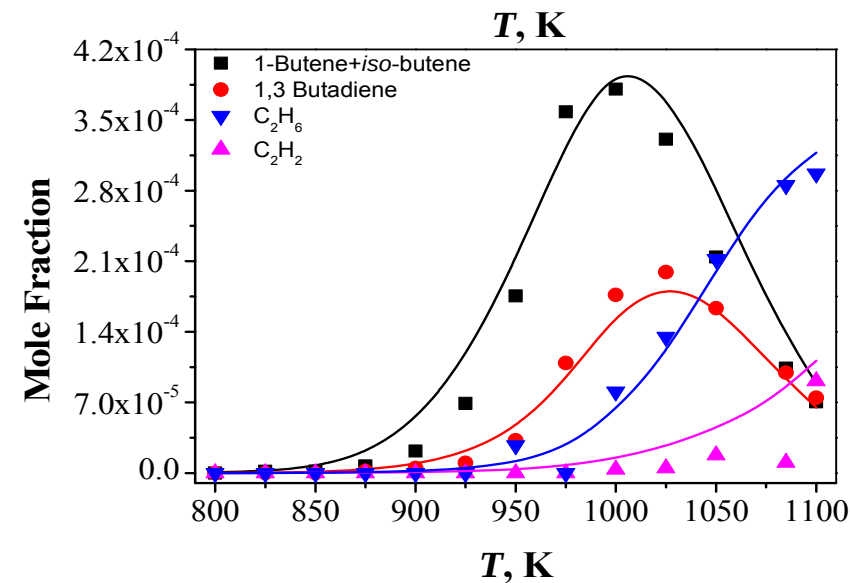
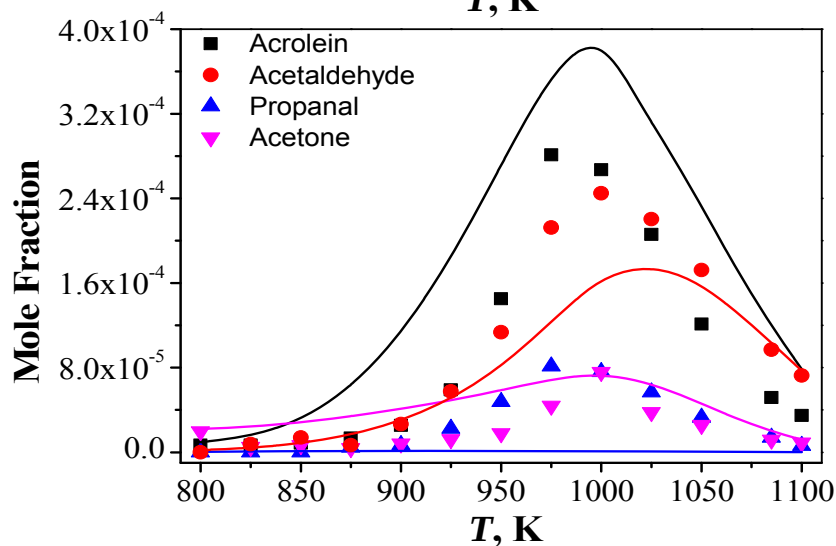
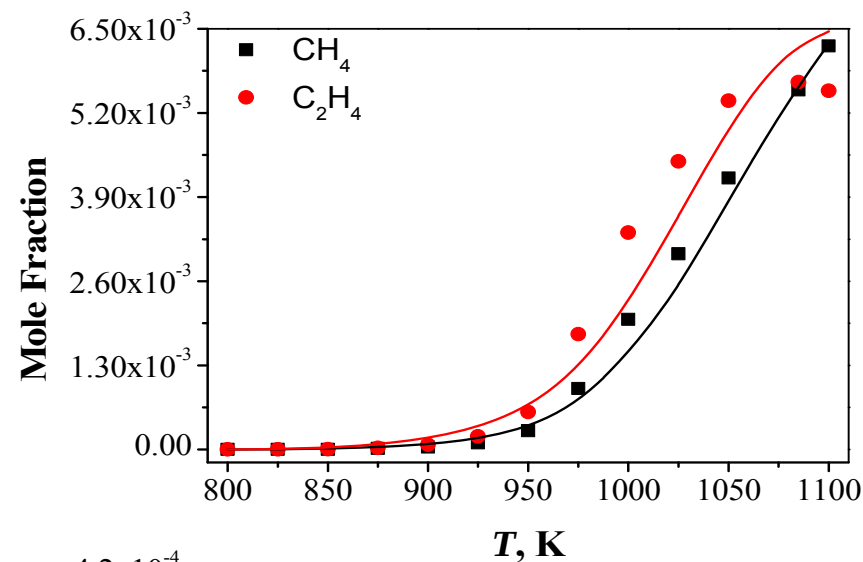
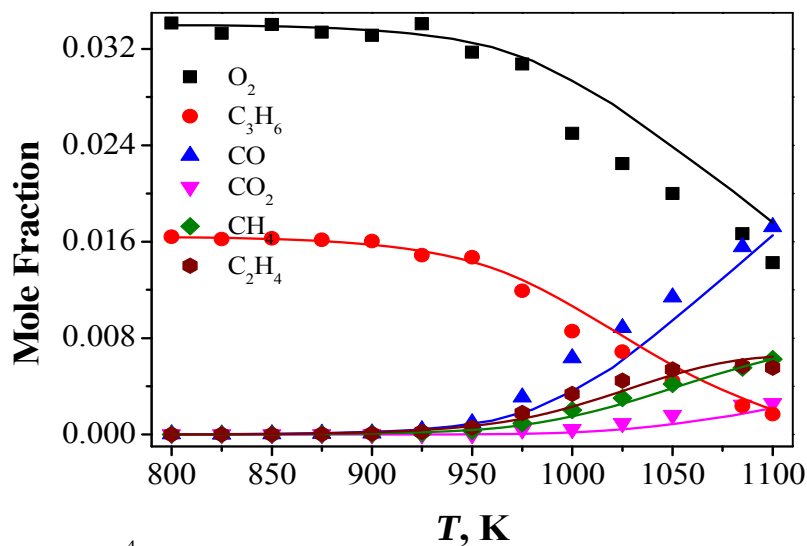


Validation in a JSR at $\phi = 0.64$



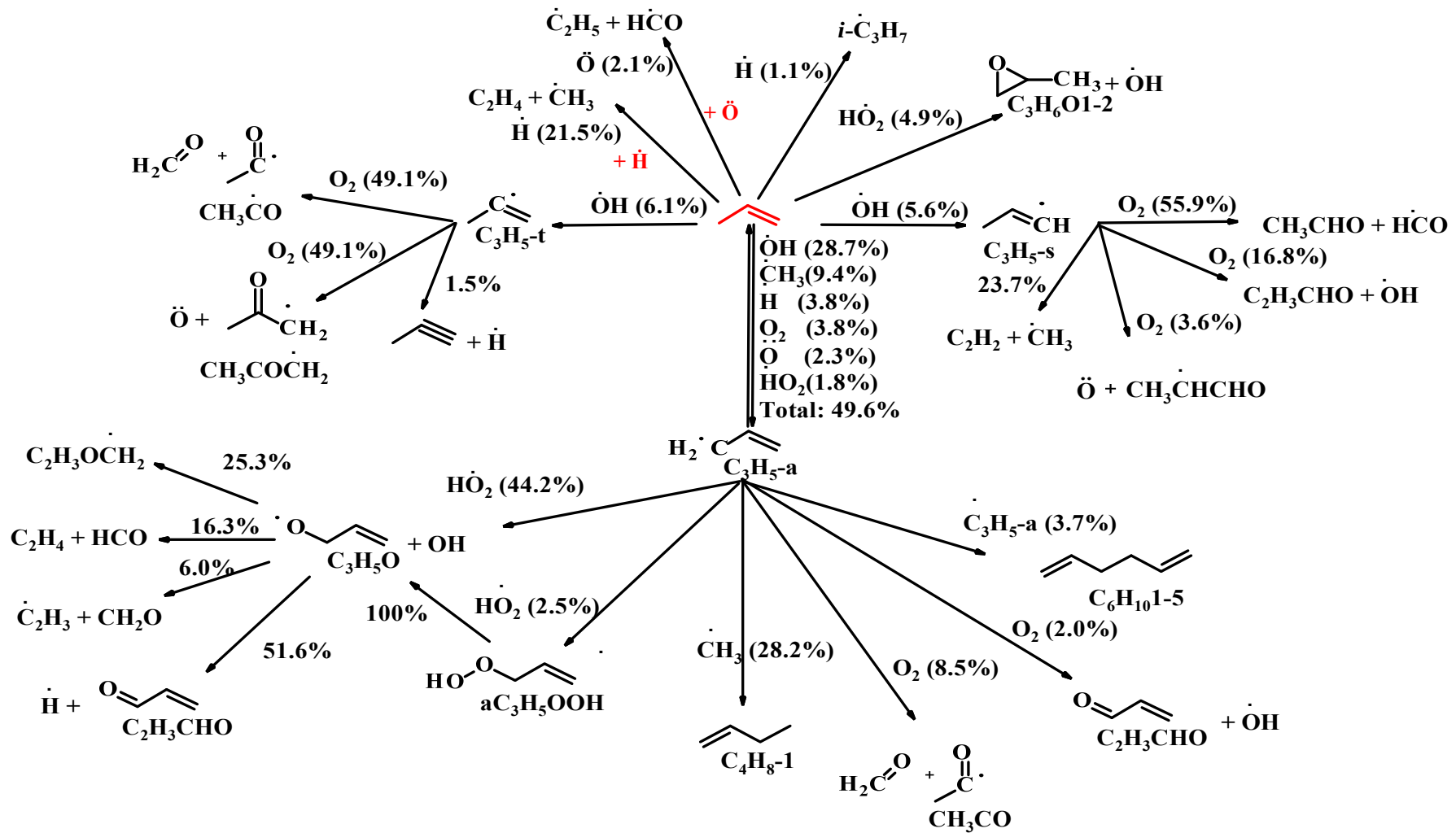


Validation in a JSR at $\phi = 2.19$



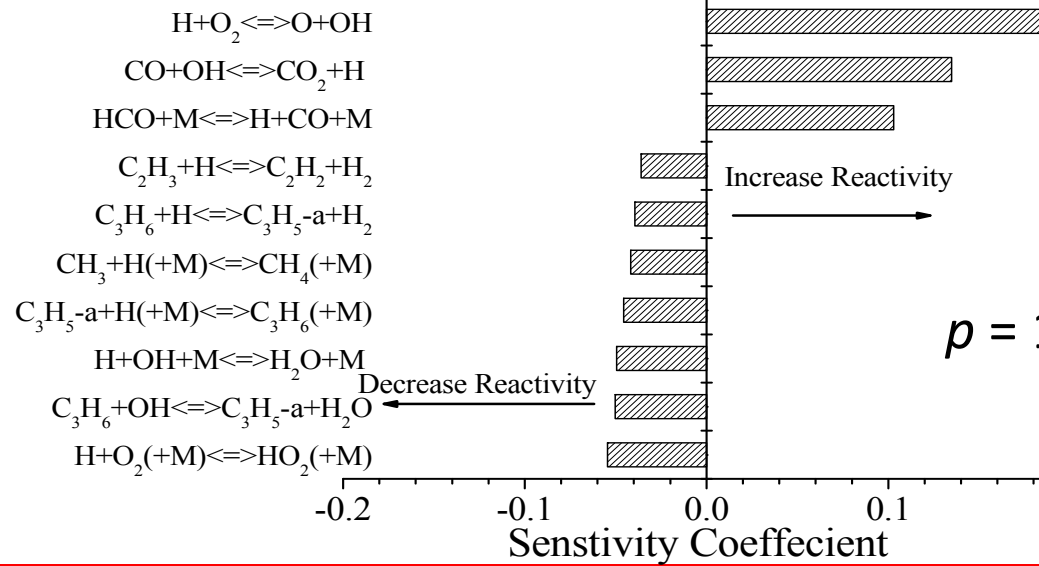
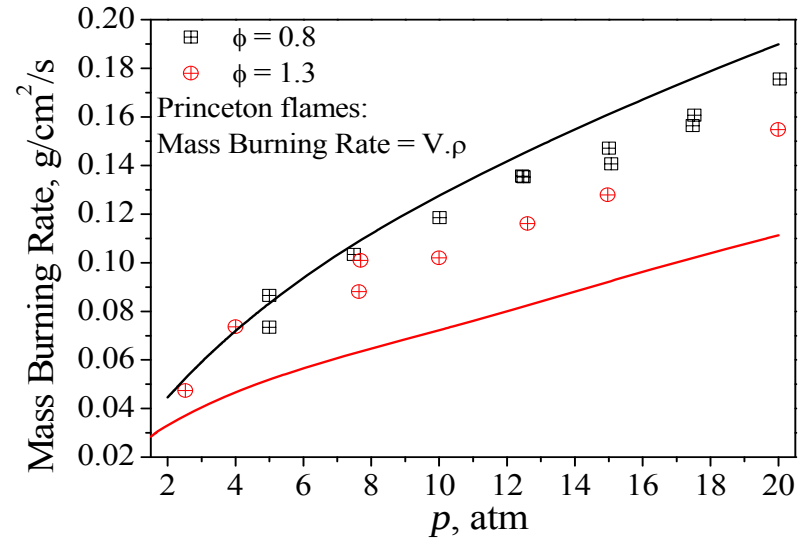
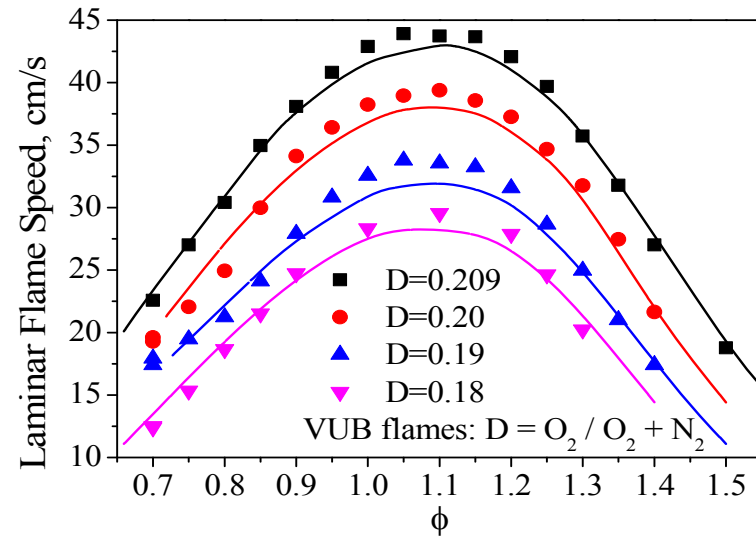
JSR flux analysis

20% fuel consumption $\phi = 2.19$, 1000 K





Validation: Flame speed and mass burning rate





Summary

- Extended to lower T and higher p
- Important reactions highlighted
- Improved performance
 - AramcoMech was validated against C_0 – C_2 species
 - Importance of only using a mechanism within the confines of its validation limits highlighted



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. CURRAN¹

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)



Mechanism Optimization



Available online at www.sciencedirect.com

ScienceDirect

Proceedings of the Combustion Institute 35 (2015) 589–596

**Proceedings
of the
Combustion
Institute**

www.elsevier.com/locate/proci

Optimization of a hydrogen combustion mechanism using both direct and indirect measurements

T. Varga^{a,b}, T. Nagy^{a,c}, C. Olm^{a,b}, I.Gy. Zsély^a, R. Pálvölgyi^a,
É. Valkó^{a,b}, G. Vincze^a, M. Cserhádi^a, H.J. Curran^d, T. Turányi^{a,*}

^a *Institute of Chemistry, Eötvös University (ELTE), Budapest, Hungary*

^b *MTA-ELTE Research Group on Complex Chemical Systems, Budapest, Hungary*

^c *Institute of Materials and Environmental Chemistry, MTA Research Centre for Natural Sciences, Budapest, Hungary*

^d *Combustion Chemistry Centre, National University of Ireland, Galway (NUIG), Ireland*



Computer is better than human...?

Comparison of error function values between our optimized and 13 recently published mechanisms by experiment type. The error function values are normalized by the number of datasets within each column.

Mechanism	Ref.	Average error function						Total (w/o He)	Total
		Shock tube	RCM	JSR	Flow reactors	Flames	Flames (w/o He)		
Optimized mechanism	This work	5.94	6.70	2.97	8.08	4.86	6.11	5.32	4.96
Kéromnès 2013	[5]	6.69	11.33	3.02	13.25	8.11	5.88	7.62	8.29
NUIG NGM 2010	[41]	7.92	17.08	3.00	7.27	7.24	9.94	9.53	8.45
Ó Conaire 2004	[1]	8.51	23.15	2.96	8.18	—	8.90	10.44	—
Konnov 2008	[2]	9.67	27.61	3.06	10.91	—	6.37	11.04	—
Hong 2011	[3]	11.45	9.15	3.01	8.15	—	18.72	12.40	—
Li 2007	[39]	7.58	43.98	2.99	7.83	7.61	7.07	12.69	12.04
Burke 2012	[4]	13.29	48.54	3.06	3.91	4.57	5.91	14.57	12.65
Saxena Williams 2006	[40]	11.06	47.28	3.02	28.30	7.60	8.13	17.05	15.43
San Diego 2014	[44]	16.80	17.75	3.00	14.90	25.22	17.62	13.86	17.22
CRECK 2012	[42]	6.61	28.42	2.93	21.44	25.49	38.30	21.32	18.58
Davis 2005	[18]	11.62	93.55	3.00	4.89	5.84	7.58	21.52	18.60
GRI 3.0 1999	[11]	49.07	115.6	2.42	11.56	—	23.97	43.78	—
Sun 2007	[43]	11.99	309.2	3.11	25.42	15.31	18.60	60.50	52.55
No. of datapoints		566	219	149	191	432	319	1390	1513
No. of data sets		43	19	9	14	62	39	121	145



Other “core” small mechanisms

- Shanghai Jiaotong University (F. Qi)
- USC Mech (H. Wang)
- San Diego Mech (F. Williams)
- Université de Nancy (F. Battin-LeClerc)
- CRECK (Politecnico di Milano: T. Faravelli, E. Ranzi)
- CNRS (P. Dagaut)
- Chemkin (Reaction Design: E. Meeks, C. Naik)
- MIT (W. Green)
- Lund University (A. Konnov)
- Tokyo University (A. Miyoshi)
- Technical University of Denmark (P. Glarborg)



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.”

Charlie Westbrook



Developing kinetic mechanisms for larger hydrocarbon fuels

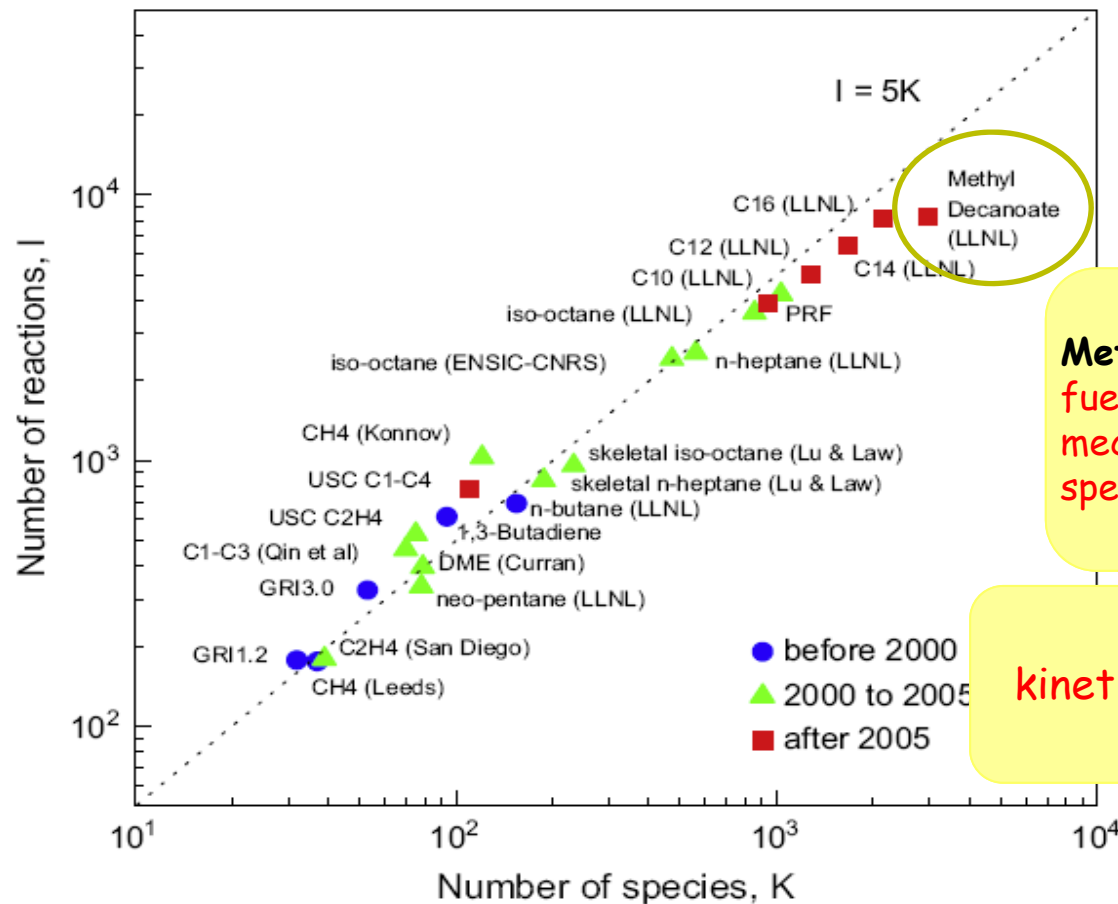




Larger Fuel Chemistry

- 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

Mechanism Size



Methyl decanoate is a biomass fuel surrogate. Detailed kinetic mechanism consists of 3036 species and 8555 reactions.

Automatic Generation of kinetic mechanisms easily produces **Large Kinetic Models**

Fig. 10. Size of selected detailed and skeletal mechanisms for hydrocarbon fuels, together with the approximate years when the mechanisms were compiled.

T.F. Lu, C.K. Law 'Toward accommodating realistic fuel chemistry in large-scale computations'
Progress in Energy and Combustion Science 35 (2009) 192–215



Mechanism Size

Mechanism size grows with molecule size

Fuel:	H ₂	CH ₄	C ₃ H ₈ (Propane)	C ₆ H ₁₄ (Hexane)	C ₁₆ H ₃₄ (Cetane)
Number of species:	7	30	100	450	1200
Number of reactions:	25	200	400	1500	7000



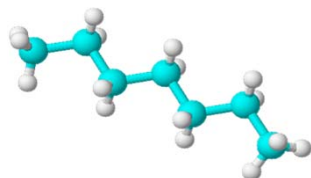
Dominance of H_2/O_2 Reactions

For nearly all hydrocarbon oxidation, no matter how large or small the fuel molecule, at high temperatures, the reactions of H_2/O_2 have the greatest sensitivity controlling the overall rate of reaction. This is true in flames, detonations, shock tubes, and many other practical combustors.



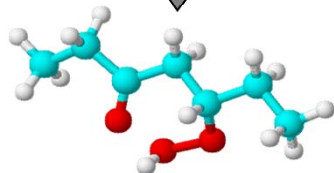
Combustion Chemistry Complexity

Low temperature

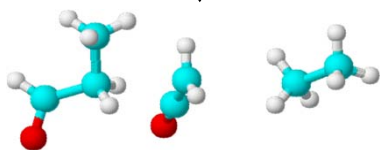


+ O₂

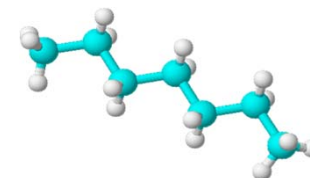
Oxidation



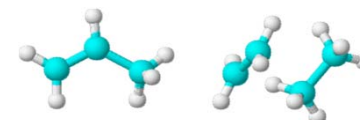
Pyrolysis



High temperature

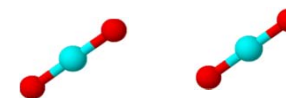


Pyrolysis

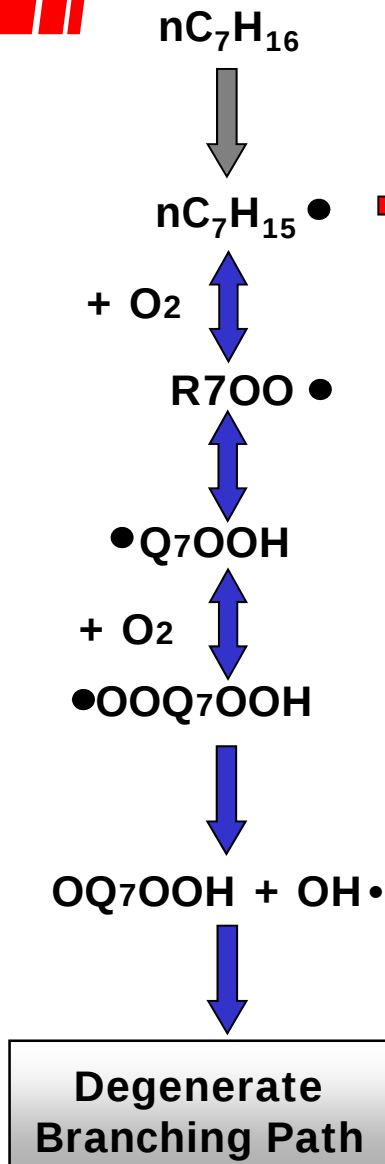


+ O₂

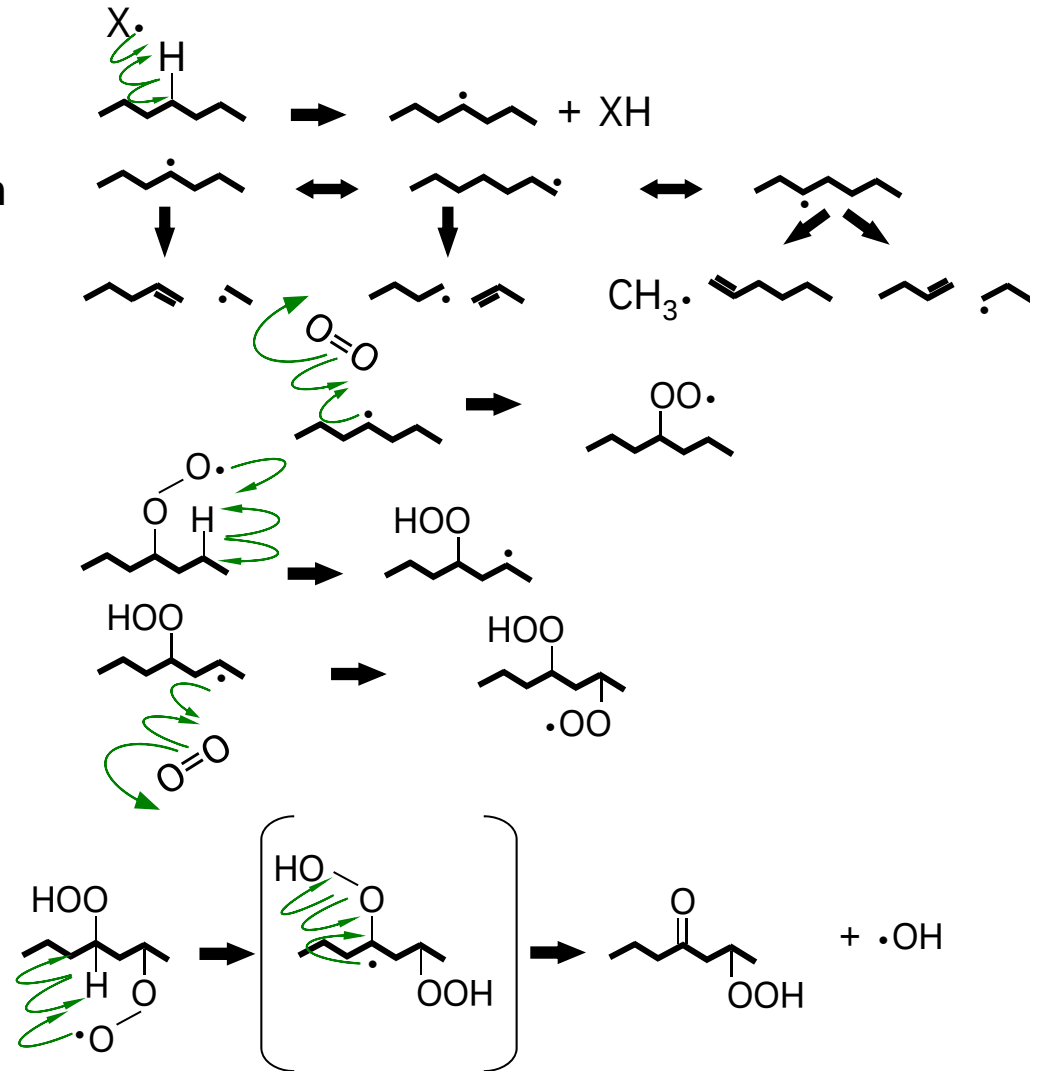
Oxidation



Oxidation of alkanes



β -Decomposition Products



Oxidation of alkanes

High Temperature

Mechanism

($E_{app} \cong 30000$ cal/mol)

β -Decomposition
Products

$HO_2\bullet + nC_7H_{14}$

$OH\bullet +$ Cyclic Ethers

$OH\bullet + \bullet RCHO + C_nH_{2n}$

Intermediate Temperature

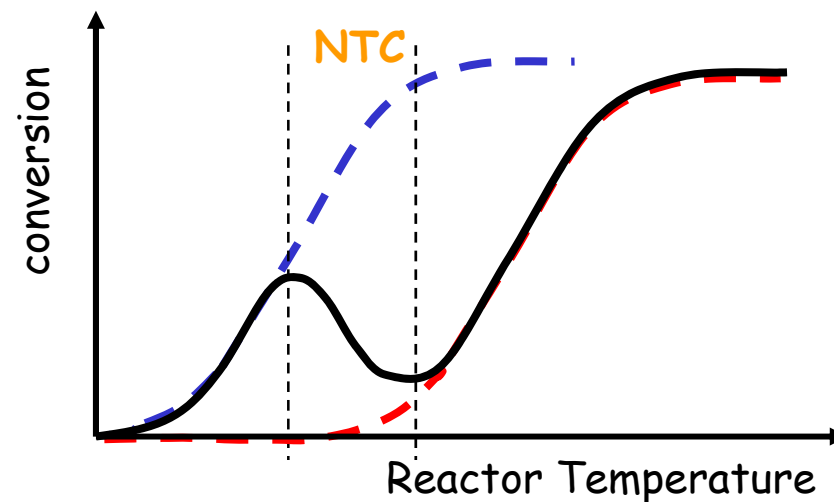
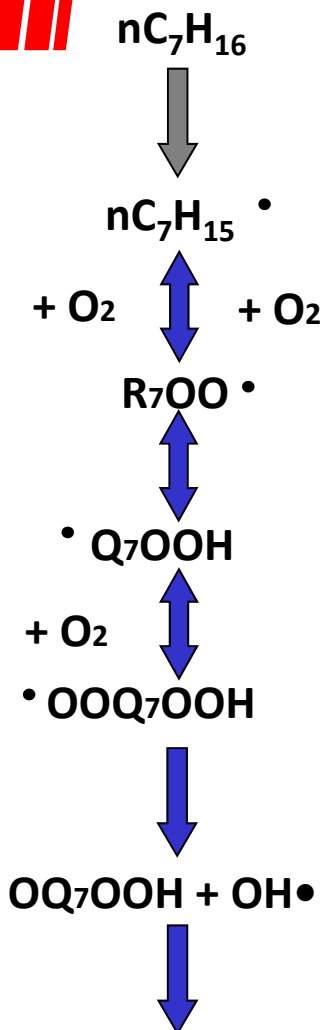
Mechanism

($E_{app} \cong 19000$ cal/mol)

Low Temperature

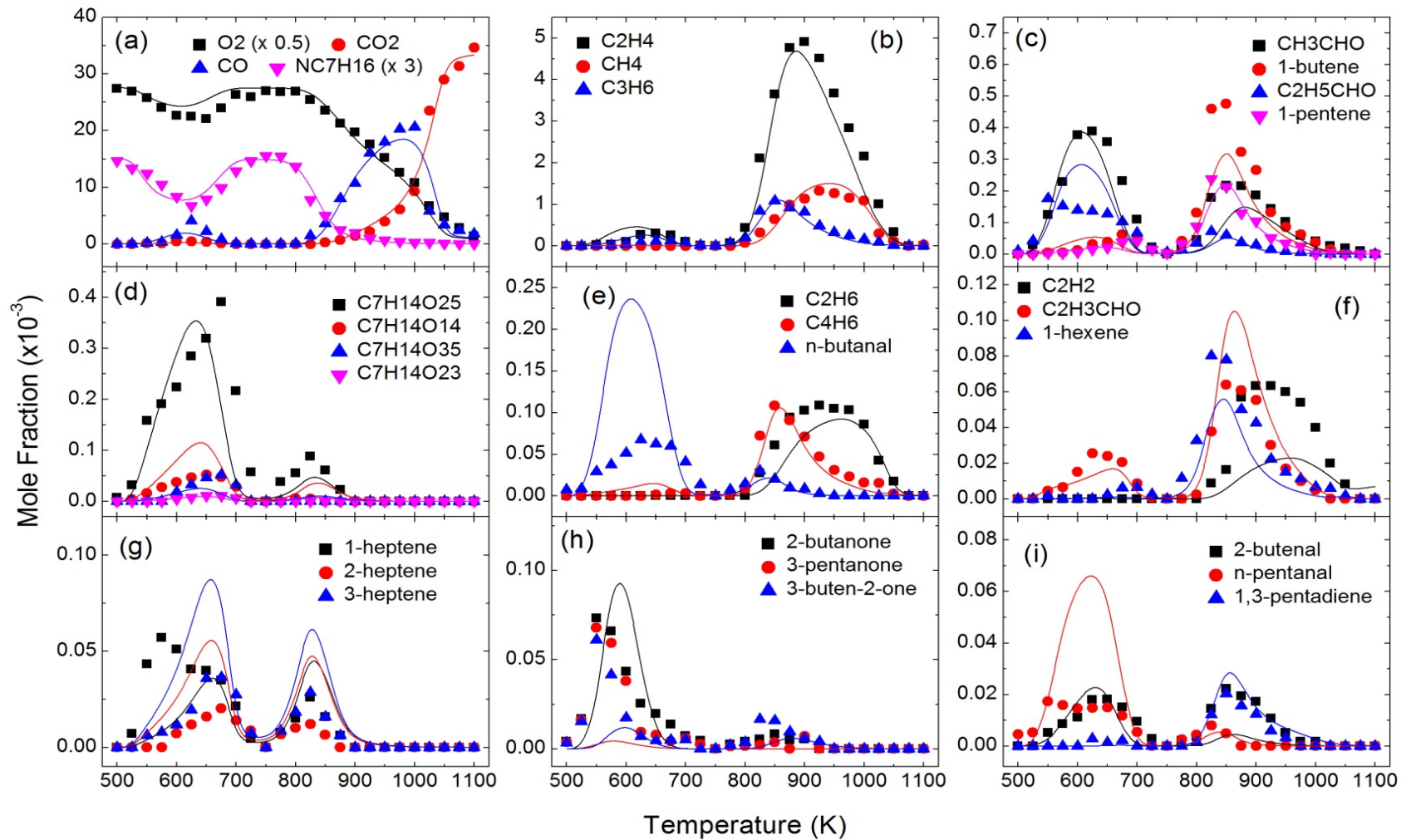
Mechanism

($E_{app} \cong 0$ cal/mol)





Example data: n-Heptane



$\phi = 1.0$, $\tau = 2.0$ s, 1.06 bar, 0.5% fuel
Herbinet et al., Combust. Flame, 159 (2012), 3455-3471



Mechanism competition

Transition from the LT to the HT mechanism ruled by the decomposition of peroxy radicals



$$\begin{array}{ll} k_{\text{add}} = 10^9 & [\text{L/mol/s}] \\ k_{\text{dec}} = 10^{13} \exp(-28000/RT) & [1/\text{s}] \end{array}$$

Competitive pathways: at high temperatures alkyl radicals are favored over the peroxy radicals, or pyrolysis is favored over oxidation.

Ceiling Temperature is the transition temperature from one mechanism to the other

At equilibrium the addition (forward) and the decomposition (reverse) reaction rates are equal:

$$r_{\text{add}} = r_{\text{dec}} \longrightarrow k_{\text{add}} [\text{R}\bullet][\text{O}_2] = k_{\text{dec}} [\text{ROO}\bullet]$$

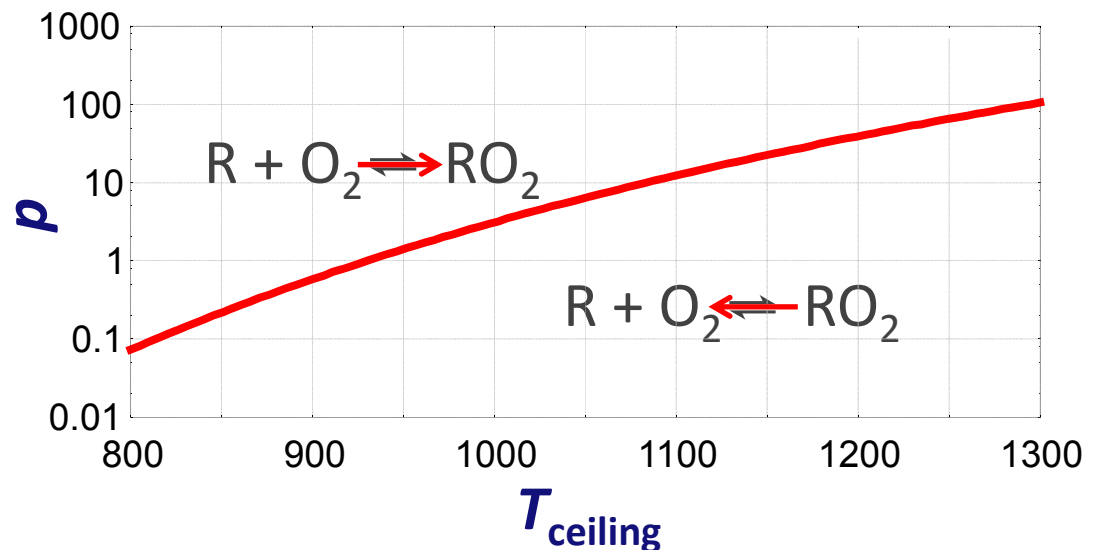


Ceiling temperature vs. pressure

$$\frac{[R\bullet]}{[ROO\bullet]} = \frac{k_{dec}}{k_{add}[O_2]} \cong \frac{10^{13} \exp(-\frac{28000}{RT})}{10^9 \frac{P}{RT} x_{O_2}}$$

$$P \cong \frac{RT}{x_{O_2}} \frac{10^{13} \exp(-\frac{28000}{RT})}{10^9}$$

p in atm, $R = 0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1}$

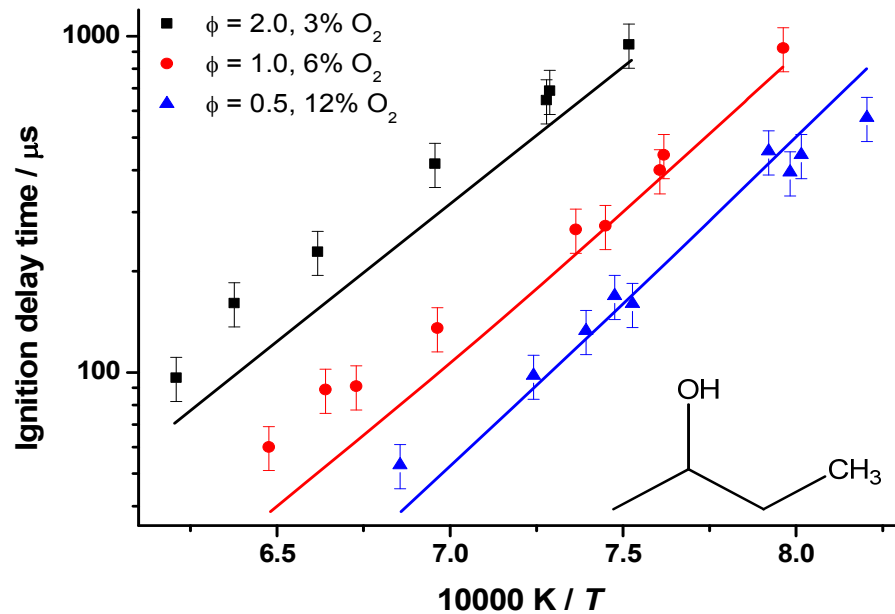


Ceiling temperature increases with pressure: higher oxygen concentration favors direct reaction of peroxy radical formation: NTC region moves toward higher temperatures

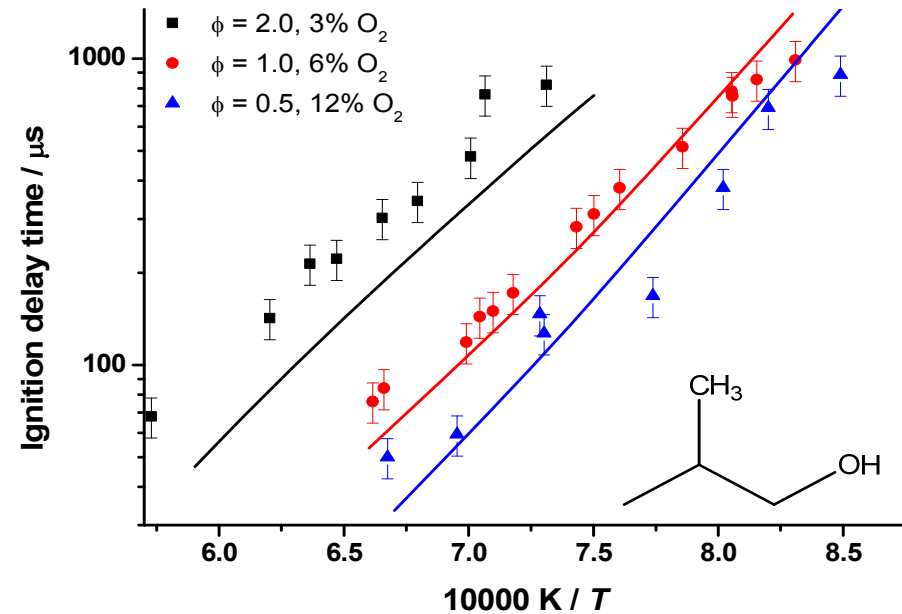
Lean Mixtures faster at High T/Low p

– Butanol isomers (ST/RCM) (Dr. Kenji Yasunaga, Ministry of Defense)

- $T = 1150\text{--}1750\text{ K}$, $p = 3.5\text{ atm}$



sec-Butanol, $p = 3.5\text{ atm}$



iso-Butanol, $p = 3.5\text{ atm}$

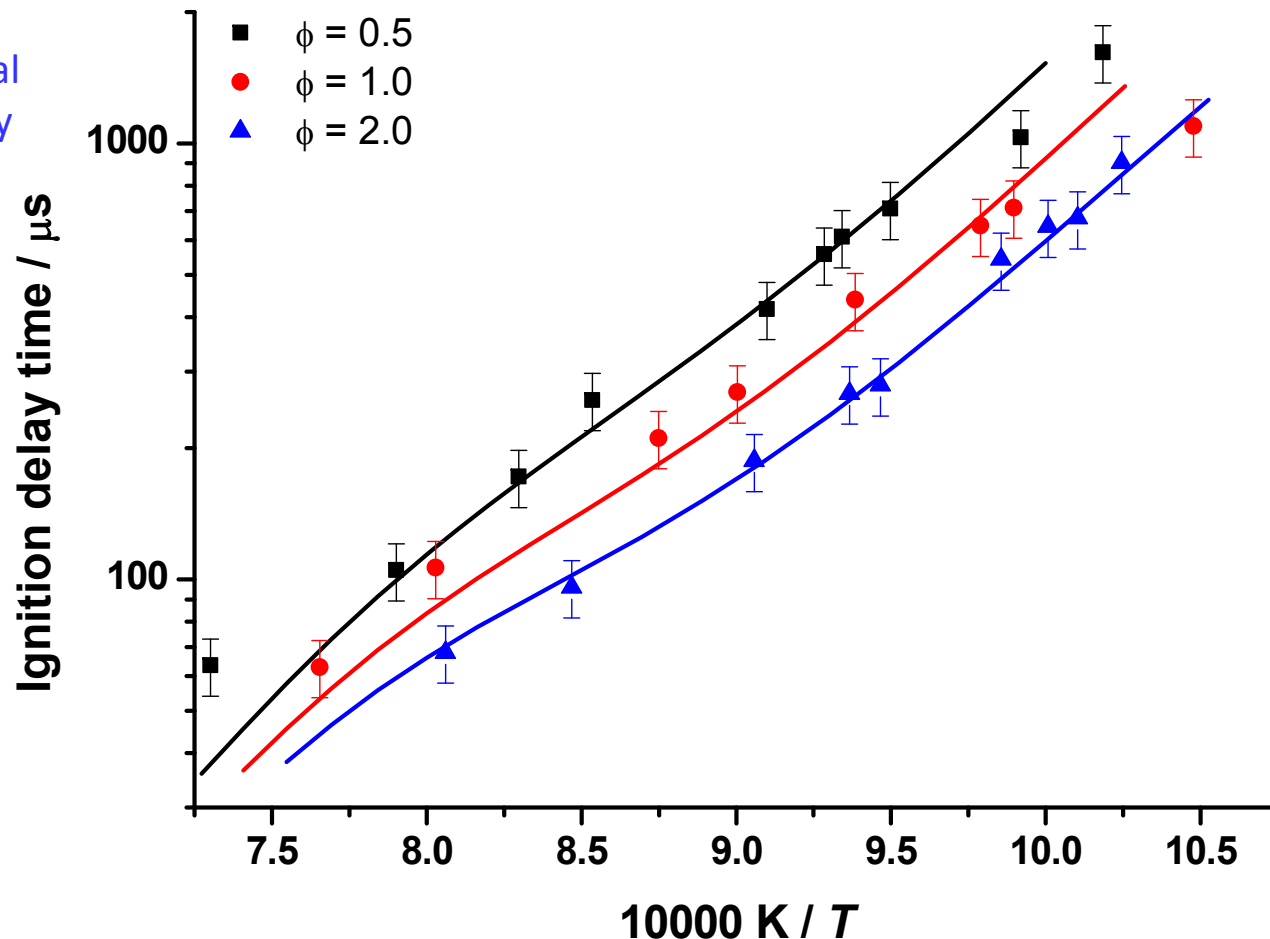
K. Yasunaga, T. Mikajiri, S.M. Sarathy, T. Koike, F. Gillespie, T. Nagy, J. M. Simmie and H. J. Curran, "A Shock Tube and Chemical Kinetic Modeling Study of the Pyrolysis and Oxidation of Butanols." *Combust. Flame*, 159(6) 2009–2027 (2012).



Rich Mixtures faster at Low T/High p

iso-Pentanol, $p = 21$ bar

Dr. Taku Tsujimura
Advanced Industrial
Science Technology

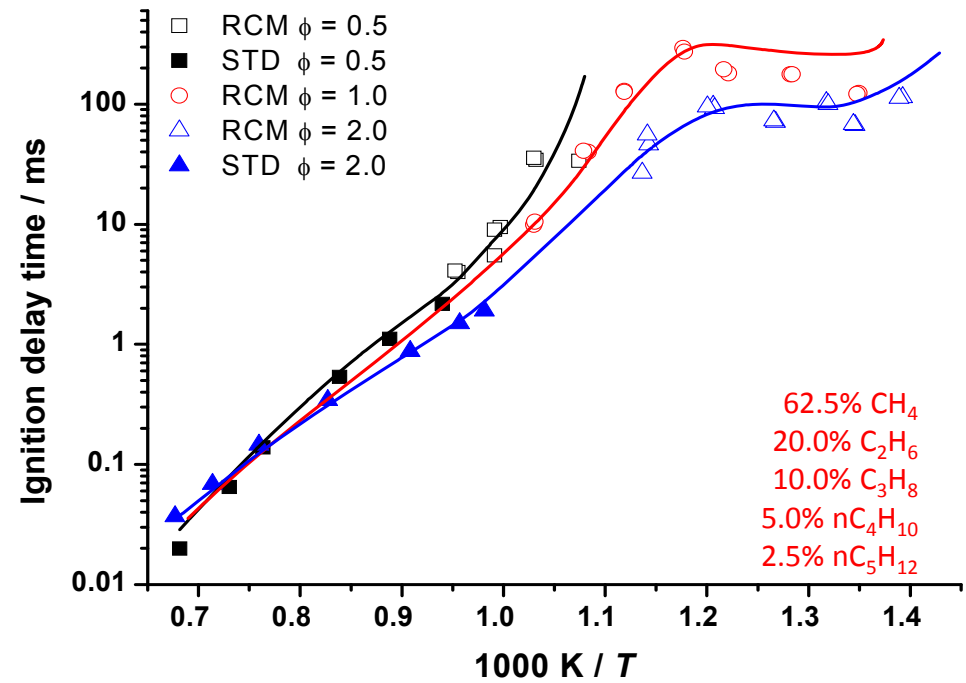
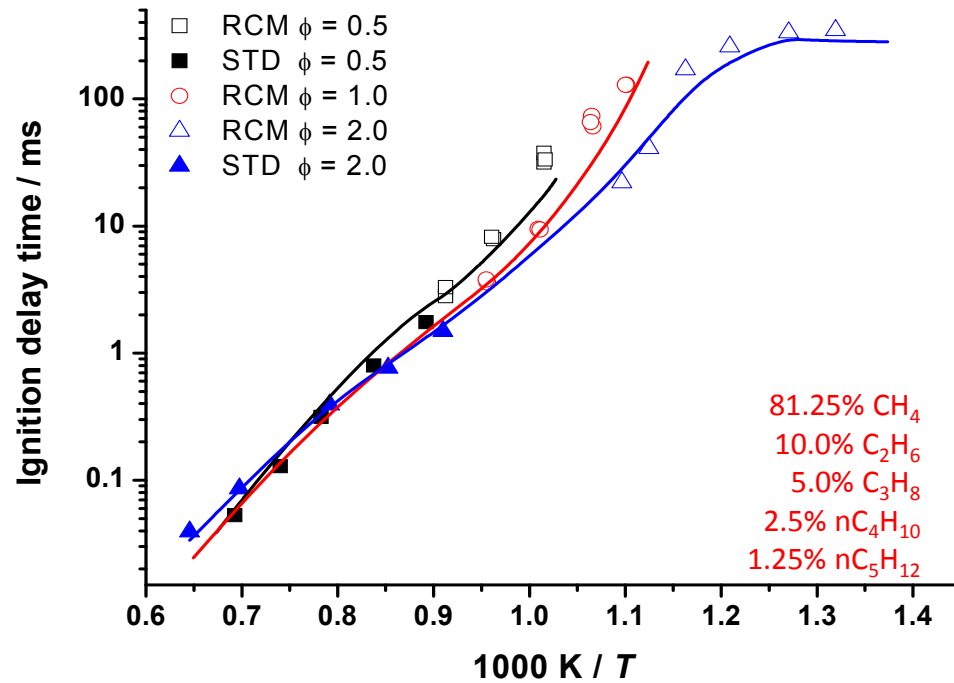


T. Tsujimura, W. J. Pitz, F. Gillespie, H. J. Curran, B. W. Weber, Y. Zhang and C.-J. Sung, Development of isopentanol reaction mechanism reproducing autoignition character at high and low temperatures. Energy Fuels (2012) 26(8) 4871–4886.



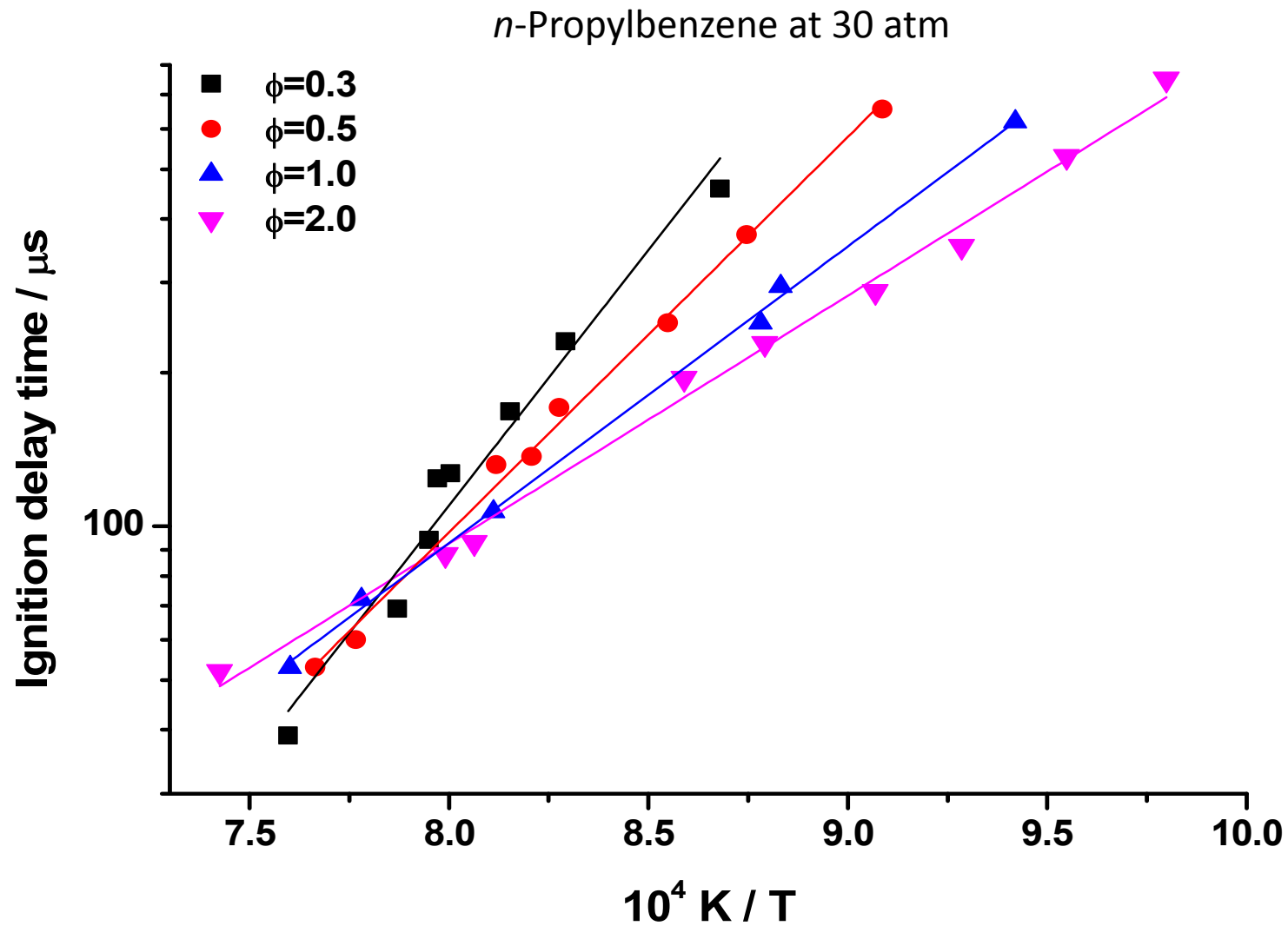
NG: Effect of Equivalence Ratio

$p = 20 \text{ atm}$



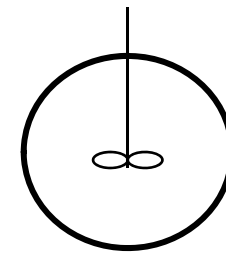
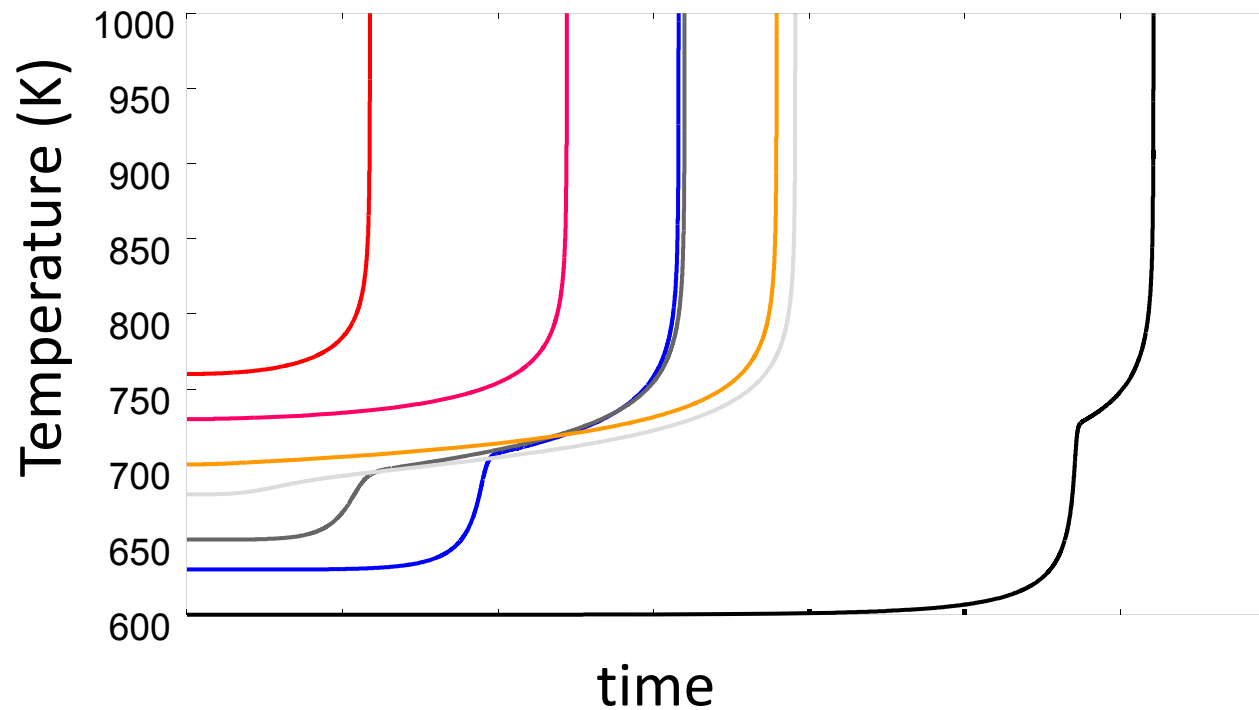


n-PB: Effect of Equivalence Ratio





Ignition of $\text{C}_3\text{H}_8/\text{O}_2$ in closed adiabatic system



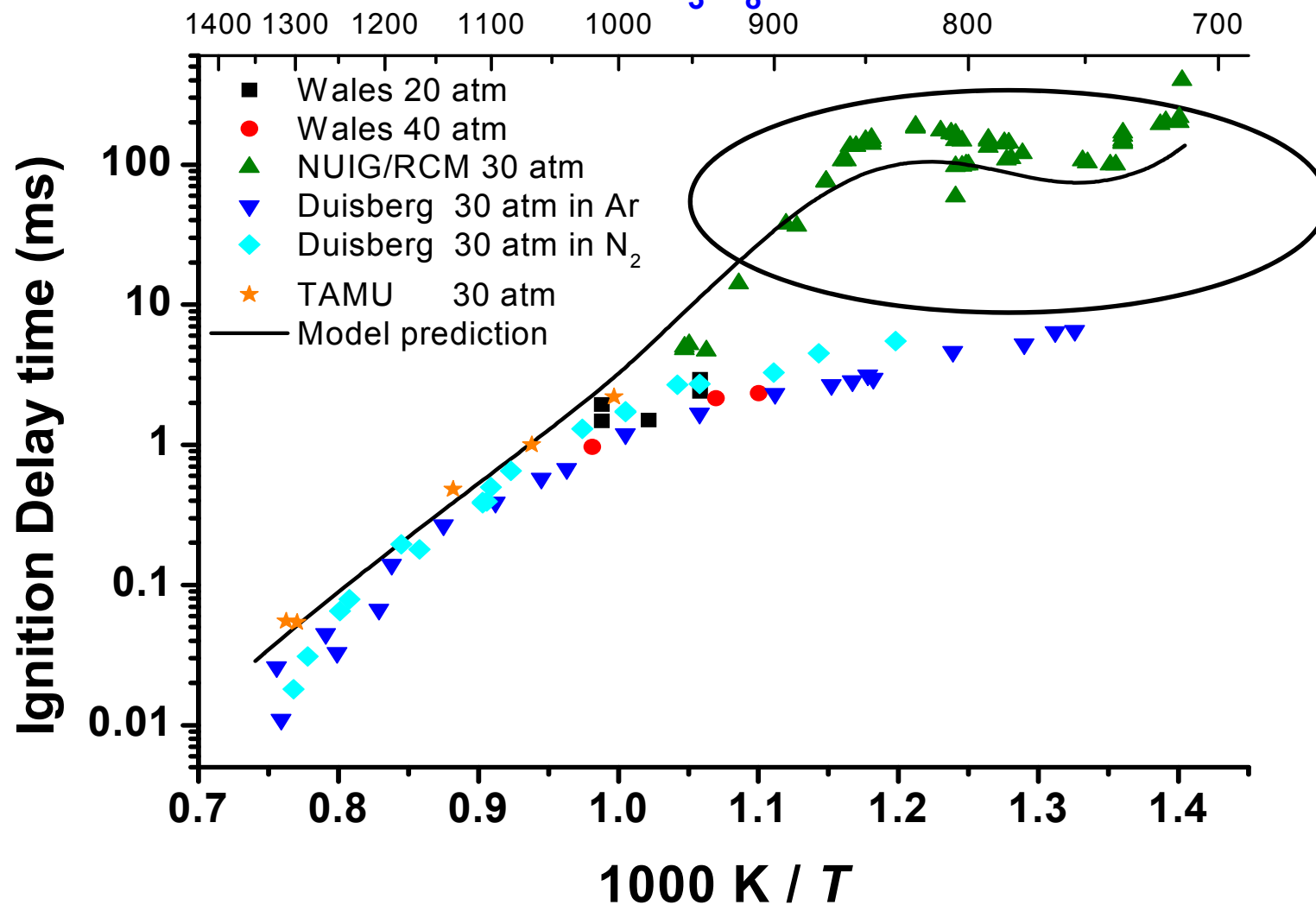
No heat exchange
No mass exchange

- One or two stage ignition.
- NTC between 650-700 K



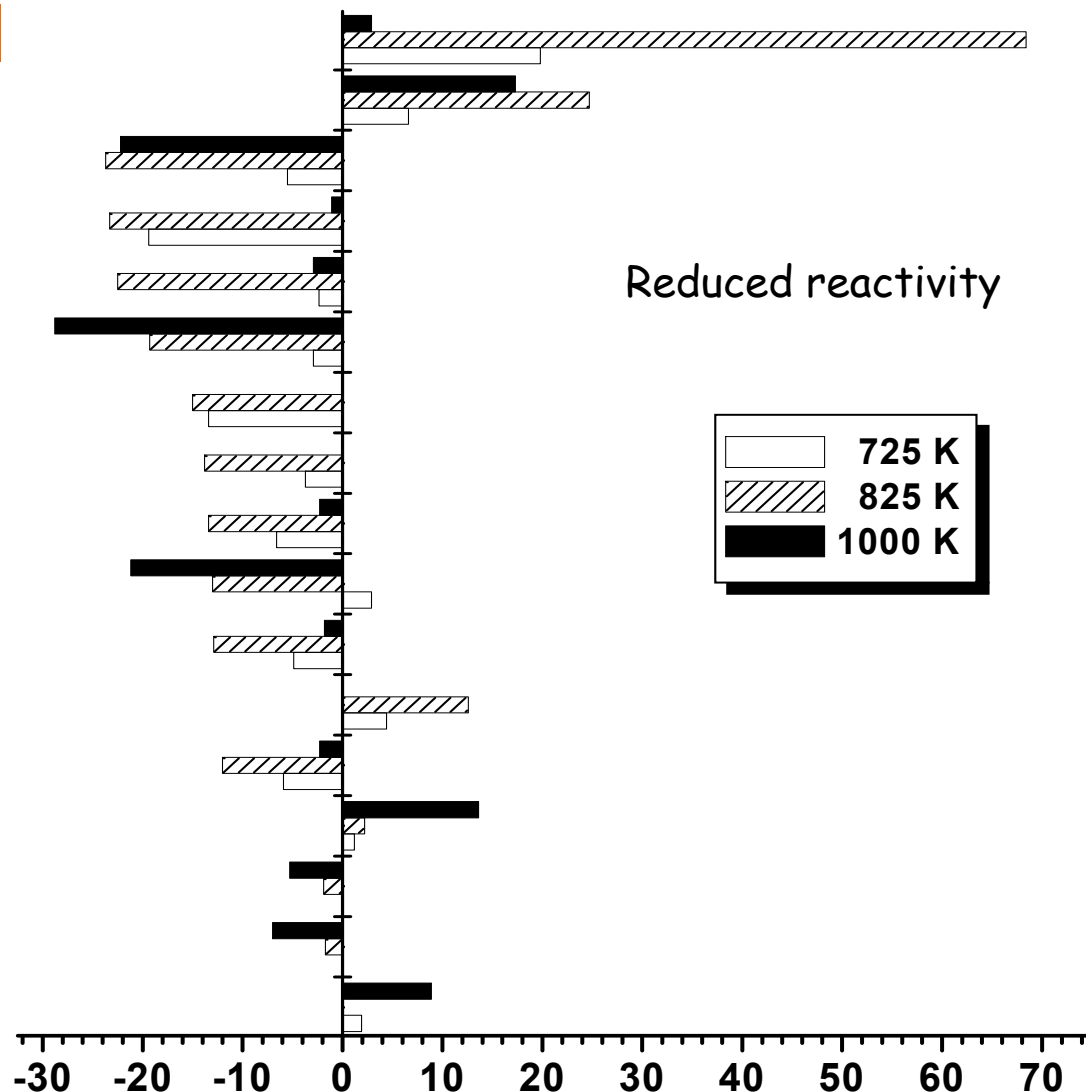
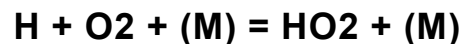
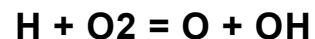
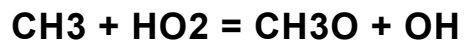
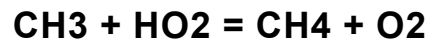
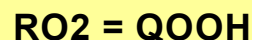
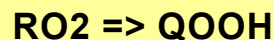
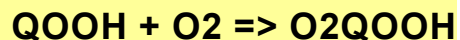
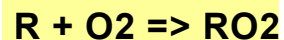
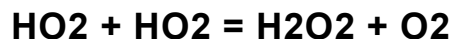
NTC Behavior

2.1% C_3H_8 , $\phi = 0.5$



High p , low T : iC_8H_{18} , $\phi = 1.0$ in air, $p = 40$ atm

R = BETA-SCISSION

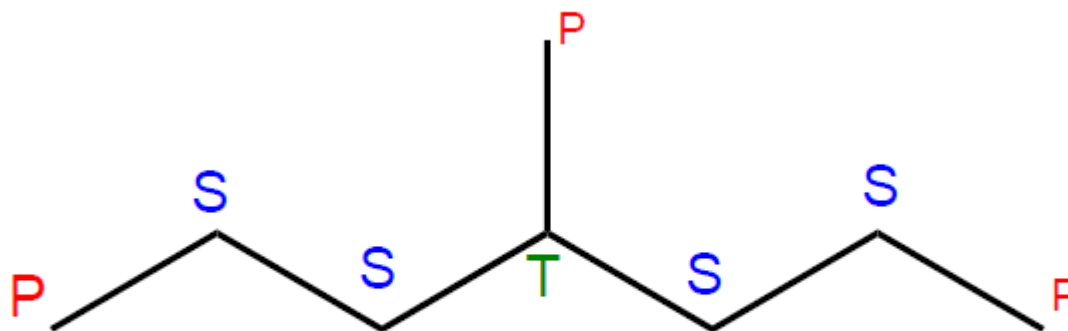


Assign reaction rate rules by reaction classes

- High temperature mechanism
 - Reaction class 1: Unimolecular fuel decomposition
 - Reaction class 2: H atom abstractions from fuel
 - Reaction class 3: Alkyl radical decomposition
 - Reaction class 4: Alkyl radical + O₂ = olefin + HO₂[•]
 - Reaction class 5: Alkyl radical isomerization
 - Reaction class 6: H atom abstraction from olefins
 - Reaction class 7: Addition of radical species to olefins
 - Reaction class 8: Alkenyl radical decomposition
 - Reaction class 9: Olefin decomposition



Test molecule: 4-methyl heptane



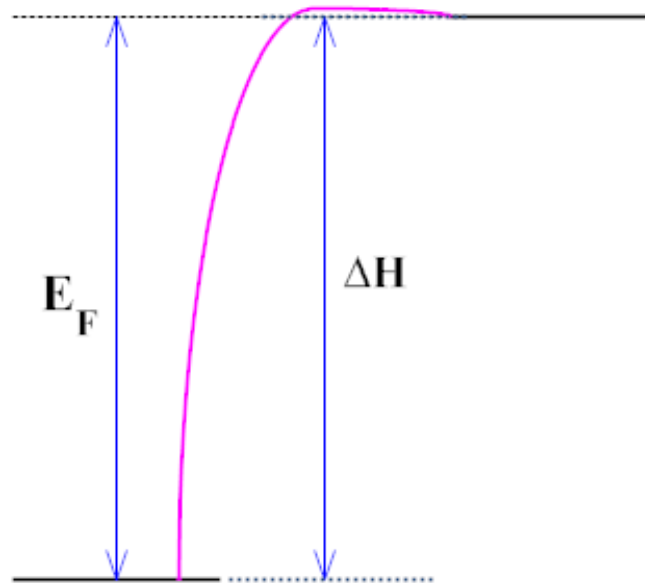
4-methylheptane

- Bond dissociation energies:
 - Primary: ~ 101.5 kcal/mol
 - Secondary: ~ 98.5 kcal/mol
 - Tertiary: ~ 96.0 kcal/mol



1: Unimolecular fuel decomposition

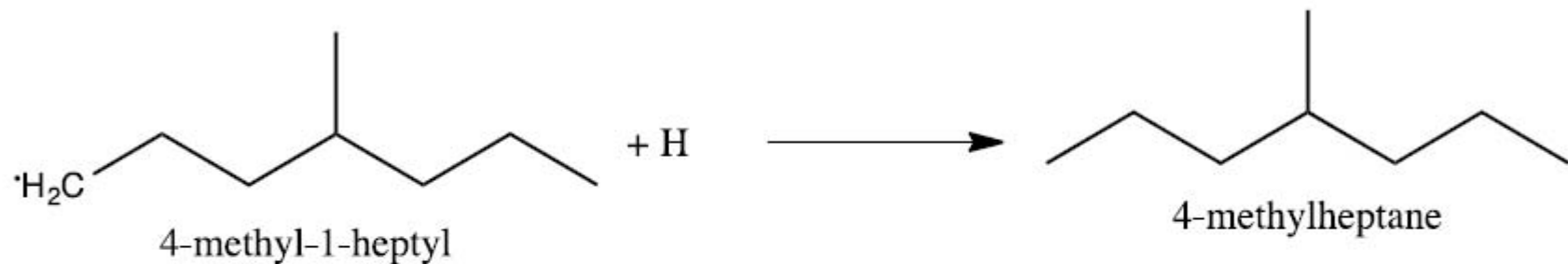
- Very important for ignition delay times in a ST
 - High p limit usually estimated in the reverse (exothermic) direction: radical-radical recombination with no E_a
- Usually need to account for fall-off in rate constant





1: Unimolecular fuel decomposition

- High p limit usually estimated in the reverse (exothermic) direction: radical-radical recombination



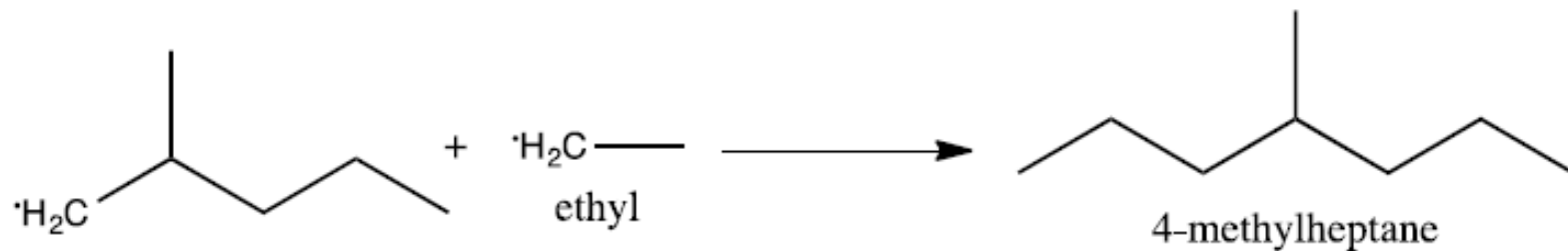
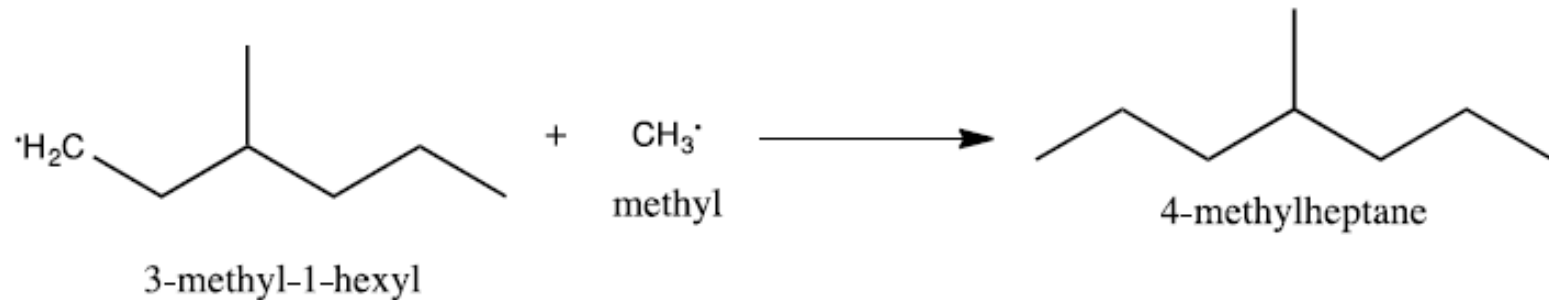
$$k = 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

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)
- There are many unique bond scissions available in 4-methylheptane



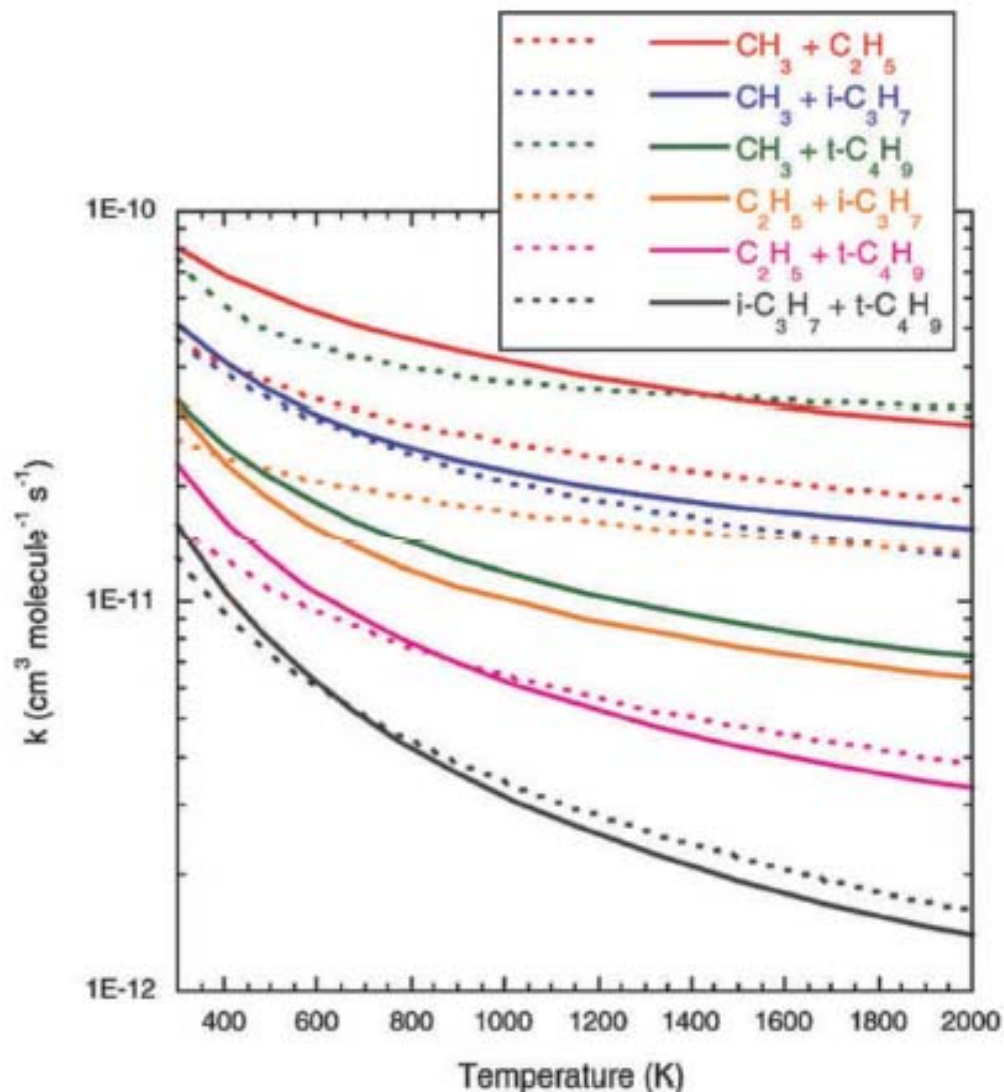
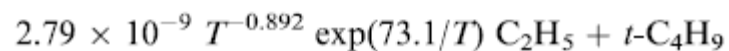
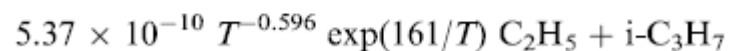
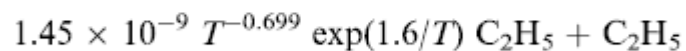
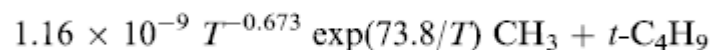
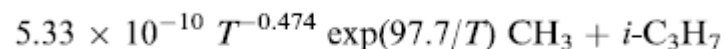
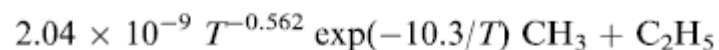
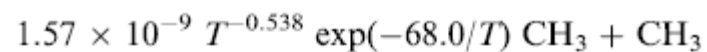


1: Unimolecular fuel decomposition

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

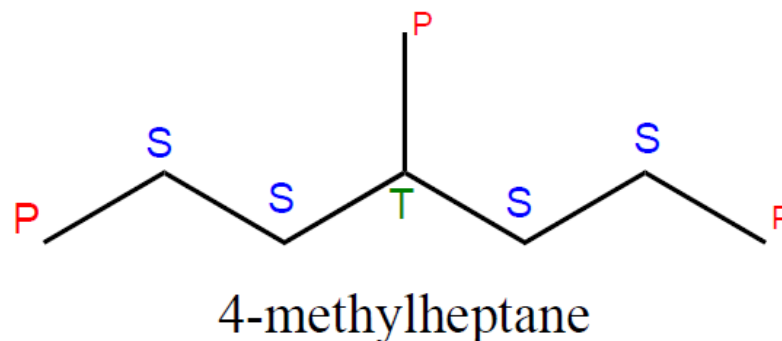
$$k_{AB} = 2(k_{AA}k_{BB})^{0.5}$$

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



2: H-atom abstraction from fuel

- Abstraction of H atoms from the fuel by radical species (e.g., $\dot{\text{H}}$, $\dot{\text{O}}\text{H}$, $\text{H}\dot{\text{O}}_2$, $\dot{\text{C}}\text{H}_3$, 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.





Reaction rate rules make the assignment of reaction rate constants manageable



Class 2

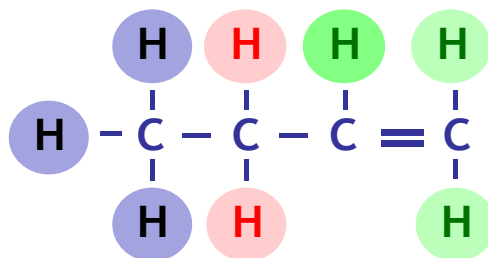
H- atom abstraction rate rules for alkanes

	C-H type	A (cm ³ mol ⁻¹ s ⁻¹)	n	E _A (cal)
$\dot{\text{H}}$	1°	2.22E+05	2.54	6,756
	2°	6.50e+05	2.40	4,471
	3°	6.02E+05	2.40	2,583
$\dot{\text{O}}\text{H}$	1°	1.76E+09	0.97	1,586
	2°	2.34E+07	1.61	-35
	3°	5.73E+10	0.51	63
$\dot{\text{C}}\text{H}_3$	1°	1.51E-01	3.65	7,154
	2°	7.55E-01	3.46	5,481
	3°	6.01E-10	6.36	893
$\text{H}\dot{\text{O}}_2$	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

Correlations between structure and reactivity

H-abstractions $RH + \cdot X \rightarrow R\cdot + HX$



Radical	Allylic H									Vinylic H					
	Primary			Secondary			Tertiary			Secondary			Tertiary		
	lgA	b	E	lgA	b	E	lgA	b	E	lgA	b	E	lgA	b	E
$\cdot O\cdot$	10.8	0.7	25	10.6	0.7	13	10.5	0.7	5	10.7	0.7	36	10.8	0.7	32
$\cdot H$	4.8	2.5	10	4.4	2.5	-7	4.4	2.5	-12	5.6	2.5	51	5.6	2.5	41
$\cdot OH$	6.0	2	-1	6.2	2	-6	6.1	2	-11	6.0	2	12	6.0	2	6
$\cdot CH_3$	-1.3	3.5	24	11.9	0	29	11.9	0	22	-1.7	3.5	54	-1.7	3.5	50
$\cdot HO_2$	3.5	2.6	58	3.5	2.6	52	4.2	2.6	45						

E_a in kJ mol^{-1}

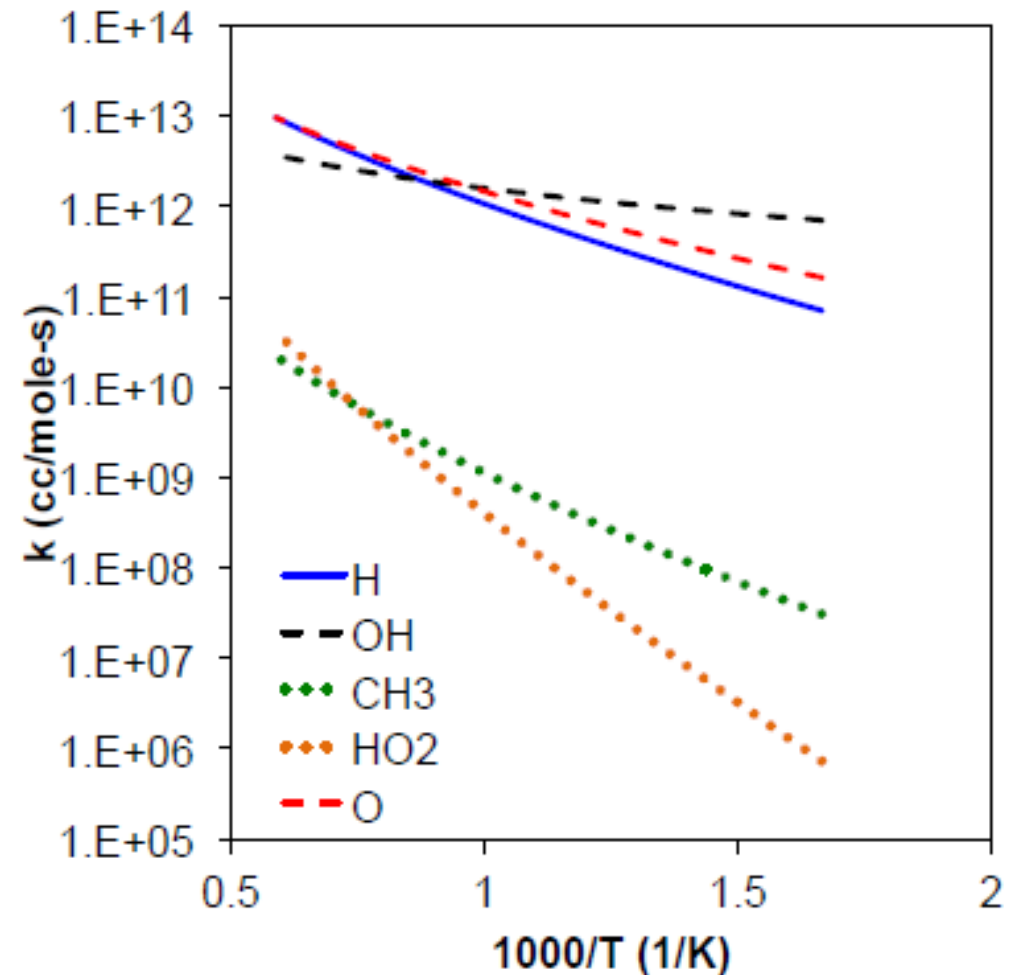
There are more complex correlations of incremental type depending on the nature of RH and $X\cdot$ (Atkinson, 1986, Ranzi et al. 1994)



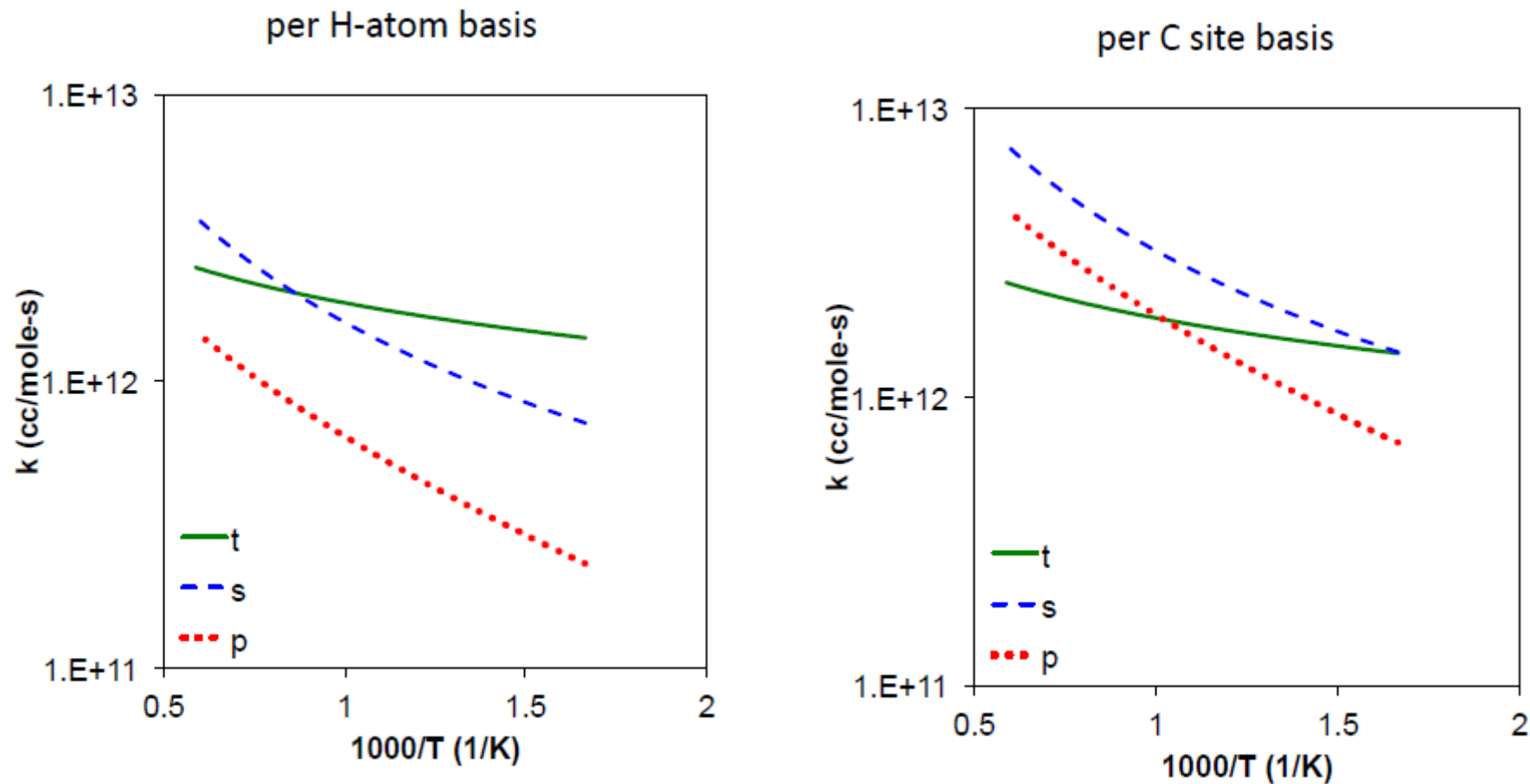
2: H-atom abstraction from fuel

- $\dot{\text{O}}\text{H}$ and $\dot{\text{H}}$ are the most reactive
- $\ddot{\text{O}}$ radical is also very reactive, but usually is in small concentration
- $\text{H}\dot{\text{O}}_2$ is notably less reactive, but leads to H_2O_2 which decomposes into two $\dot{\text{O}}\text{H}$ radicals

per H-atom basis from a secondary site



2: H-atom abstraction by $\dot{\text{O}}\text{H}$ radicals



2: H-atom abstraction by $\dot{\text{O}}\text{H}$ radicals

- Finer considerations take into account next-nearest-neighbour (NNN) configurations and different types of H atoms

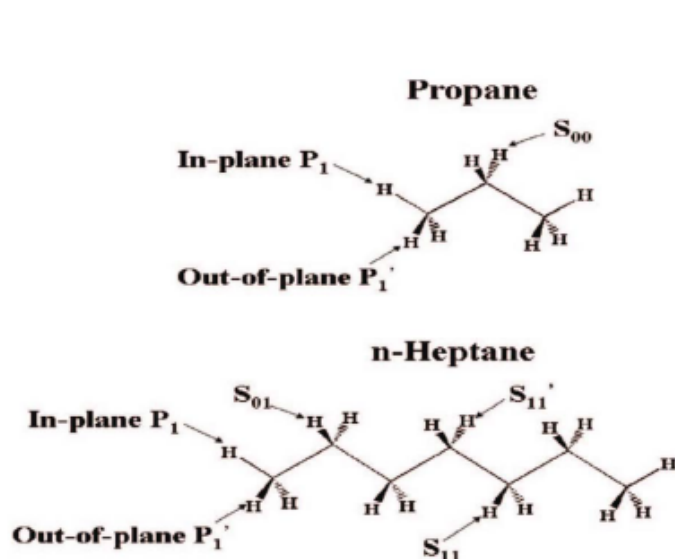


Figure 10. Types of primary and secondary C—H bonds in propane and *n*-heptane.

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		
<i>n</i> -butane		2	4		4	
<i>n</i> -pentane		2	4		4	2
<i>n</i> -hexane		2	4		4	4
<i>n</i> -heptane		2	4		4	4
<i>n</i> -octane		2	4		4	4
<i>n</i> -nonane		2	4		4	4
<i>n</i> -decane		2	4		4	4
<i>n</i> -undecane		2	4		4	4
<i>n</i> -dodecane		2	4		4	4
<i>n</i> -tridecane		2	4		4	4
<i>n</i> -tetradecane		2	4		4	4
<i>n</i> -pentadecane		2	4		4	4
<i>n</i> -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 S₀₁ H ato

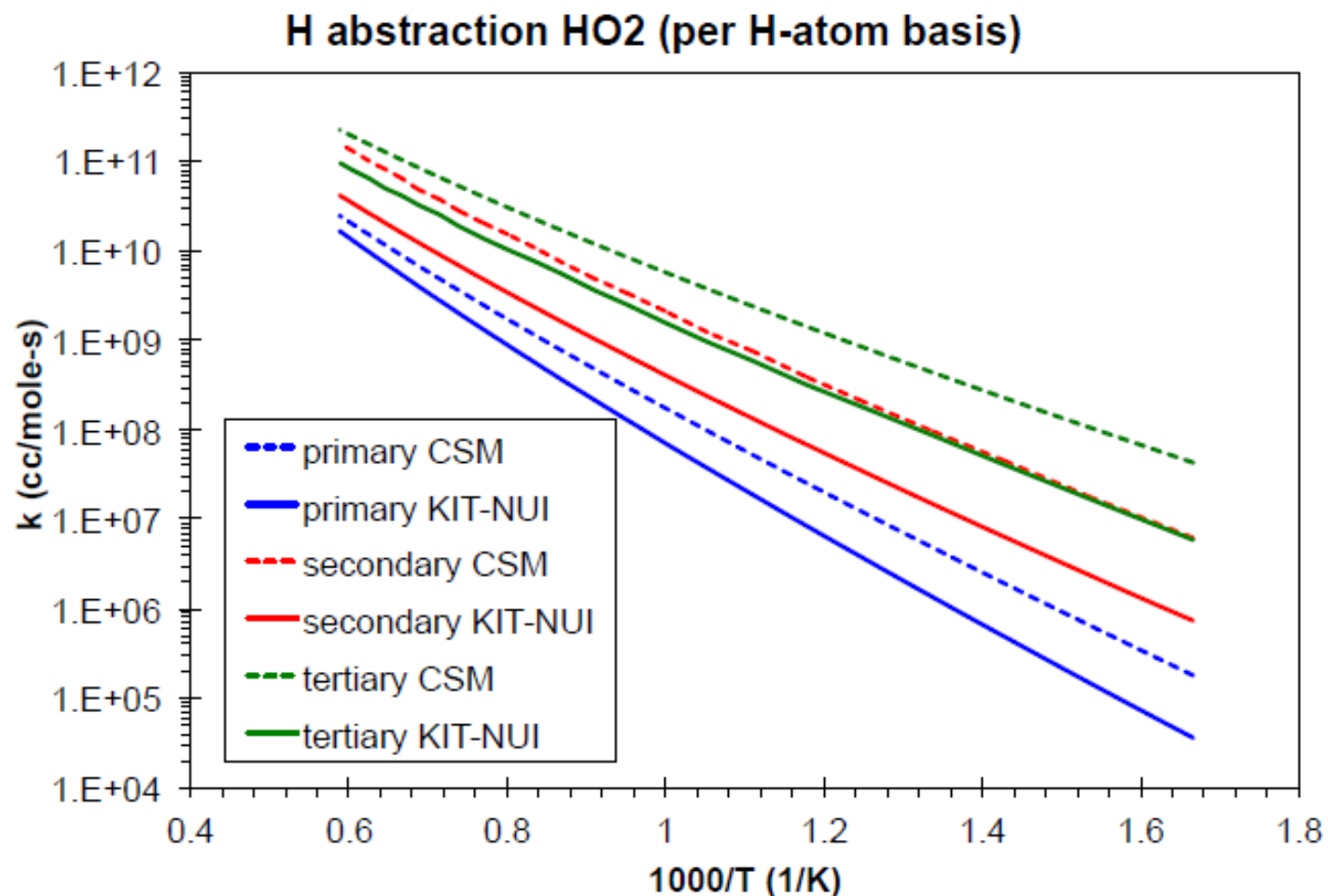
TABLE 9: Summary of Rate Parameters for Total Rate Constants (298–2000 K) According to the Expression $k = AT^n \exp(-B/T)$ cm³ molecule⁻¹ s⁻¹

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

Sivaramakrishnan et al. J Phys. Chem. A 2009 113(17) 5047-5060.



Uncertainty in fuel + $\text{H}\dot{\text{O}}_2$ 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)



Need more accurate rates constants for: $\text{H}\dot{\text{O}}_2 + \text{alkanes}$
Uncertainty in rate of a factor of 3 - 6

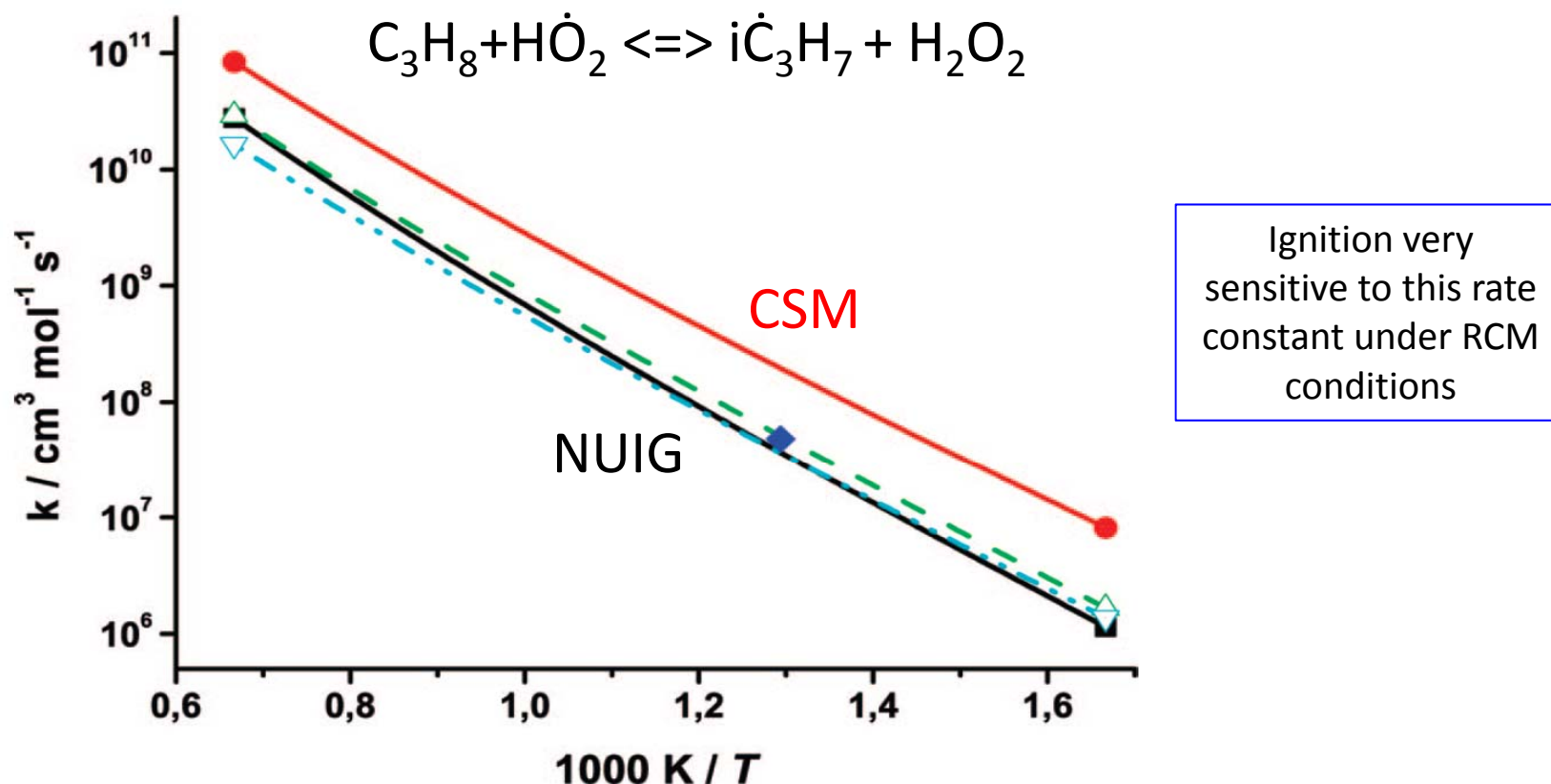


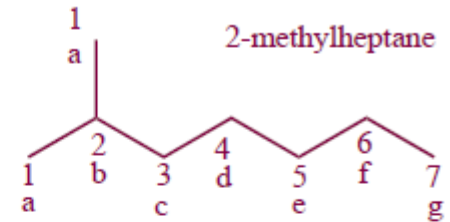
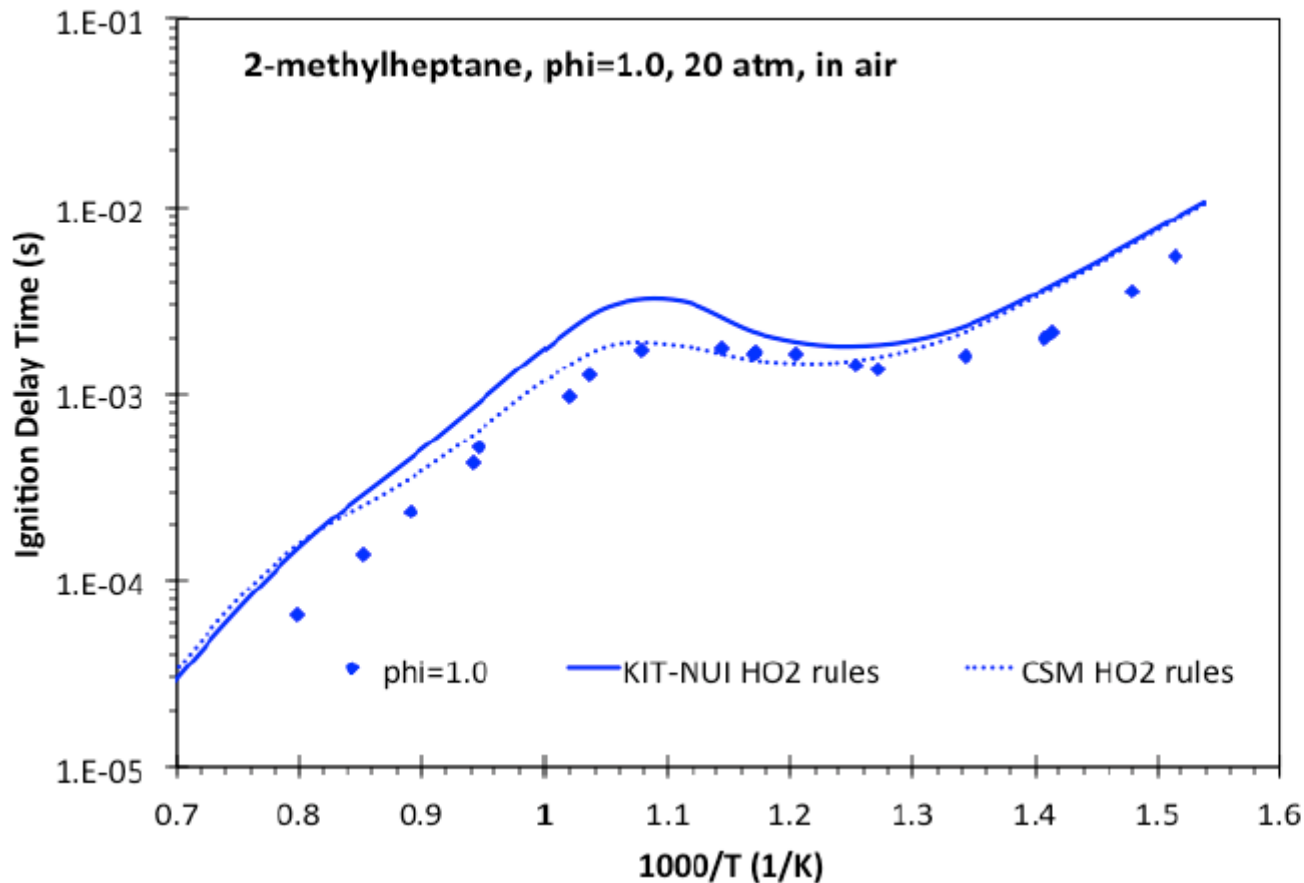
Figure 6. $k(\text{C}_3\text{H}_8 + \text{HO}_2^\bullet \rightarrow i\text{-C}_3\text{H}_7^\bullet + \text{H}_2\text{O}_2)$. This work (—■—), Carstensen¹⁸ (—●—), Scott⁸ (--Δ--), Orme¹⁴ (-••▽-••), Baldwin¹¹ (◆).





Uncertainty in fuel + $\text{H}\dot{\text{O}}_2$ 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.



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

$$\Delta^\ddagger G = \Delta^\ddagger G_0 + a\Delta_r G_0$$

Allow to calculate k (Hammett equation)

Evans-Polanyi relationships

$$E_a = \Delta^\ddagger H_0 + a \Delta_r H_0$$

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



Evans-Polanyi type correlations

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



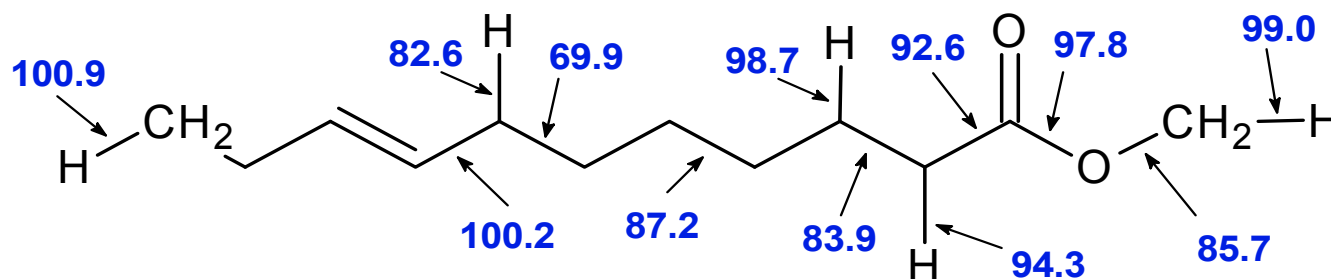
$$k = n_{\text{H}} A T^n \exp \left(-\{E_0 - f(\Delta H_0 - \Delta H)\} / RT \right) \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

n_{H} number of equivalent abstractable H-atoms

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

$\text{R}\cdot$	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

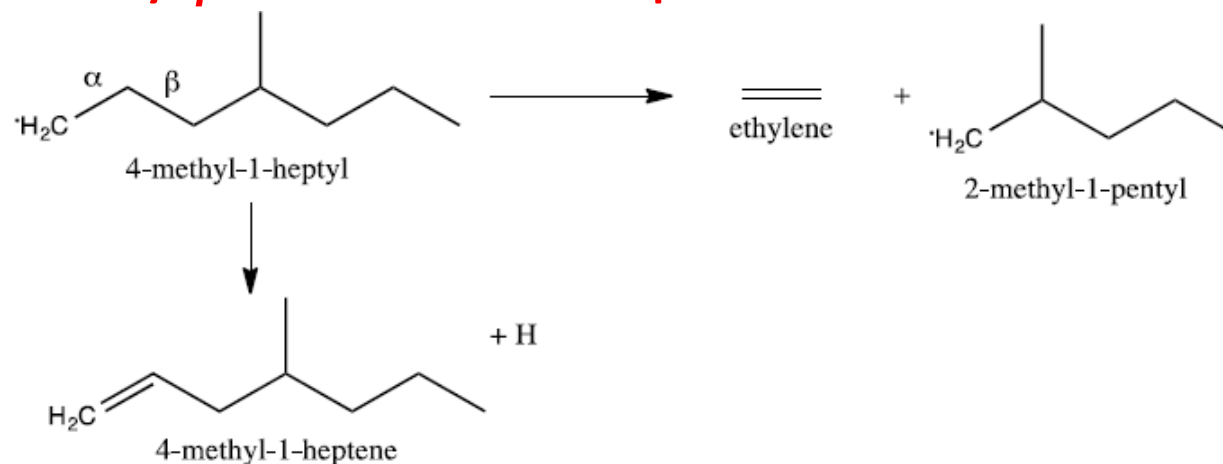
Importance of thermo
data and BDE





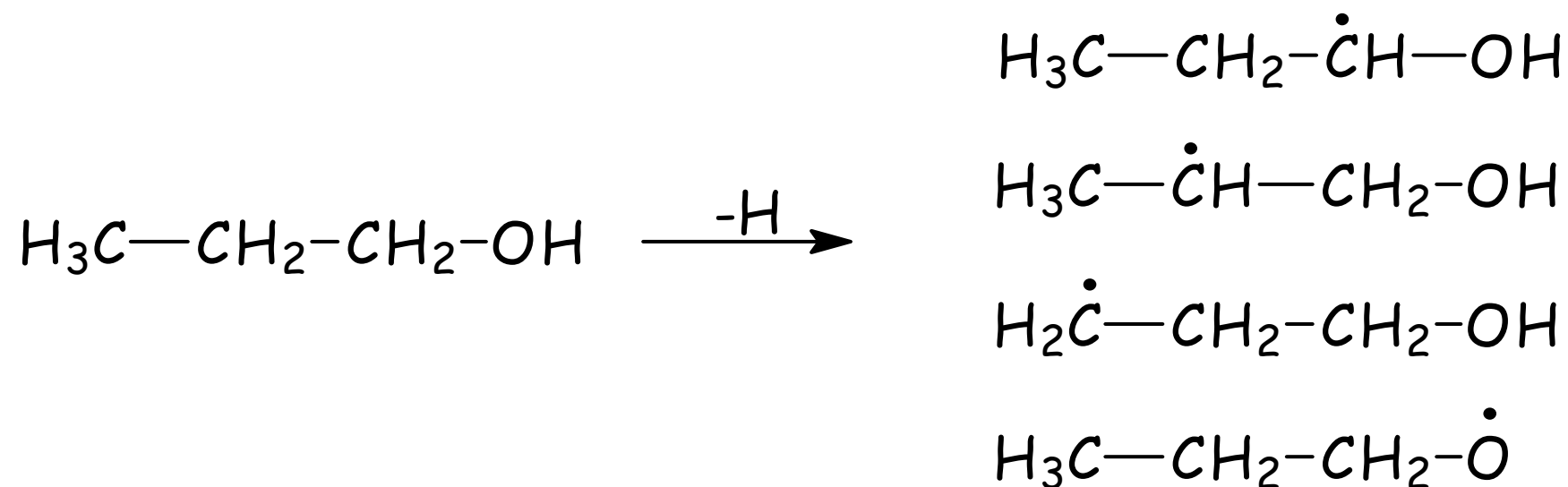
3: Alkyl radical decomposition

- Alkyl radicals undergo β -scission of C–C and C–H bonds to form a radical and an alkene.
- Bond **once removed** (i.e., β) from the radical site breaks to form a stable molecule and a radical.
- β -scissions of C–H bonds are negligible compared to C–C bond scission at $T \gtrsim 2000$ K.
- How many β -scissions are possible?

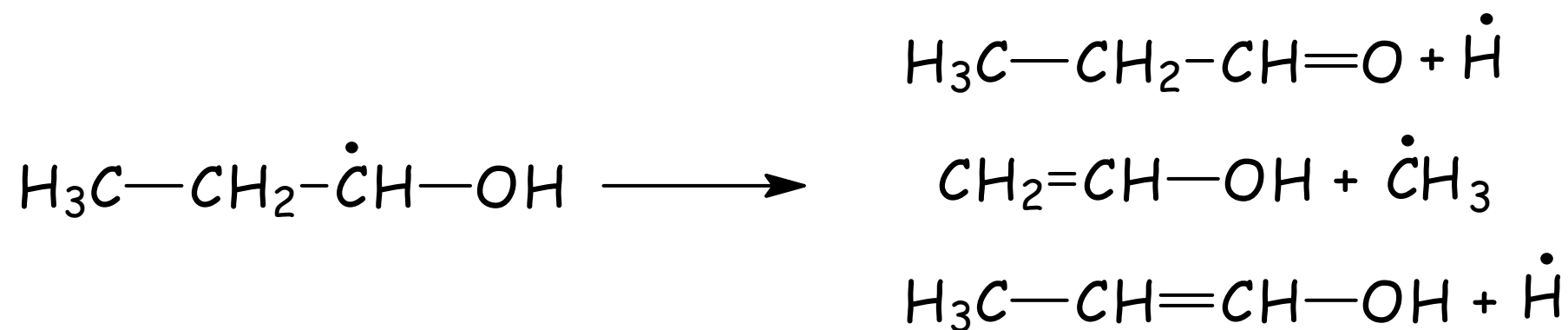




Alkyl radical decomposition



n-Propanol α -radical decomposition





“Enols Are Common Intermediates in Hydrocarbon Oxidation”

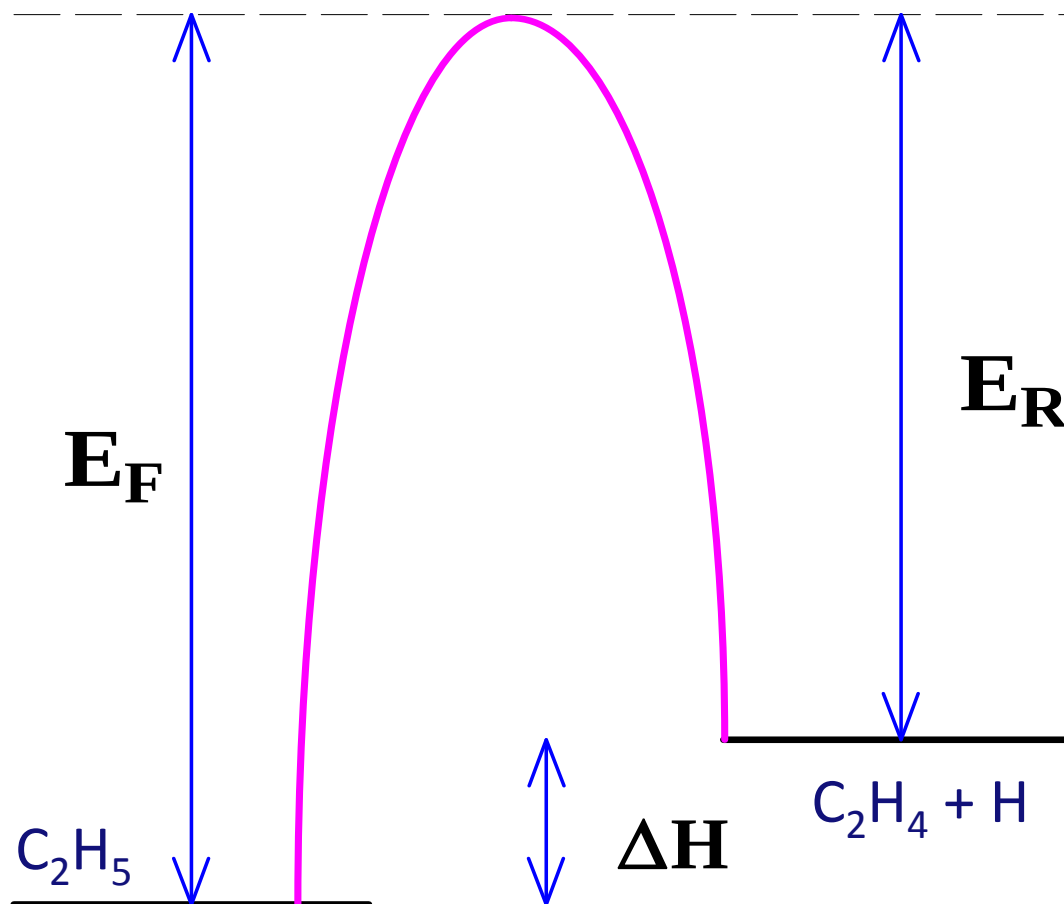
Craig A. Taatjes, *et al. Science* **308**, 1887 (2005)

Photoionization mass spectrometry of flames

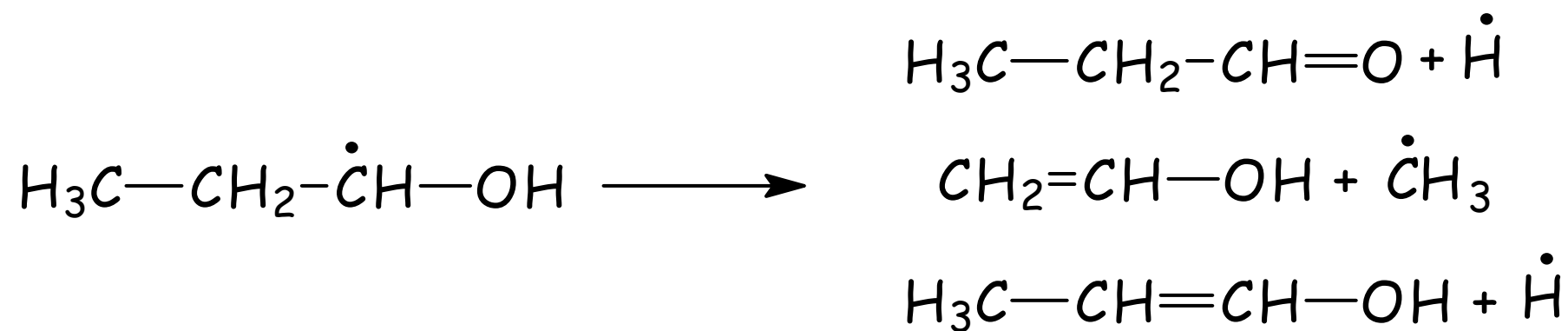
- Detected substantial quantities of 2, 3, & 4-carbon enols
- Ethenol detected for: allene, propyne, benzene, cyclohexane, 1,3-butadiene, ethanol, propene, cyclopentene, ethene and 1-propanol
- Ethenol below detection for: ethane, methane, propane, and 2-propanol flames



Alkyl radical decomposition



n-Propanol α -radical decomposition





Alkyl radical decomposition

Reaction	A-factor	T ⁿ	E _a (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.

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



Hydrogen addition

Reaction	$\Delta H^{\circ,\ddagger}$ / 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	$\Delta H^{\circ,\ddagger}$ / 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	—

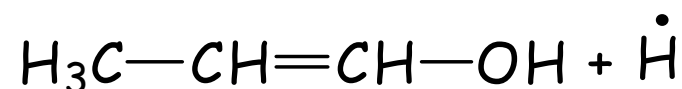
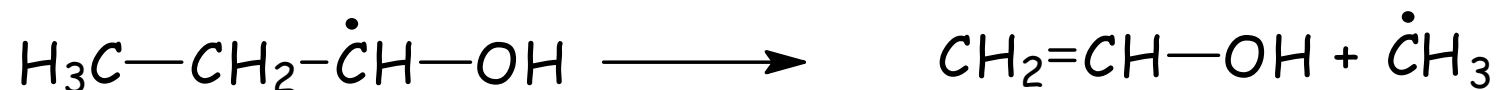
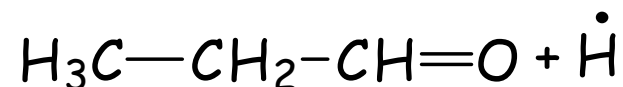


Ethyl addition

Reaction	$\Delta H^{0,\ddagger}$ / kcal mol ⁻¹	
	CBS-QB3	CBS-APNO
CH ₂ =CH(OH)	6.28	6.33
CH(OH)=CH ₂	7.74	7.86



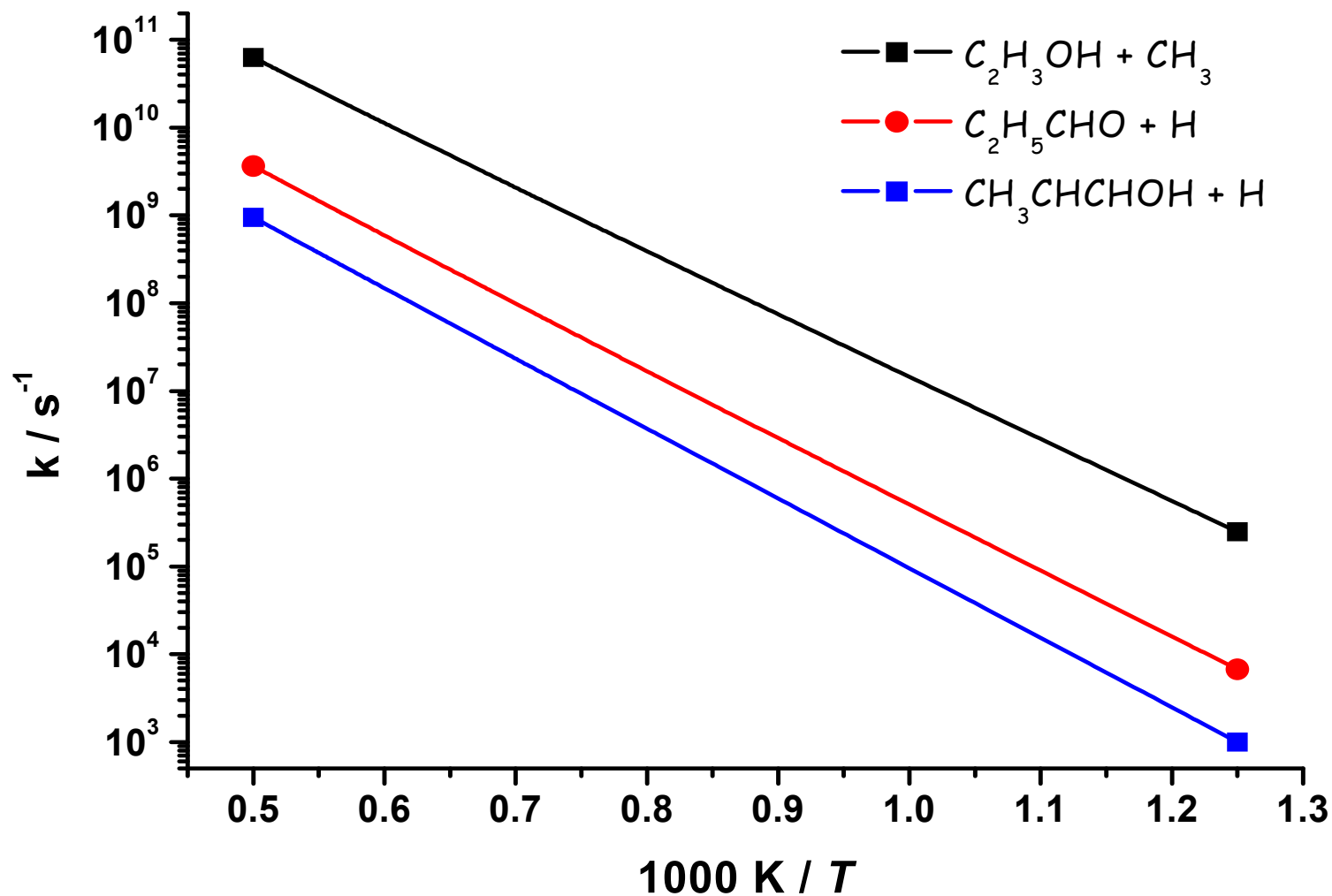
$\text{CH}_3\text{CH}_2\text{CHOH} = \text{products?}$



Reaction	A_r	n_r	Ea_r
$\text{CH}_3\text{CH}_2\text{CH}=\text{O} + \text{H}$	8.00×10^{12}	0.00	9500.
$\text{CH}_2=\text{CHOH} + \text{CH}_3$	1.76×10^4	2.48	6130.
$\text{CH}_3\text{CH}=\text{CHOH} + \text{H}$	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.

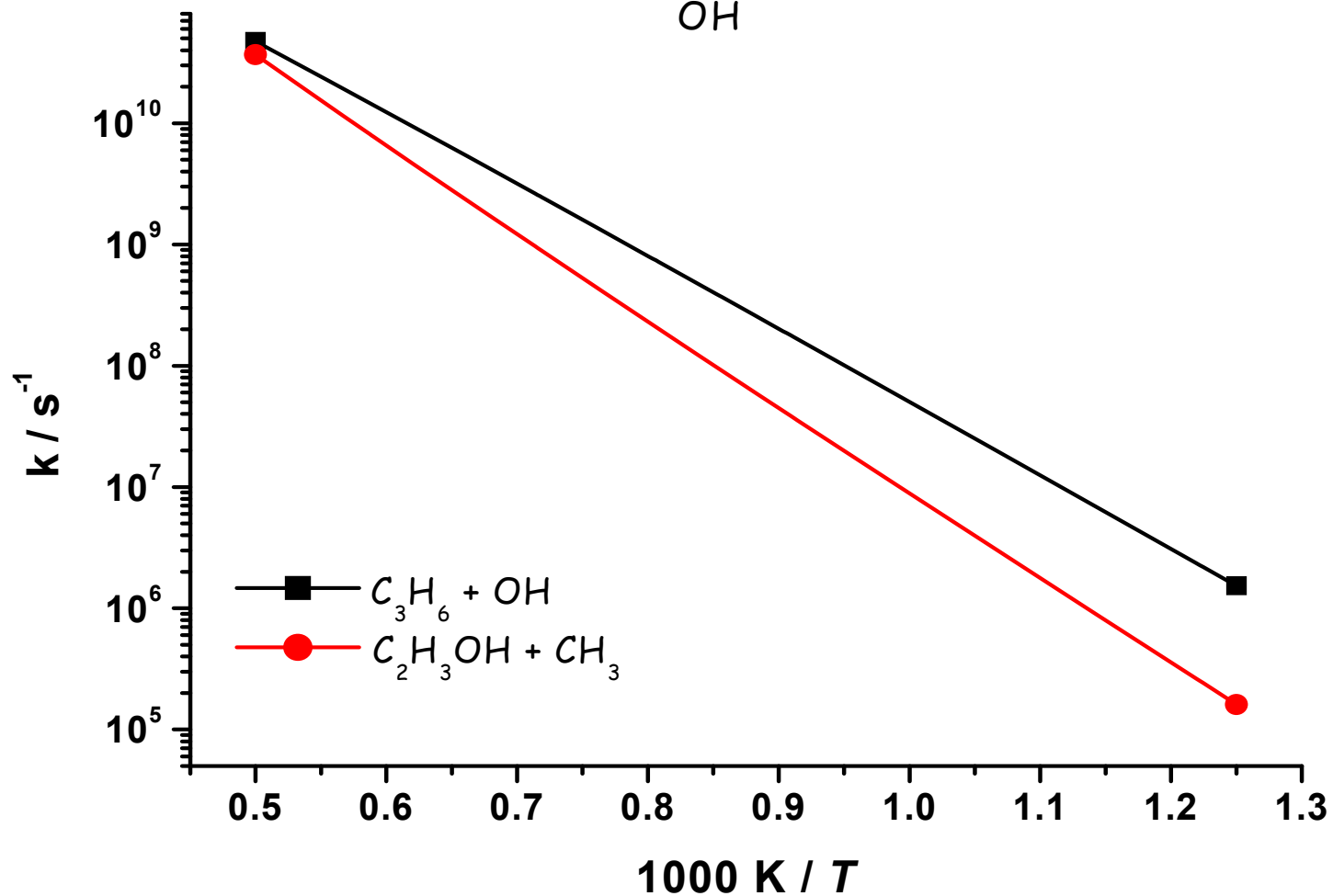
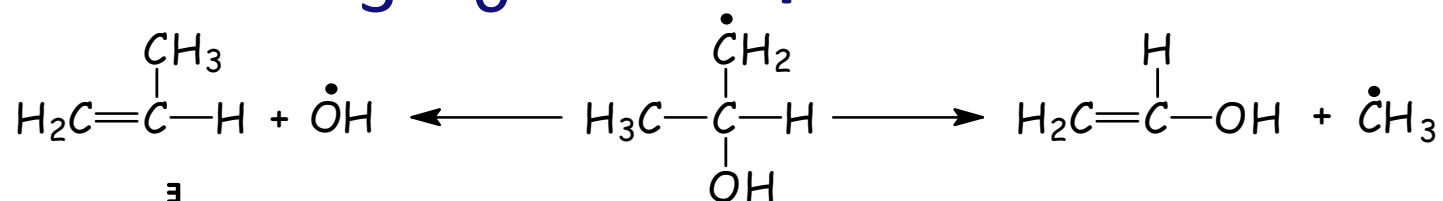


$\text{CH}_3\text{CH}_2\text{CHOH} = \text{products?}$





iC₃H₆OH = products?





Evans-Polanyi type correlations

Correlation for the **decomposition of alkyl free radicals by β -scission**,
determined from the **theoretical calculation** (CBS-QB3 level of theory)
of a series of reference reactions (Sirjean, 2007)



$$E_a = 0.60 \Delta_r H_0 + 14.8 \text{ kcal/mol}$$

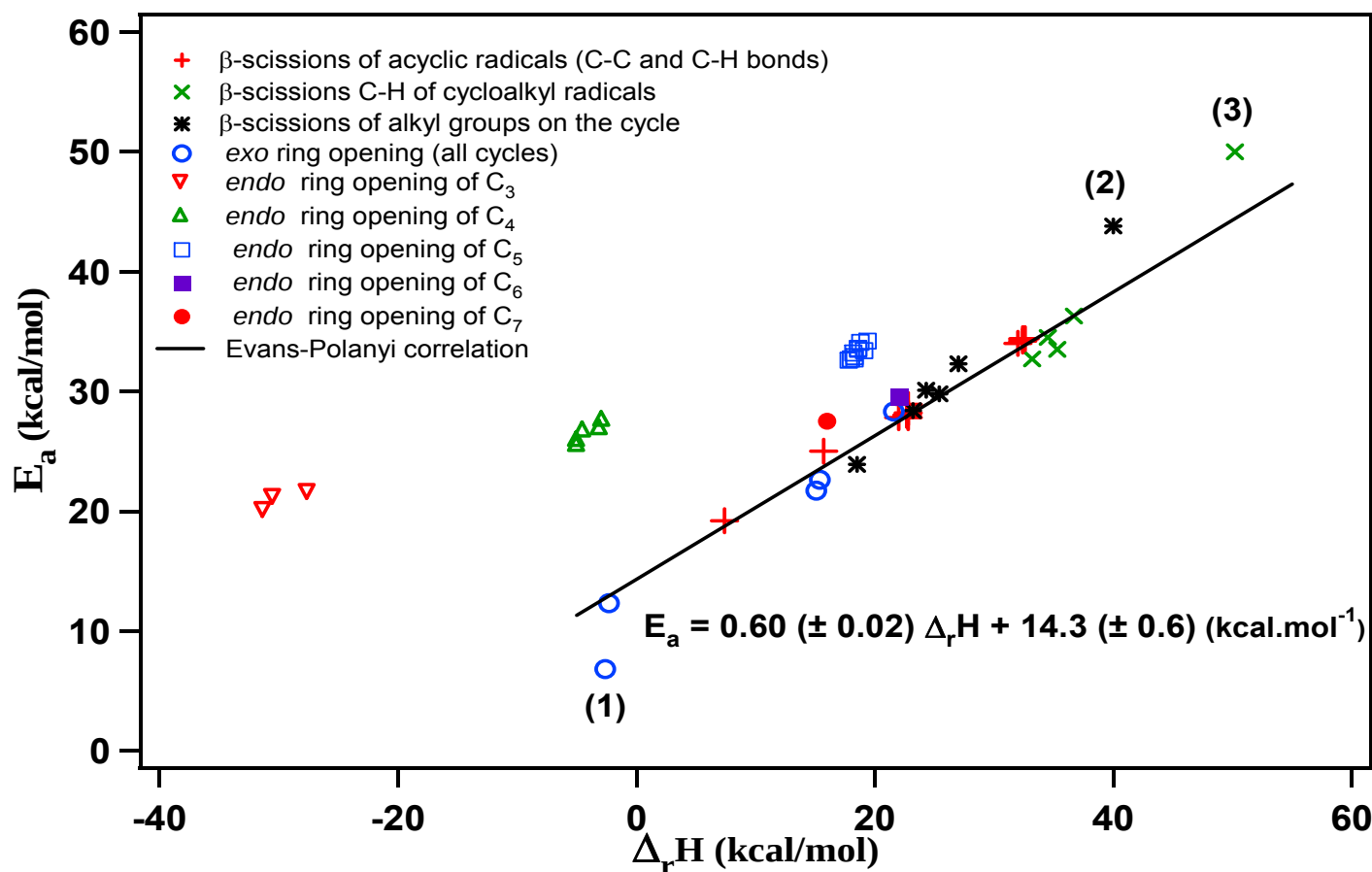
Reactions of acyclic radicals used to built the correlation

Reactions	$\Delta_r H^\circ$ (kcal/mol)	E_a (kcal/mol)	Reactions	$\Delta_r H^\circ$ (kcal/mol)	E_a (kcal/mol)
$\cdot C_3H_7 \rightarrow \cdot CH_3 + C_2H_4$	22,8	28,9	1-penten-5-yl $\rightarrow \cdot C_3H_5 + C_2H_4$	7,4	19,2
$\cdot C_4H_9 \rightarrow \cdot C_2H_5 + C_2H_4$	22,0	27,8	$\cdot C_3H_7 \rightarrow C_3H_6 + H$	32,0	34,0
$\cdot C_5H_{11} \rightarrow \cdot C_3H_7 + C_2H_4$	22,8	28,2	$\cdot C_4H_9 \rightarrow C_4H_8 + H$	32,6	34,4
$\cdot C_6H_{13} \rightarrow \cdot C_4H_9 + C_2H_4$	22,7	28,0	$\cdot C_5H_{11} \rightarrow C_5H_{10} + H$	32,5	34,4
$\cdot C_7H_{15} \rightarrow \cdot C_5H_{11} + C_2H_4$	22,7	28,0	$\cdot C_6H_{13} \rightarrow C_6H_{12} + H$	32,4	34,4
1-hexen-6-yl $\rightarrow$ 1-buten-4-yl + C_2H_4	22,8	27,8	$\cdot C_7H_{15} \rightarrow C_7H_{14} + H$	32,4	34,2
1-hexen-3-yl $\rightarrow$ 1,3-butadiene + $\cdot C_2H_5$	15,7	25,0			



β -scission alkyl free radicals

Correlation adapted to a large number of β -scissions but not to some ring opening.

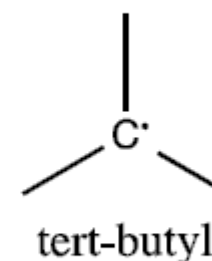
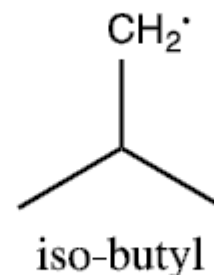
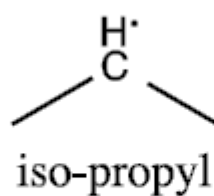
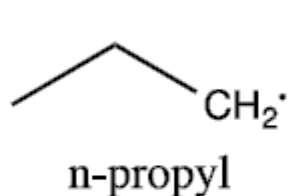




3: Alkyl radical decomposition

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

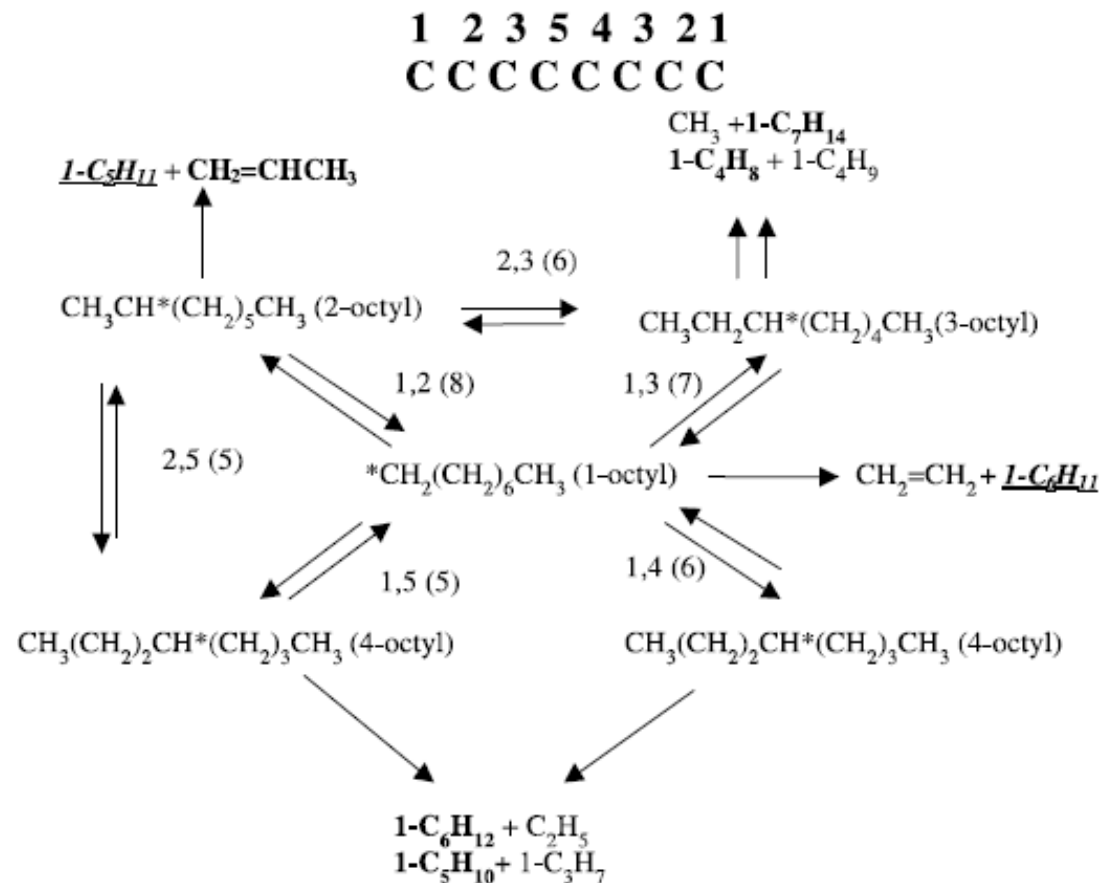
Reaction	A ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$)	n	E_A (kcal)	Analogous reaction from Curran et al. IJCK 2006
$\text{H} + \text{C}_8\text{H}_{16}\text{-1-4} = \text{C}_8\text{H}_{17}\text{-1-4}$	2.50E+11	0.51	2,620	$\text{H} + \text{C}_3\text{H}_6 = \text{nC}_3\text{H}_7$
$\text{H} + \text{C}_8\text{H}_{16}\text{-2-4} = \text{C}_8\text{H}_{17}\text{-2-4}$	4.24E+11	0.51	1,230	$\text{H} + \text{C}_3\text{H}_6 = \text{iC}_3\text{H}_7$
$\text{H} + \text{C}_8\text{H}_{16}\text{-3-4} = \text{C}_8\text{H}_{17}\text{-4-4}$	1.06E+12	0.51	1,230	$\text{H} + \text{iC}_4\text{H}_8 = \text{tC}_4\text{H}_9$



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

4: Alkyl radical isomerization

- Alkyl radical decompositions cannot be separated from radical isomerizations



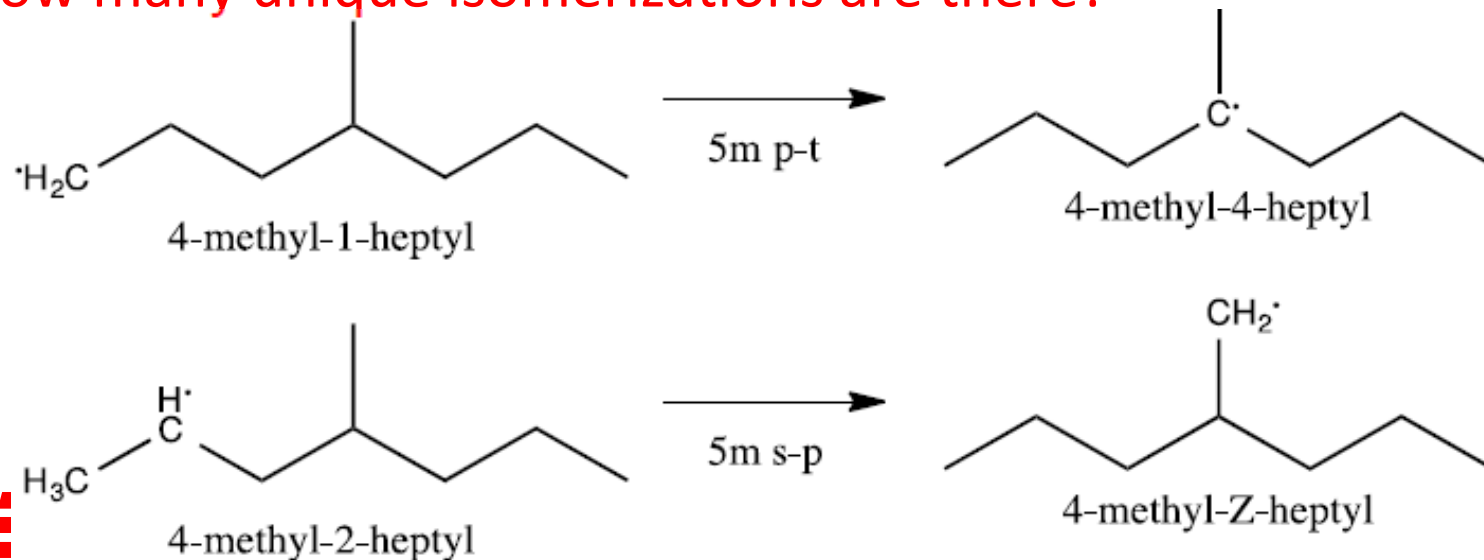
- These reactions involved transfer of H-atoms within the molecule
- Typically more important under fuel rich conditions and at temperatures where decomposition are less favored

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



4: Alkyl radical isomerization

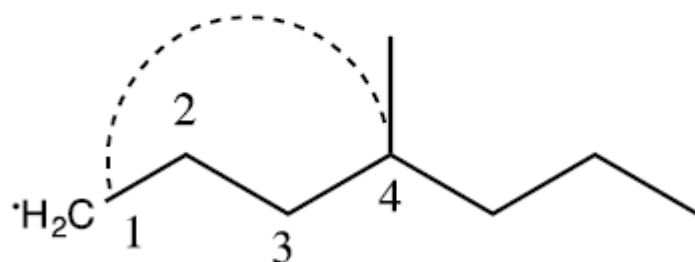
- The rate constant for these reactions depends on the nature of the broken C-H bond (i.e., primary, secondary, or tertiary) and on the ring strain energy barrier.
- Isomerization reactions involving 5-member, 6-member, and 7-member transition state ring are most important
- Radical isomerizations involving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





4: Alkyl radical isomerization

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



1,4 isomerization ties up 3 rotors

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

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

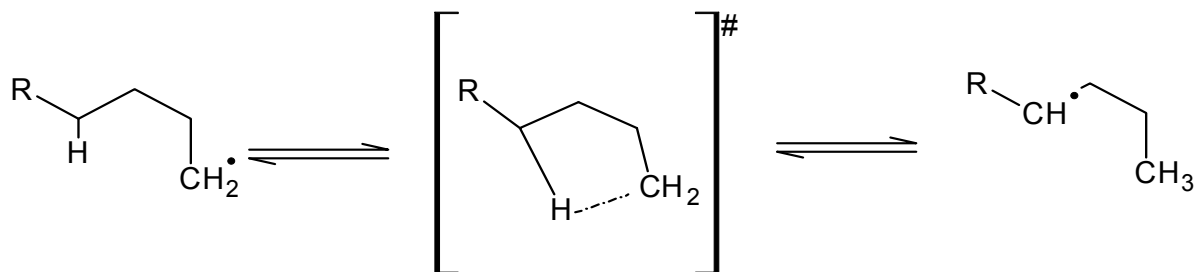
Ring-Strain Corrections, E_{rs}^c

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

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

Isomerization of free radicals: activation energy



$$E_a = E_{\text{ring}} + E_{\text{abstr}}$$

E_{abstr} Energy contribution of the internal H-abstraction

E_{ring} Strain energy of the ring created in the TS

Data for the isomerization of an alkyl radical

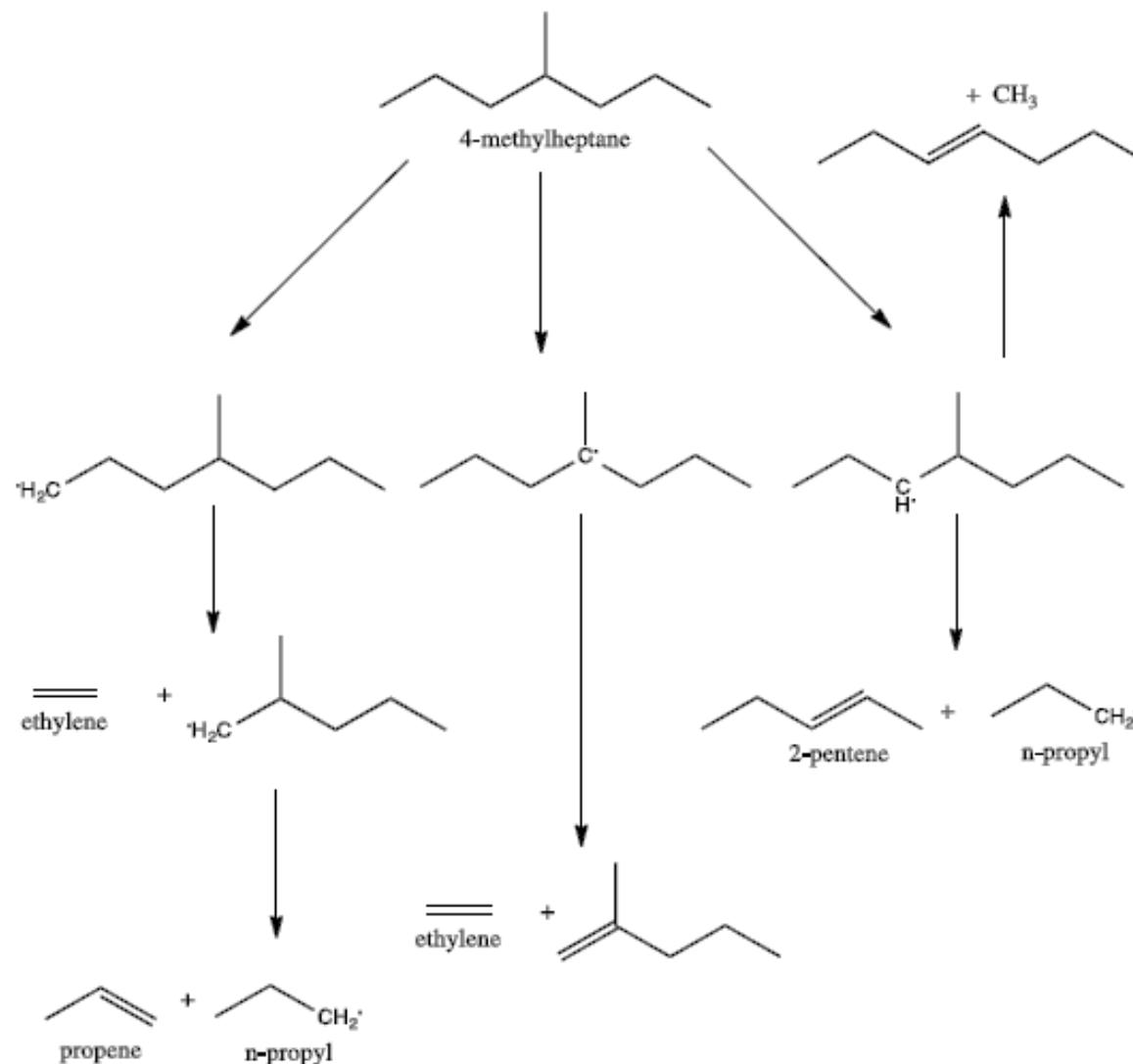
	H _p	H _s	H _t
E_{abstr}	13500	11000	9000

Atoms in the cyclic TS	4	5	6	7	8	9
E_{ring}	26000	6300	1000	6400	9900	12800



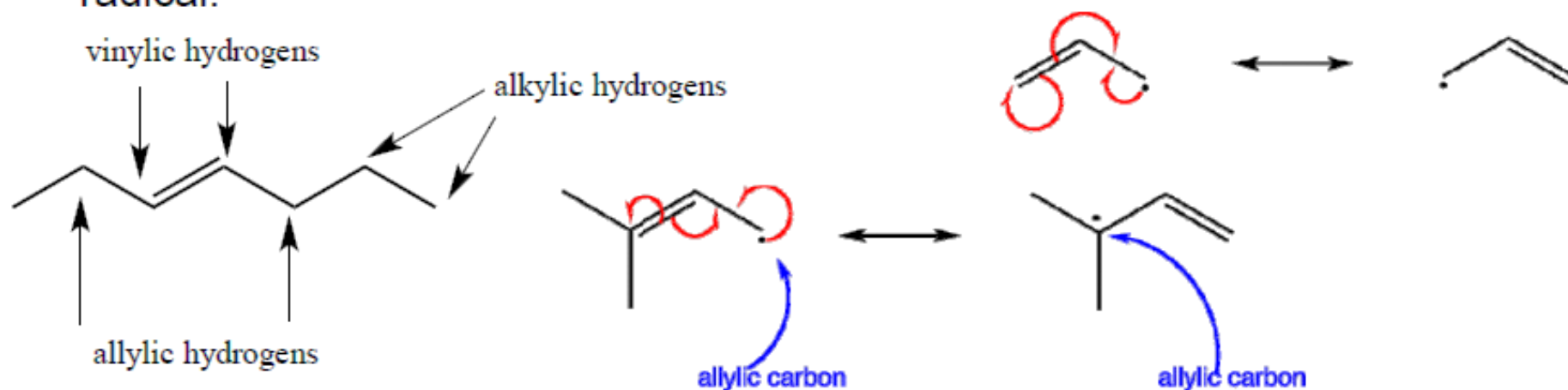
So where are we now?

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



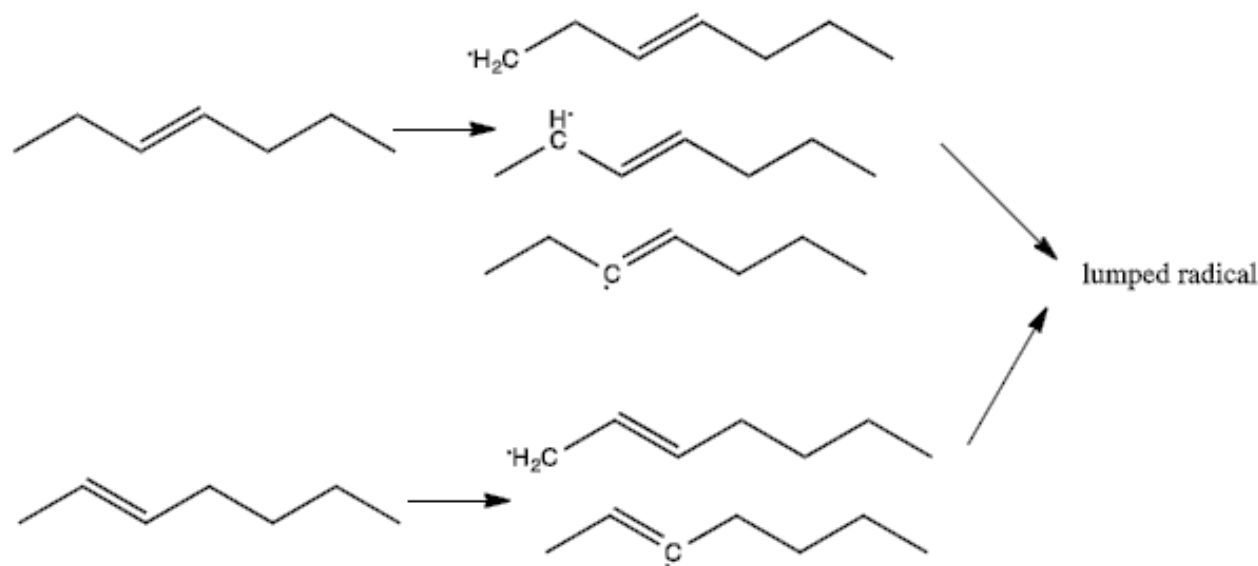
H atom abstraction from alkenes

- The addition of a double bond in alkene molecules presents additional complexity in describing/modeling their combustion chemistry.
- H-abstraction from the β -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.



/// H atom abstraction from alkenes

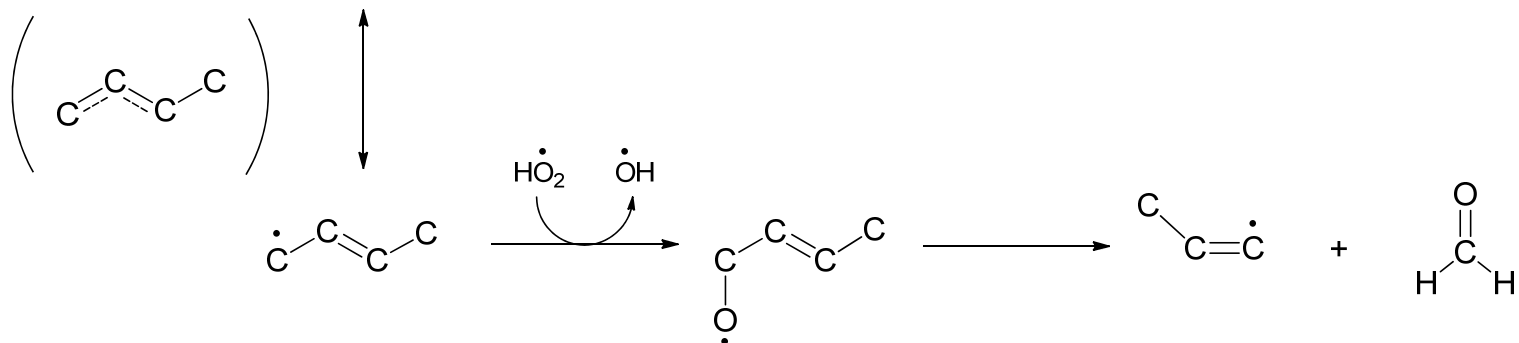
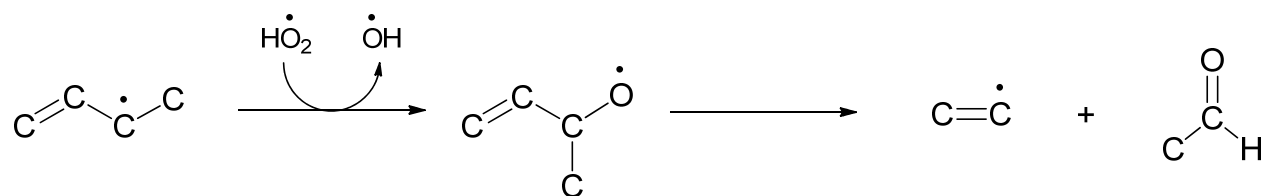
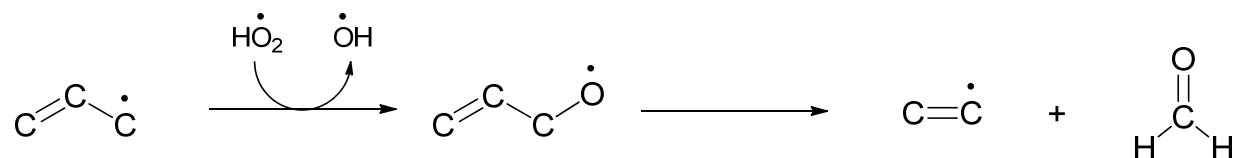
- When alkenes are an intermediate (i.e., not the fuel), one can treat abstraction reactions from large alkenes in a simplified manner
- Neglect the presence of primary, secondary, tertiary, allylic, and vinylic C-H sites, so abstraction reactions by radical species (i.e., H, OH, CH₃, HO₂, and O) lead 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.





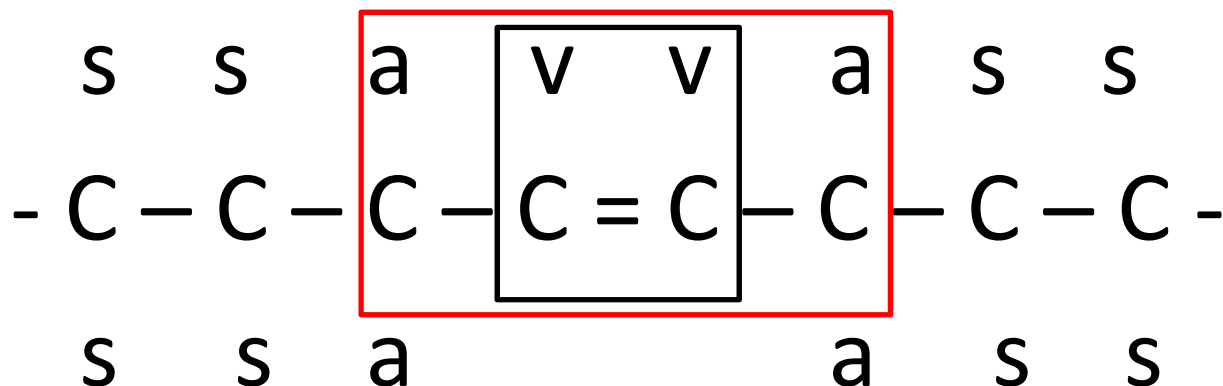
Allylic radical decomposition

- Allylic radicals either undergo β -scission or react with HO_2 radicals to generate allyloxy and OH radicals.
- Allyloxy radicals decompose via β -scission to generate an aldehyde and a vinylic radical.





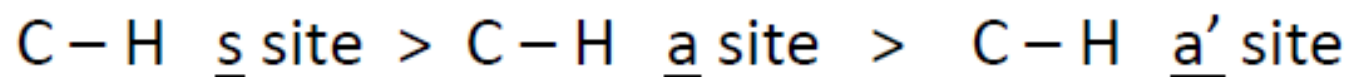
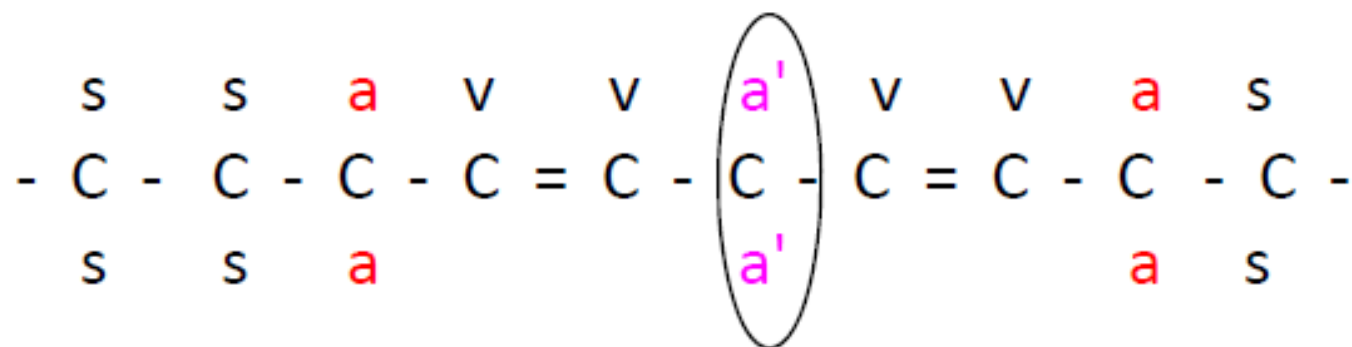
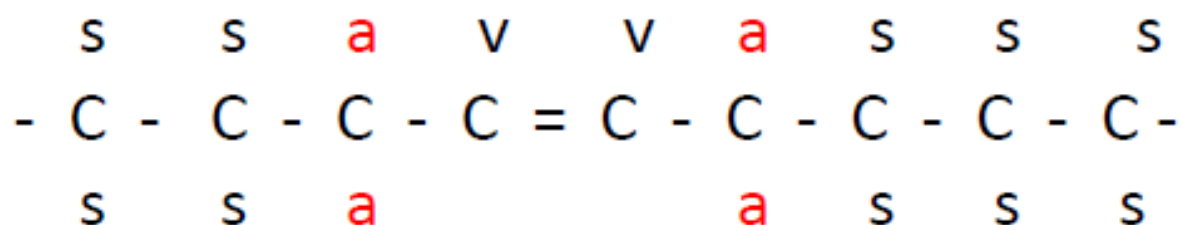
C = C double bonds reduce low T reactivity



- Inserting one C=C double bonds changes the reactivity of 4 carbons atoms in the C chain
- Allylic C – H bond sites are weaker than most others
- Therefore they are preferentially abstracted by radicals
- O₂ is also very weakly bound at allylic sites and falls off rapidly, inhibiting low T reactivity

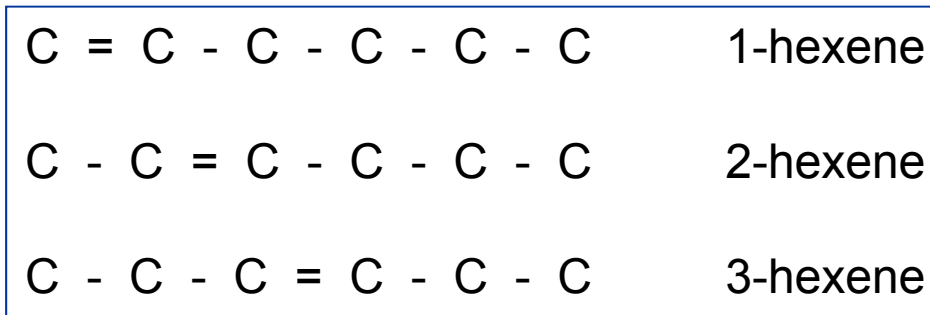


Two double bonds make a huge difference





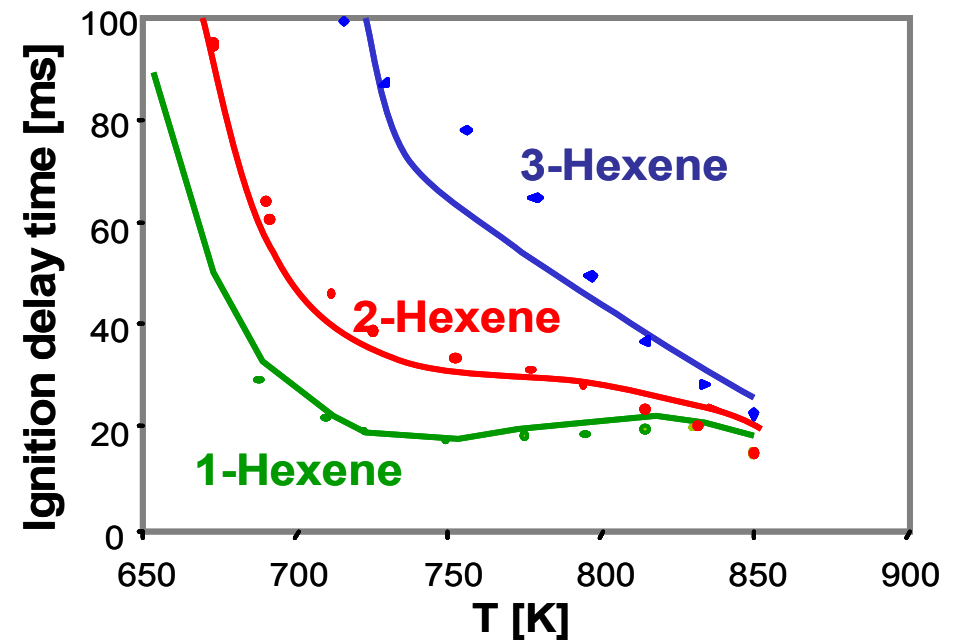
Observed reactivity effect in hexene fuels



RO_2 isomerization initiates
low temperature reactivity

Moving the double bond towards the center
of the molecule “inhibits” RO_2 kinetics

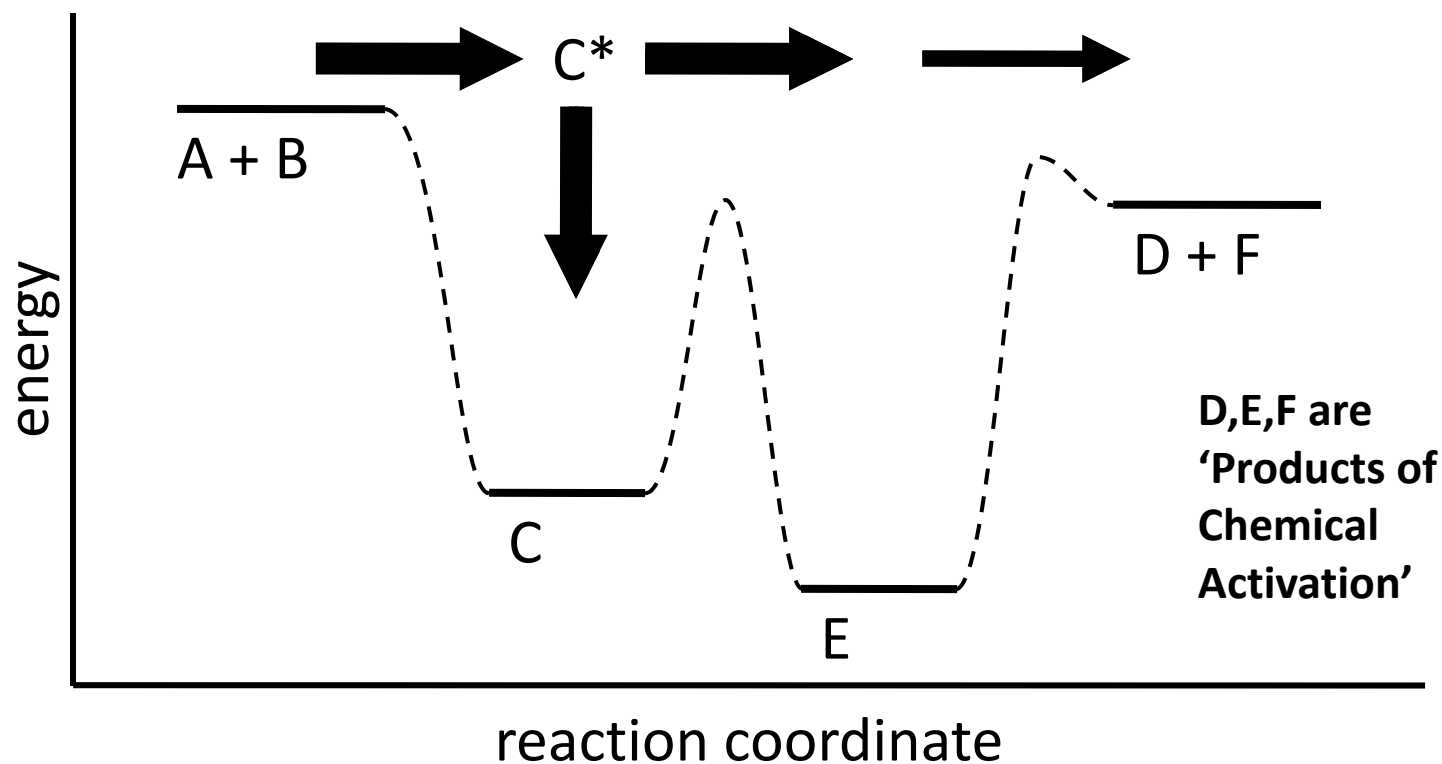
Ignition delay times in a rapid compression
machine of hexene isomers
(0.86-1.09 MPa, $\Phi=1$):



Experimental data: Vanhove et al. PCI 2005
Simulations: Mehl, Vanhove, Pitz, Ranzi Combustion and Flame 2008



Reaction Co-ordinate Diagram



High pressure: collisional stabilization dominates

Reaction classes for low temperature reactions

Low temperature mechanism

Reaction class 10: Alkyl radical addition to O_2 ($R + O_2$)

Reaction class 11: $R + R'O_2 = R\dot{O} + R'\dot{O}$

Reaction class 12: Alkylperoxy radical isomerization

Reaction class 13: $R\dot{O}_2 + H\dot{O}_2 = ROOH + O_2$

Reaction class 14: $R\dot{O}_2 + H_2O_2 = ROOH + H\dot{O}_2$

Reaction class 15: $R\dot{O}_2 + CH_3\dot{O}_2 = R\dot{O} + CH_3\dot{O} + O_2$

Reaction class 16: $R\dot{O}_2 + R'\dot{O}_2 = R\dot{O} + R'\dot{O} + O_2$

Reaction class 17: $ROOH = R\dot{O} + \dot{O}H$

Reaction class 18: $R\dot{O}$ Decomposition

Reaction class 19: $QOOH = \text{Cyclic Ether} + \dot{O}H$

Reaction class 20: $QOOH = \text{Olefin} + H\dot{O}_2$

Reaction class 21: $QOOH = \text{Olefin} + \text{Aldehyde or Carbonyl} + \dot{O}H$

Reaction class 22: Addition of $QOOH$ to molecular oxygen O_2

Reaction class 23: $\dot{O}_2QOOH$ isomerization to carbonylhydroperoxide + $\dot{O}H$

Reaction class 24: Carbonylhydroperoxide decomposition

Reaction class 25: Reactions of cyclic ethers with $\dot{O}H$ and $H\dot{O}_2$

Correlations between structure and reactivity

It is assumed that the equivalent sites in different molecules react at the same speed. Constants determined for some reference molecules

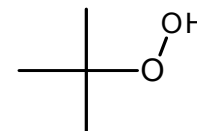
Decomposition of hydroperoxides $\text{ROOH} \rightarrow \text{RO}\cdot + \cdot\text{OH}$

Weak O-O bond (43 kcal/mol).

Experimental measurement for tBuOOH (Sahetchian et al., 1992)

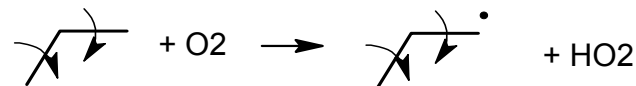
Used for all ROOH molecules

$$k = 4.0 \times 10^{15} \exp(-42500 / RT)$$

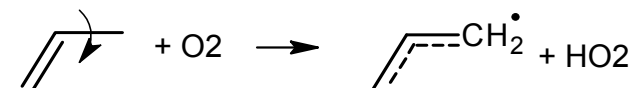


Bimolecular initiations $\text{RH} + \text{O}_2 \rightarrow \text{R}\cdot + \text{HO}_2\cdot$ (Ingham et Walker, 1994)

$\text{R}\cdot$ alkyl $k = 7.0 \times 10^{12} \exp(-\Delta_r H^\circ / RT)$



$\text{R}\cdot$ allyl $k = 7.0 \times 10^{11} \exp(-\Delta_r H^\circ / RT)$



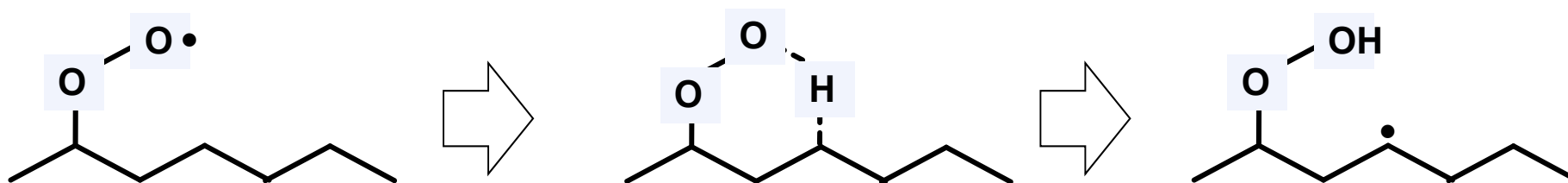
taking into account the loss of a rotor in the second case



Low temperature chemistry: $\text{ROO} \rightleftharpoons \text{QOOH}$ isomerizations

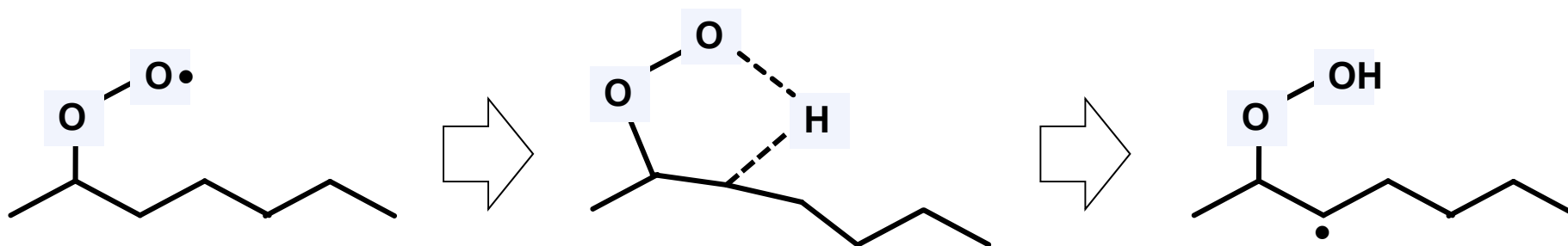
Class 12

6 Member ring isomerization

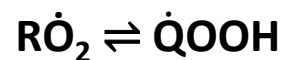


$$K_6 = 2.5\text{E}+10 \cdot \exp(-20450/\text{RT})$$

5 Member ring isomerization



$$K_5 = 2.0\text{E}+11 \cdot \exp(-26450/\text{RT})$$



Ring size	Site			
		A	n	E
5	Primary	1.00×10^{11}	0.00	29400
	Secondary	1.00×10^{11}	0.00	26850
	Tertiary	1.00×10^{11}	0.00	24100
6	Primary	1.25×10^{10}	0.00	24400
	Secondary	1.25×10^{10}	0.00	20850
	Tertiary	1.25×10^{10}	0.00	19100
7	Primary	1.56×10^9	0.00	22350
	Secondary	1.56×10^9	0.00	19050
	Tertiary	1.56×10^9	0.00	17050

H. J. Curran, P. Gaffuri, W. J. Pitz, C. K. Westbrook
Combust. Flame **2002**, 129, 253–280.

High-Pressure Rate Rules for Alkyl + O₂ Reactions. 1. The Dissociation, Concerted Elimination, and Isomerization Channels of the Alkyl Peroxy Radical

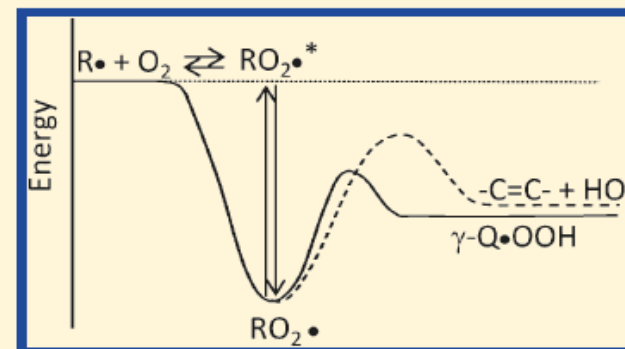
Stephanie M. Villano,[†] Lam K. Huynh,[‡] Hans-Heinrich Carstensen,[†] and Anthony M. Dean^{*,†}

[†]Chemical and Biological Engineering Department, Colorado School of Mines, Golden, Colorado 80401, United States

[‡]International University, Vietnam National University – HCMC and Institute for Computational Science and Technology at HCMC, Vietnam

S Supporting Information

ABSTRACT: The reactions of alkyl peroxy radicals (RO₂) play a central role in the low-temperature oxidation of hydrocarbons. In this work, we present high-pressure rate estimation rules for the dissociation, concerted elimination, and isomerization reactions of RO₂. These rate rules are derived from a systematic investigation of sets of reactions within a given reaction class using electronic structure calculations performed at the CBS-QB3 level of theory. The rate constants for the dissociation reactions are obtained from calculated equilibrium constants and a literature review of experimental rate constants for the reverse association reactions. For the concerted elimination and isomerization channels, rate constants are calculated using canonical transition state theory. To determine if the high-pressure rate expressions from this work can directly be used in ignition models, we use the QRRK/ MSC method to calculate apparent pressure and temperature dependent rate constants for representative reactions of small, medium, and large alkyl radicals with O₂. A comparison of concentration versus time profiles obtained using either the pressure dependent rate constants or the corresponding high-pressure values reveals that under most conditions relevant to combustion/ ignition problems, the high-pressure rate rules can be used directly to describe the reactions of RO₂.

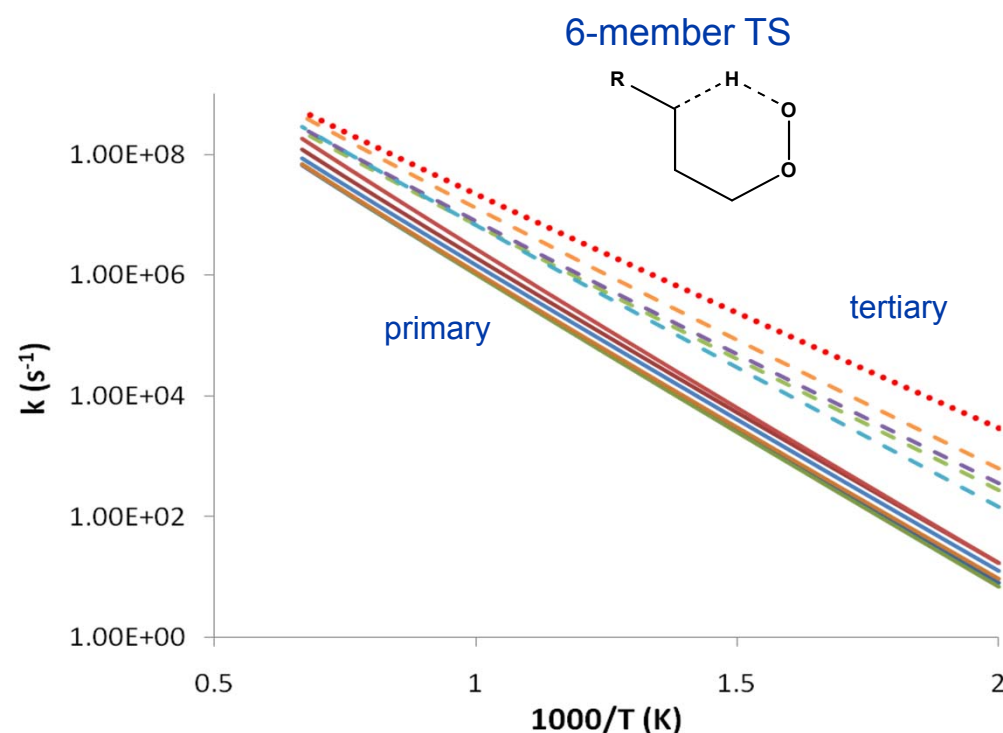
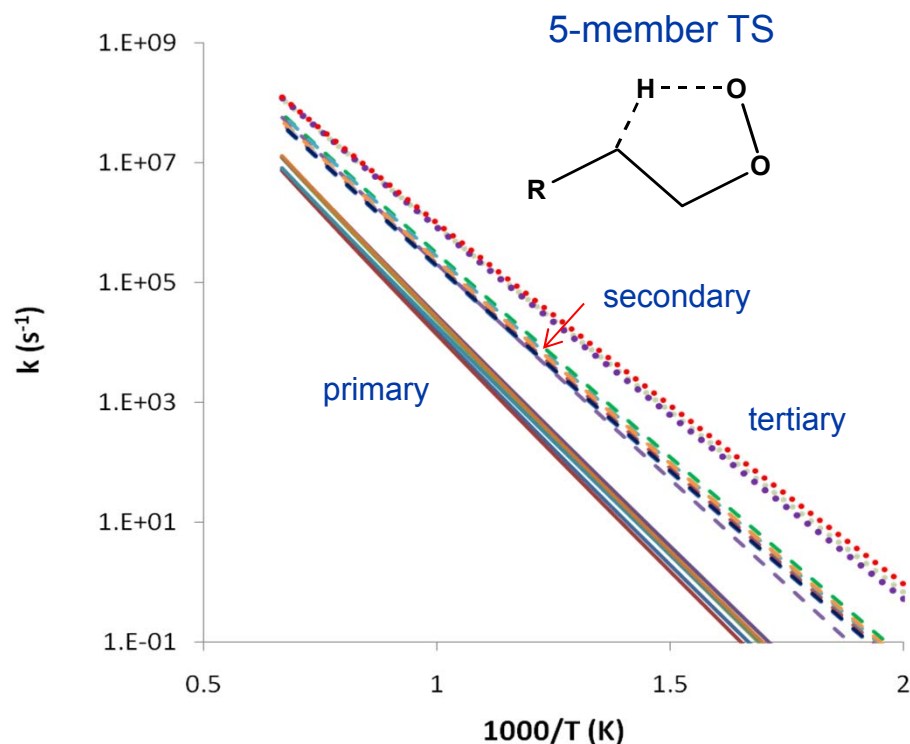




RO_2 isomerizations: Rate constants from computational chemistry

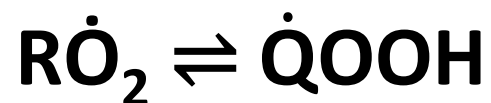
(Dean, Carstensen et al. Colorado School of Mines)

Class 12



S. M. Villano, L. K. Huynh, H. –H. Carstensen, A. M. Dean
J. Phys. Chem. A **2011**, *115*, 13425–13442

- Activation energy depends on ring size *and* overall thermochemistry
- Amenable to rule generation



Curran *et al.*

Villano *et al.*

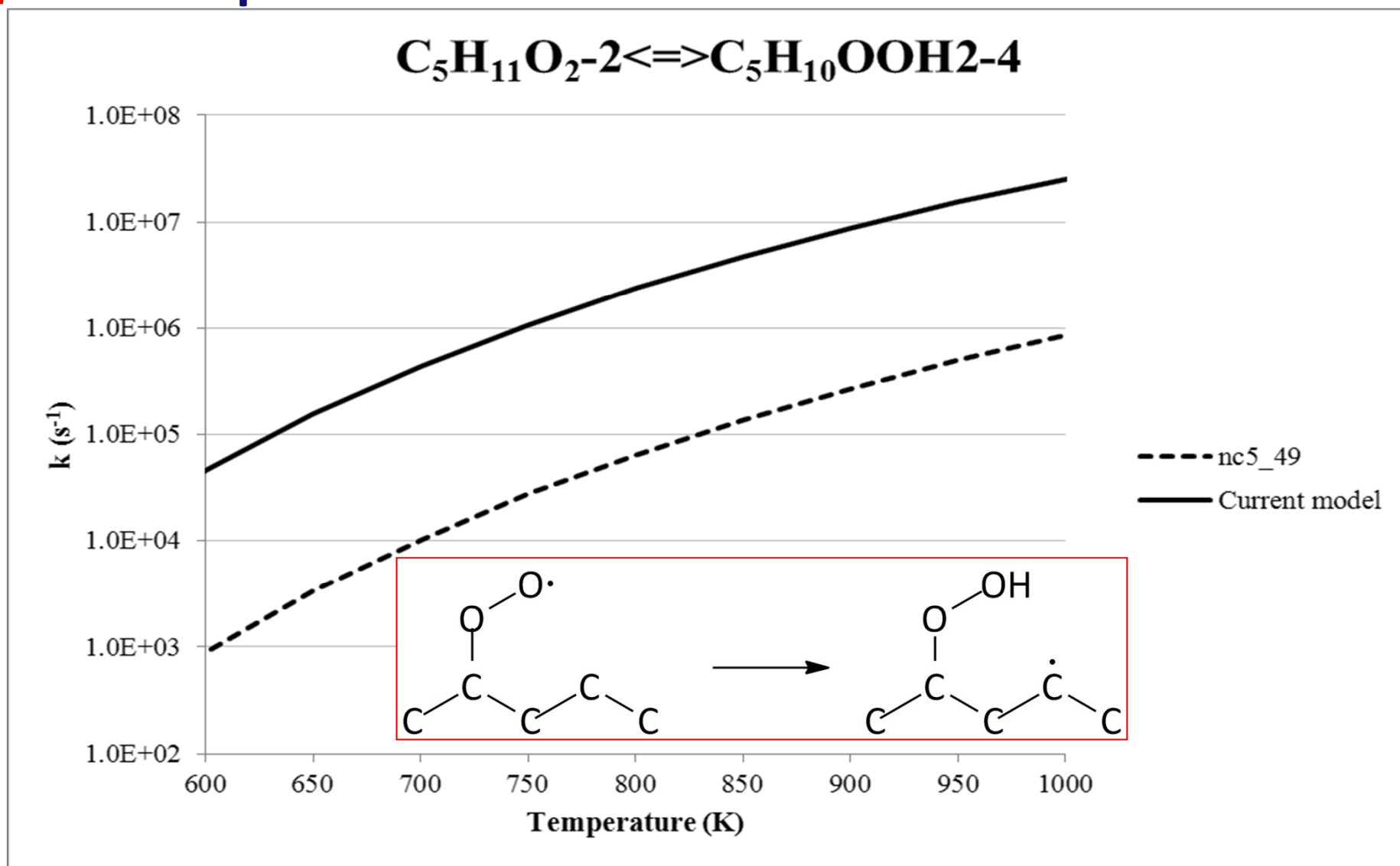
Ring size	Site	Curran <i>et al.</i>			Villano <i>et al.</i>		
		<i>A</i>	<i>n</i>	<i>E</i>	<i>A</i>	<i>n</i>	<i>E</i>
5	Primary	1.00×10^{11}	0.00	29400	2.17×10^6	1.73	32000
	Secondary	1.00×10^{11}	0.00	26850	4.87×10^7	1.36	28600
	Tertiary	1.00×10^{11}	0.00	24100	2.52×10^7	1.39	25300
6	Primary	1.25×10^{10}	0.00	24400	1.62×10^7	1.23	21500
	Secondary	1.25×10^{10}	0.00	20850	4.65×10^7	1.11	18200
	Tertiary	1.25×10^{10}	0.00	19100	1.45×10^8	0.94	15800
7	Primary	1.56×10^9	0.00	22350	3.42×10^5	1.48	20200
	Secondary	1.56×10^9	0.00	19050	5.16×10^5	1.41	16400
	Tertiary	1.56×10^9	0.00	17050	2.02×10^7	0.90	14600

H. J. Curran, P. Gaffuri, W. J. Pitz, C. K. Westbrook
Combust. Flame **2002**, 129, 253–280.

S. M. Villano, L. K. Huynh, H. -H. Carstensen, A. M. Dean
J. Phys. Chem. A **2011**, 115, 13425–13442.



Comparison of rate coefficients





Developing Chemical Kinetic Mechanisms for fuel Oxidation at Low Temperatures and high Pressures



Prof Henry Curran

John Bugler, Kuiwen Zhang, Emma Silke

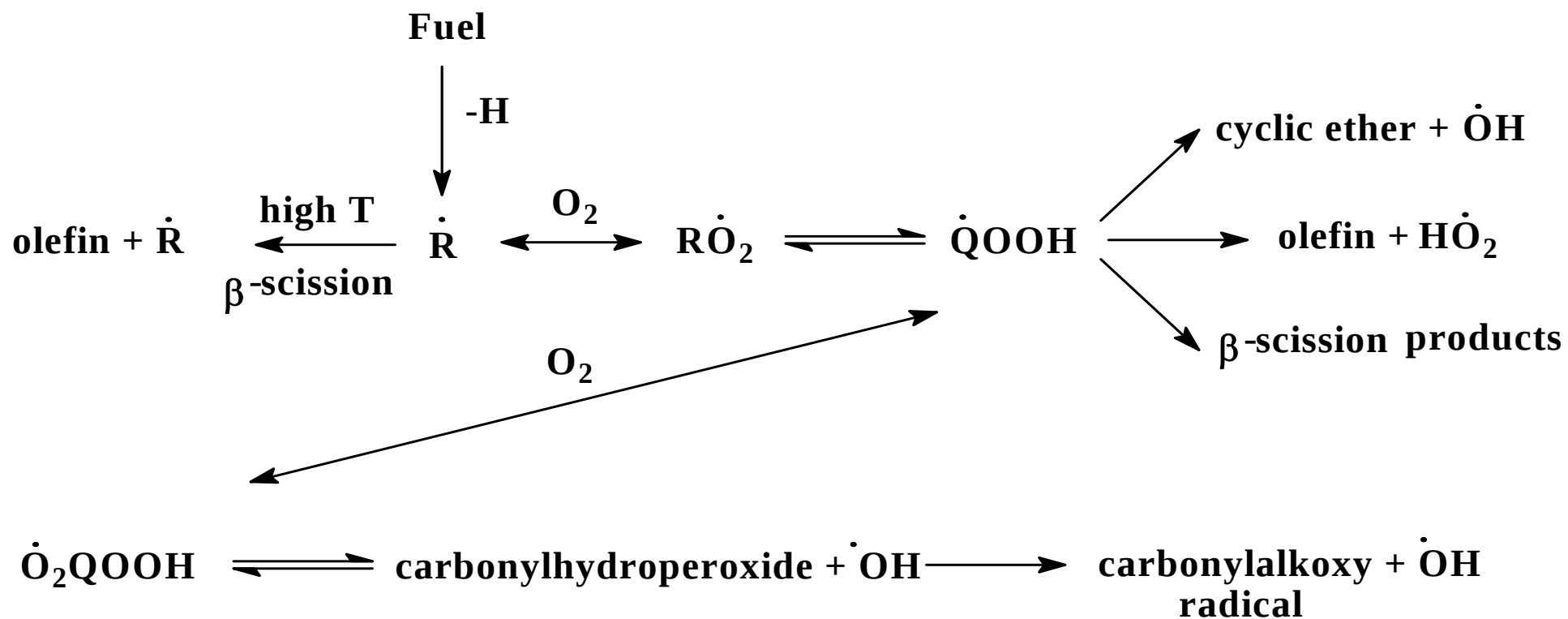
Combustion Chemistry Centre



J. Bugler, K.P. Somers, E.J. Silke, H.J. Curran Revisiting the Kinetics and Thermodynamics of the Low-Temperature Oxidation Pathways of Alkanes: A Case Study of the Three Pentane Isomers *Journal of Physical Chemistry A* **(2015)** in press

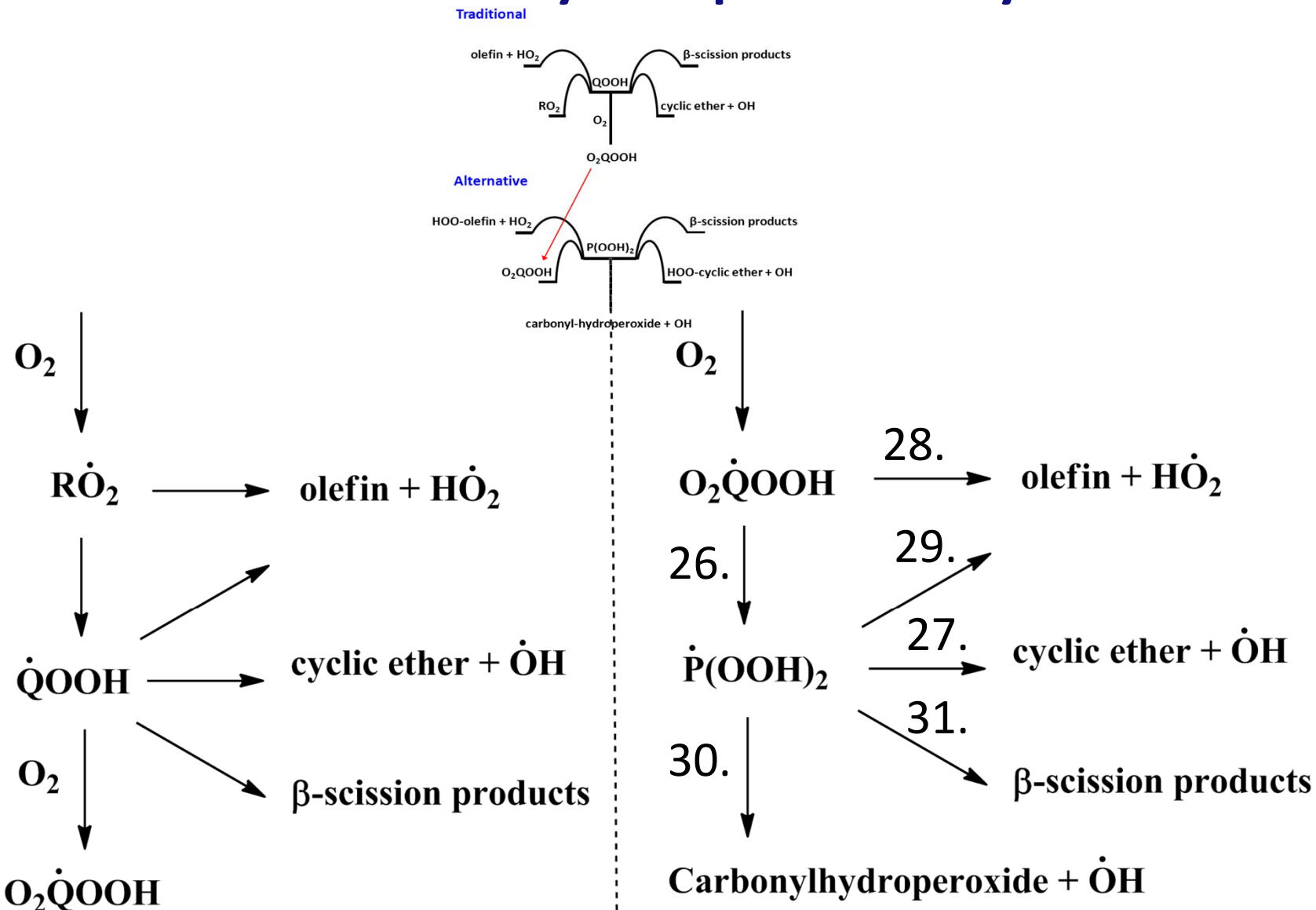


Generic Fuel Reaction Scheme





Similarity of pathways



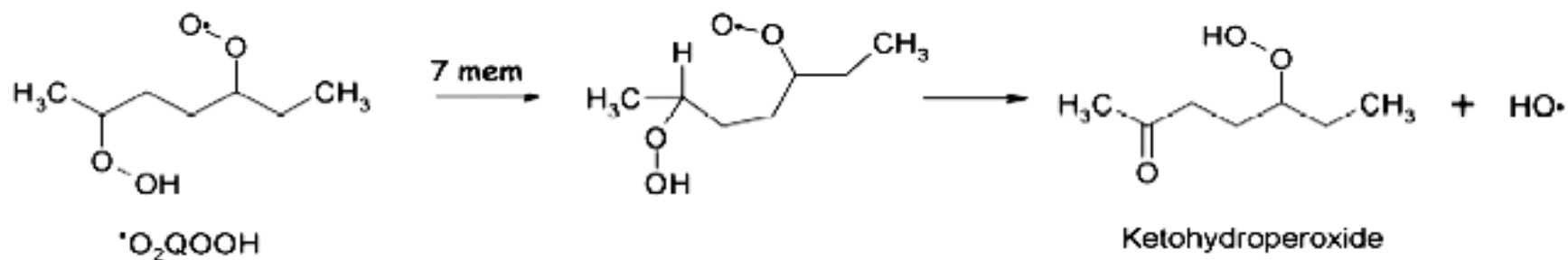


New reaction classes

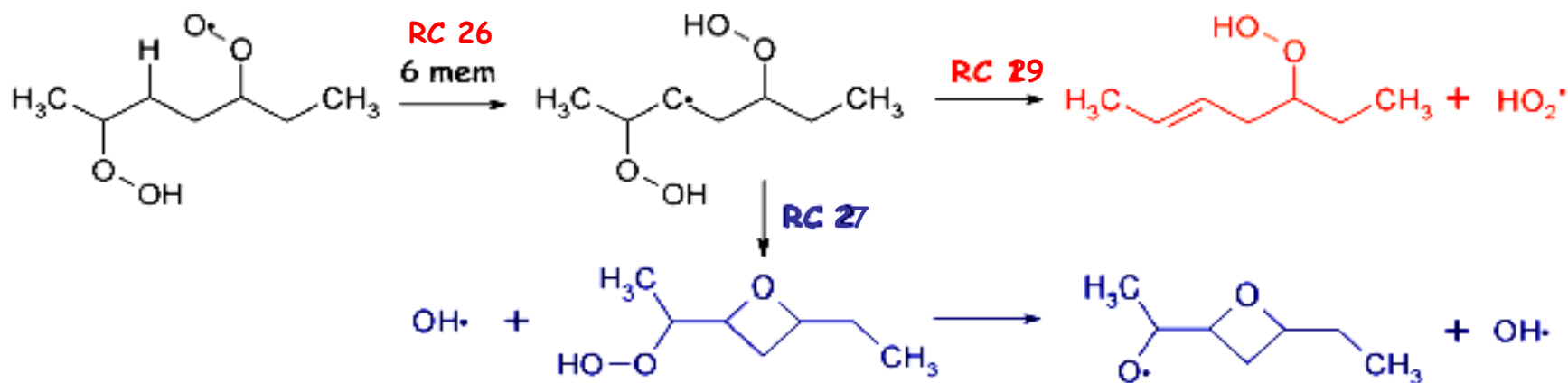
- 26. $\dot{\text{O}}_2\text{QOOH} \rightleftharpoons$ alternative H-atom isomerisation
- 27. $\dot{\text{P}}(\text{OOH})_2 \rightarrow$ cyclic ether + $\dot{\text{O}}\text{H}$
- 28. $\dot{\text{O}}_2\text{QOOH} \rightarrow$ olefin + $\text{H}\dot{\text{O}}_2$
- 29. $\dot{\text{P}}(\text{OOH})_2 \rightarrow$ olefin + $\text{H}\dot{\text{O}}_2$
- 30. $\dot{\text{O}}_2\text{QOOH} \rightleftharpoons$ carbonylhydroperoxide + $\dot{\text{O}}\text{H}$
- 31. $\dot{\text{P}}(\text{OOH})_2 \rightarrow$ β -scission products
- 32. QOOH intramolecular isomerisation
- 33. $\text{R}\dot{\text{O}}_2 \rightarrow$ Olefin + $\text{H}\dot{\text{O}}_2$ (concerted elimination)



$\dot{\text{O}}_2\text{QOOH} \rightleftharpoons$ alternative isomerisation



Conventional chemistry

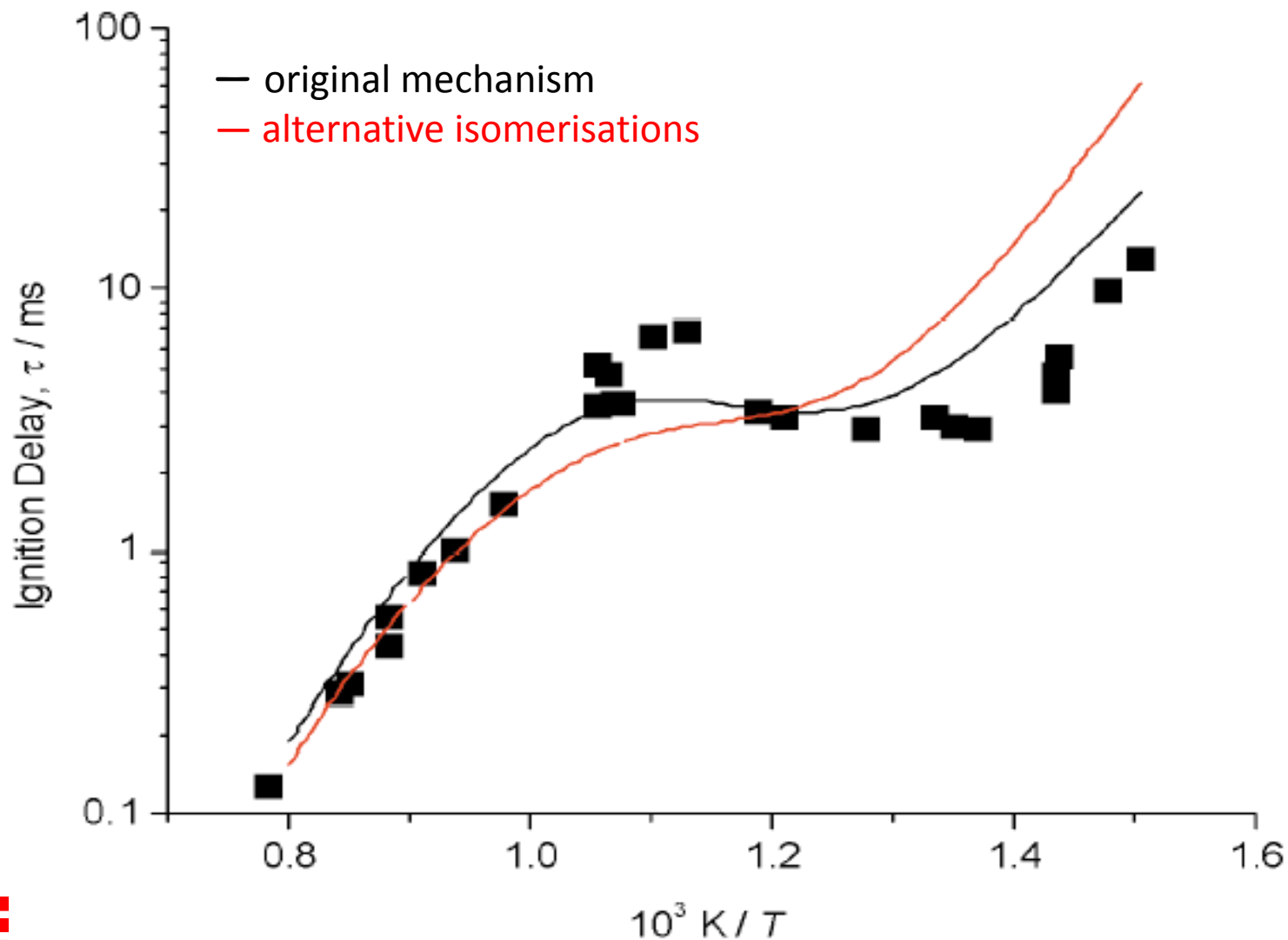


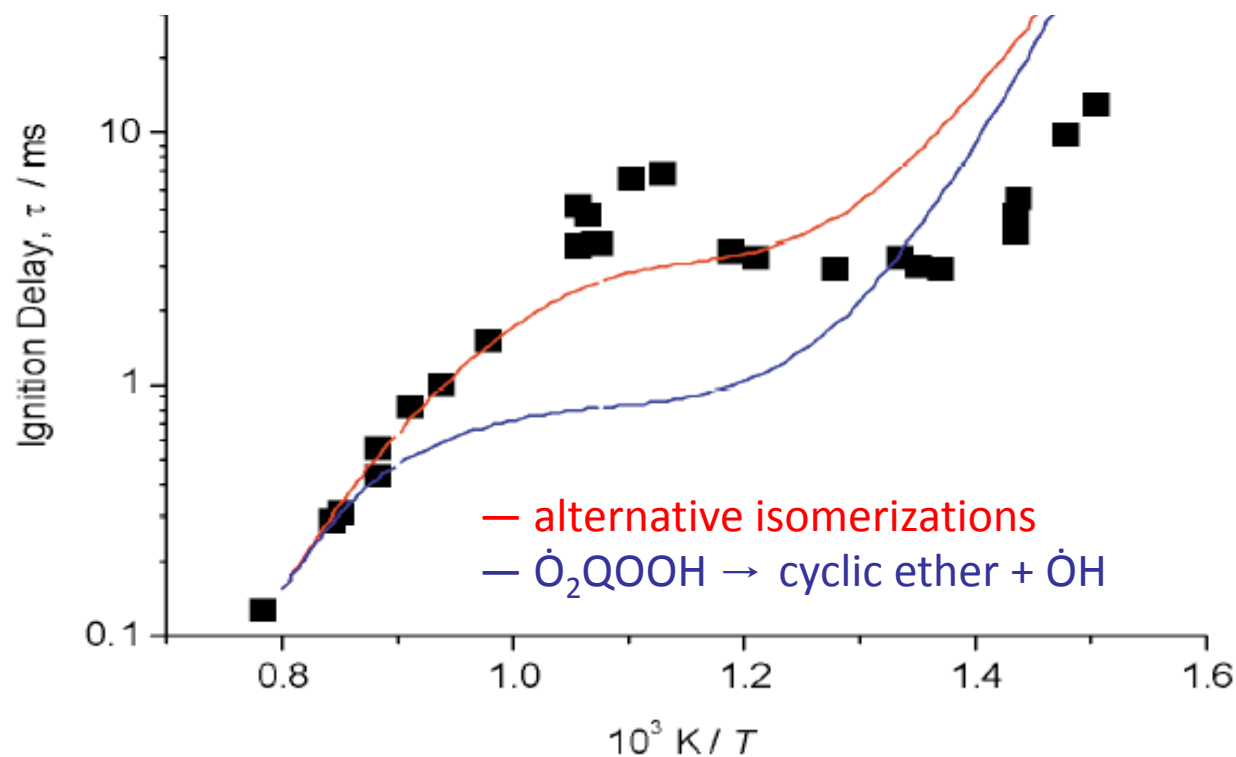
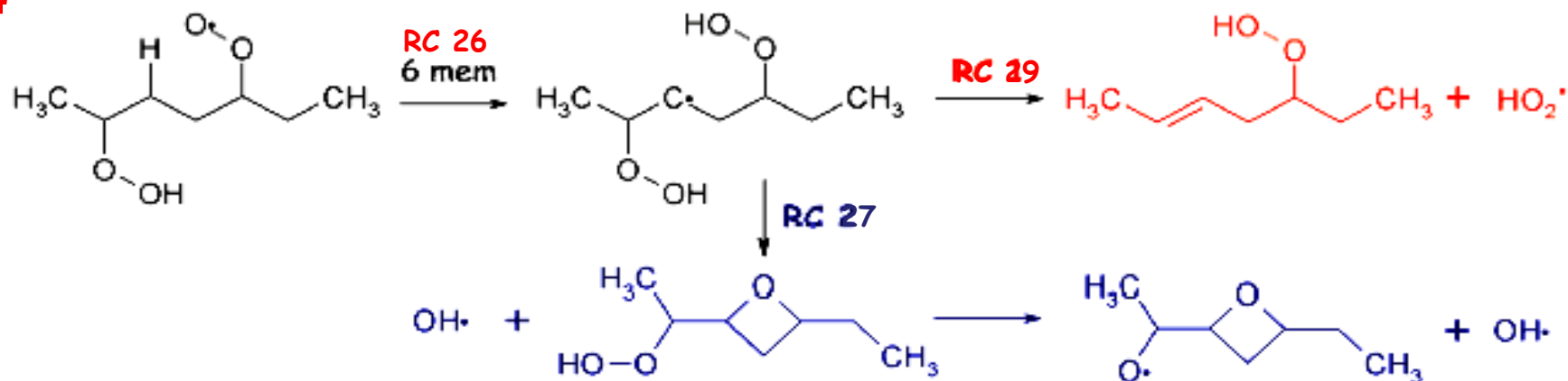
Alternative chemistry

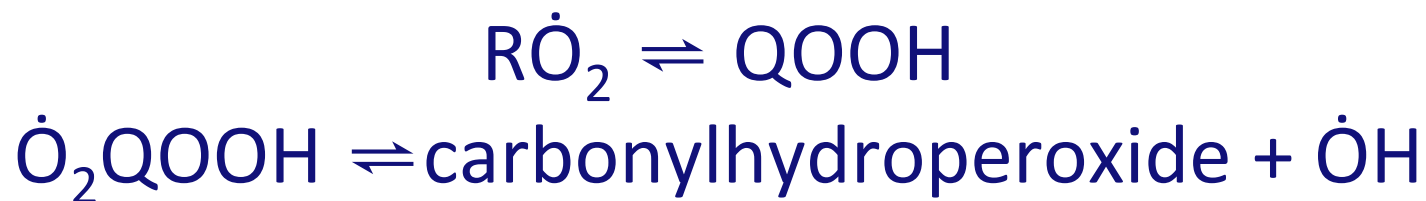


$\dot{\text{O}}_2\text{QOOH} \rightleftharpoons$ alternative isomerization

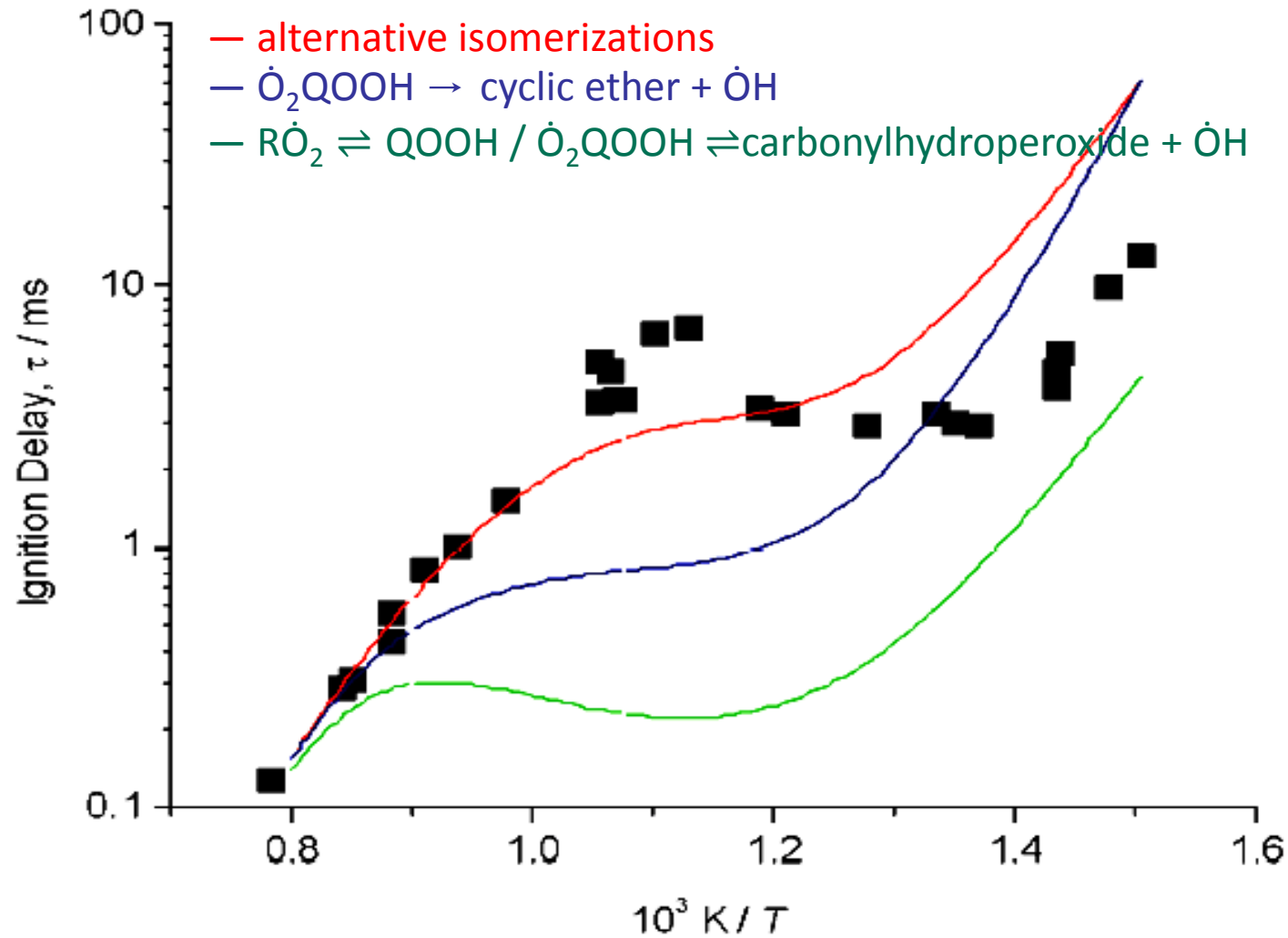
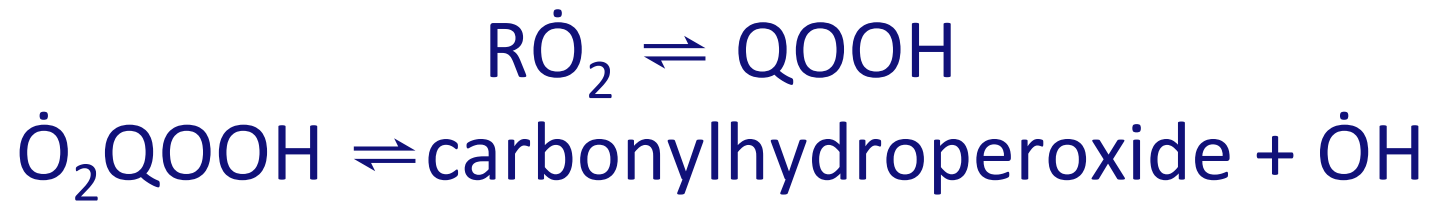
1.0% nC_7H_{16} , $\phi = 1.0$ in 'air', $P = 13.5$ bar





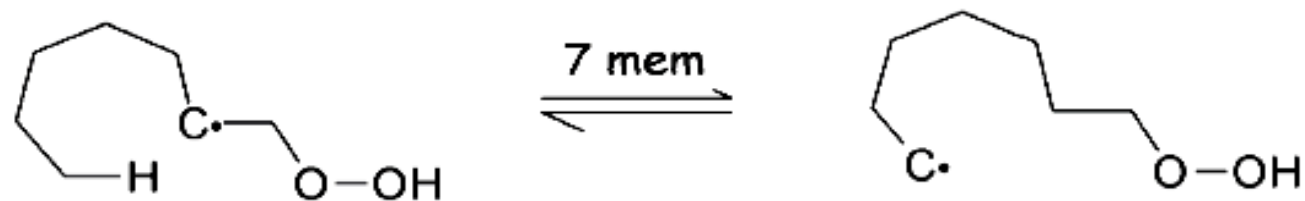
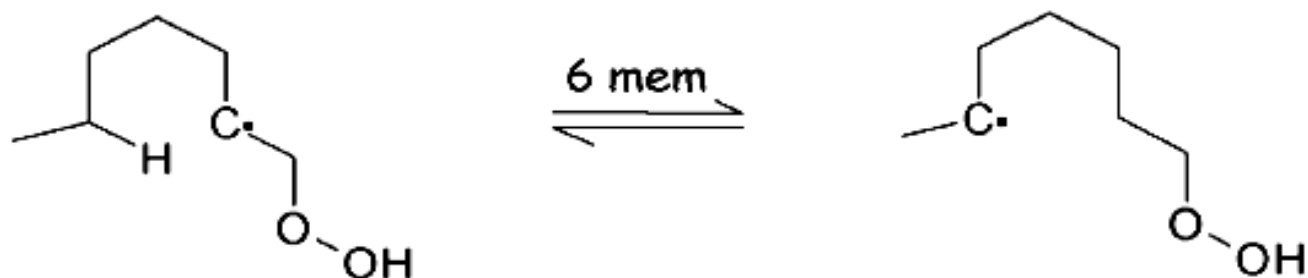
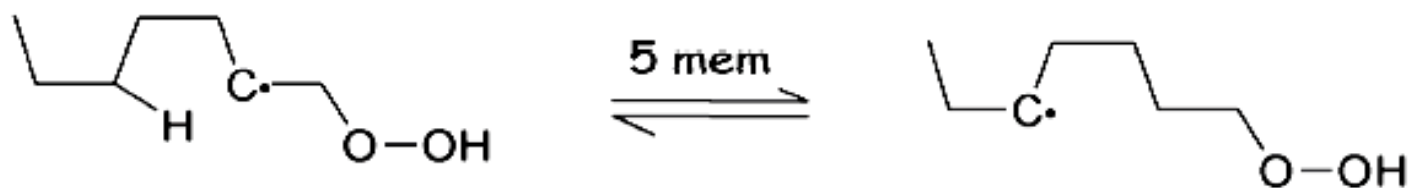


- R. Sumathi and W.H. Green
 - *ab-initio* calculations at the CBS-QB3 level
- Rate constants for isomerization significantly faster (x 10) than Curran recommendations





QOOH Intramolecular isomerisation





QOOH Intramolecular isomerisation

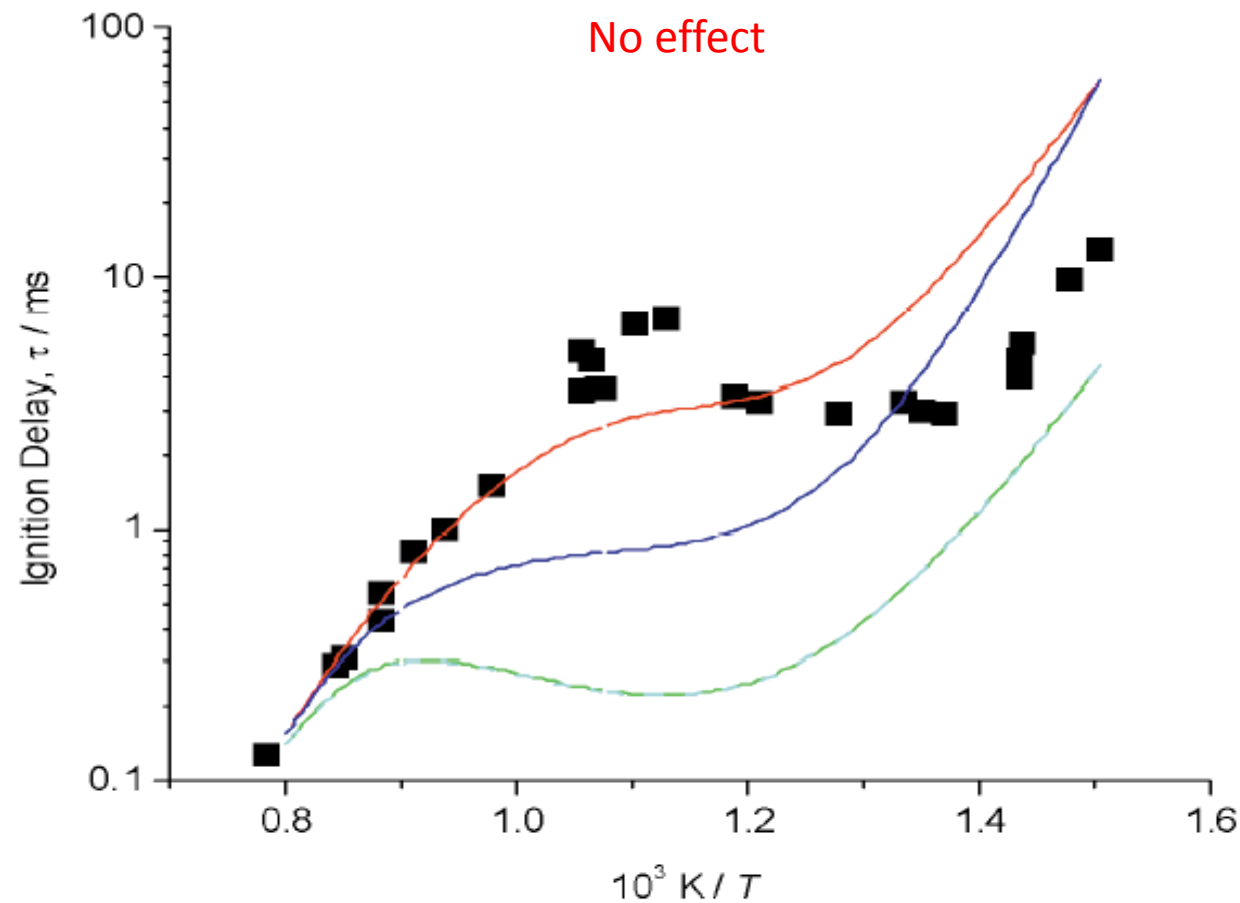


Figure 5.13: *n*-Heptane, $\phi = 1.0$ and ~ 13.5 bar: ■ Ciezki *et al* [58], — *this study* plus reaction class 1, — reaction class 1 and 2, — reaction class 1, 2, 5 and 6, - - - reaction class 1, 2, 5, 6 and 7.

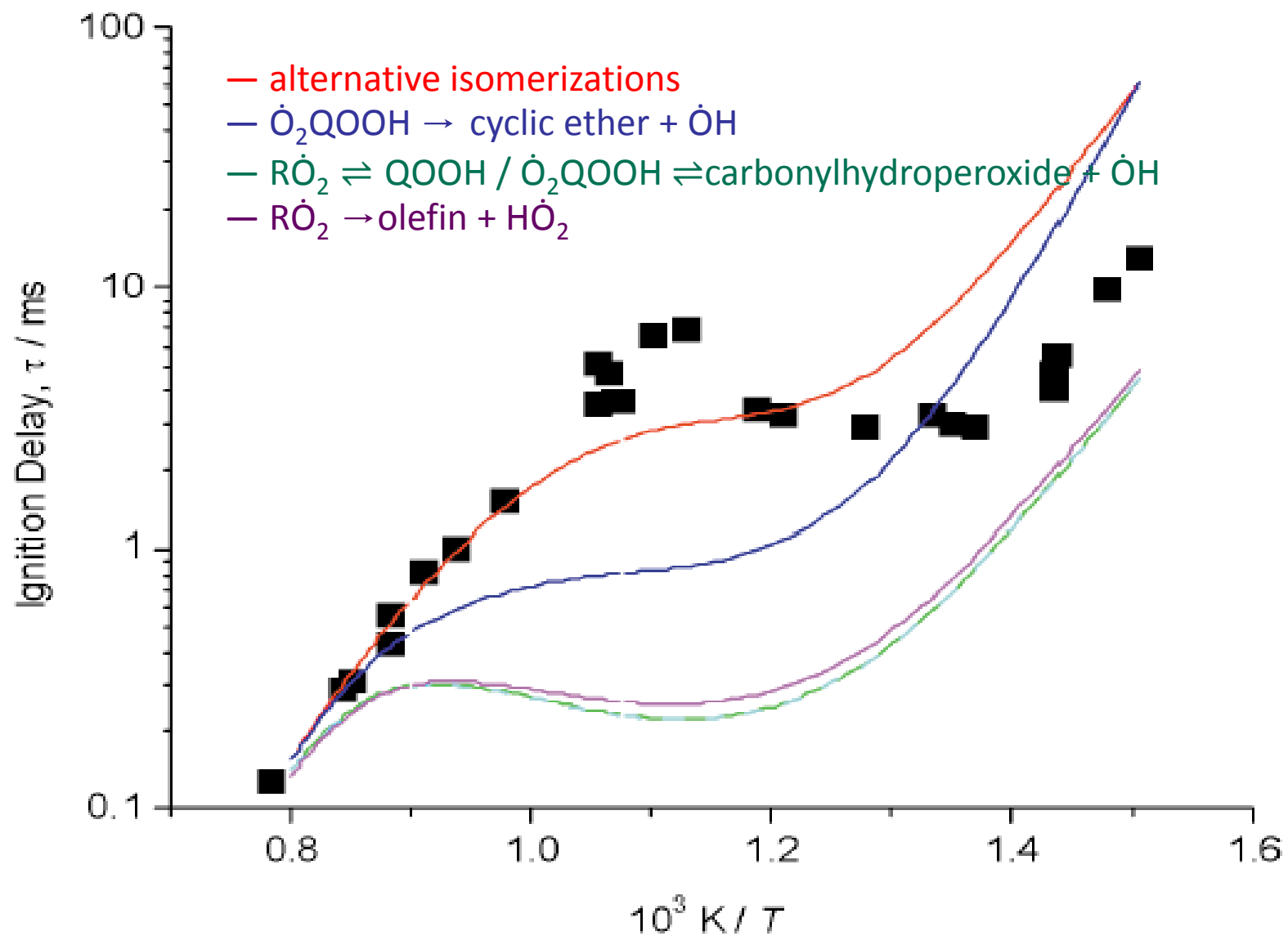




Reaction	A	n	$\mathcal{E}_a$
$nC_3H_7\dot{O}_2 = C_3H_6 + H\dot{O}_2$	1.89×10^7	1.51	29636.
$iC_3H_7\dot{O}_2 = C_3H_6 + H\dot{O}_2$	1.56×10^9	1.16	30866.

Barckholtz, T. A., Bozzelli, J. W. and Chen, C. “Modelling the Negative Temperature Coefficient in the Low Temperature Oxidation of Propane” *3rd Joint Meeting of U.S. Sections of Combustion Institute* 2003.

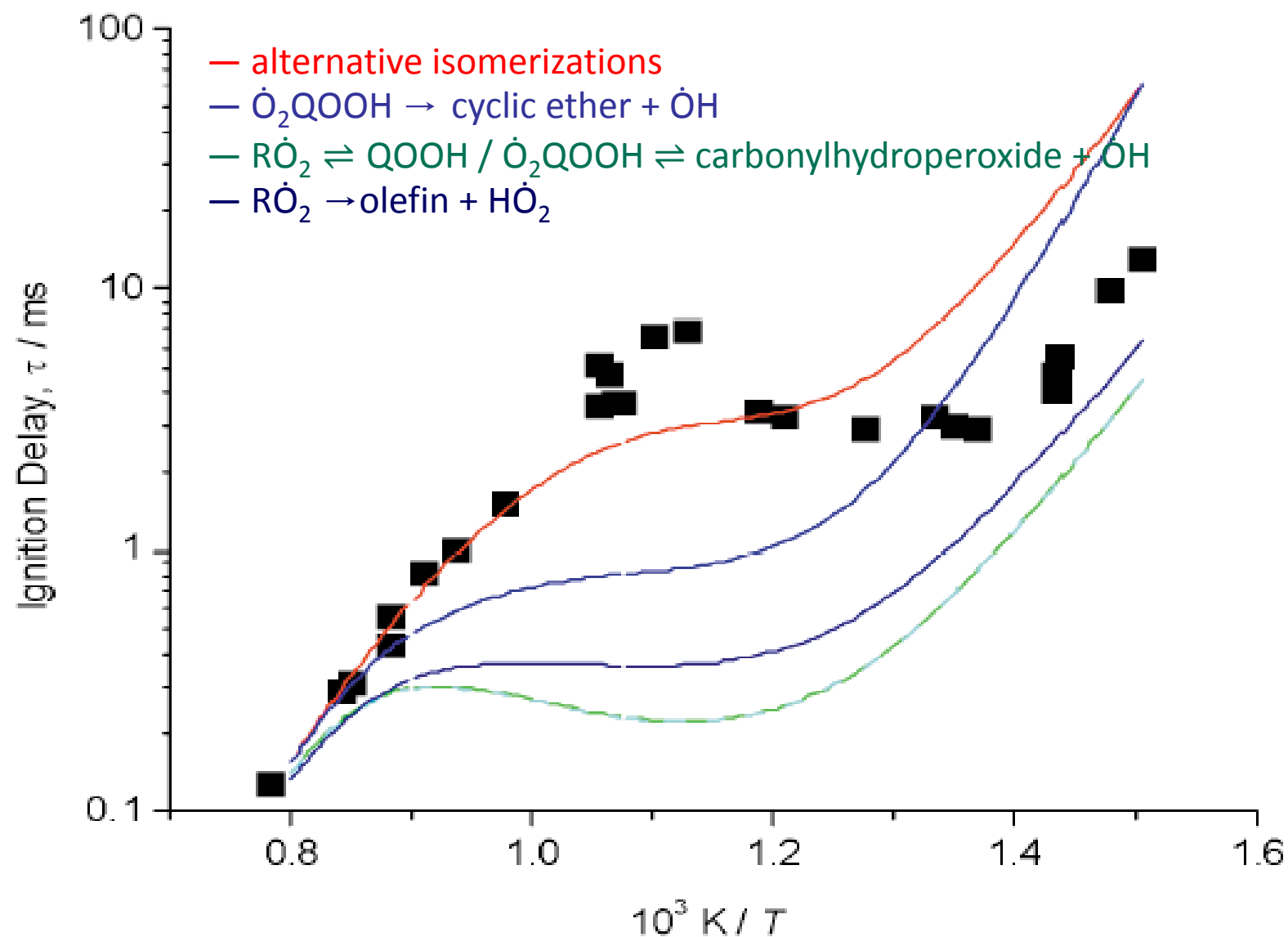






Reaction	A	n	$\mathcal{E}_a$
$nC_3H_7\dot{O}_2 = C_3H_6 + H\dot{O}_2$	1.89×10^7	1.51	27636.
$iC_3H_7\dot{O}_2 = C_3H_6 + H\dot{O}_2$	1.56×10^9	1.16	28866.

Naik, C. “Modelling the Low to Intermediate Temperature Oxidation and Pyrolysis of Hydrocarbons” *Ph.D. Thesis* 2004, Chemical Engineering Dept., Colorado School of Mines, USA.

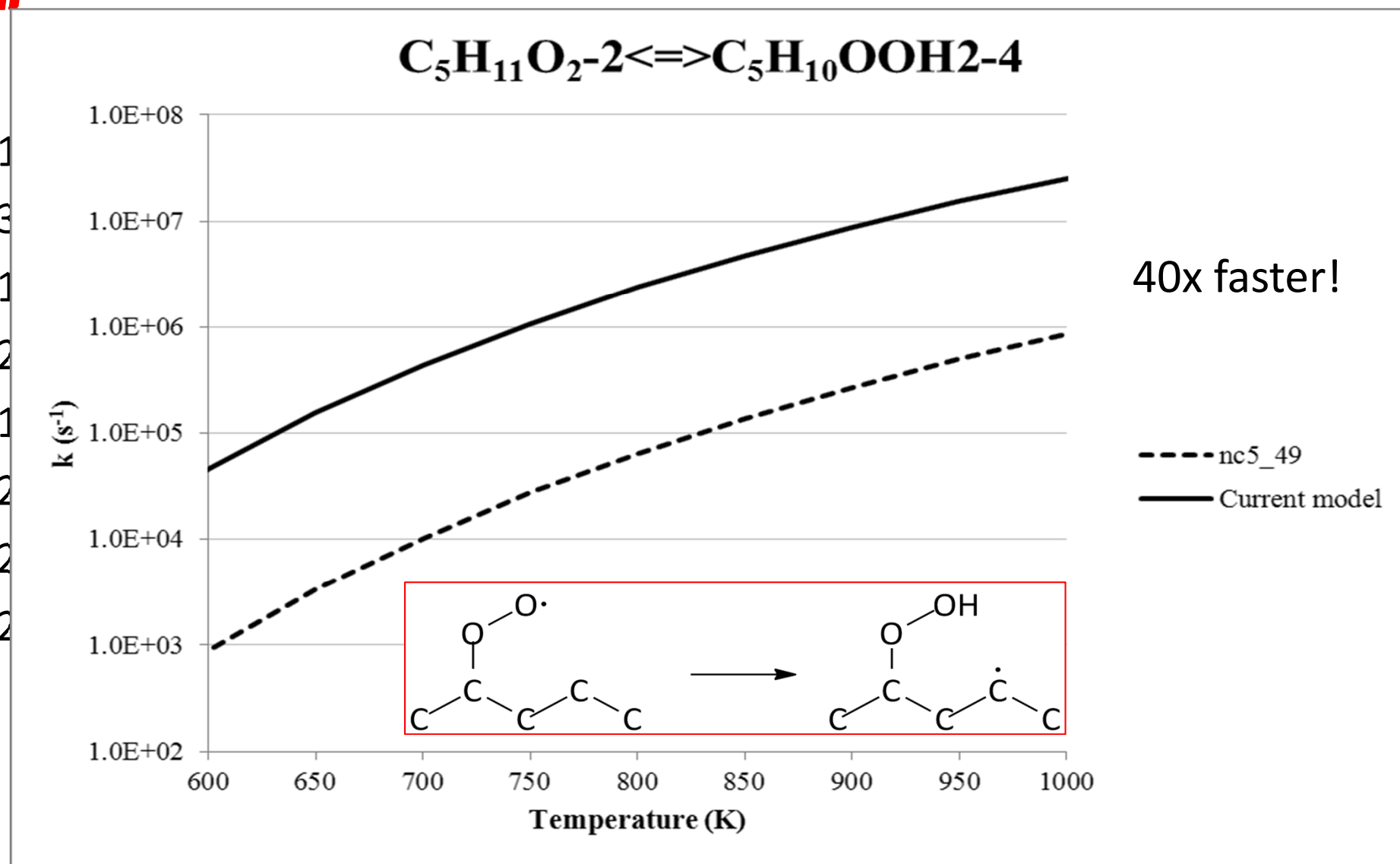




Updates to *n*-Pentane mechanism

All solid lines in graphs represent constant
volume simulations

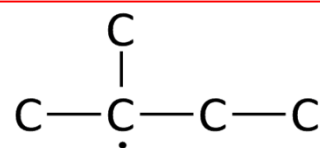
Updates to Kinetics



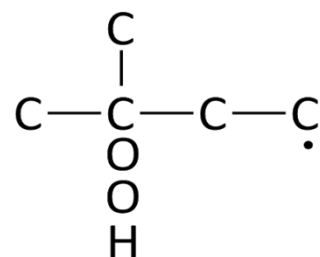


New classes

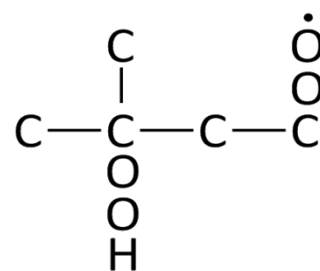
- 28. $\dot{O}_2QOOH = \text{olefin} + H\dot{O}_2$
- 26. $\dot{O}_2QOOH = \dot{P}(OOH)_2$ (an isomerisation)
- 29. $\dot{P}(OOH)_2 = \text{olefin} + H\dot{O}_2$
- 27. $\dot{P}(OOH)_2 = \text{cyclic ether} + H\dot{O}_2$
- 31. $\dot{P}(OOH)_2 = \beta\text{-scission products}$



O_2



O_2



$H\dot{O}_2$)

+ $H\dot{O}_2$)

cyclic ether + $\dot{O}H$)

β -scission products)



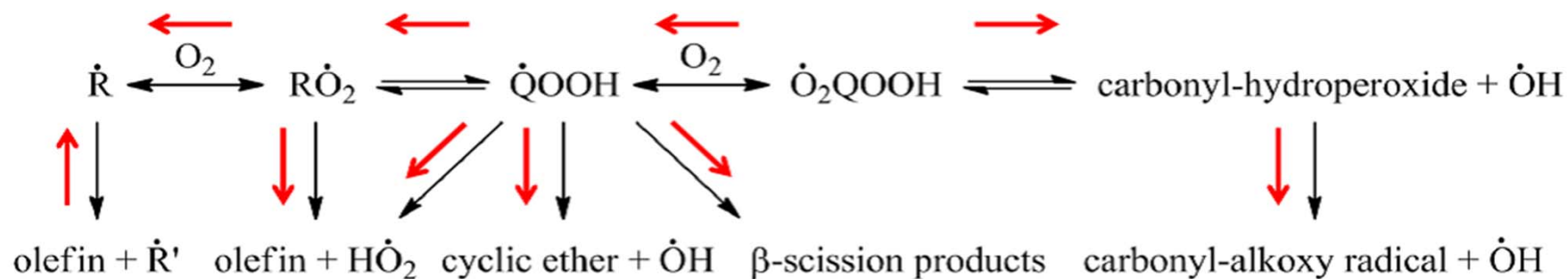
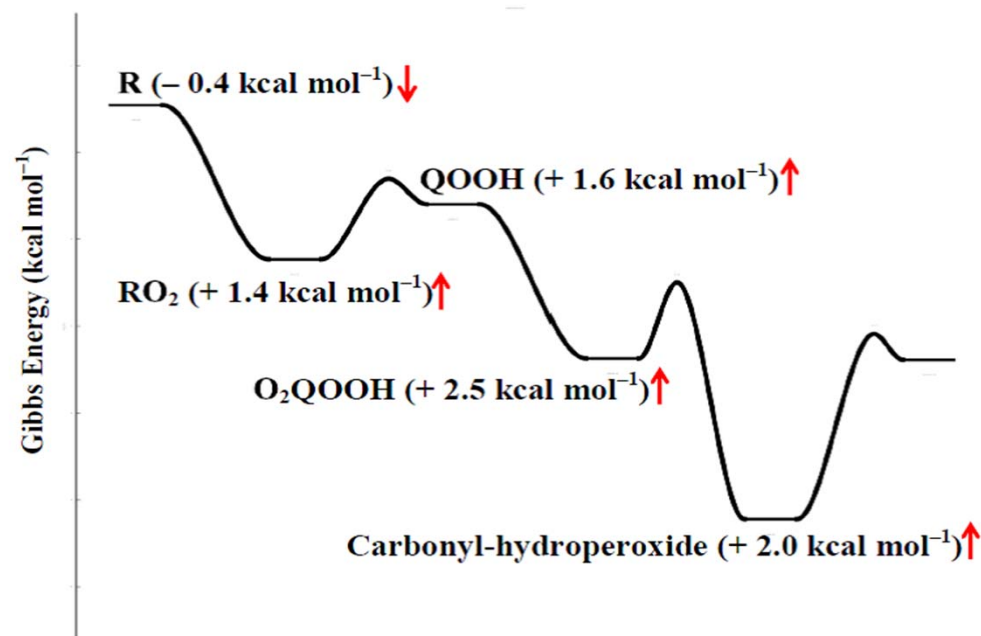
Effect of thermochemistry

- Thermochemistry updated from Burke et al.

S. Burke, J. M. Simmie, H. J. Curran
J. Phys. Chem. Ref. Data **2015**, 44, 013101.

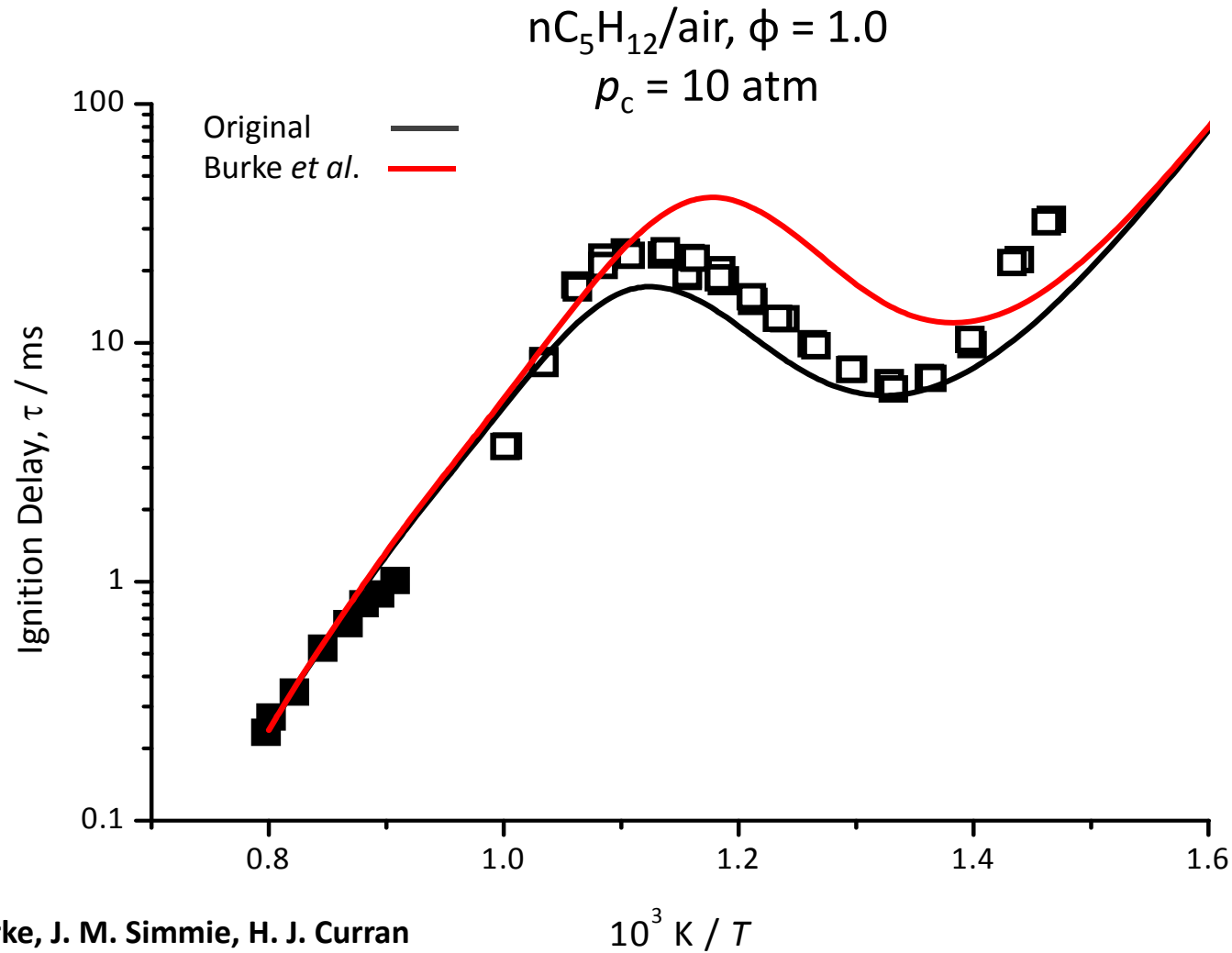


Effect of thermochemistry

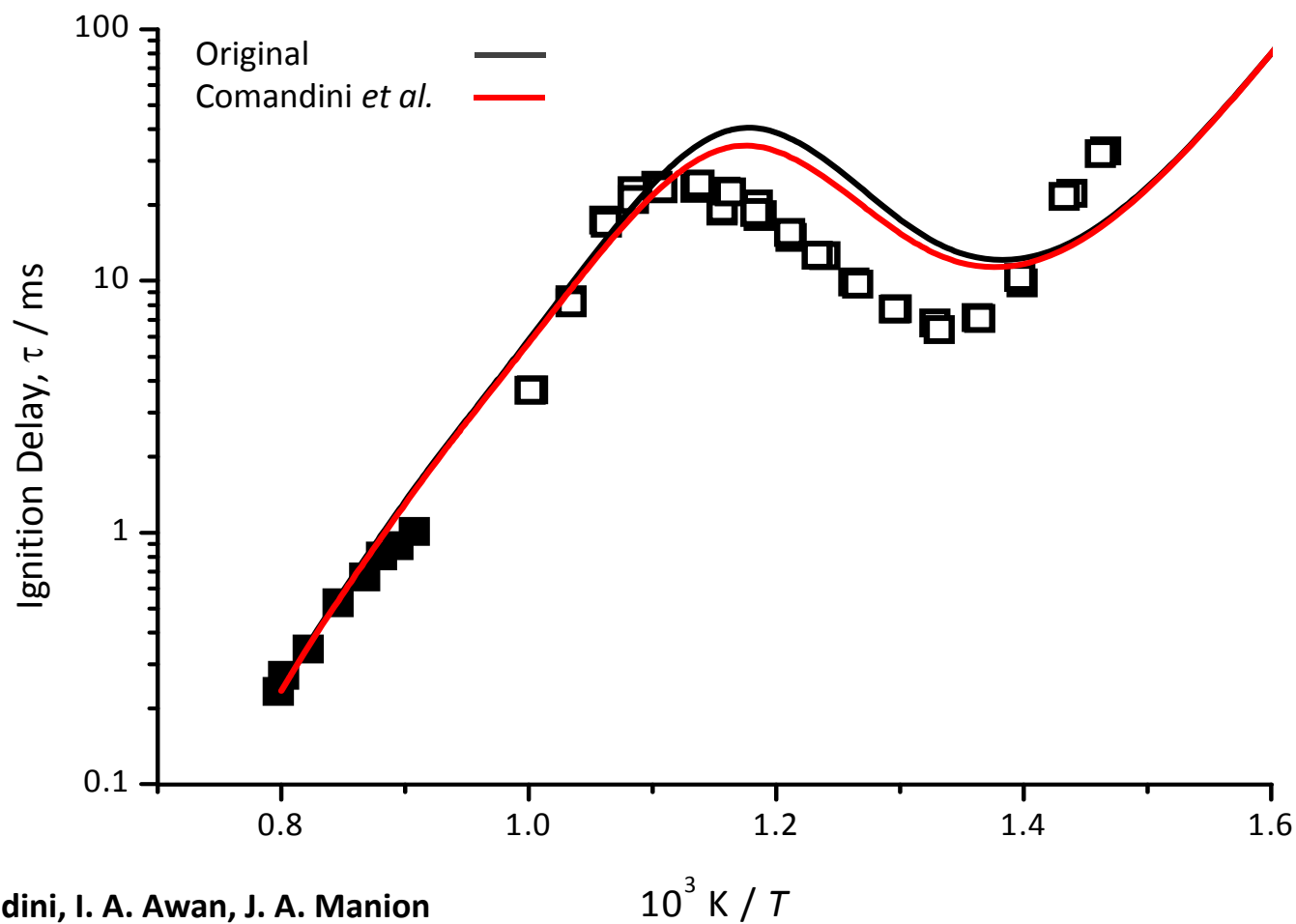




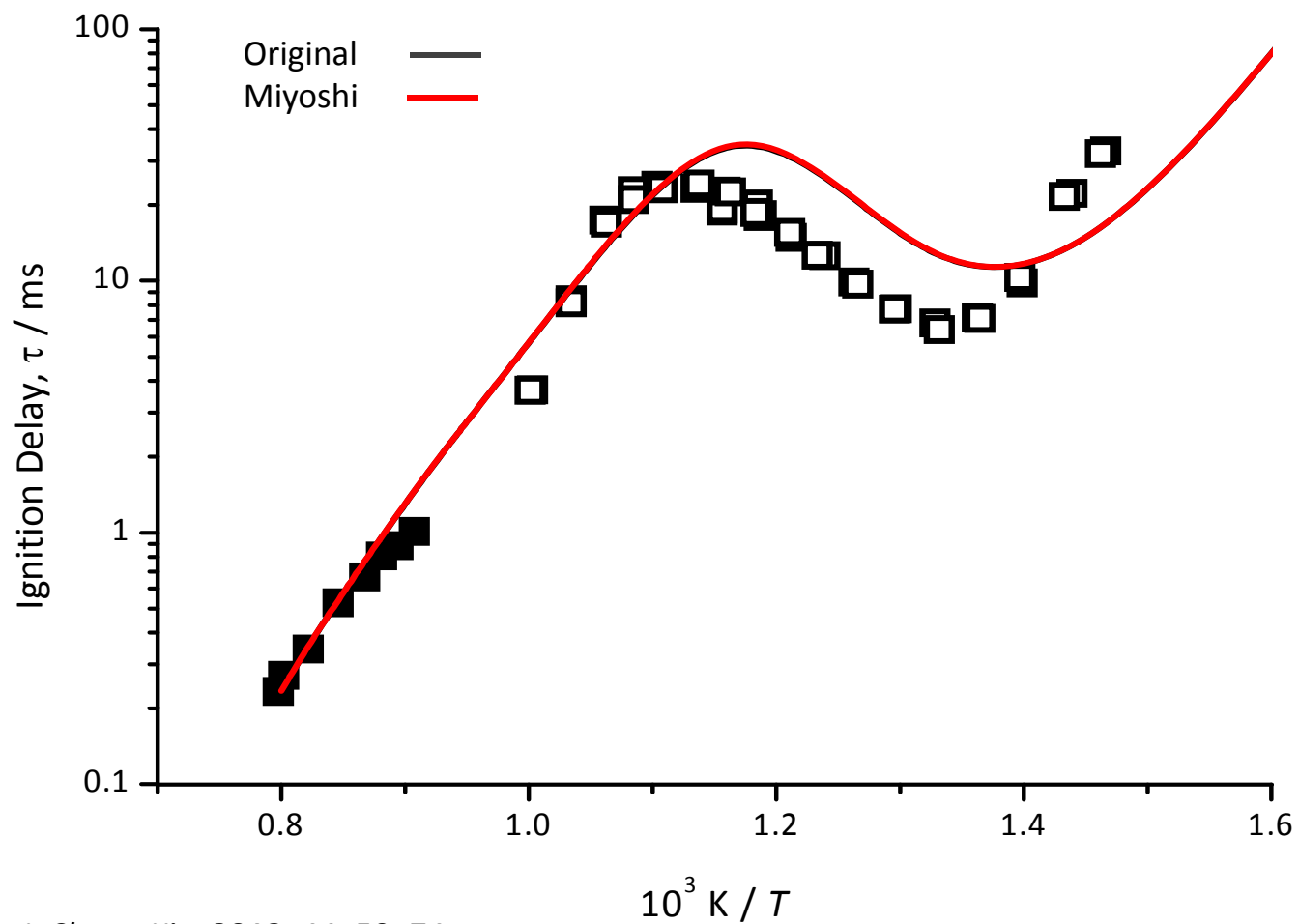
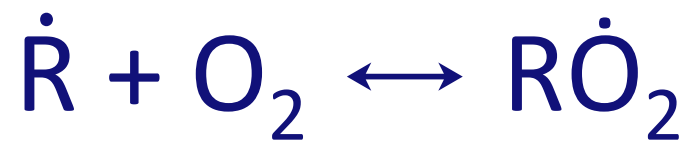
Effect of Thermochemistry



S. Burke, J. M. Simmie, H. J. Curran
J. Phys. Chem. Ref. Data **2015**, 44, 013101.

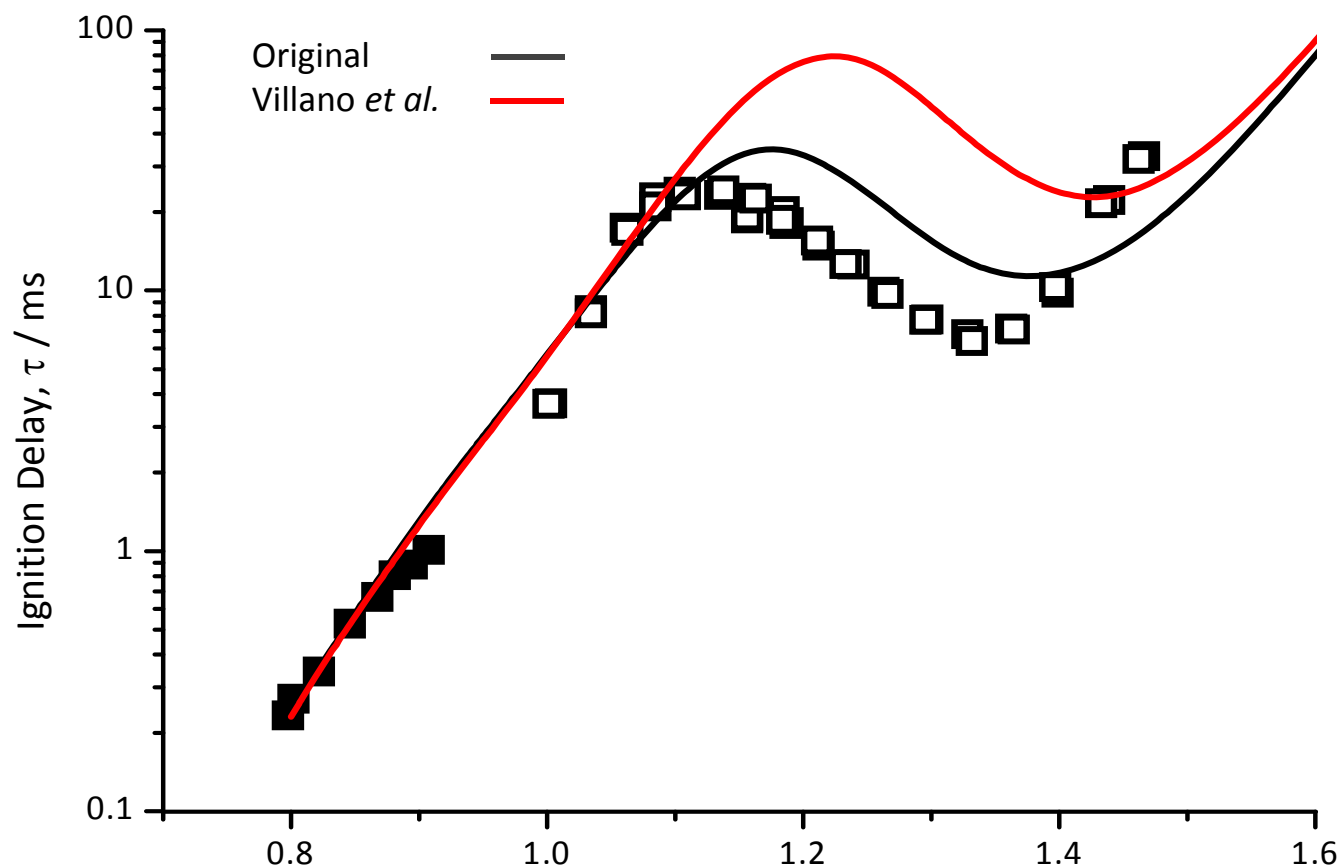


A. Comandini, I. A. Awan, J. A. Manion
Chem. Phys. Lett. **2012**, 552, 20–26

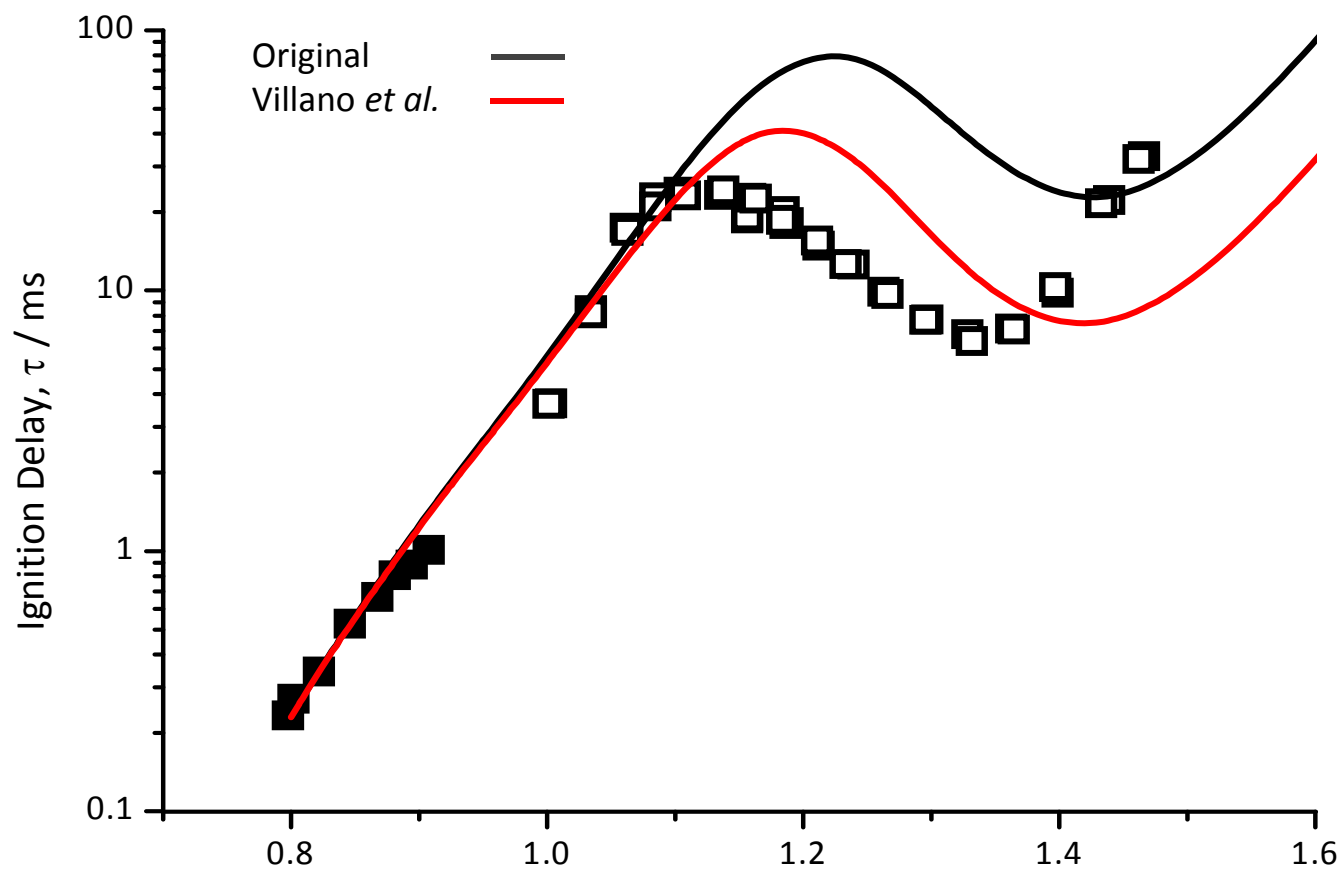
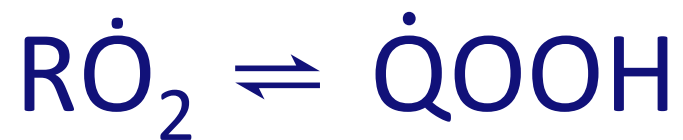


A. Miyoshi *Int. J. Chem. Kin.* **2012**, 44, 59–74



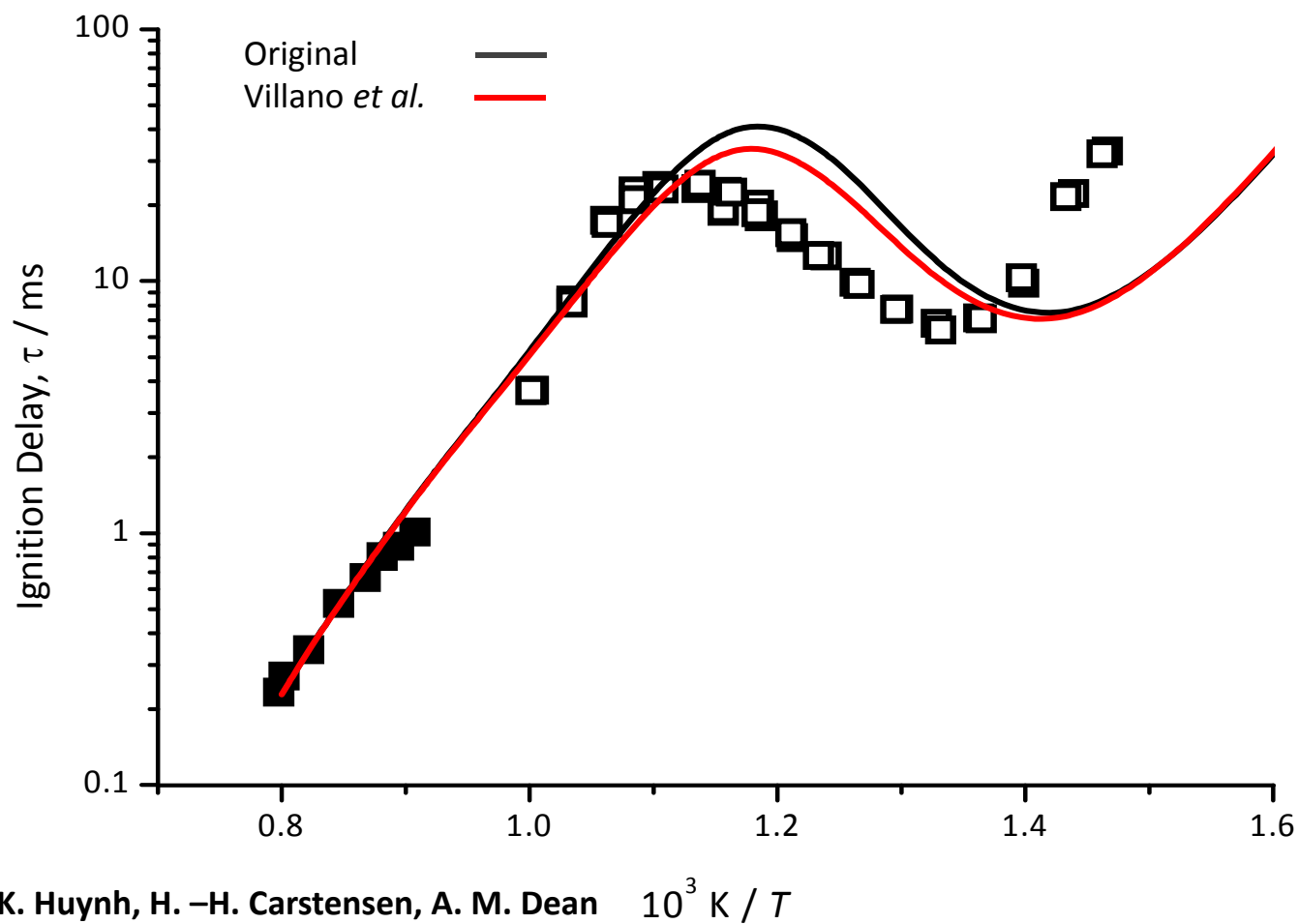


S. M. Villano, L. K. Huynh, H. -H. Carstensen, A. M. Dean $10^3 \text{ K} / T$
J. Phys. Chem. A **2011**, *115*, 13425–13442



S. M. Villano, L. K. Huynh, H. –H. Carstensen, A. M. Dean $10^3 \text{ K} / T$
J. Phys. Chem. A **2011**, *115*, 13425–13442

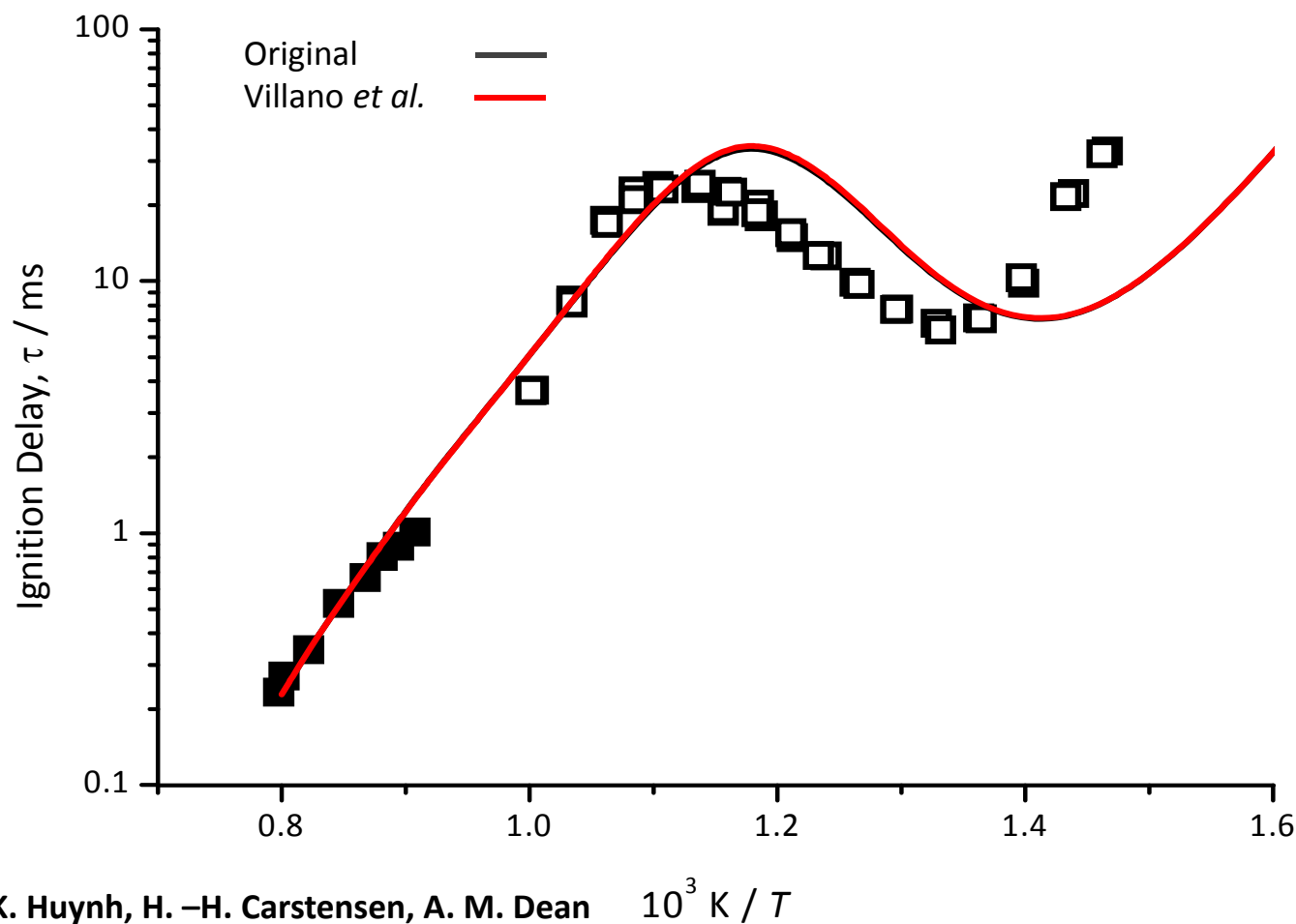




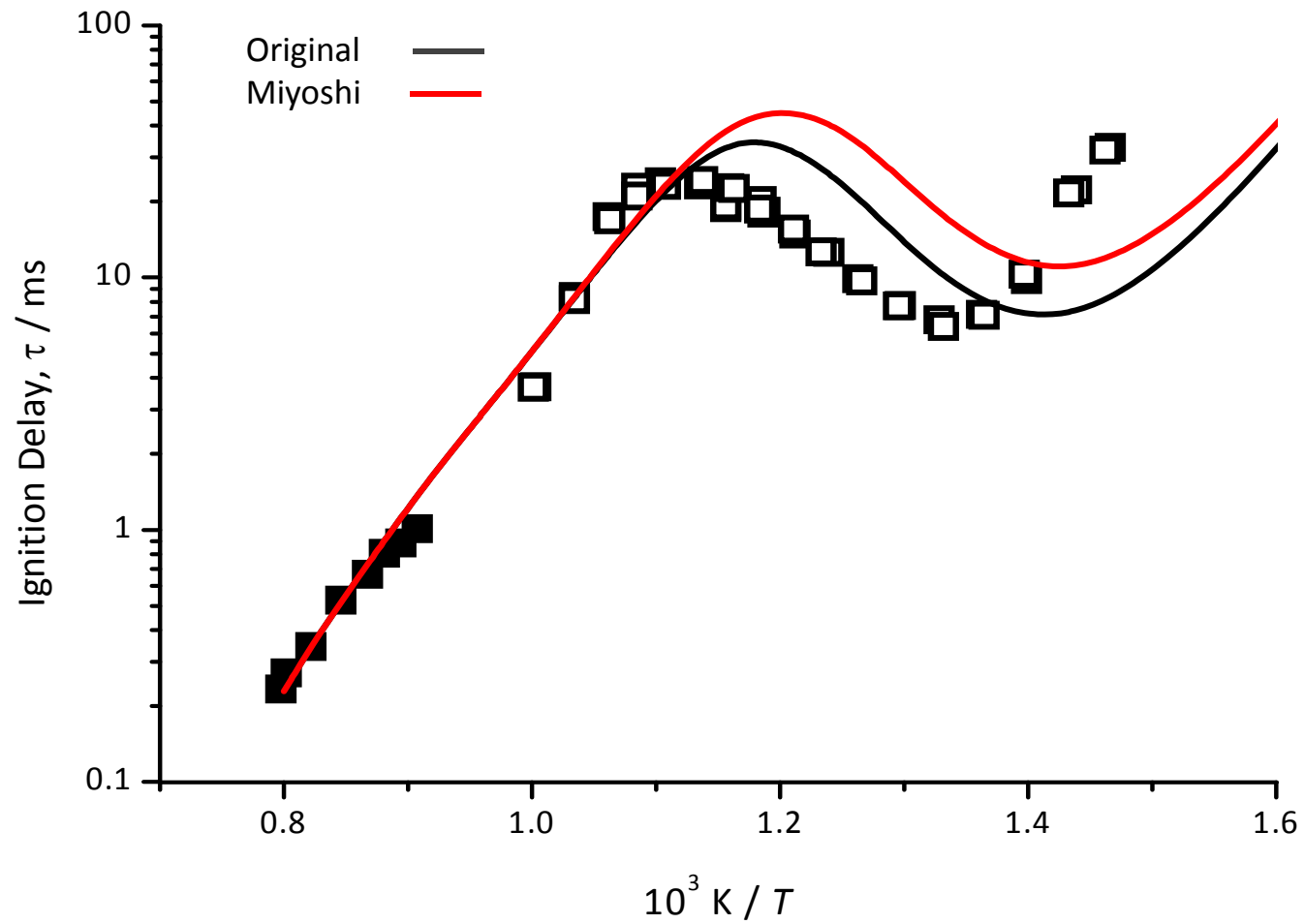
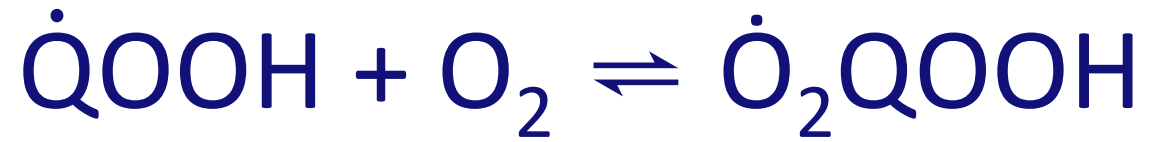
S. M. Villano, L. K. Huynh, H. -H. Carstensen, A. M. Dean $10^3 \text{ K} / T$
J. Phys. Chem. A **2012**, 116, 5068–5089



$\dot{Q}OOH \rightleftharpoons \beta$ -scission products



S. M. Villano, L. K. Huynh, H. –H. Carstensen, A. M. Dean
J. Phys. Chem. A **2012**, 116, 5068–5089

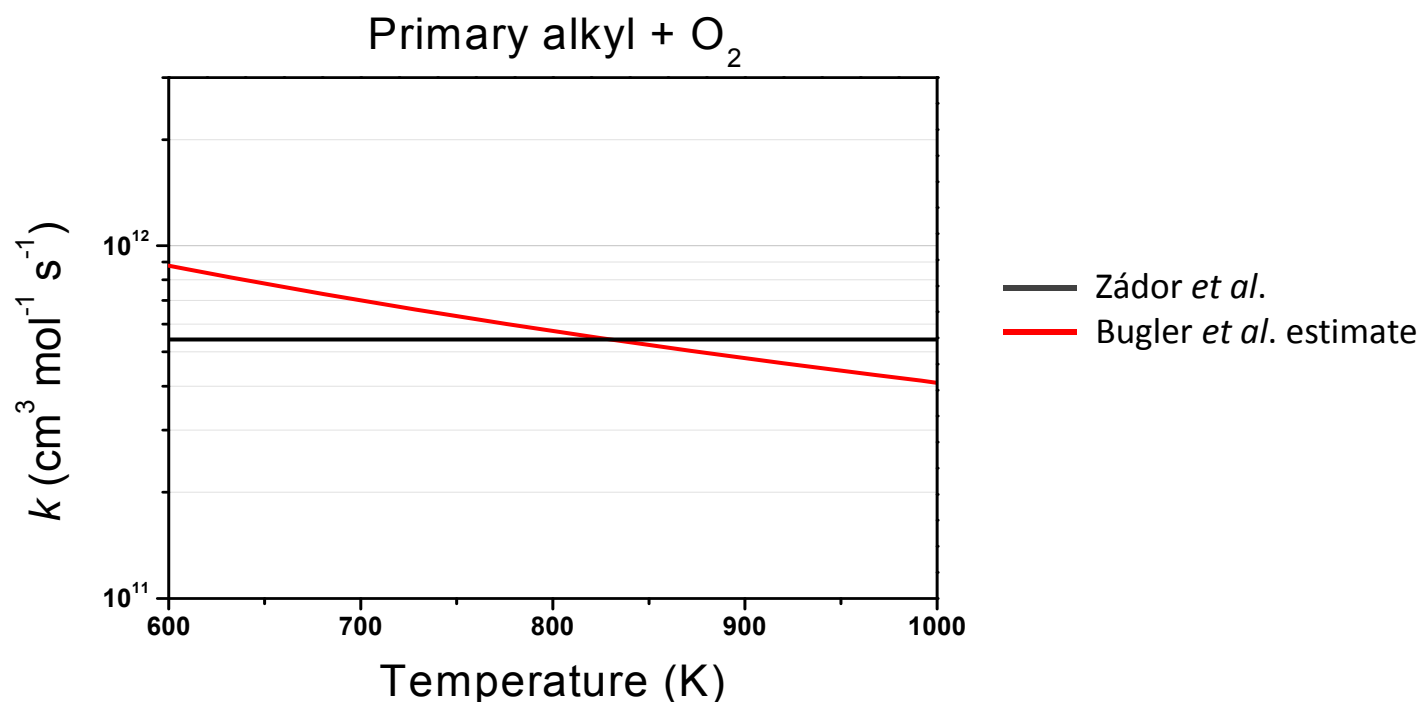


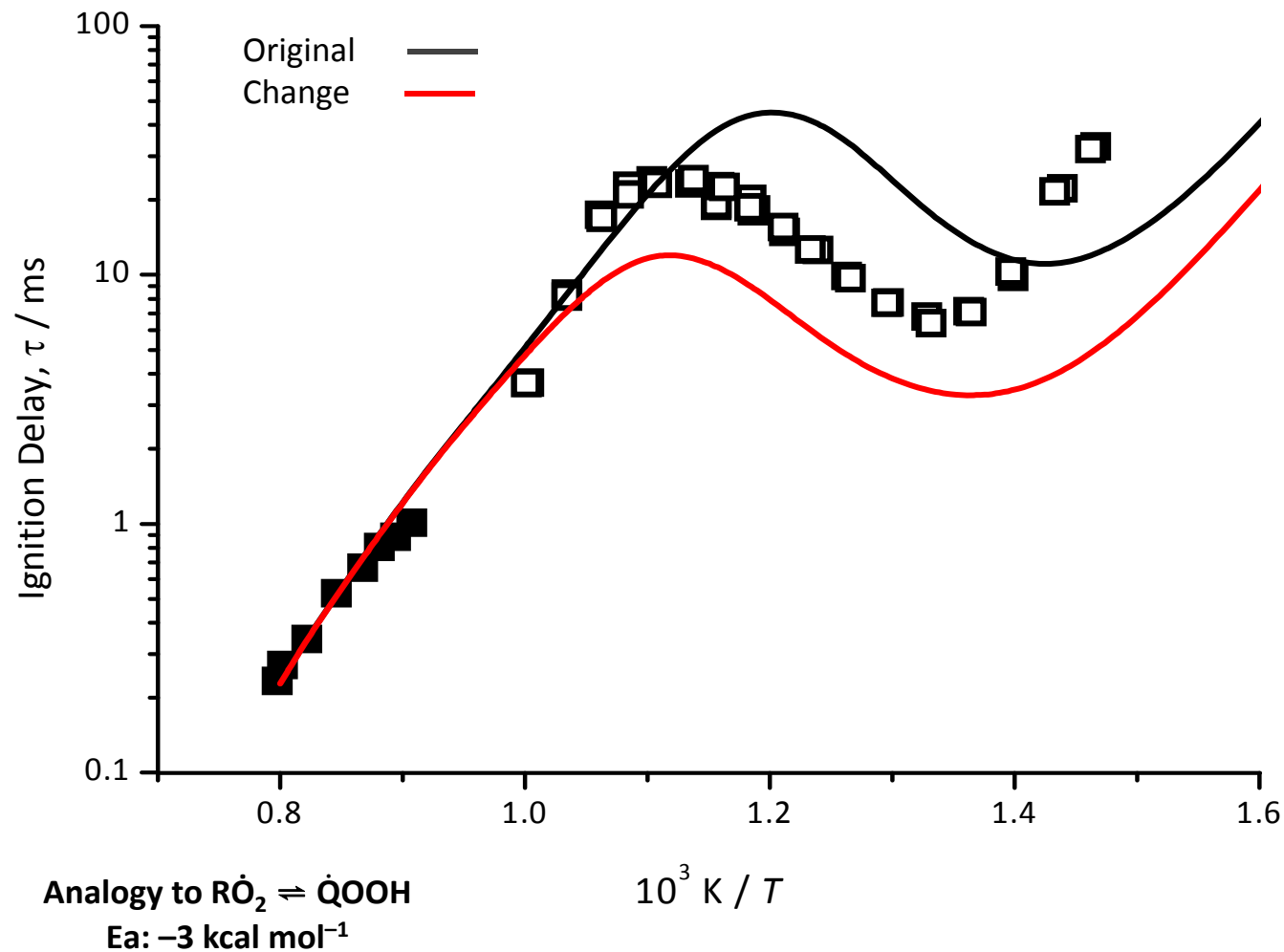
Analogy to $\dot{\text{R}} + \text{O}_2 \rightleftharpoons \text{R}\dot{\text{O}}_2$





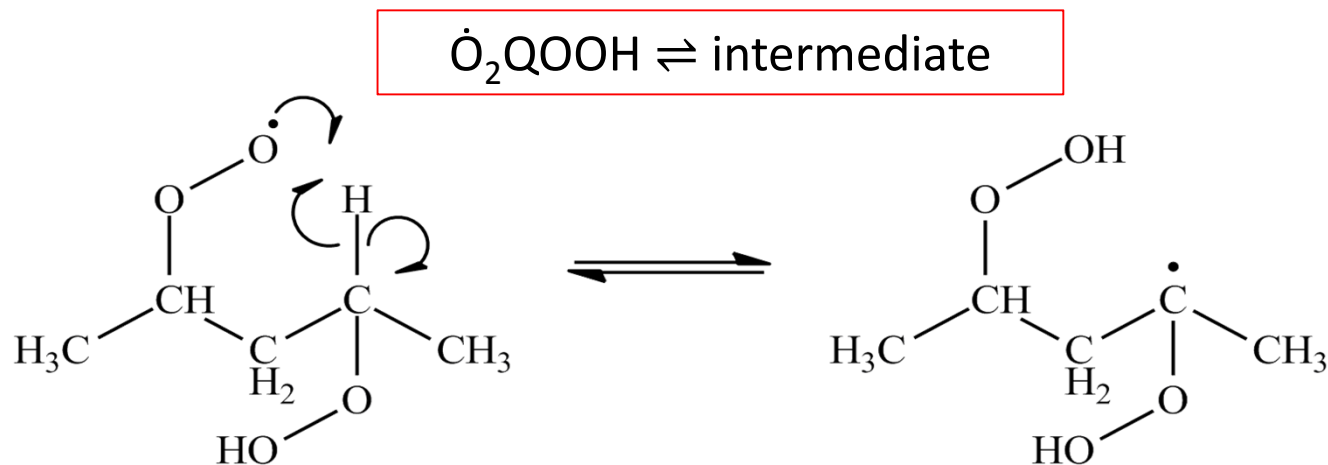
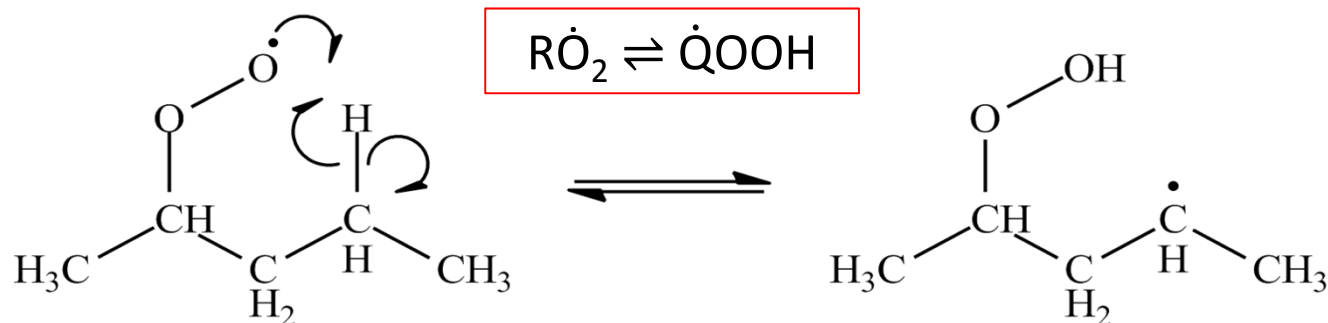
- Rate constants estimated by analogy to $\dot{\text{R}} + \text{O}_2$
- Reduced by approximately factor of 2
- Good agreement with recent experimental and theoretical determinations from Sandia National Laboratories¹



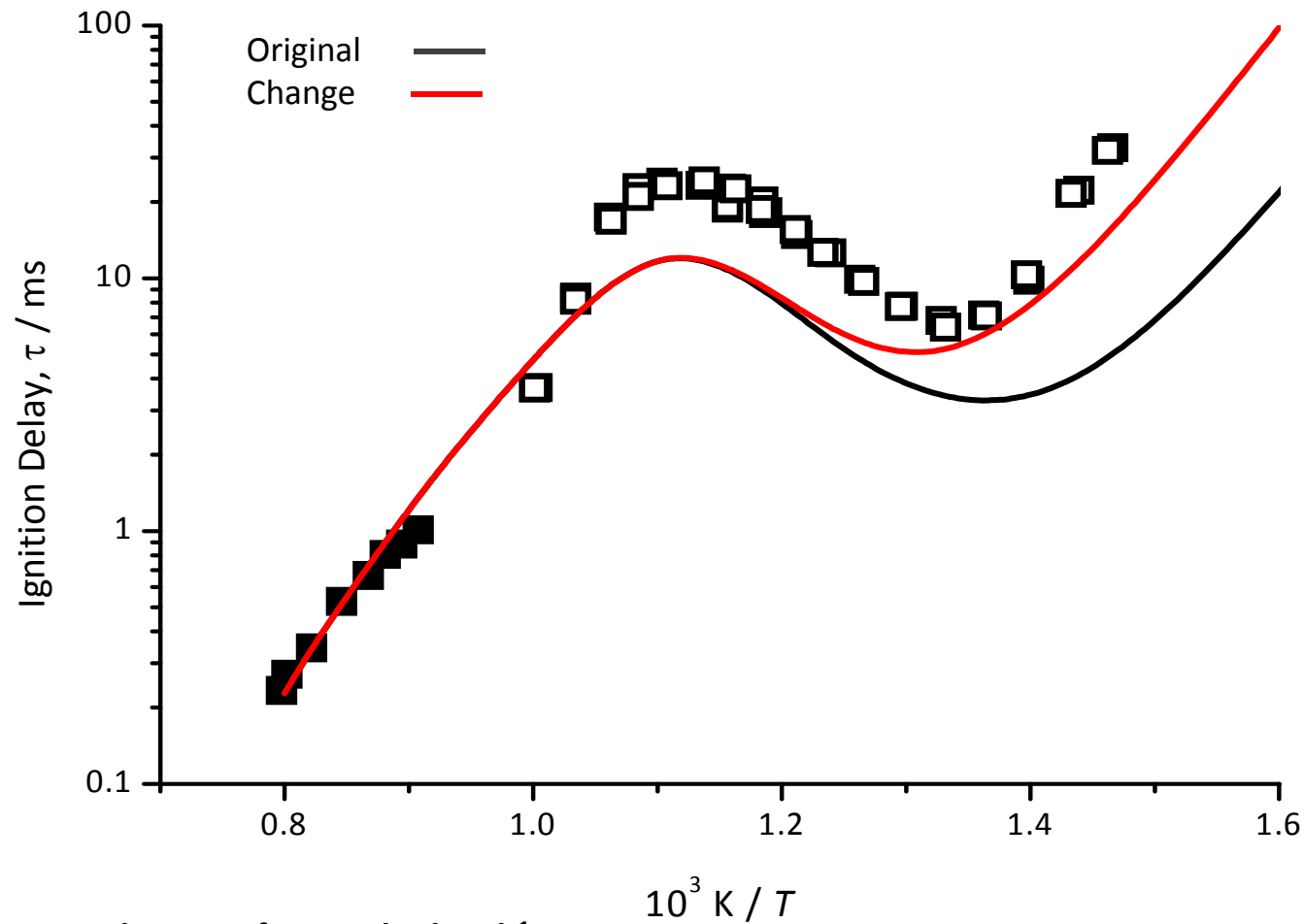




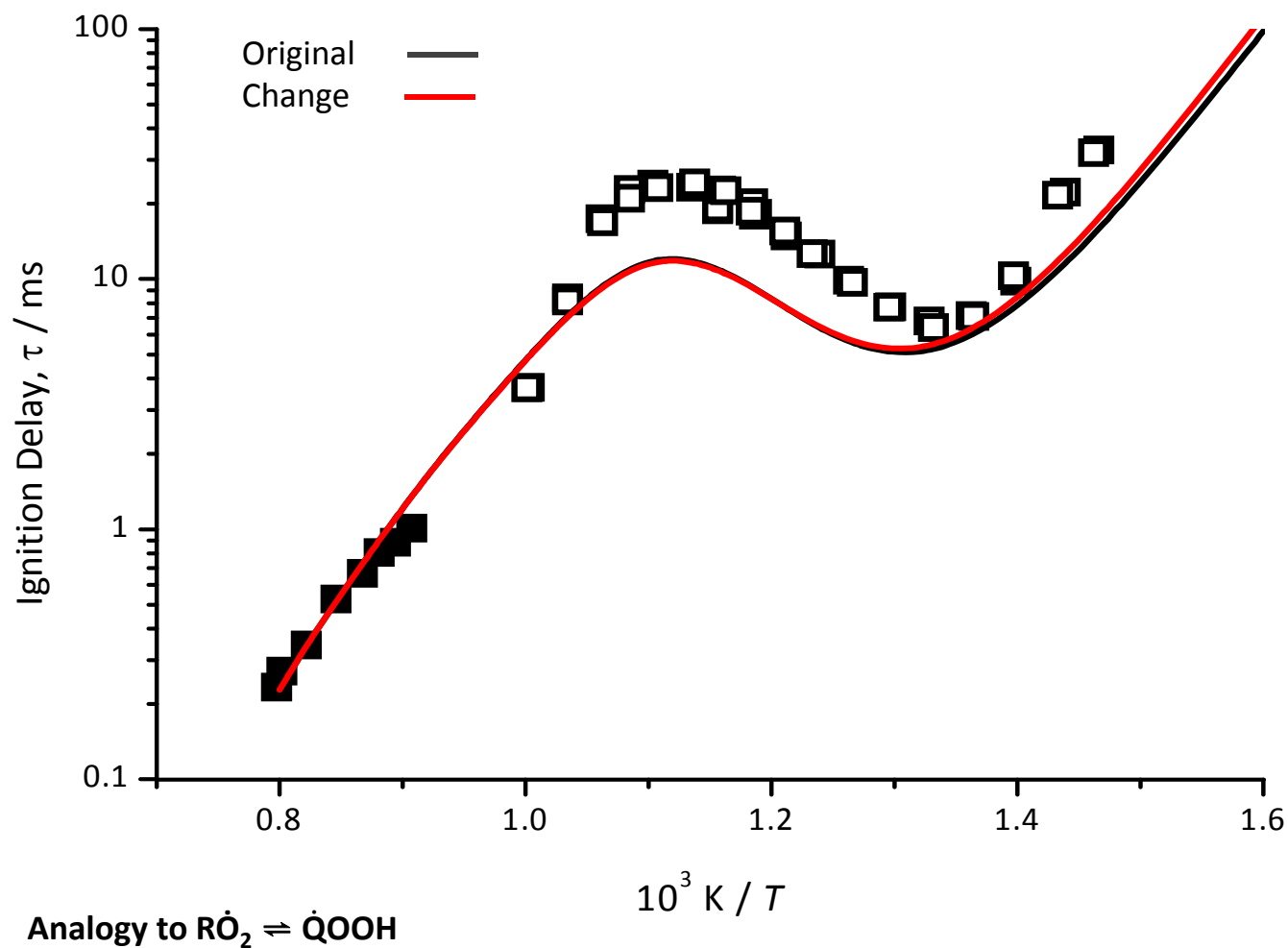
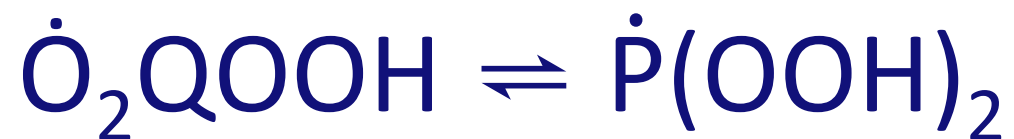
1st and 2nd Isomerisations

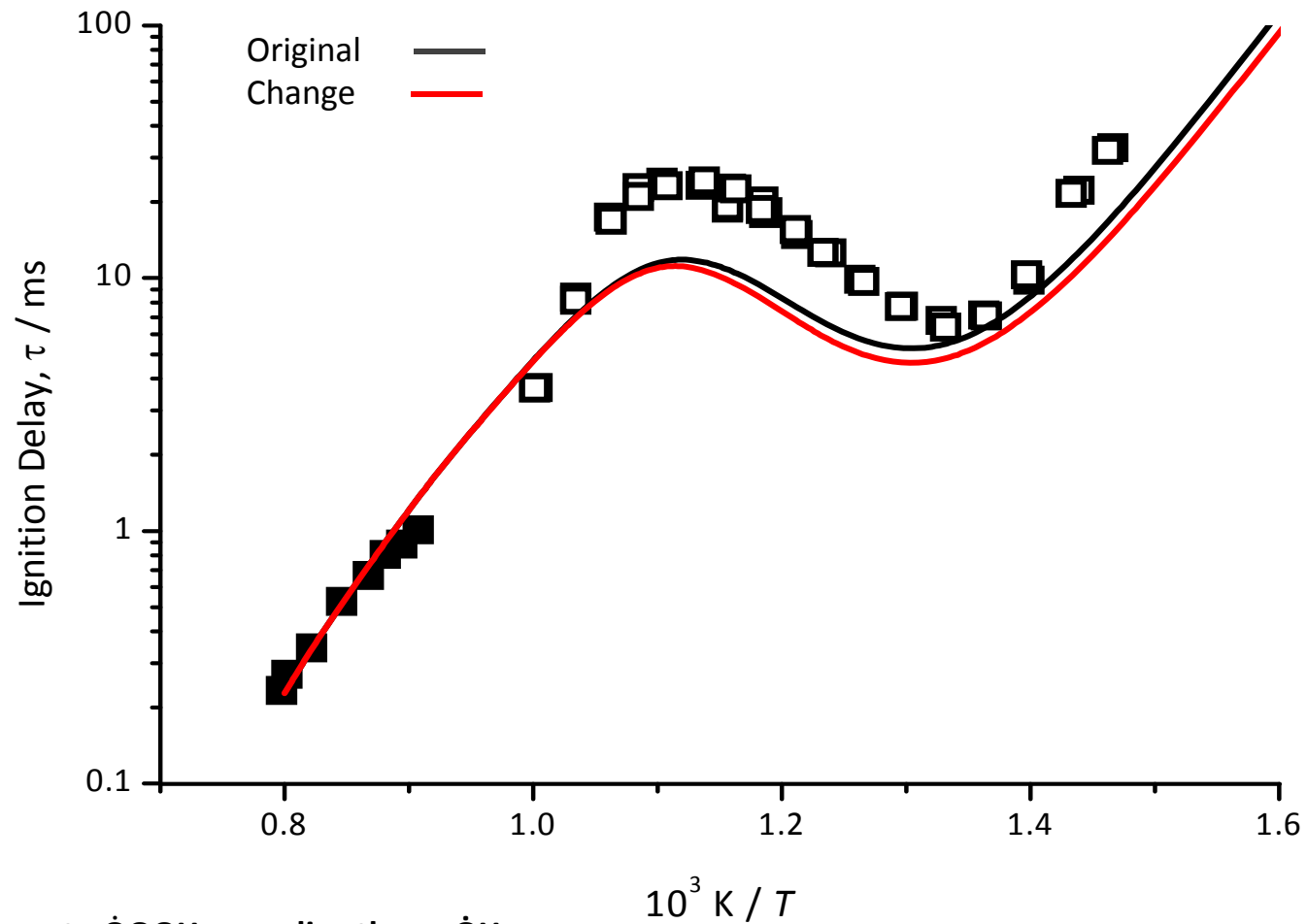


Activation energy:
 -3 kcal mol^{-1} relative to $\text{R}\dot{\text{O}}_2 \rightleftharpoons \dot{\text{Q}}\text{OOH}$

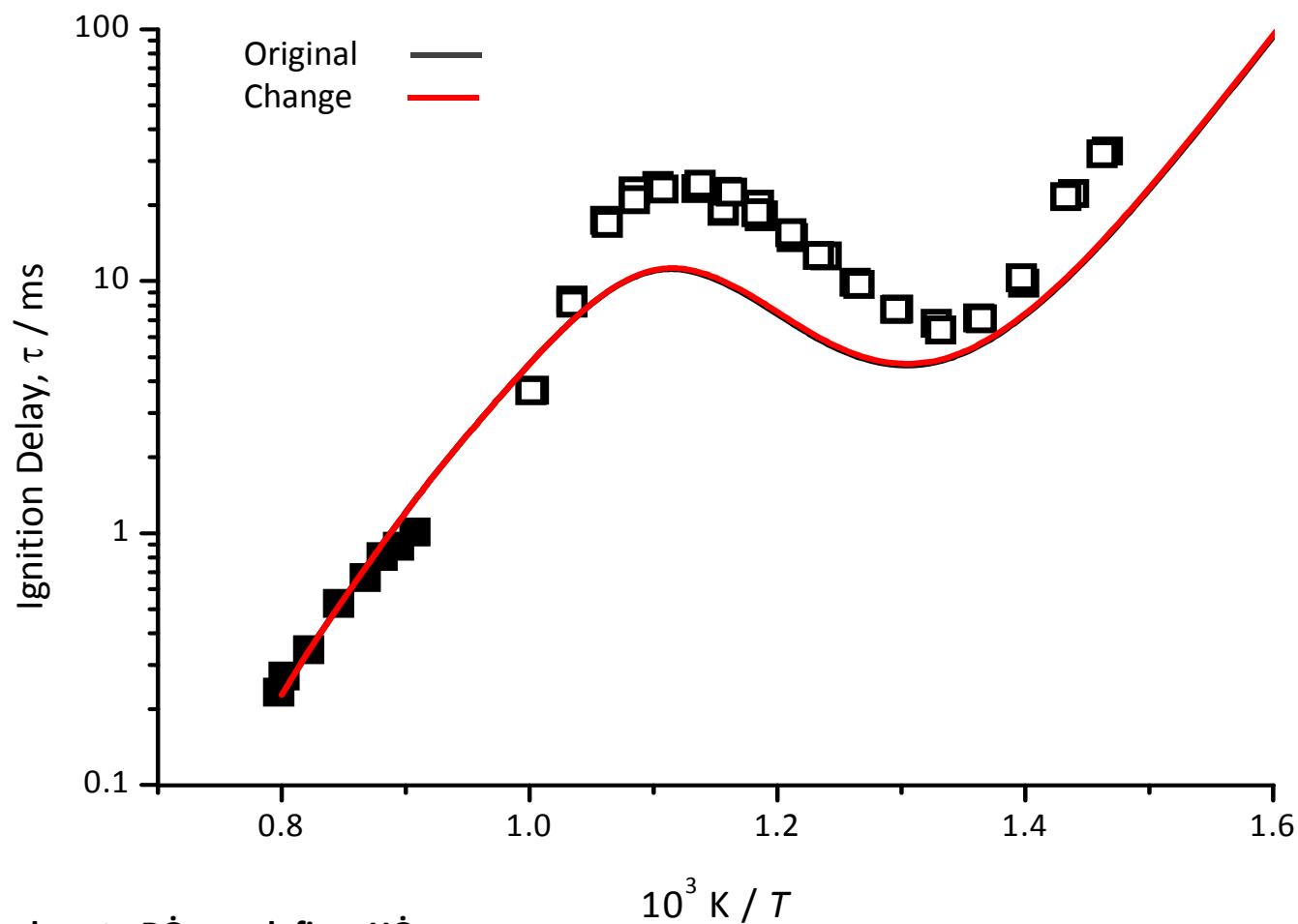
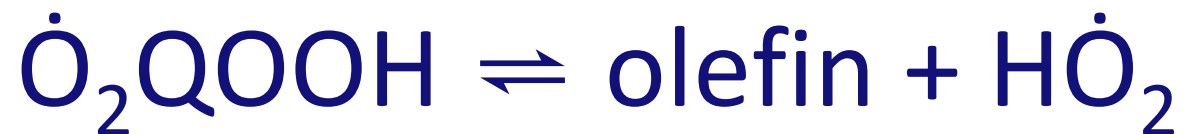


Ea: increased to ~ 43 from 39 kcal mol^{-1}





Analogy to $\dot{\text{Q}}\text{OOH} \rightleftharpoons \text{cyclic ether} + \dot{\text{O}}\text{H}$



Analogy to $\text{R}\dot{\text{O}}_2 \rightleftharpoons \text{olefin} + \text{H}\dot{\text{O}}_2$

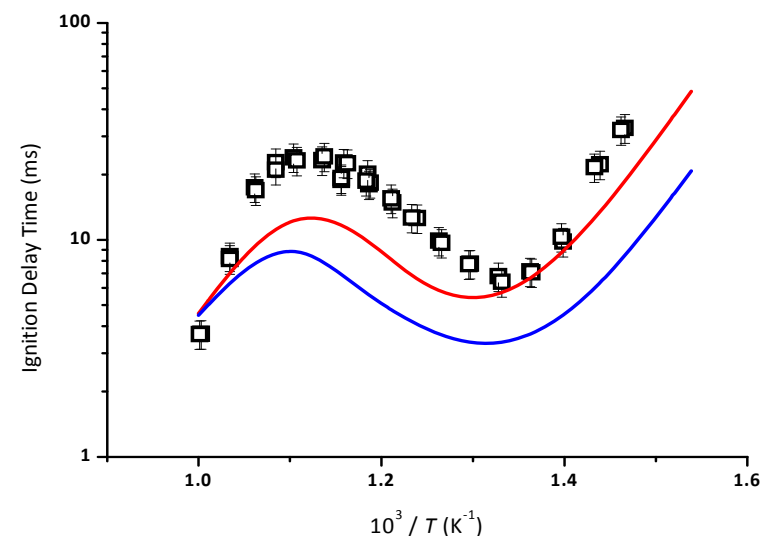
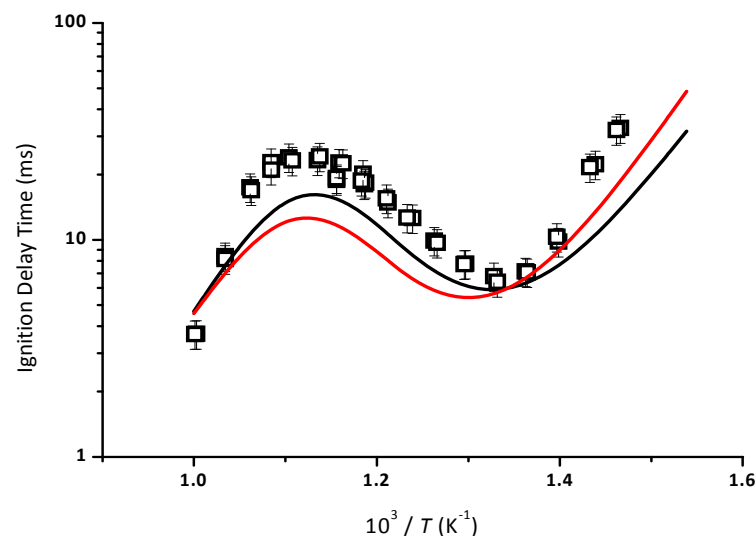




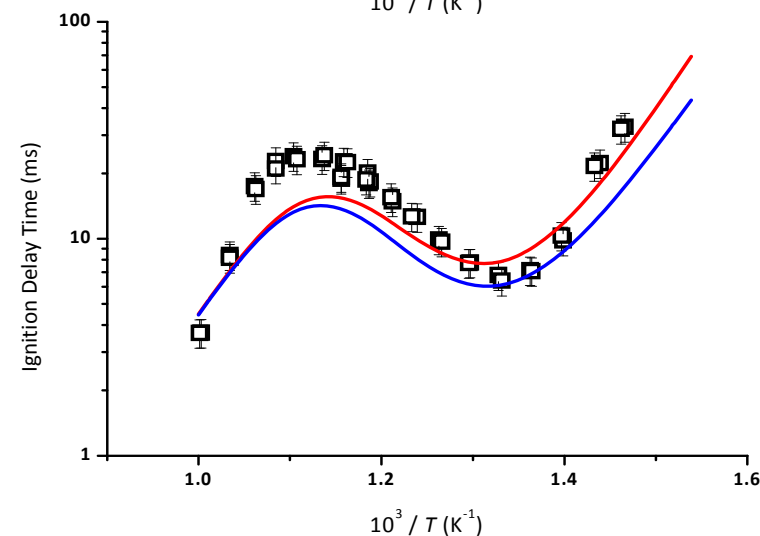
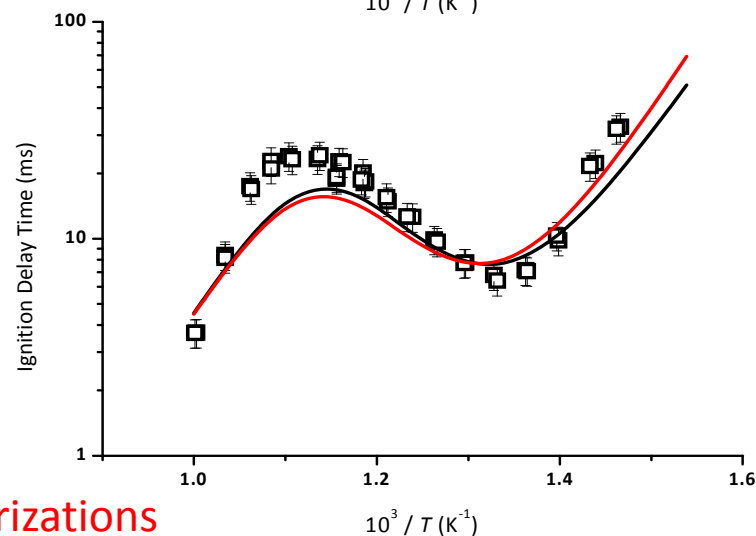
Effect of Alternative Pathways

nc5_49

Healy *et al.*
JPCA 2010 24:1521



Current mechanism

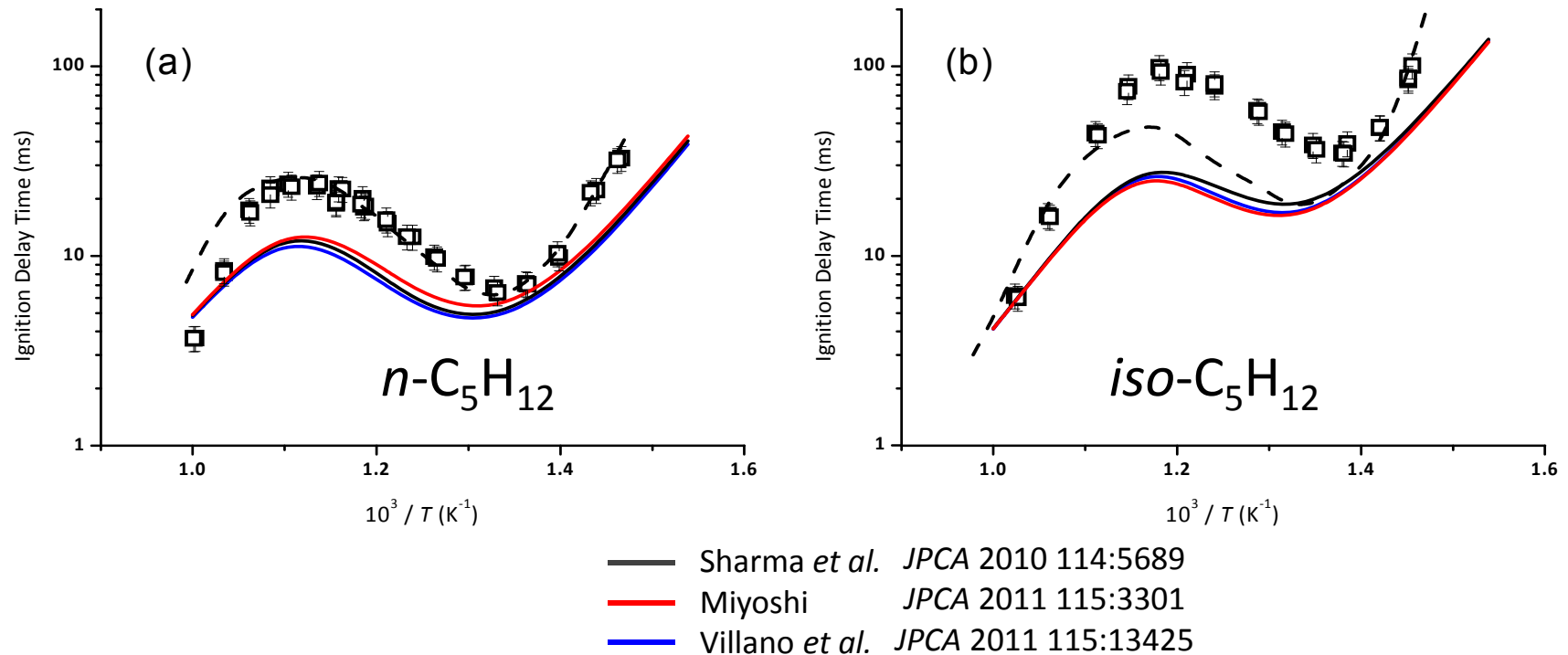


— alternative isomerizations

— $\text{P}(\text{OOH})_2 \rightarrow \text{cyclic ether} + \dot{\text{O}}\text{H}$



Fuel/'air', $\phi = 1.0$, 10 atm

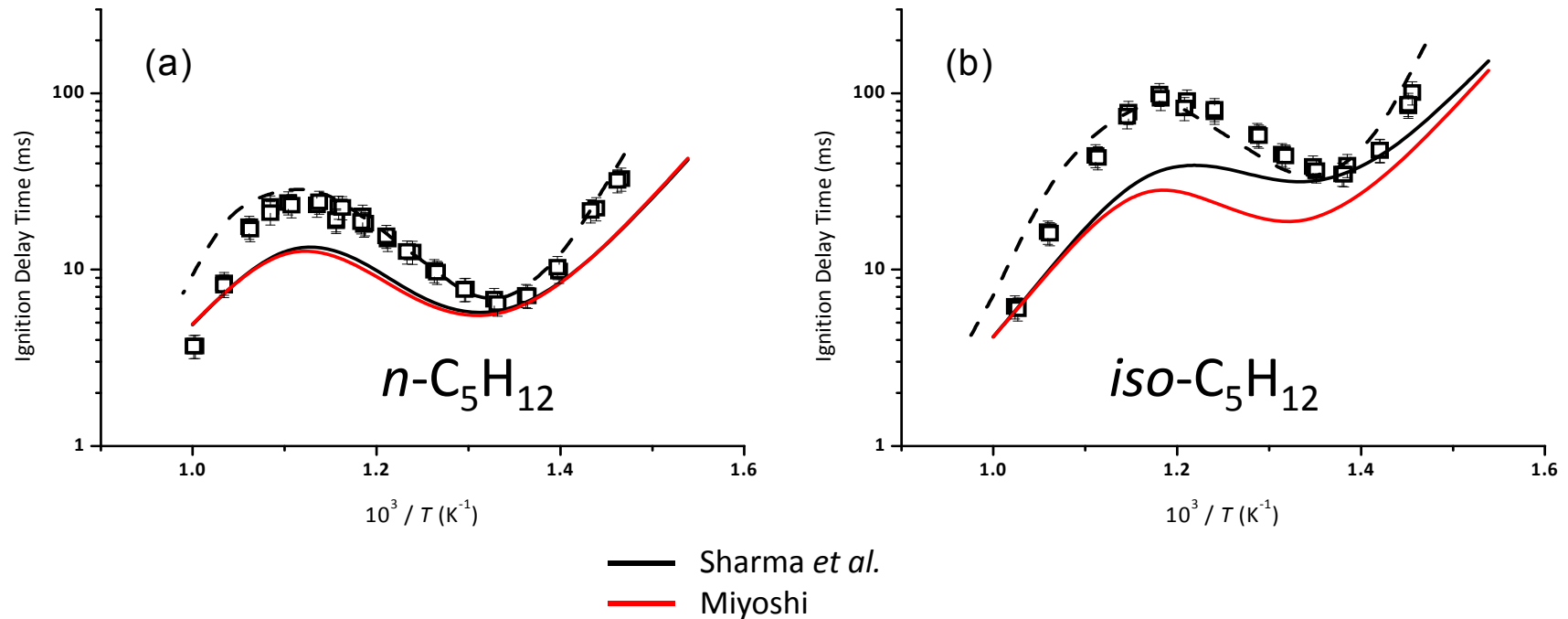


$\text{R}\dot{\text{O}}_2 = \dot{\text{Q}}\text{OOH}$: TST calculations

$\dot{\text{O}}_2\text{QOOH} = \text{Carbonyl-hydroperoxide} + \dot{\text{O}}\text{H}$: analogy to $\text{R}\dot{\text{O}}_2 = \dot{\text{Q}}\text{OOH}$ (E_a : -3 kcal mol^{-1})



Fuel/'air', $\phi = 1.0$, 10 atm



$\text{R}\dot{\text{O}}_2 = \dot{\text{Q}}\text{OOH}$: TST calculations

$\dot{\text{O}}_2\text{QOOH} = \text{Carbonyl-hydroperoxide} + \dot{\text{O}}\text{H}$: TST calculations

Sharma *et al.* *JPCA* 2010 114:5689

Miyoshi *JPCA* 2011 115:3301

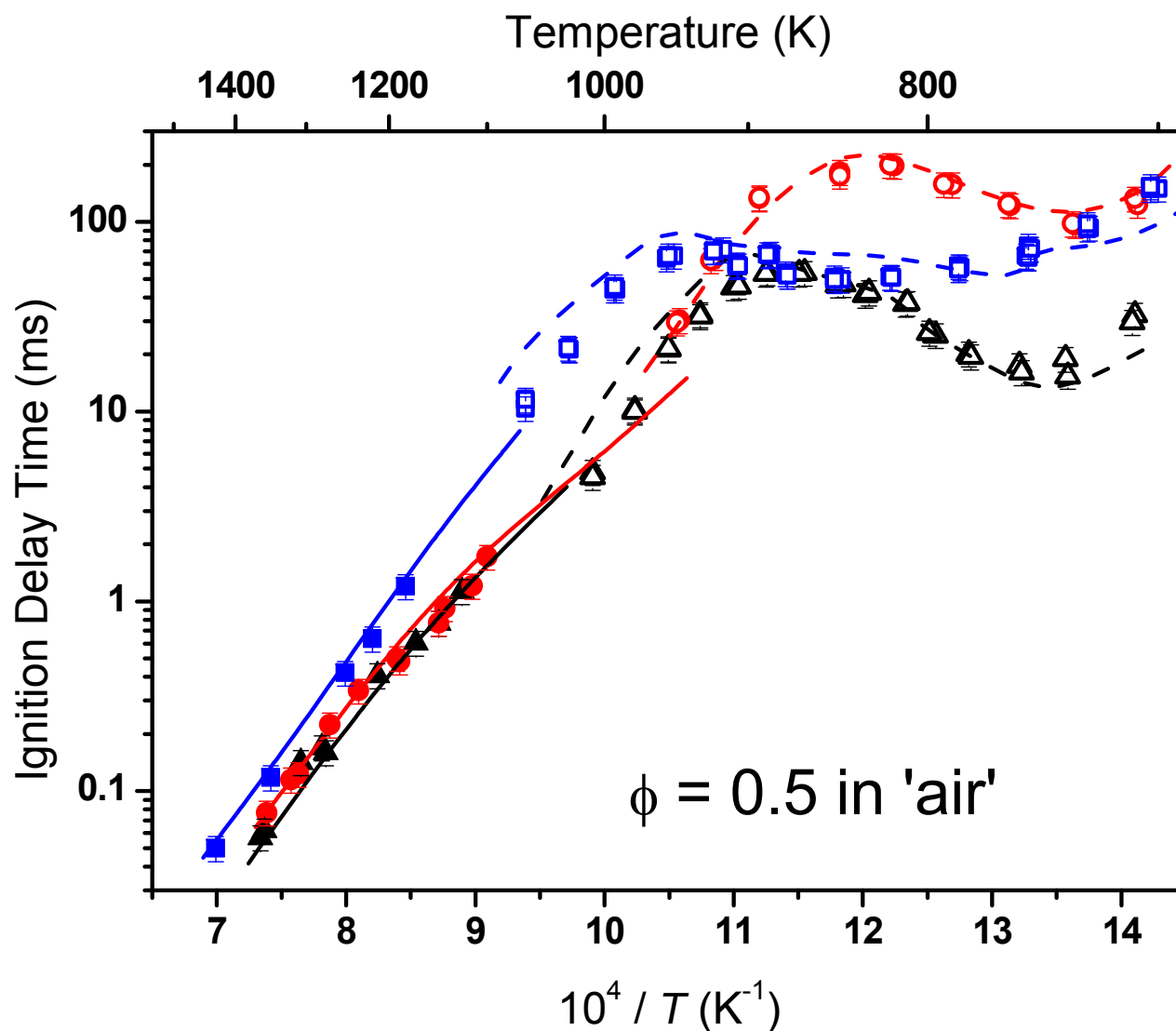


1st and 2nd Isomerisations

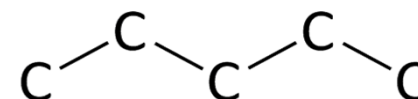
- Curran *et al.* recommends $E_a -3 \text{ kcal mol}^{-1}$ independent of ring size
- Sharma *et al.* calculations:
 - 5-membered TS rings: $\sim -3.3 \text{ kcal mol}^{-1}$ $\uparrow k$
 - 6-membered TS rings: $\sim -1.7 \text{ kcal mol}^{-1}$ $\downarrow k$
 - 7-membered TS rings: $\sim -0.4 \text{ kcal mol}^{-1}$ $\downarrow k$
- Isomerisations through 6-membered transition state rings still dominate



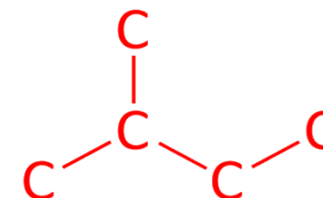
Model vs Experiments



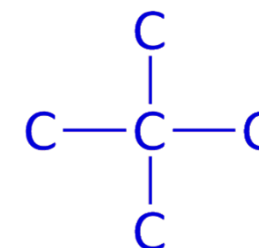
***n*-Pentane**



***iso*-Pentane**



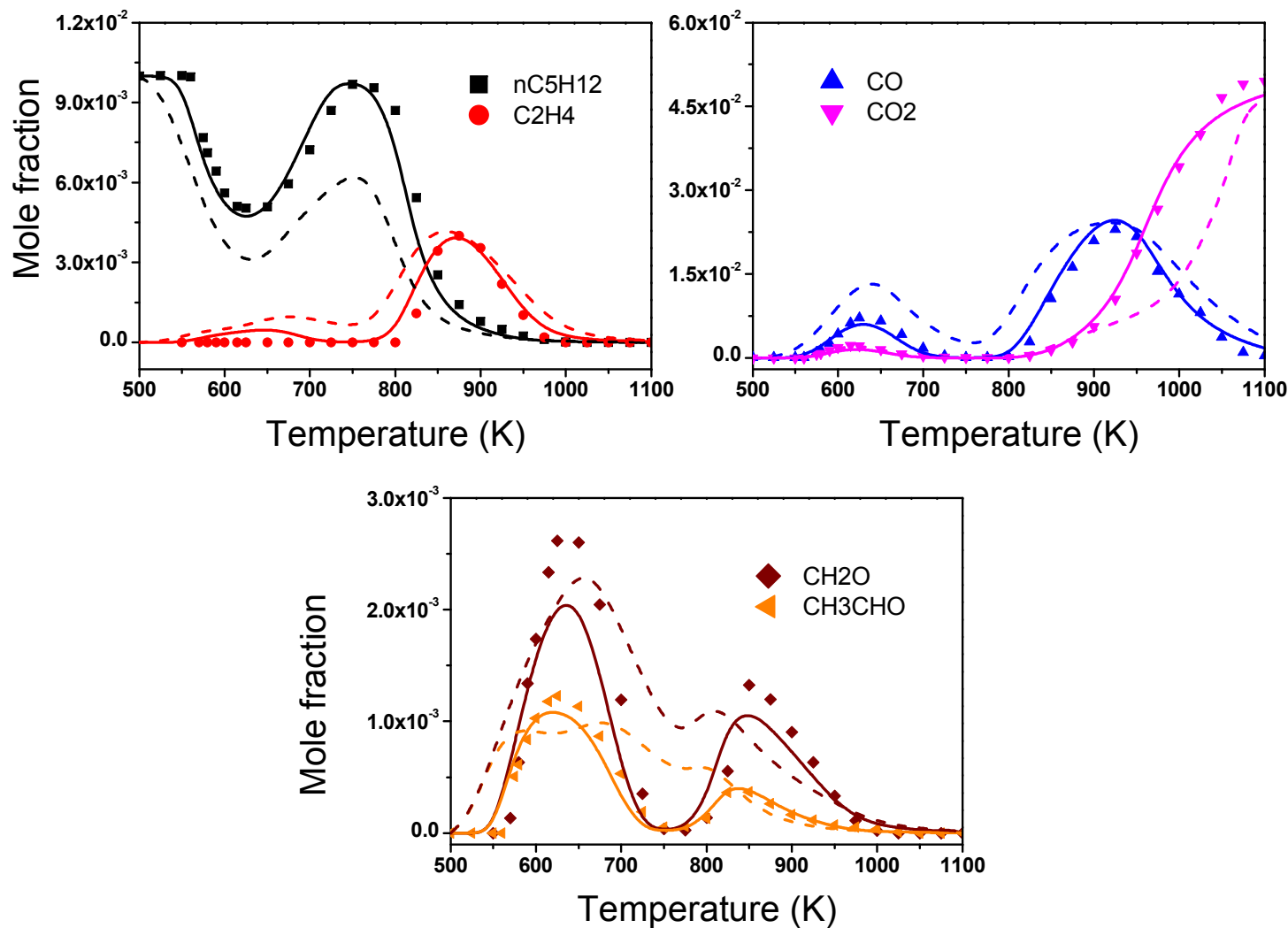
***neo*-Pentane**





Speciation data

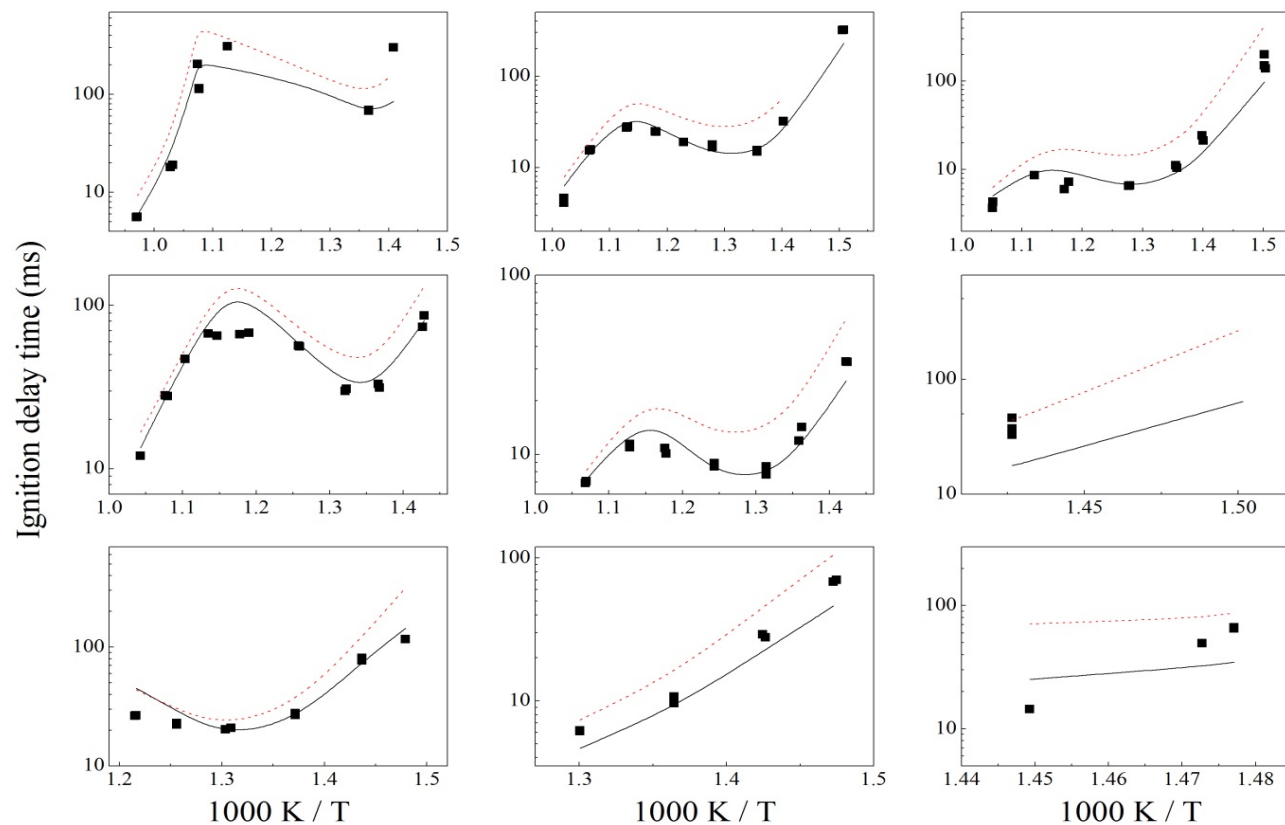
Jet-stirred reactor data: 1% $n\text{-C}_5\text{H}_{12}$, 16% O_2 , 83% N_2 , $p = 1$ atm





Improvement in C₄ chemistry

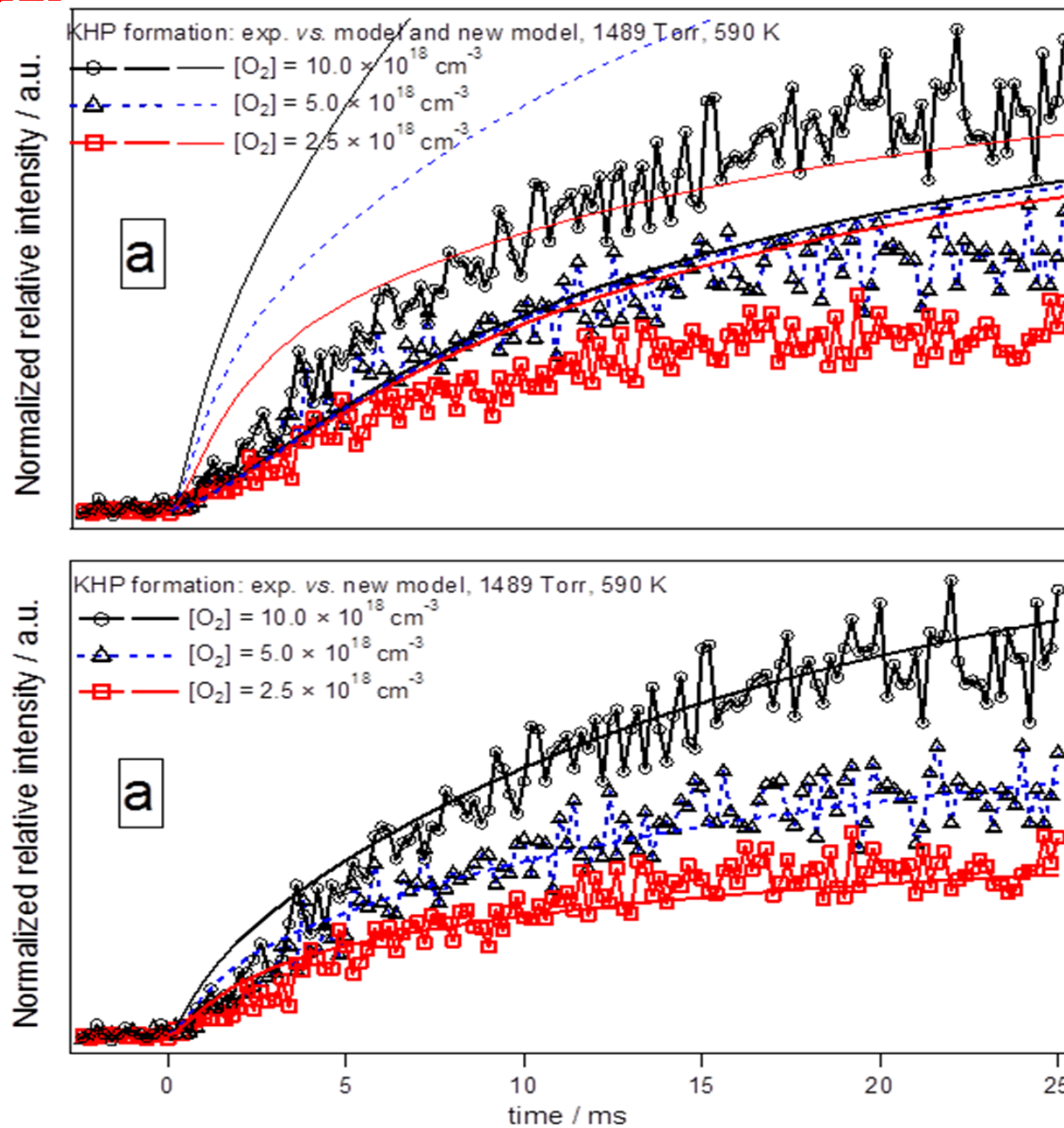
- n-butane ignition delay time in RCM under $\phi = 0.5, 1.0$ and 2.0 (rows); $p = 10, 20$ and 30 atm (columns)



Experimental data:
D. Healy, et al., Combustion and
Flame, (2010) 157(8) 1526–1539

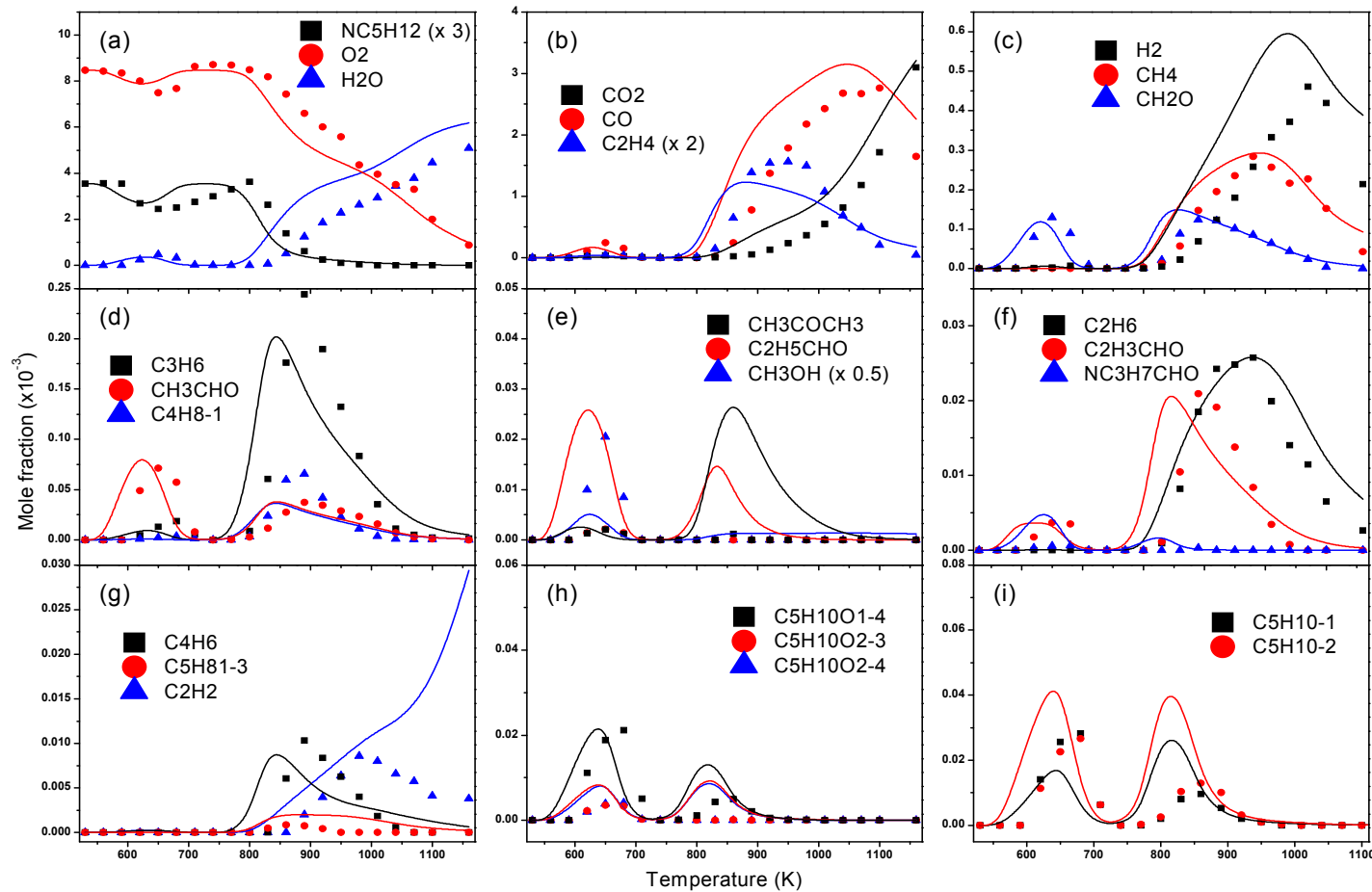
Black solid line: current mechanism
Red dashed line: Aramco 1.3 mech

Validation: iso-Butane



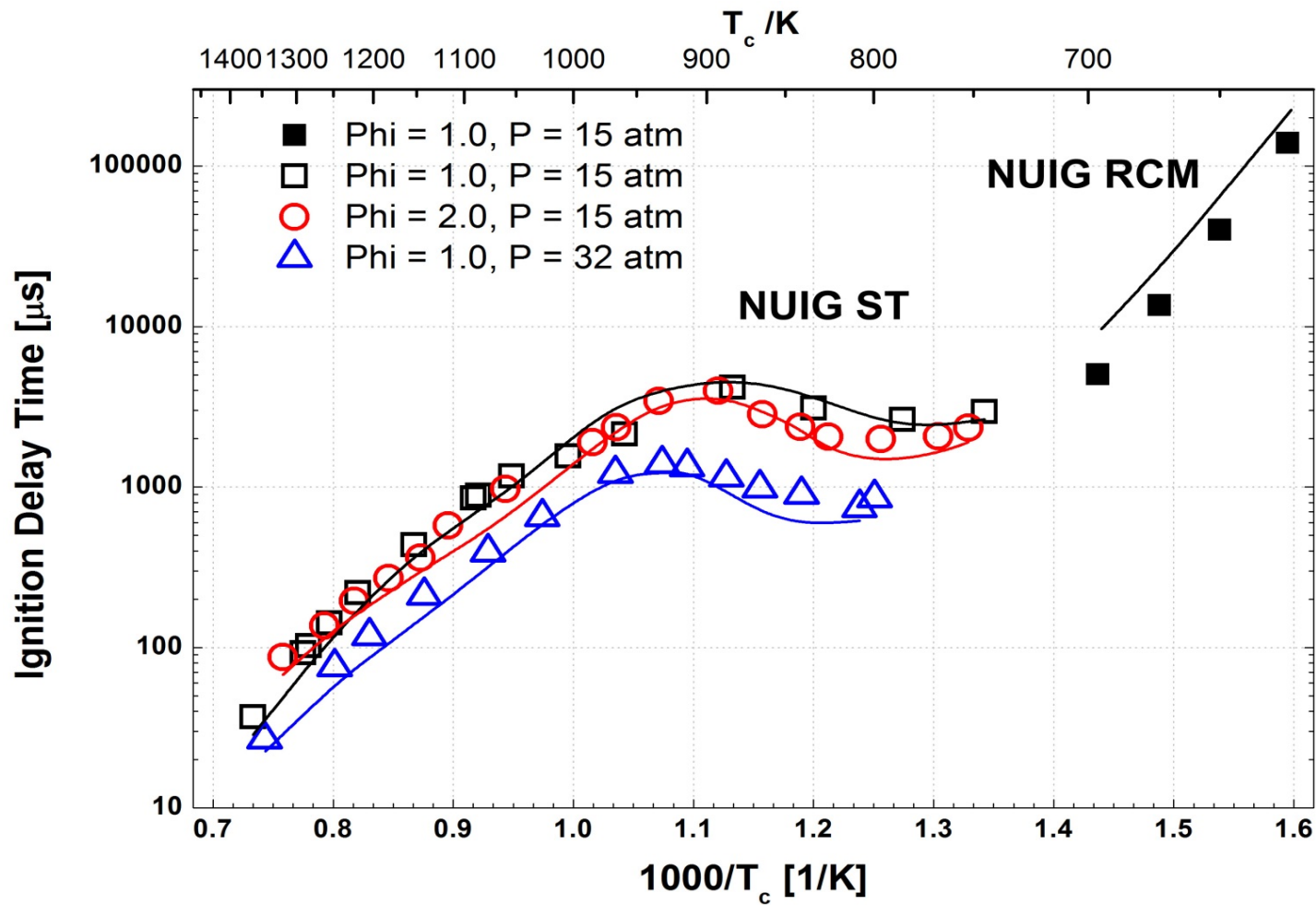
Arkke J. Eskola, Oliver Welz, John D. Savee,
David L. Osborn, Craig A. Taatjes
Synchrotron photoionization measurements
of fundamental autoignition reactions:
Product formation in low-temperature
isobutane oxidation
Proc. Combust. Inst., (2013) 34, 385–392

Validation: n-Pentane

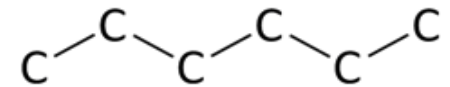


JSR experiment from Philippe Dagaut at Orléans
 $\phi = 1.0$, $\tau = 0.7$ s, 10 atm, 0.1% fuel

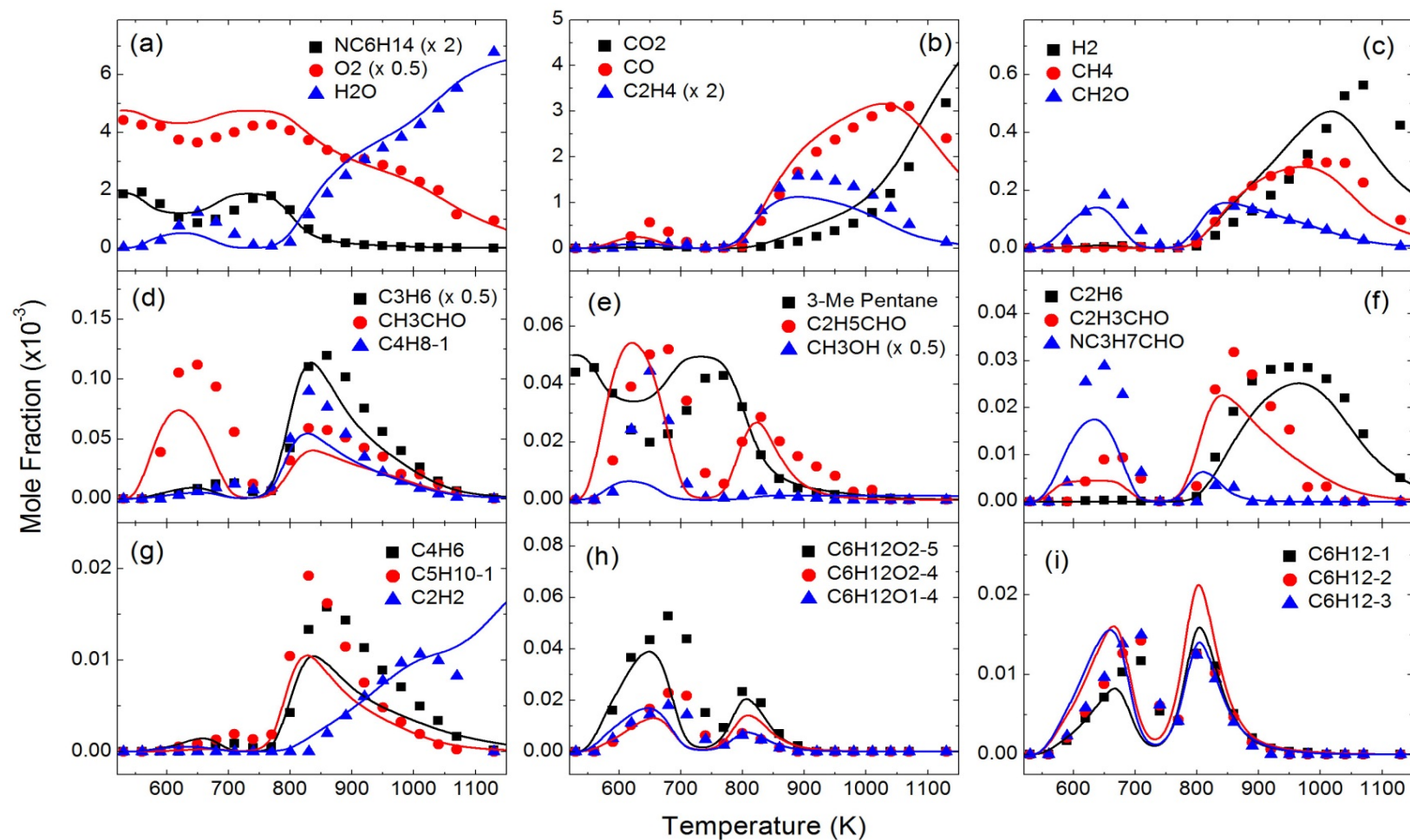
Validation: n-Hexane



n-Hexane



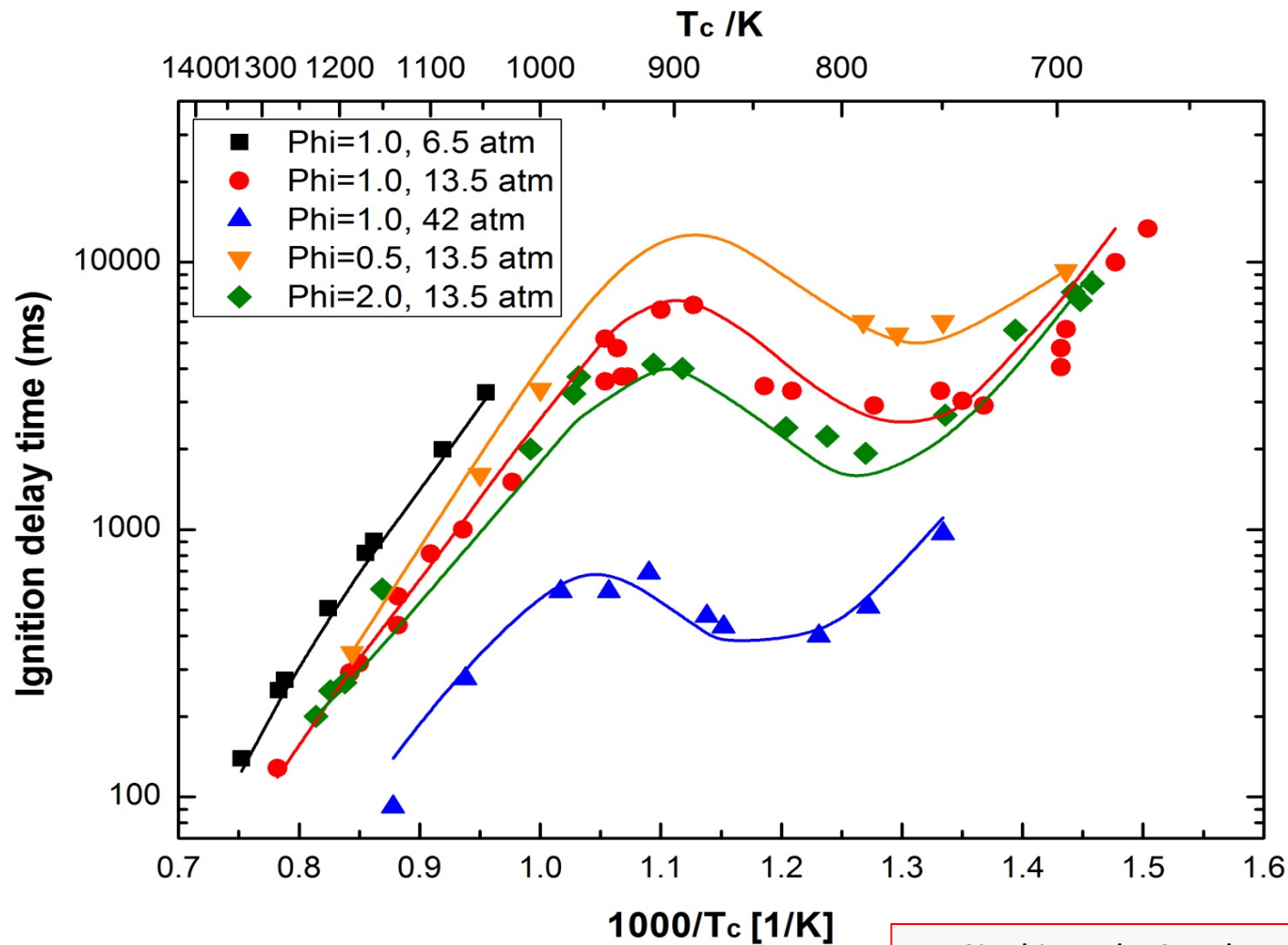
Validation: n-Hexane



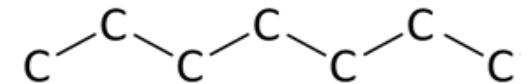
JSR experiment Philippe Dagaut at Orléans
 $\phi = 1.0$, $\tau = 0.7$ s, 10 atm, 0.1% fuel



Validation: n-Heptane



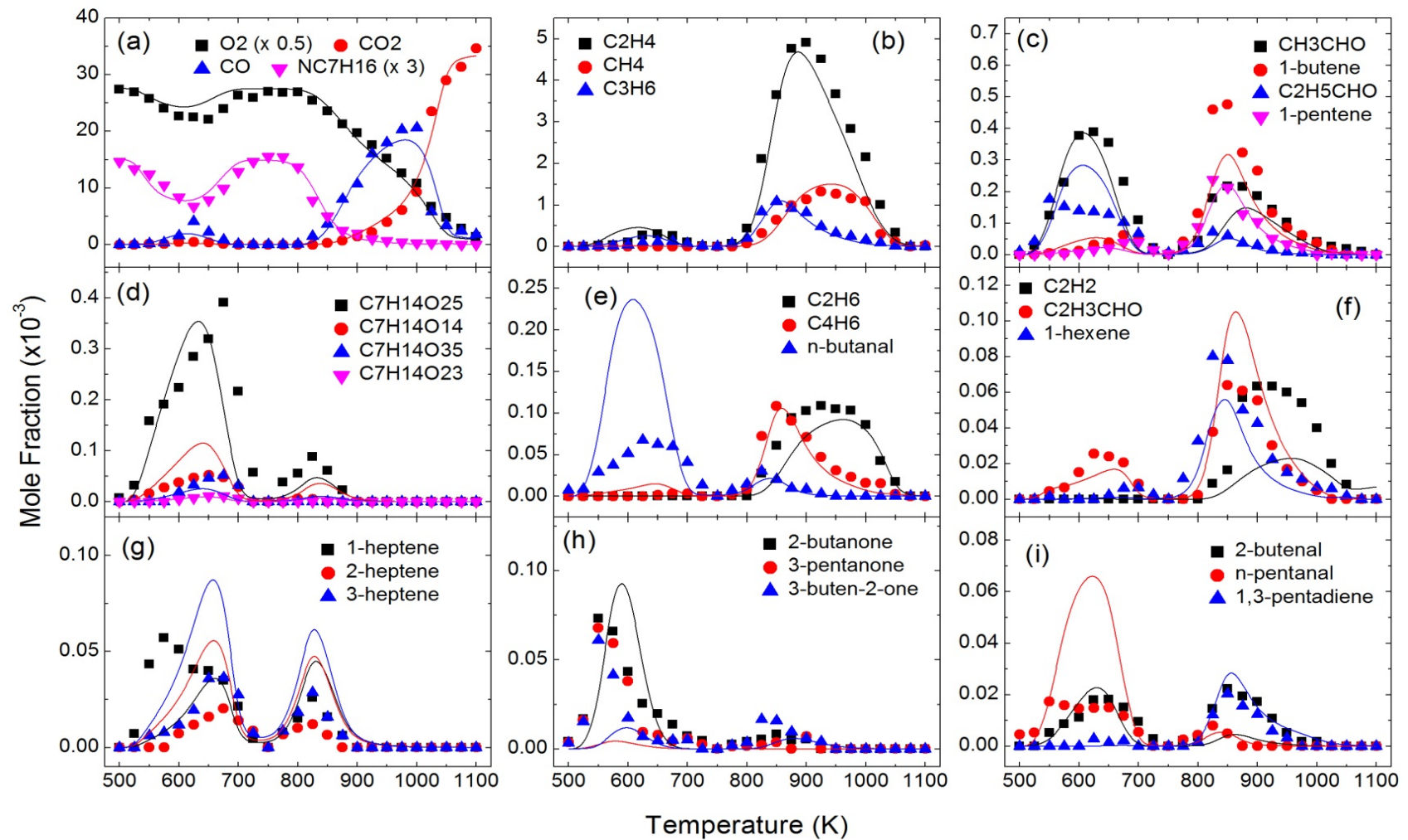
n-Heptane



Ciezki et al., Combust. Flame, 93 (1993) 421-433



Validation: n-Heptane



$\phi = 1.0$, $\tau = 2.0$ s, 1.06 bar, 0.5% fuel
Herbinet et al., Combust. Flame, 159 (2012) 3455-3471.



Conclusions

- Re-evaluated our understanding of low-temperature oxidation of alkanes
- Developed rate rules for reaction classes important in low-temperature regime
- We have found that “alternative” pathways have little effect on simulation results
- Found the source of long-standing discrepancy between mechanisms of straight and branched alkanes



Future work

- Re-visit the PRF models
- Apply new thermochemical properties, rate constants and alternative pathways to larger alkanes



Interesting features of biofuel combustion



The world is looking for new sources of energy

- Wind power
- Solar radiation
- Geothermal power
- Sea waves
- Nuclear power
- Fusion reactors
- Any others ? Probably
- But combustion is a big contributor



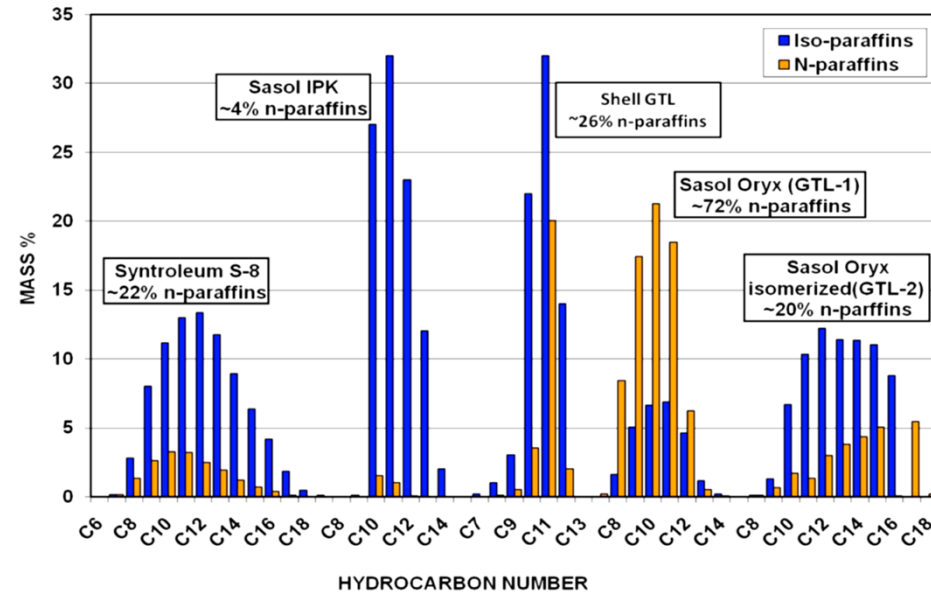
Combustion is responsible for most of the power generation in the world

- 85% of EU power production
- 90+% of transportation power
- Perhaps 100 years of fossil fuels remain
- Alternative energy sources are not very mature
 - estimate of 50 – 100 years needed for development
- Combustion is a relatively mature science
- The challenge:
 - limit the adverse impacts of fossil fuels
 - buy time for alternative energy



Future HC fuels - many sources

- Some petroleum will still be available
- Oil sands, oil shale
- Coal-to-liquids
- Fischer – Tropsch
- Natural gas
- Hydrogen
- Bio-derived fuels
 - Ethanol, butanol, algae
 - Biodiesel from vegetable and animal oils
- Chemical kinetics to understand and simulate
 - complex behaviour (ignition, NTC, cool flames...)
 - reactivity (extent of conversion, heat release)
 - product / pollutant formation





Energy Crisis—Solutions?

- Oxygenated fuel $\Rightarrow$ cleaner burning
 - Renewable, “Carbon neutral” fuel
 - Some can be used with existing diesel engines & distribution systems

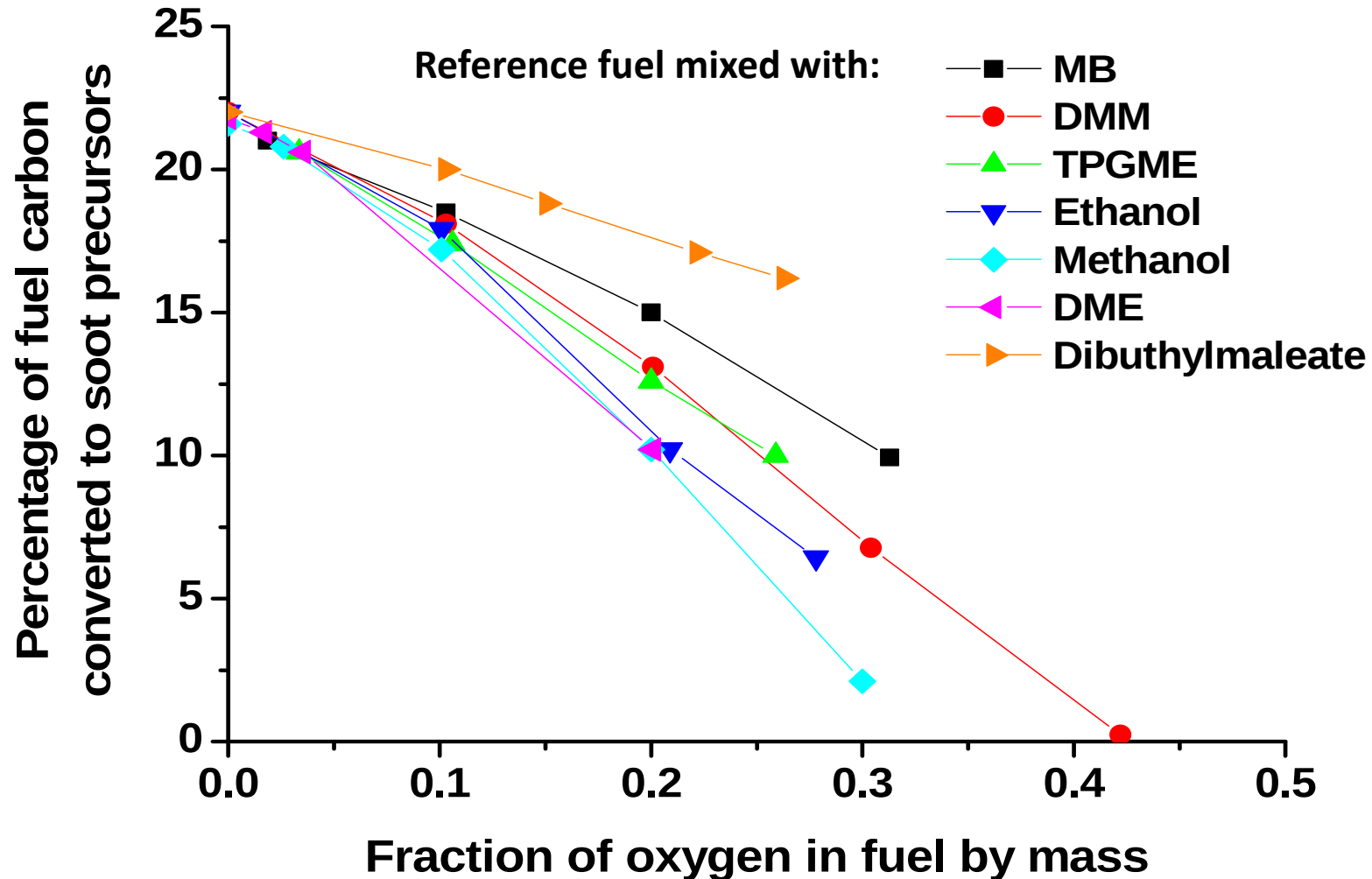
Emission	PM	CO	HC	NOx
Change	-47%	-48%	-67%	+10%

US EPA Draft technical report, EPA420-P-02-001 ; 2002

- 1st generation biofuels have drawbacks:
 - Emissions / atmospheric pollutants
 - Many cannot be burned “pure” in an un-modified engine
 - Food vs. Fuel debate
- Questions over production processes:
 - Raw materials, costs, distribution
 - lifecycle carbon footprint
 - land usage change
- Need renewable liquid fuels which overcome these issues and have desirable performance in ICEs



How well an oxygenated fuel works depends on its molecular structure



Miyamoto *et al.* Paper No. SAE 980506 (1998).

Westbrook *et al.* J. Phys. Chem. A (2006) 110: 6912–6922.



Oxygenated fuels

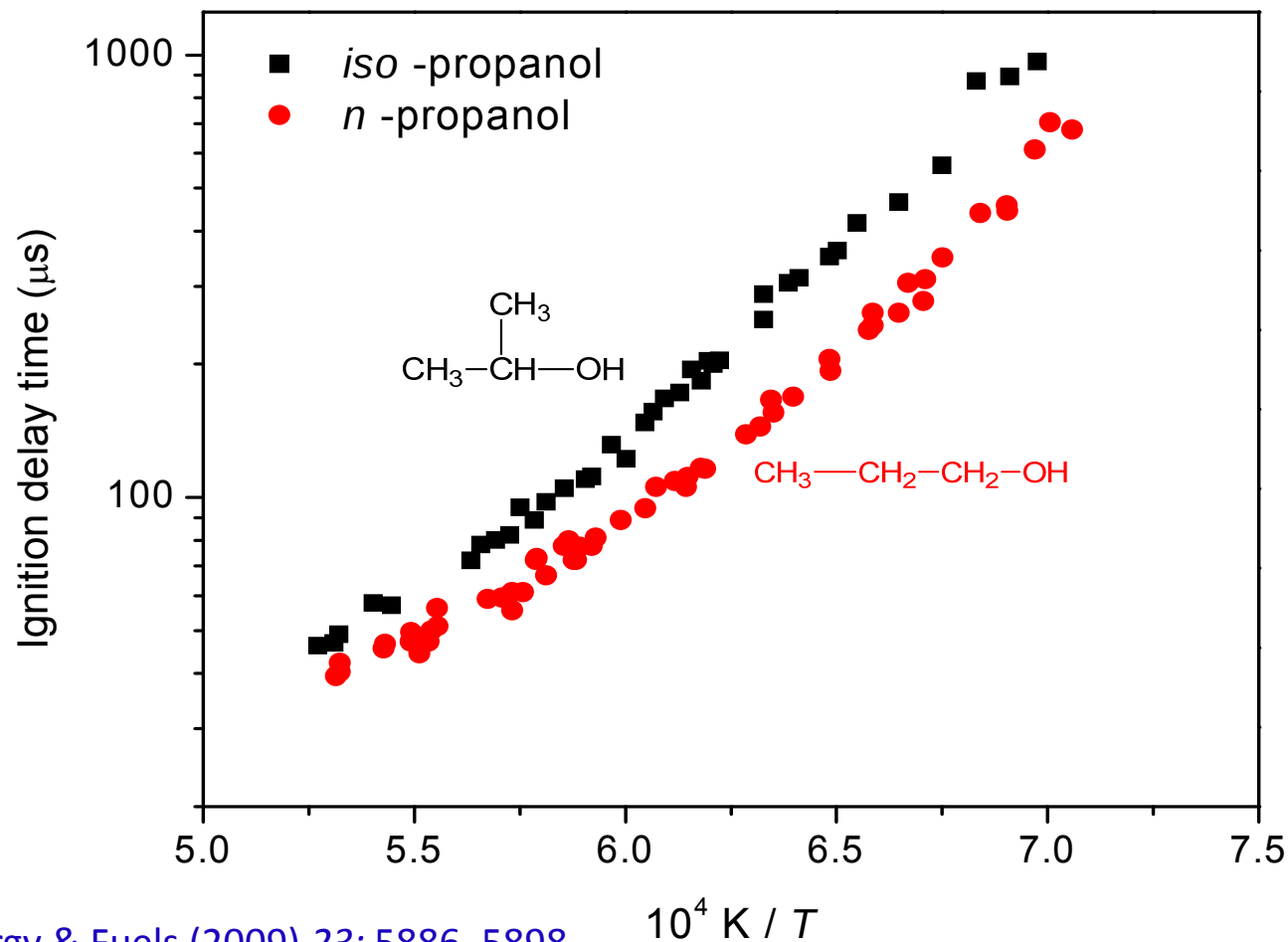
- Alcohols (methanol, ethanol, propanol, butanol)
- Ethers (DME, DEE, EME, MTBE, ETBE)
- Esters (methyl and ethyl esters)
- Ketones (acetone, EMK, DEK)
- Furans (methyl furan, di-methyl furan)



Propanol isomers – shock tube study

Comparison of reactivity of the isomers

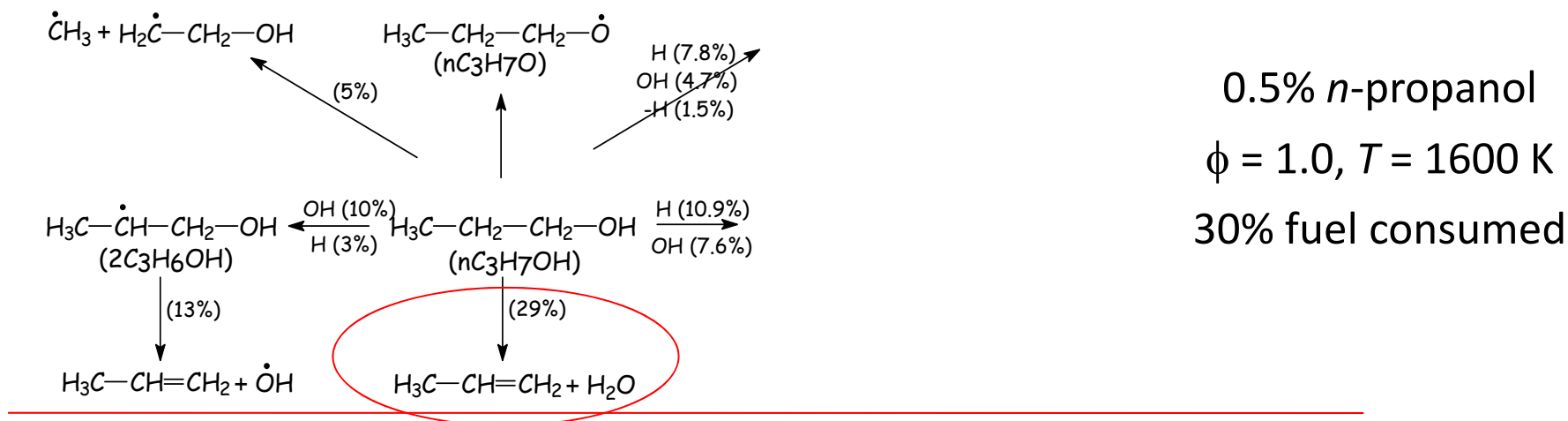
0.5% fuel, 2.25% O₂, $\phi = 1.0$, P = 1 atm



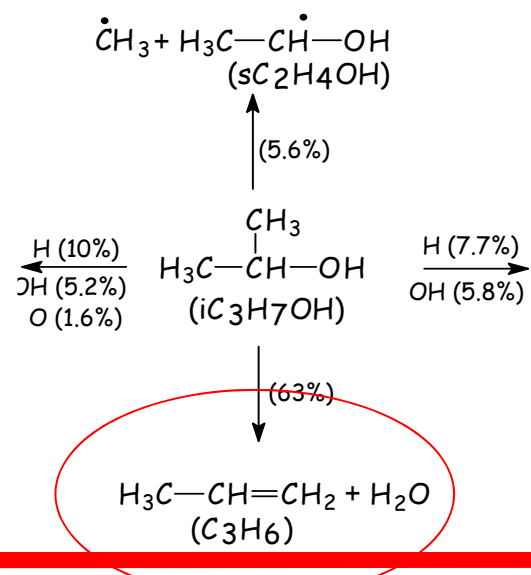
Johnson *et al.* Energy & Fuels (2009) 23: 5886–5898.



Water elimination is much more important for iso-propanol



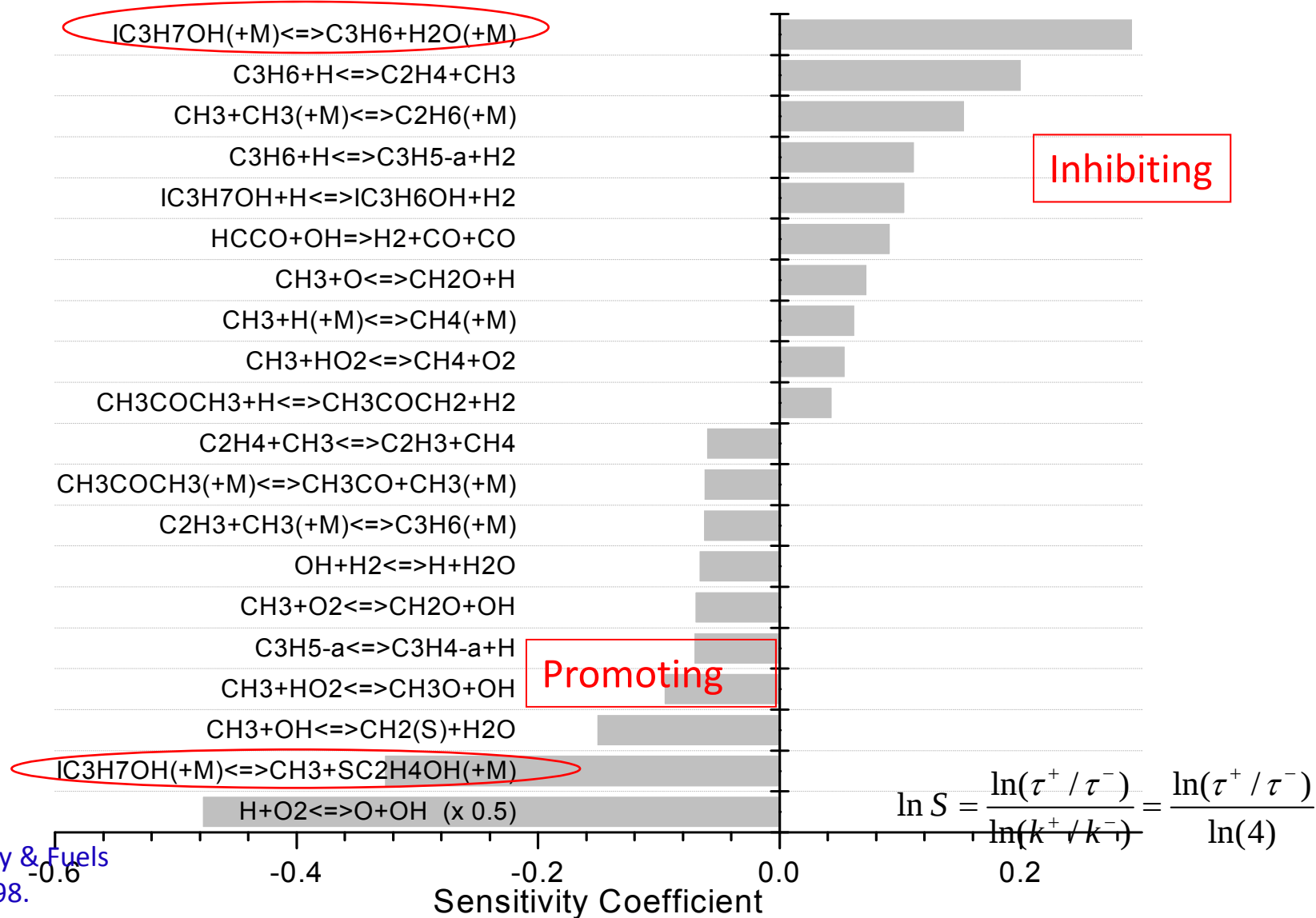
0.5% *iso*-propanol
 $\phi = 1.0$, $T = 1600$ K
 30% fuel consumed



Johnson *et al.* Energy & Fuels
 (2009) 23: 5886–5898.



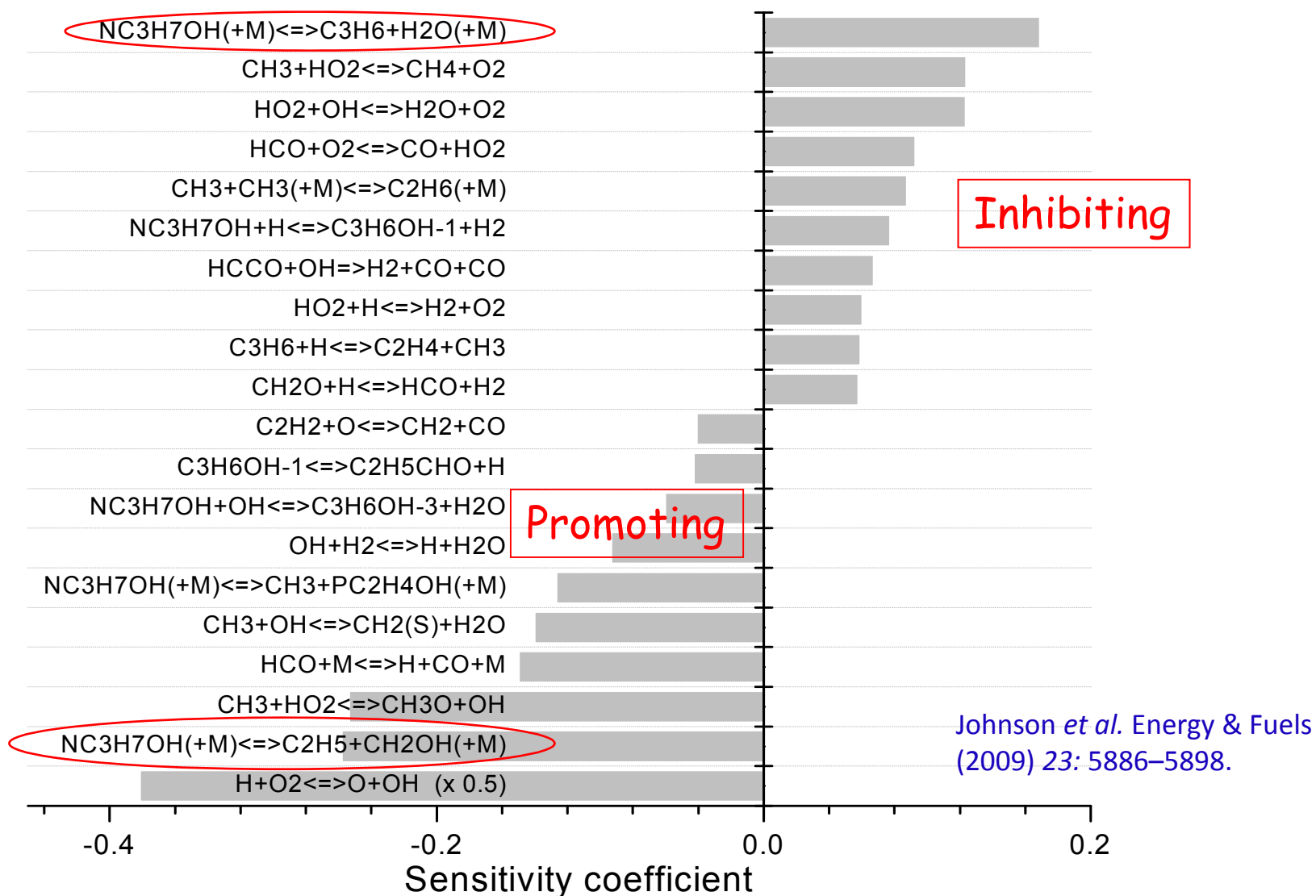
iso-propanol –Sensitivity analysis in ST



Johnson et al. Energy & Fuels
(2009) 23: 5886–5898.

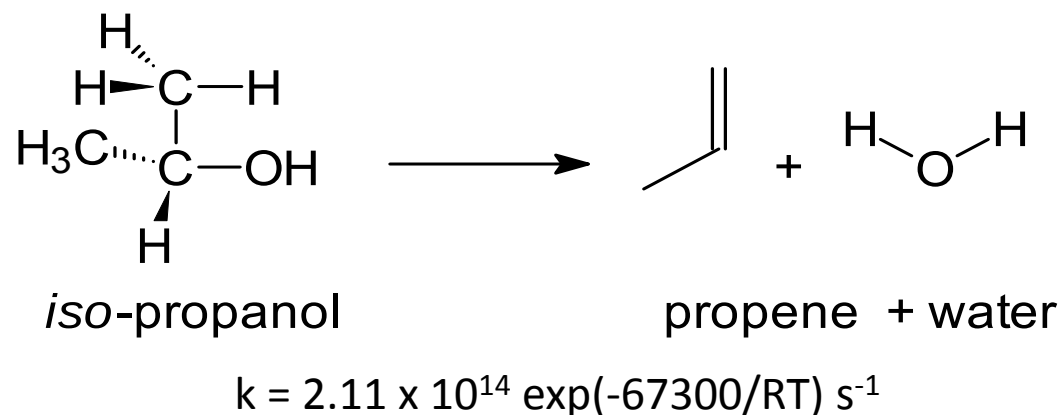
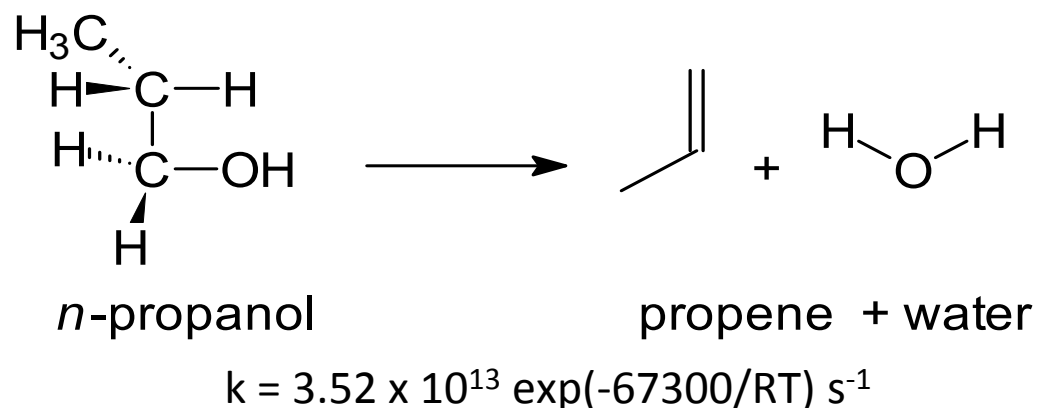


n-propanol –Sensitivity analysis in ST





Alcohol molecular elimination

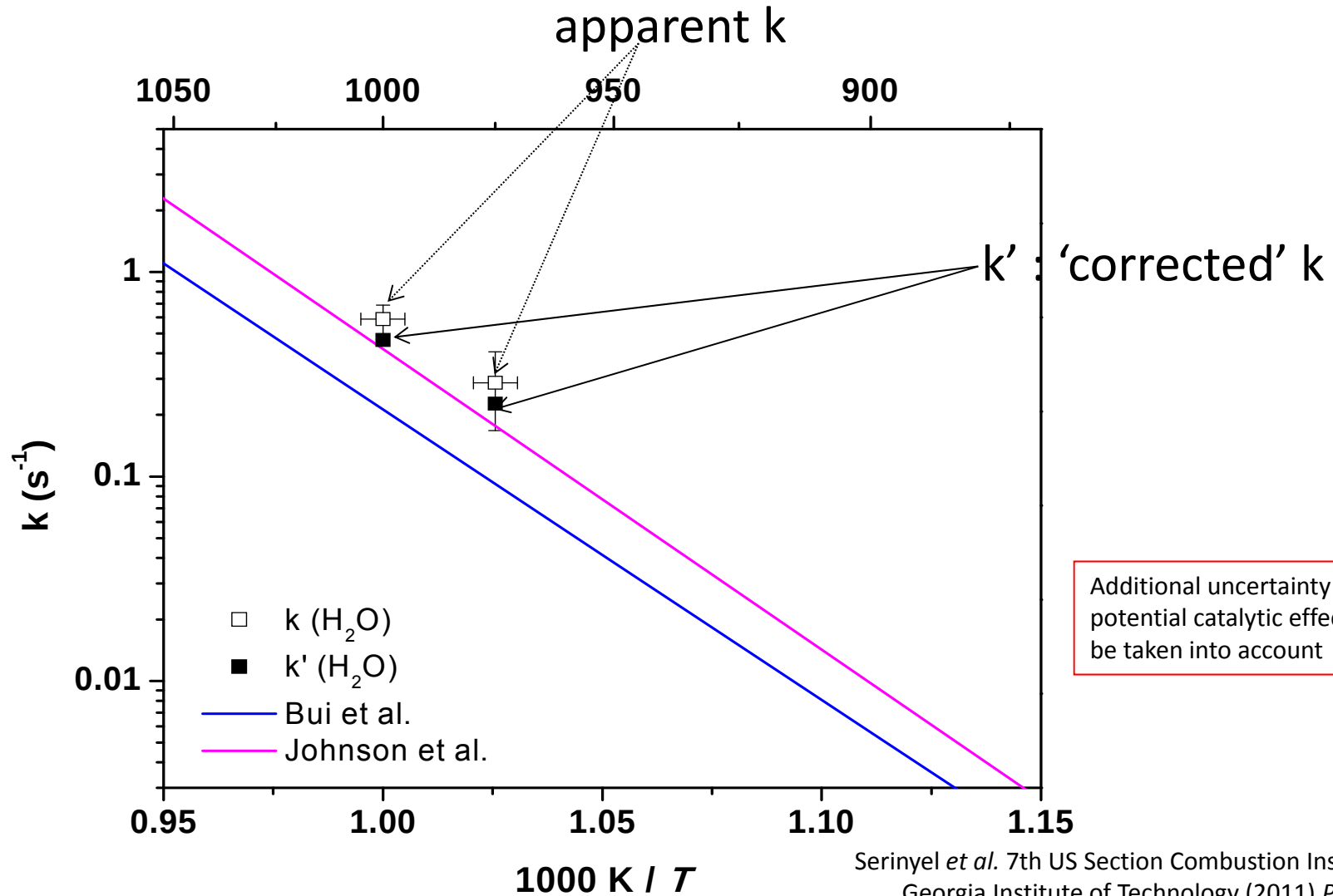


Tsang, W. Int. J. Chem. Kinet. (1976) 8: 173–192.



iso-propanol – Flow Reactor Study

Rate constant of molecular elimination

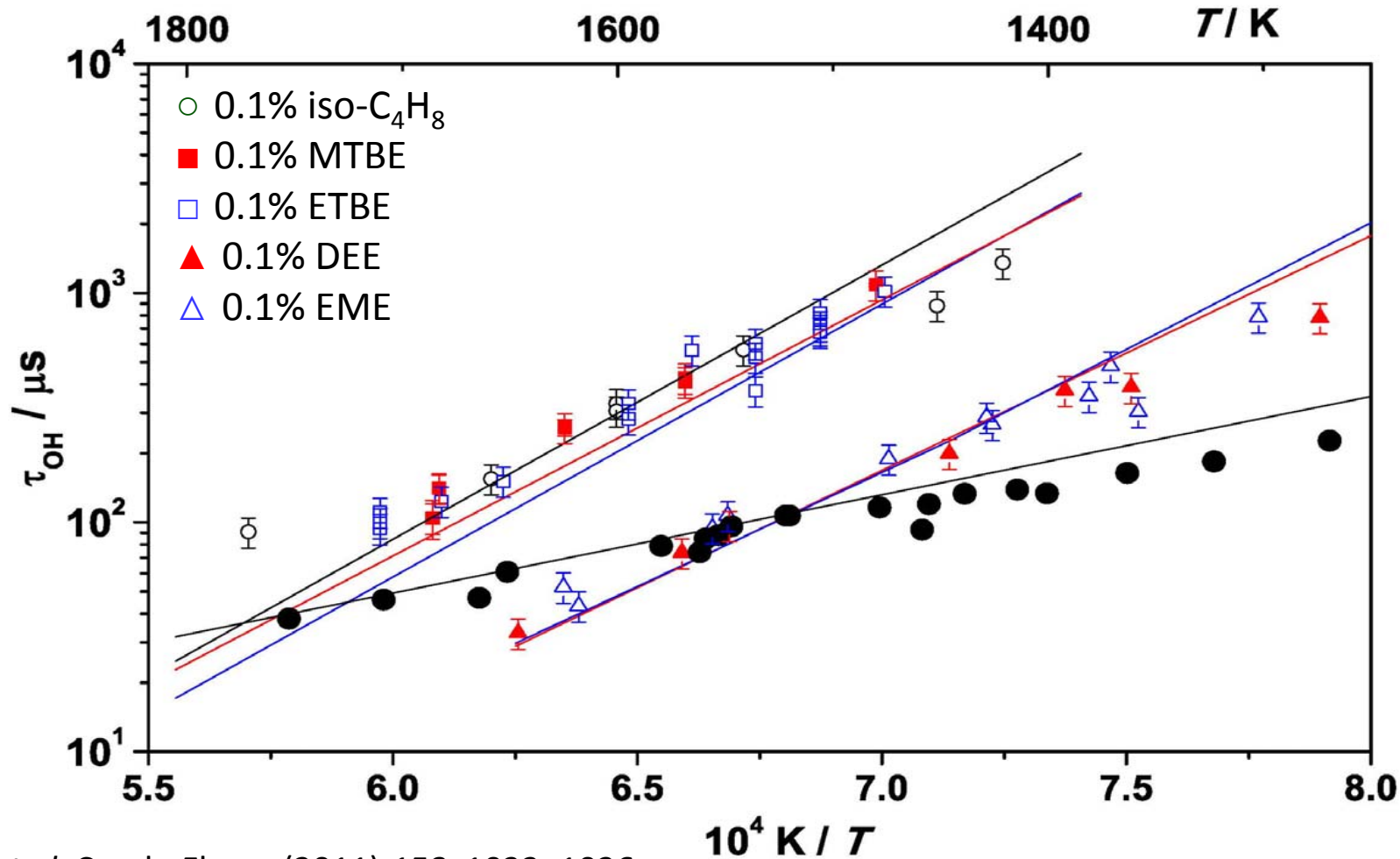


Serinyel *et al.* 7th US Section Combustion Institute Meeting
Georgia Institute of Technology (2011) *Paper 3A04*



Reactivity of ethers

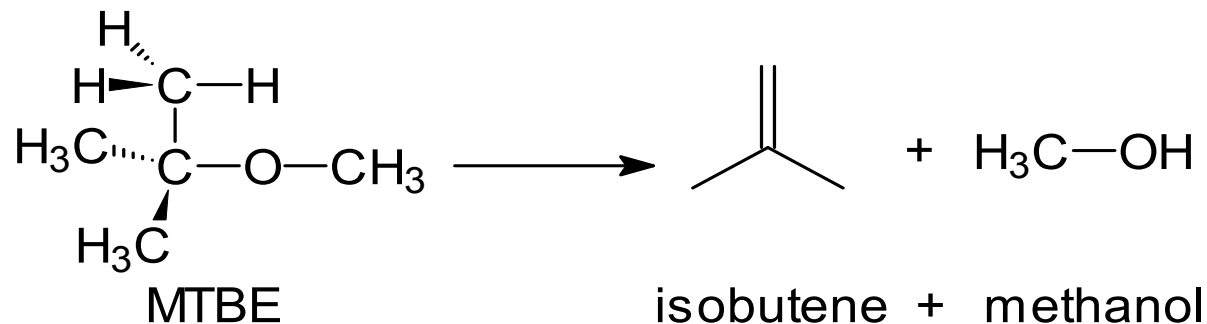
● 1% H₂, 1% O₂ in Ar, $p_5 = 1.4\text{--}2.6$ atm



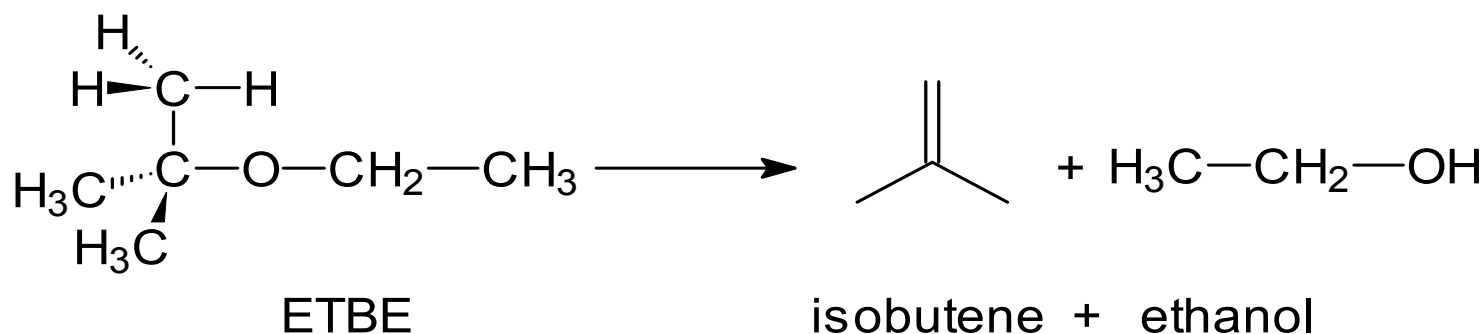
Yasunaga *et al.* Comb. Flame (2011) 158: 1032–1036.



Ether molecular elimination



$$k = 1.70 \times 10^{14} \exp(-60800/RT) \text{ s}^{-1}$$



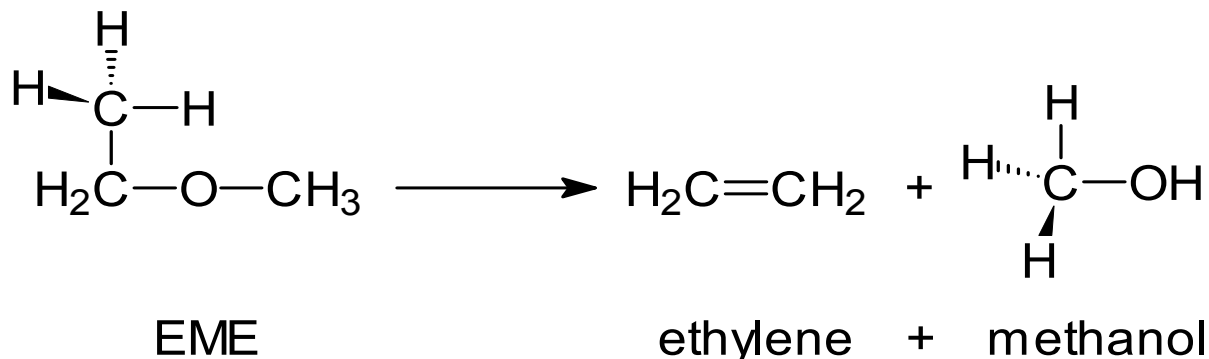
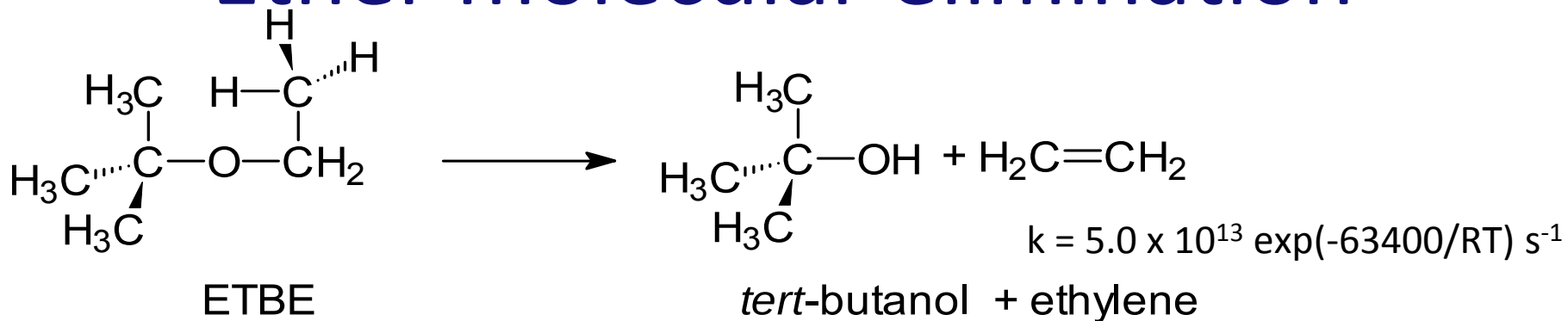
$$k = 1.70 \times 10^{14} \exp(-60600/RT) \text{ s}^{-1}$$

Yasunaga *et al.* Comb. Flame (2011) 158: 1032–1036.

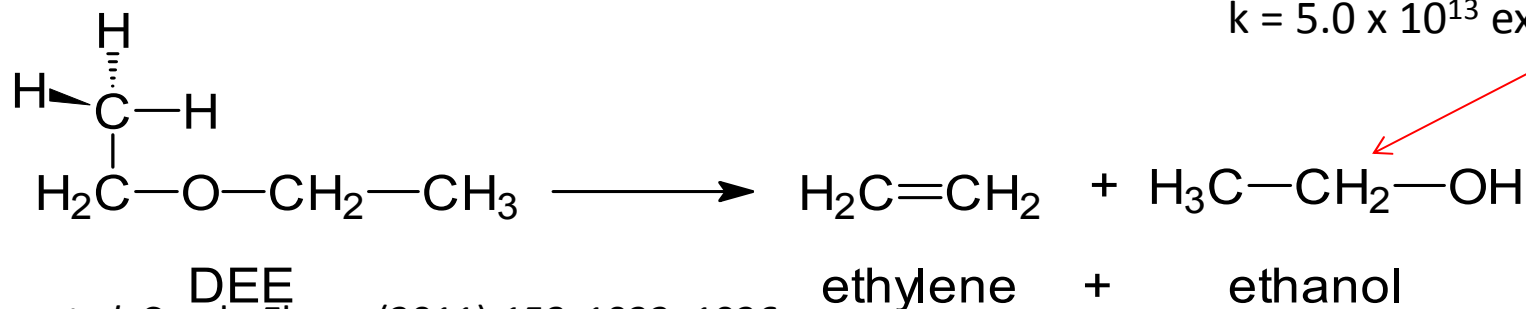
MP4/cc-pVTZ//MP2/cc-pVTZ level of theory with zero point corrections



Ether molecular elimination



$$k = 5.0 \times 10^{13} \exp(-65200/RT) \text{ s}^{-1}$$

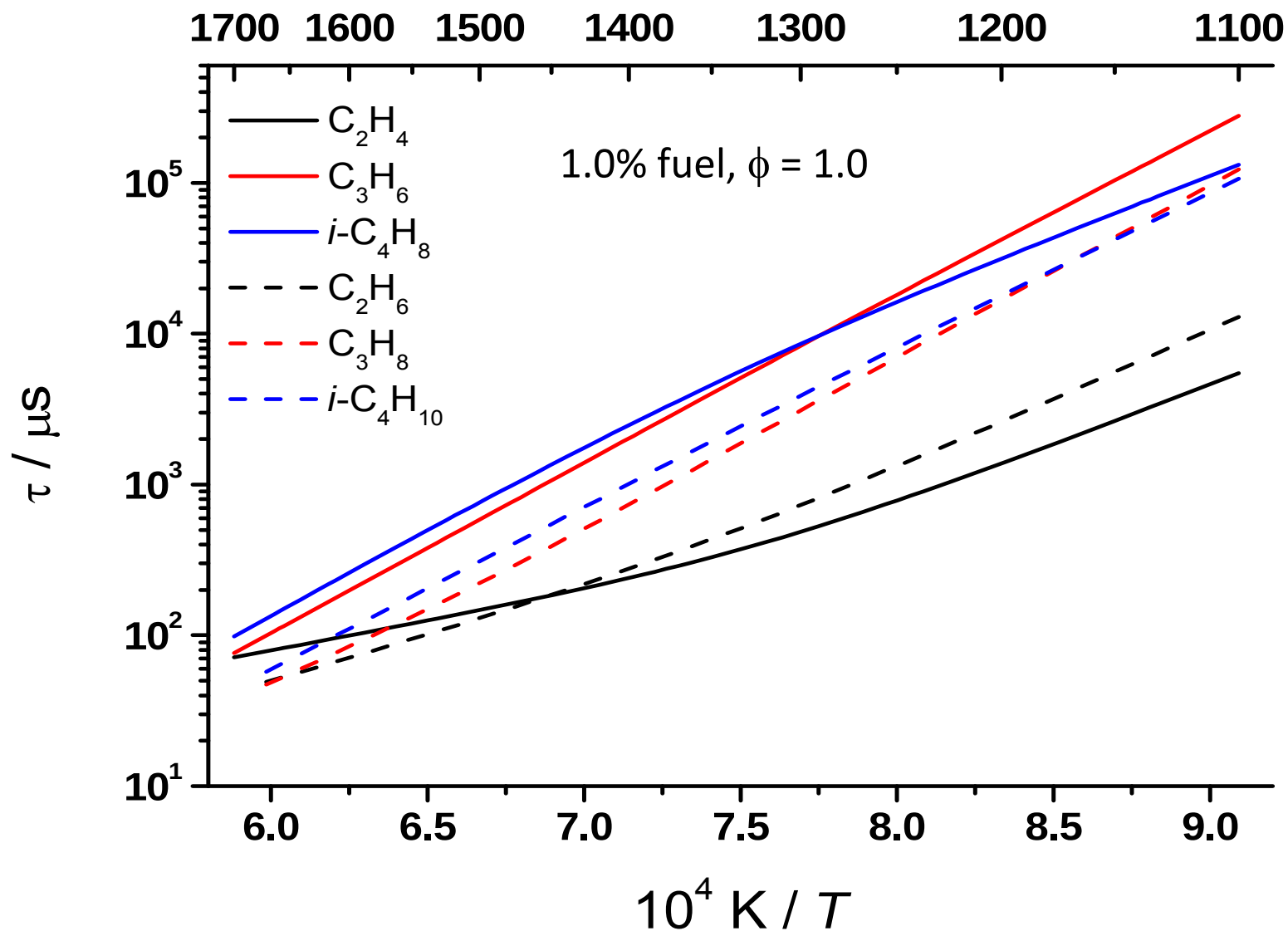


Yasunaga *et al.* Comb. Flame (2011) 158: 1032–1036.

MP4/cc-pVTZ//MP2/cc-pVTZ level of theory with zero point corrections



Ethylene is very fast to ignite





Relative reactivity of fuels

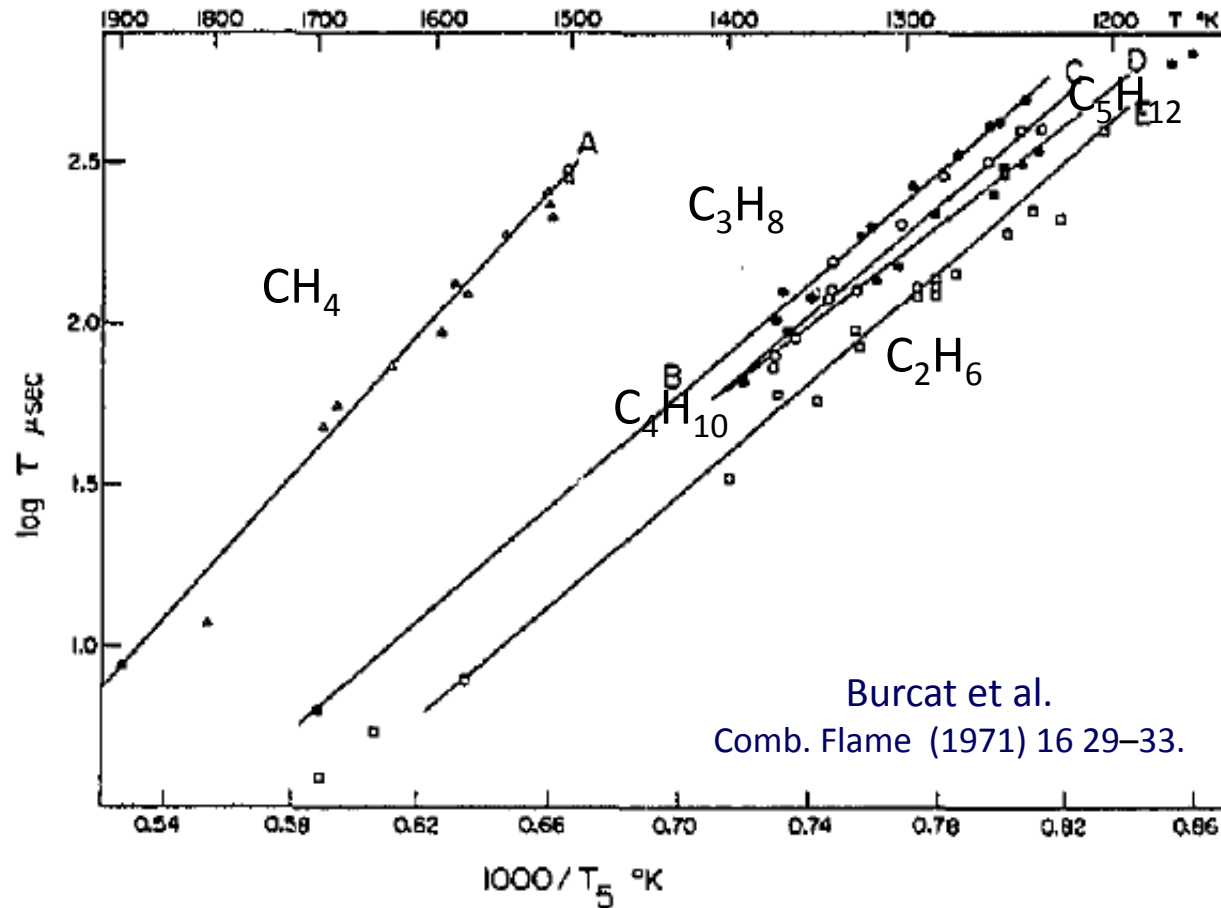
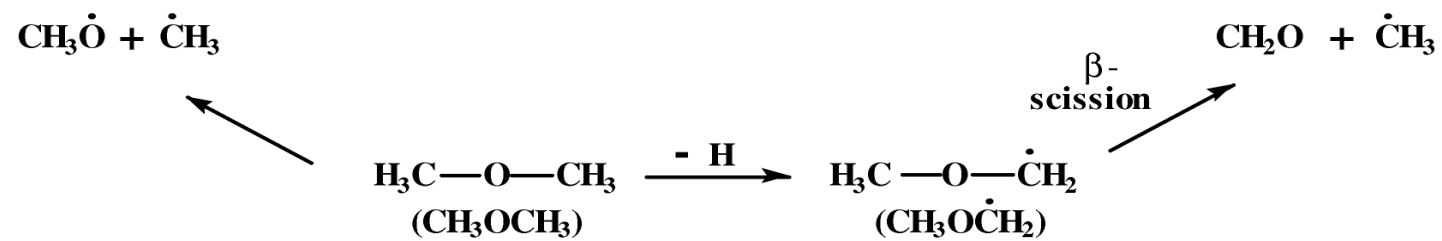
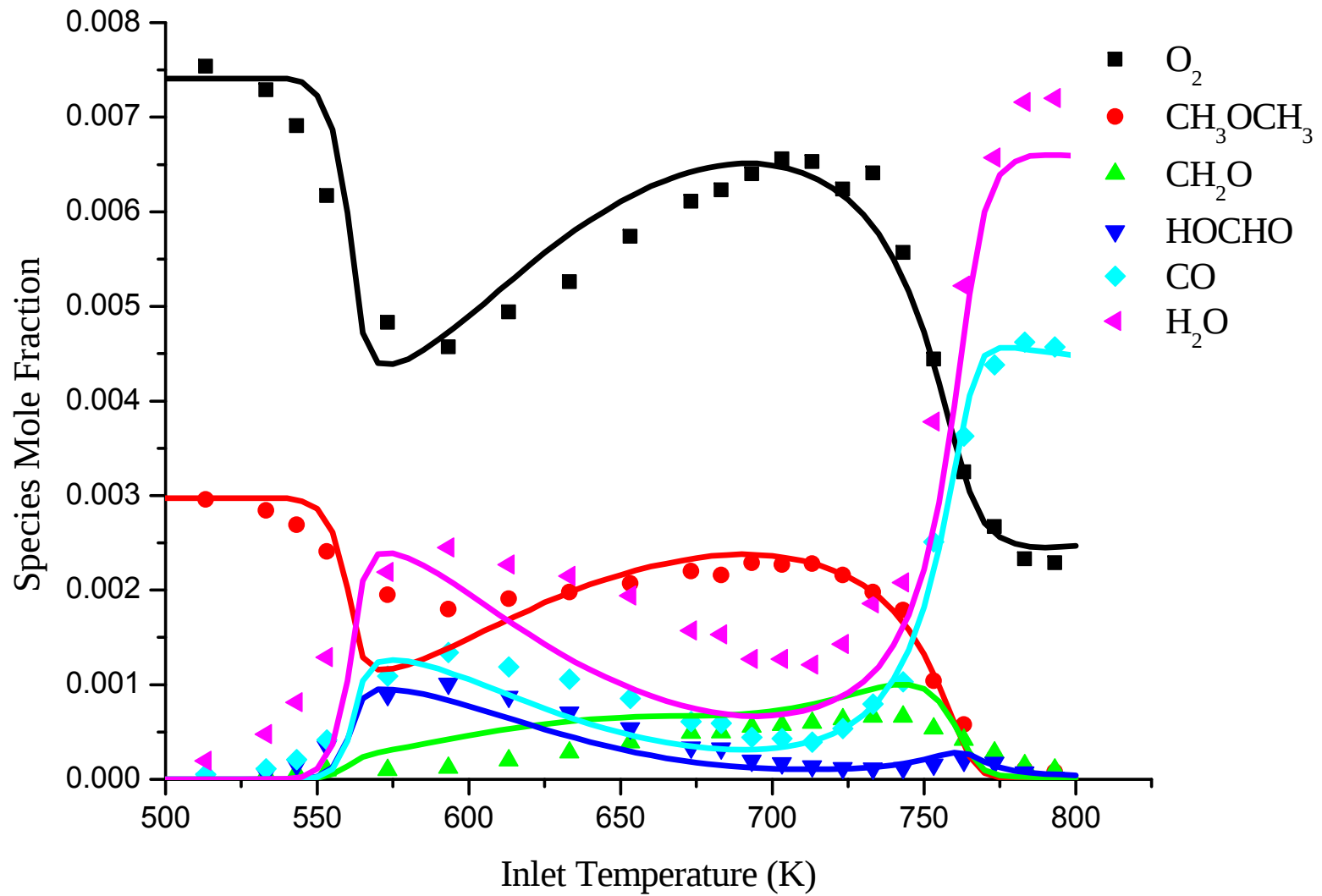


Figure 1. A plot of $\log \tau$ versus $1/T_5$ for five alkane-oxygen-argon mixtures; $p_1 \sim 185 \pm 15$ torr. A. 7.7% CH_4 + 15.4% O_2 ; B. 3.22% C_3H_8 + 16.1% O_2 ; C. 2.5% C_4H_{10} + 16.25% O_2 ; D. 2.04% C_5H_{12} + 16.3% O_2 ; E. 4.54% C_2H_6 + 15.91% O_2 .





3030 ppm DME, $\phi = 1.19$, $p = 12.5$ atm, $\tau = 1.8$ s.

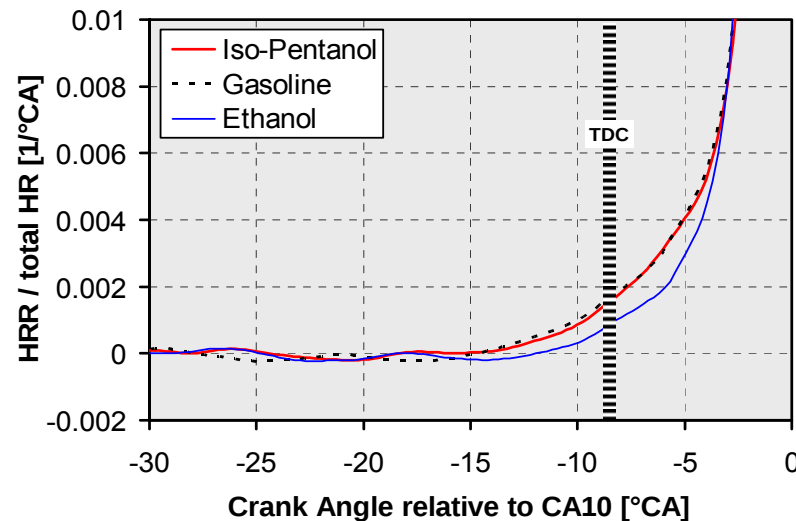




Isopentanol ($C_5H_{12}O$) is a promising next-generation biofuel



- Efficient production routes from biomass exist (Connor *et al*, Adv. Microbiol. Biotechnol. 2010)
- Isopentanol has favorable characteristics as HCCI fuel (Dec *et al*, SAE technical paper 2010)

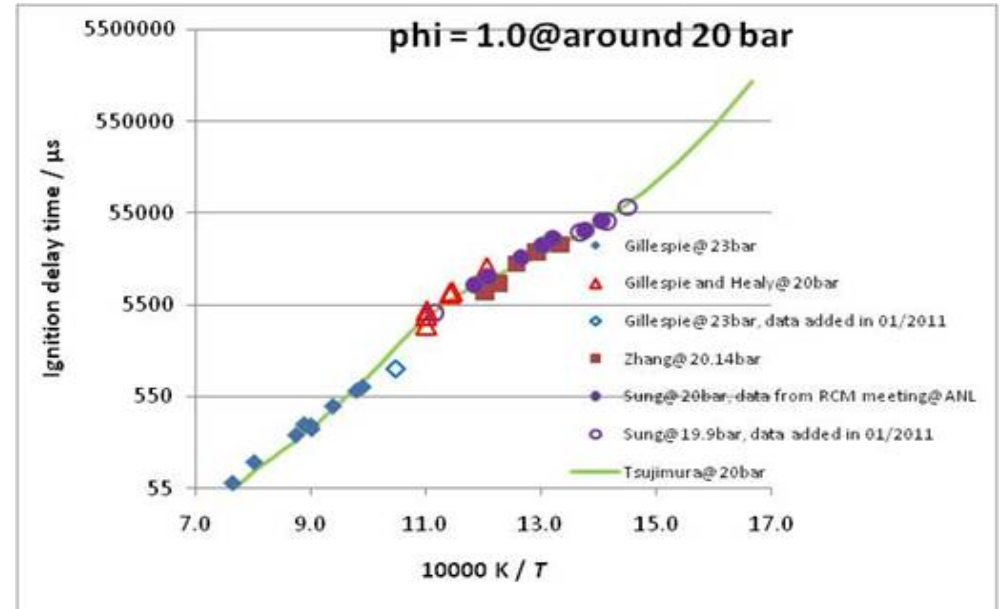
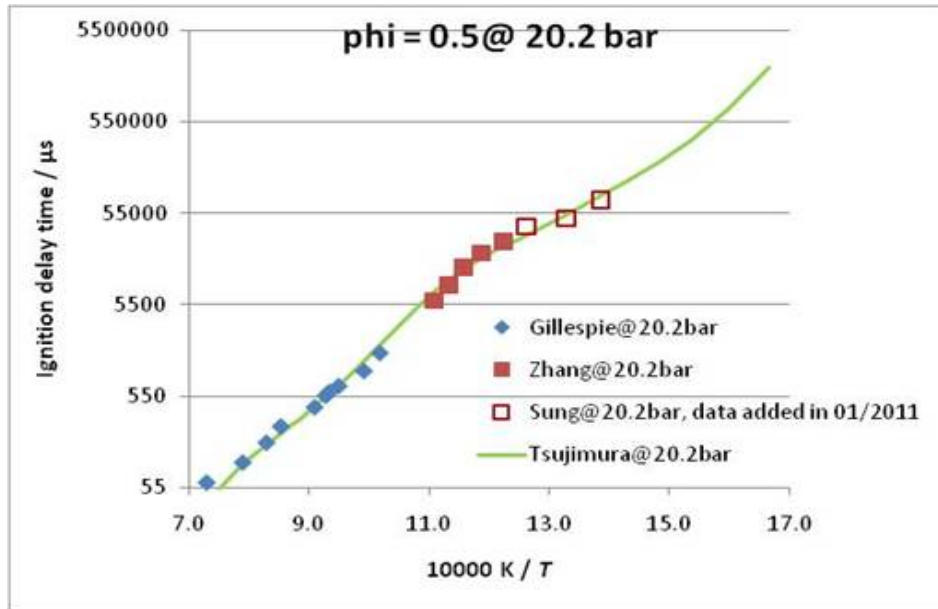


Isopentanol shows
ITHR similar to
gasoline

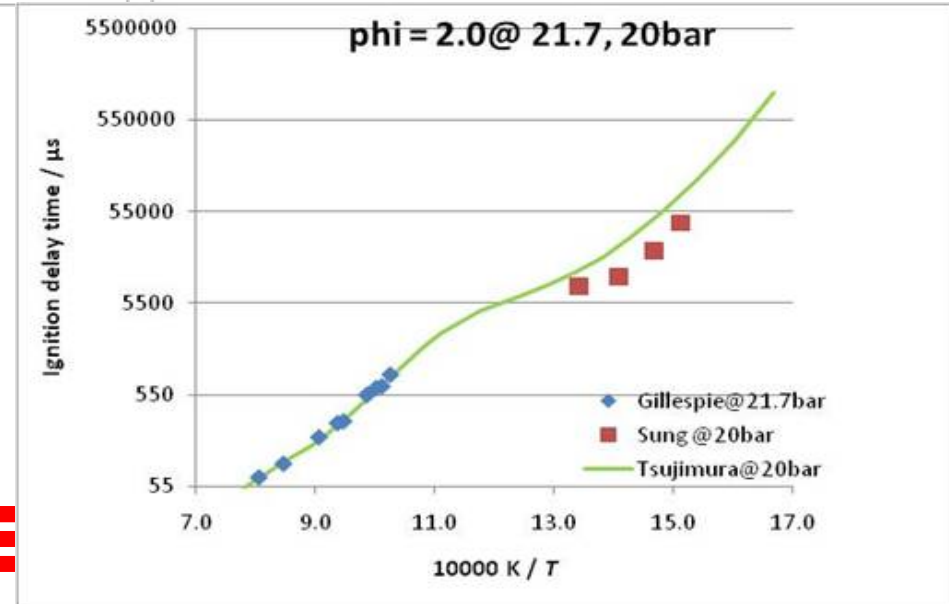
- HCCI engines rely on autoignition
- Low-temperature oxidation ($R + O_2$) chemistry plays a central role
- $R + O_2$ chemistry of novel biofuels has to be known to understand and predict their combustion characteristics

Welz *et al*. 7th US Section Combustion Institute Meeting
Georgia Institute of Technology (2011) Paper 1B14

Isopentanol Oxidation

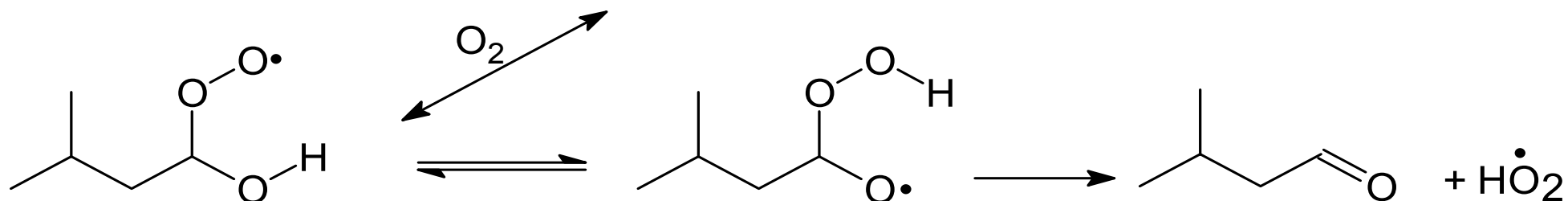
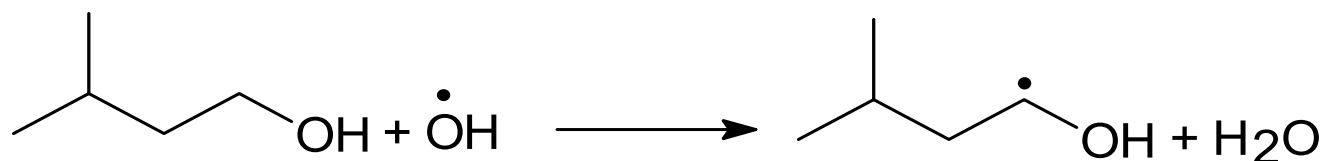
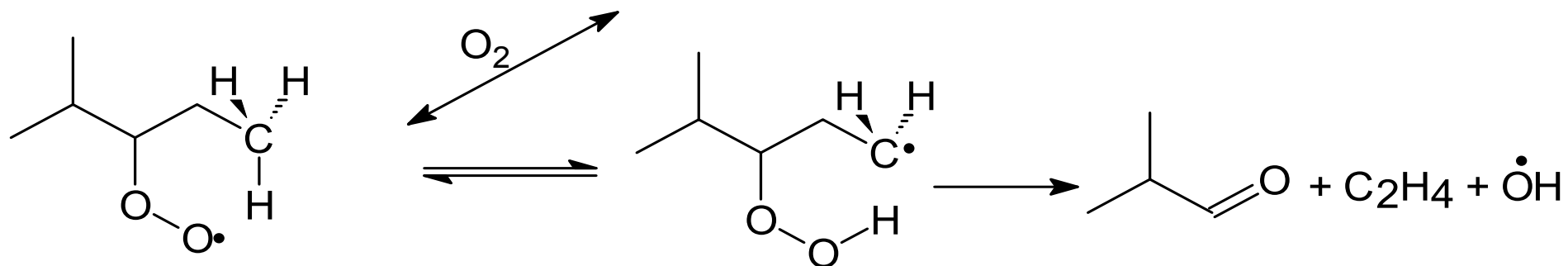
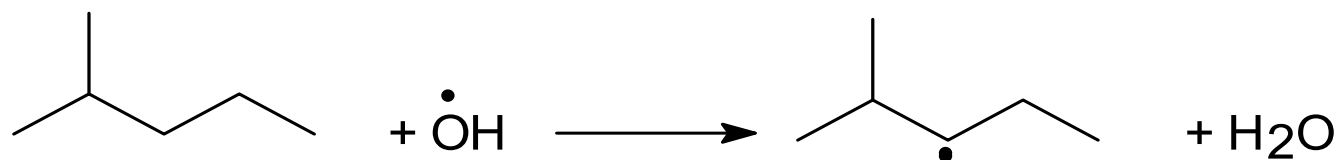


T. Tsujimura, W.J. Pitz, F. Gillespie, H.J. Curran, B.W. Weber, Y. Zhang, C-J. Sung, "Development of *iso*-Pentanol Reaction Mechanism Reproducing Autoignition Character at High and Low Temperatures", Energy Fuels (2012) 26(8) 4871–4886.



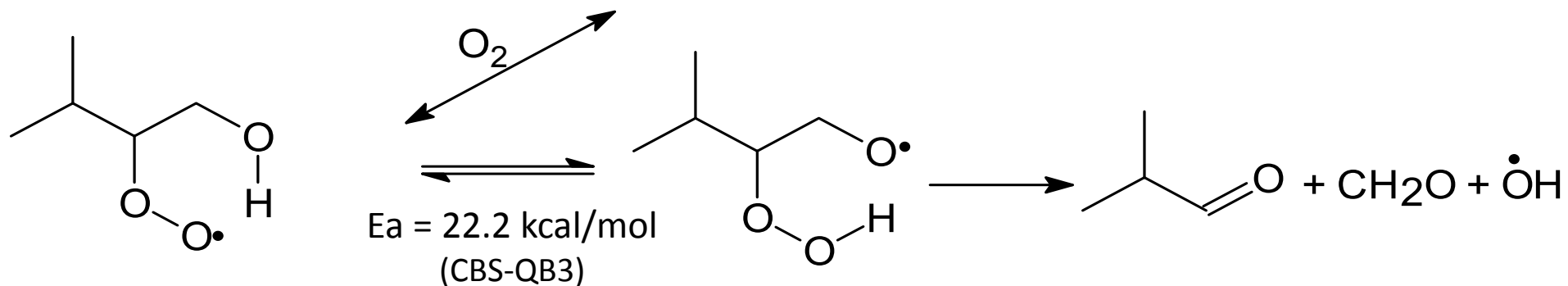
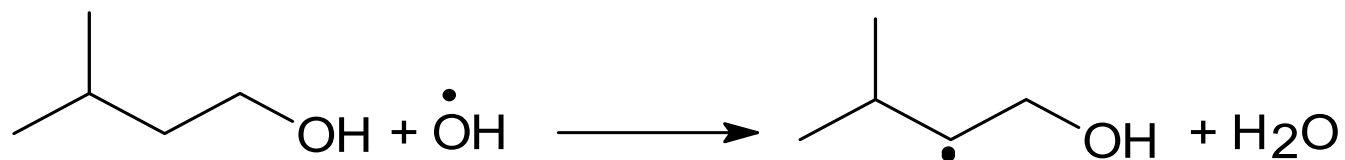
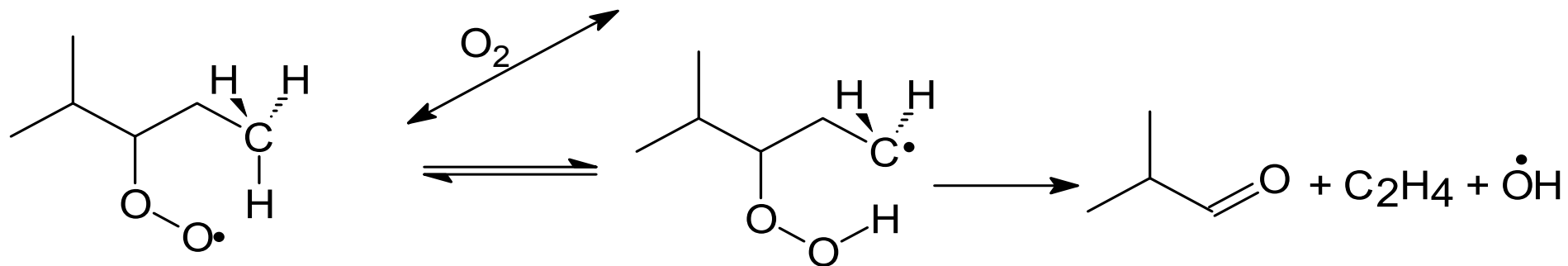
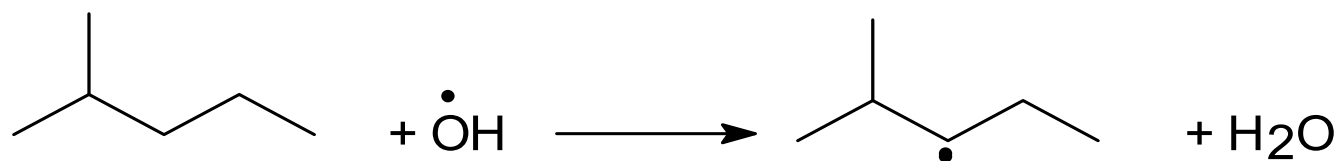


Isopentanol Oxidation



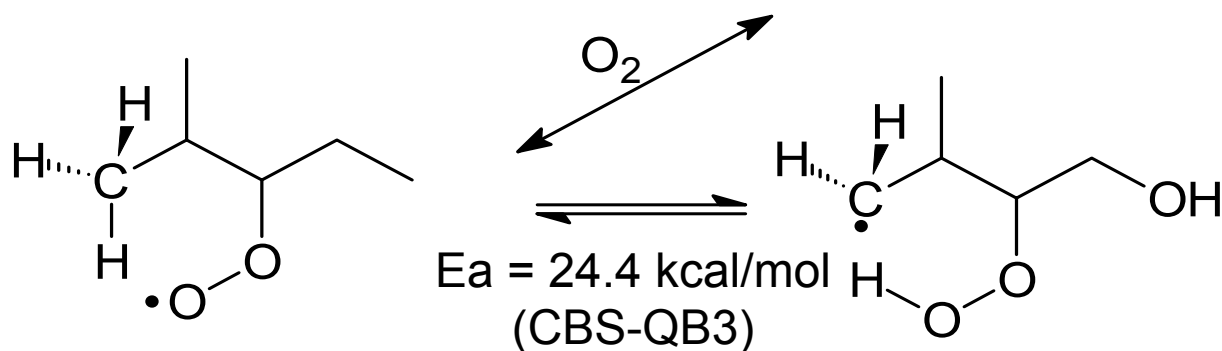
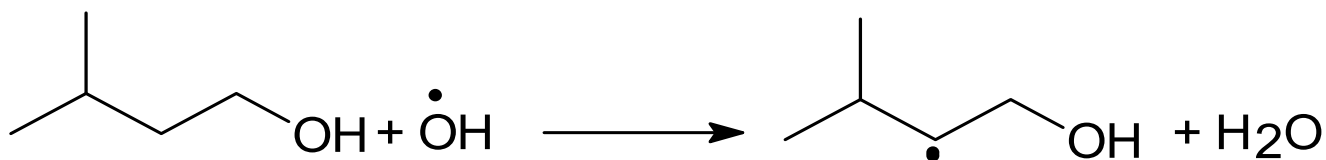
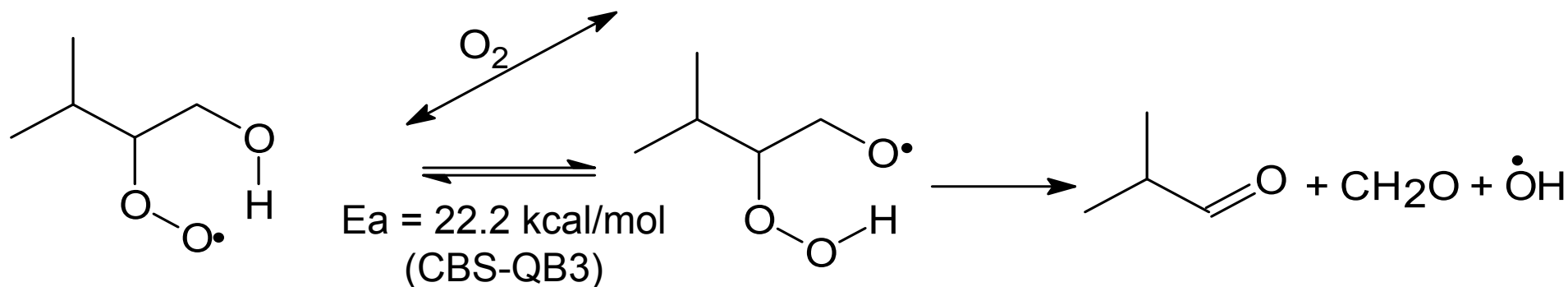
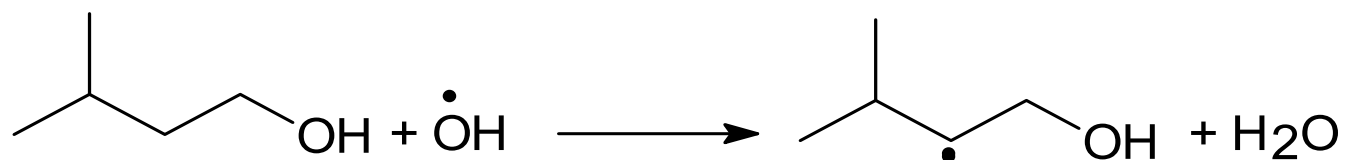


Isopentanol Oxidation



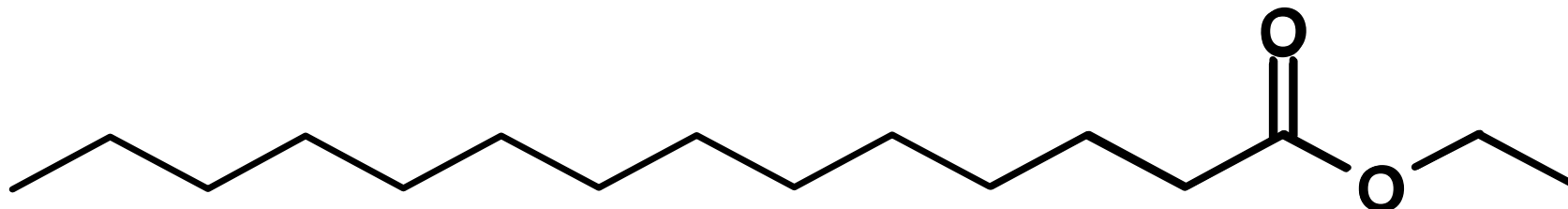


Isopentanol Oxidation

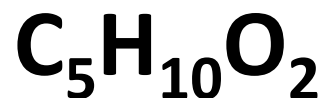




Combustion of Model Biodiesels



Ethyl tetradecanoate

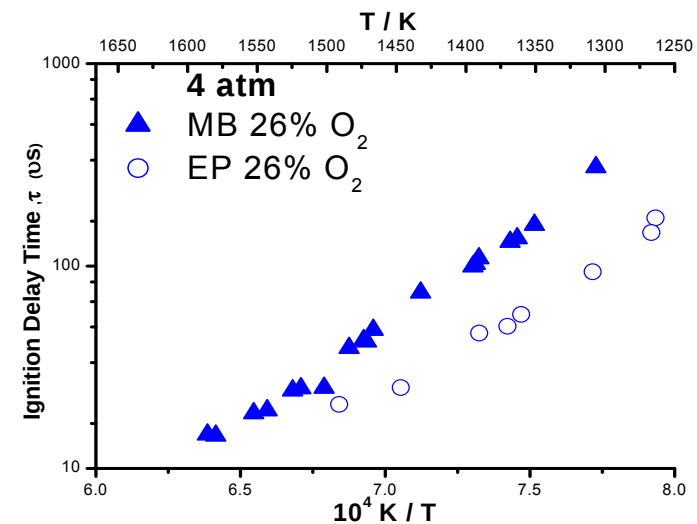
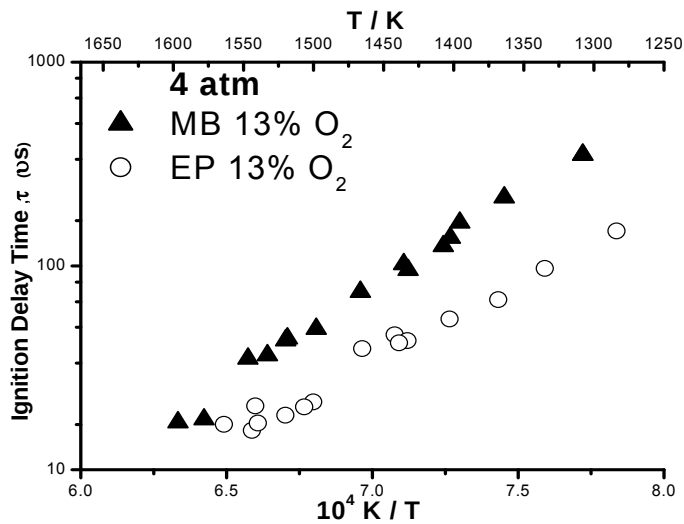
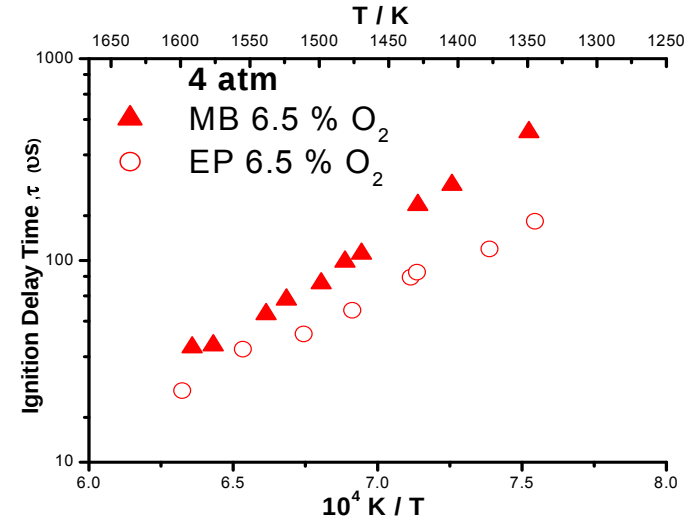
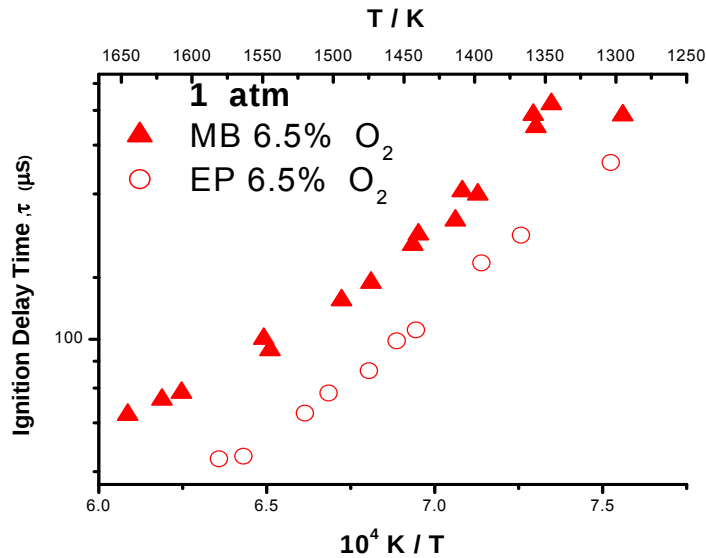


methyl butanoate (MB)

ethyl propanoate (EP)



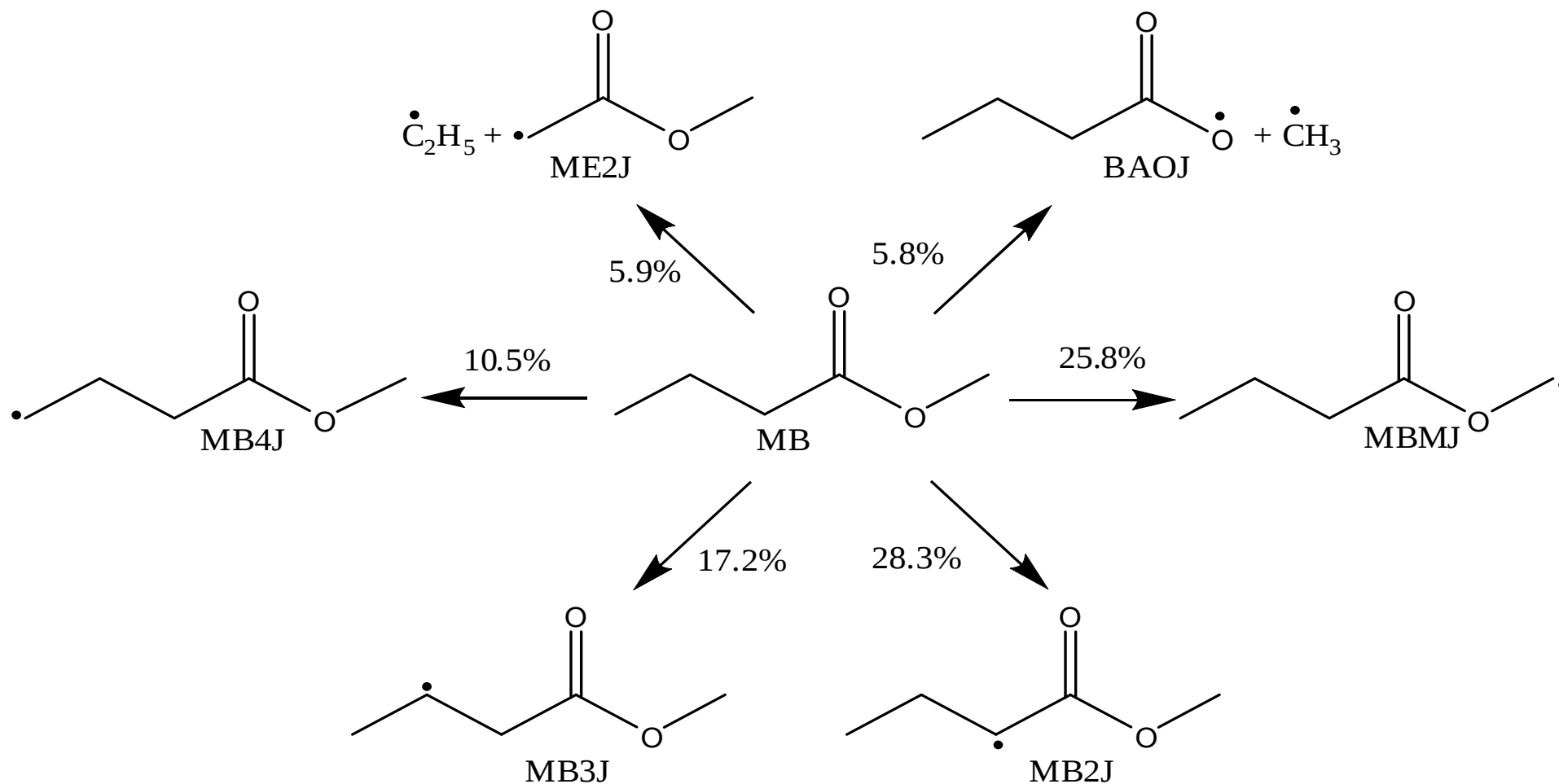
Comparison – MB vs EP





MB Consumption

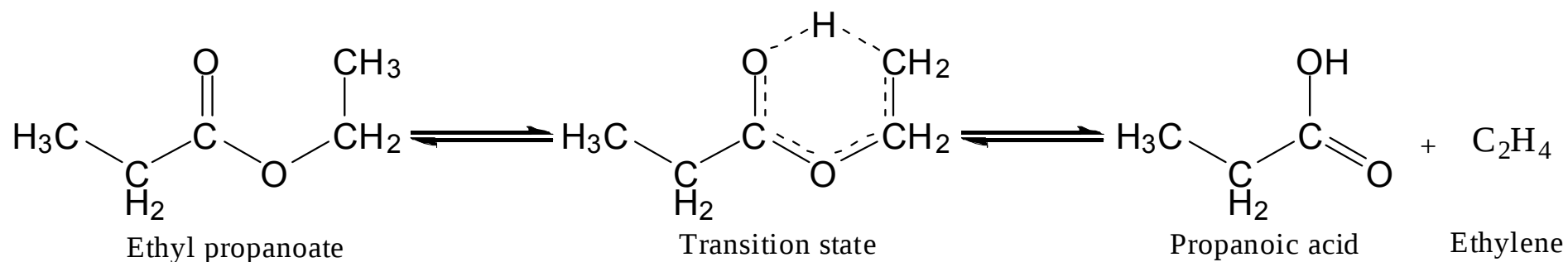
1.0 % MB 6.5% O₂ 1600 K , 1 atm $\Rightarrow$ 50 % MB consumed





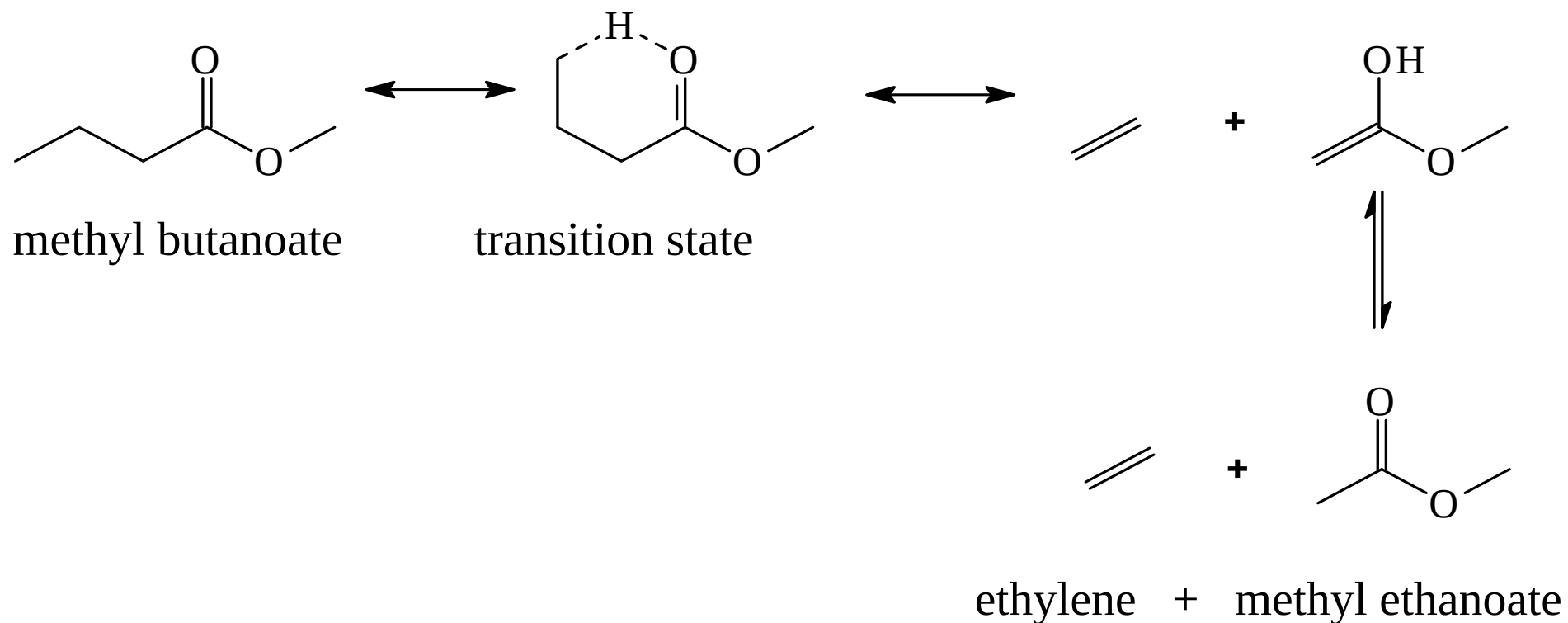
EP decomposition

1.0 % EP 6.5% O₂ 1600 K , 1 atm $\Rightarrow$ 50 % EP consumed



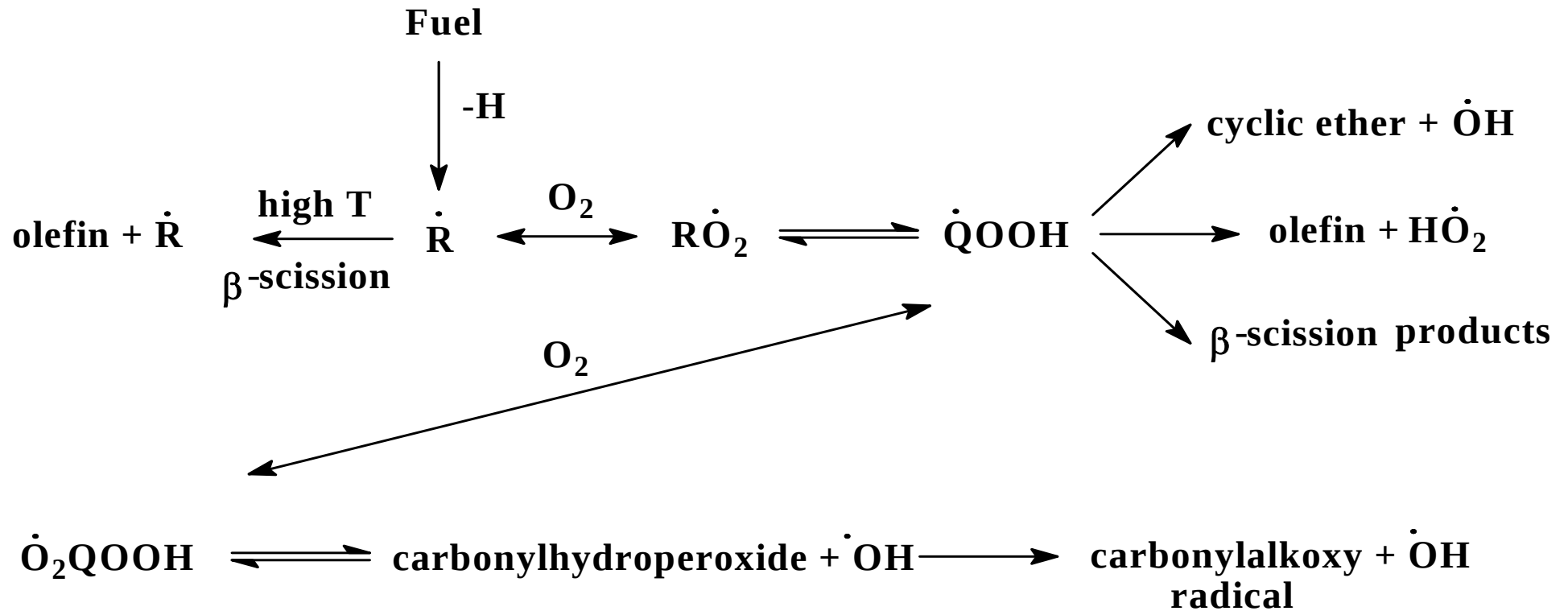


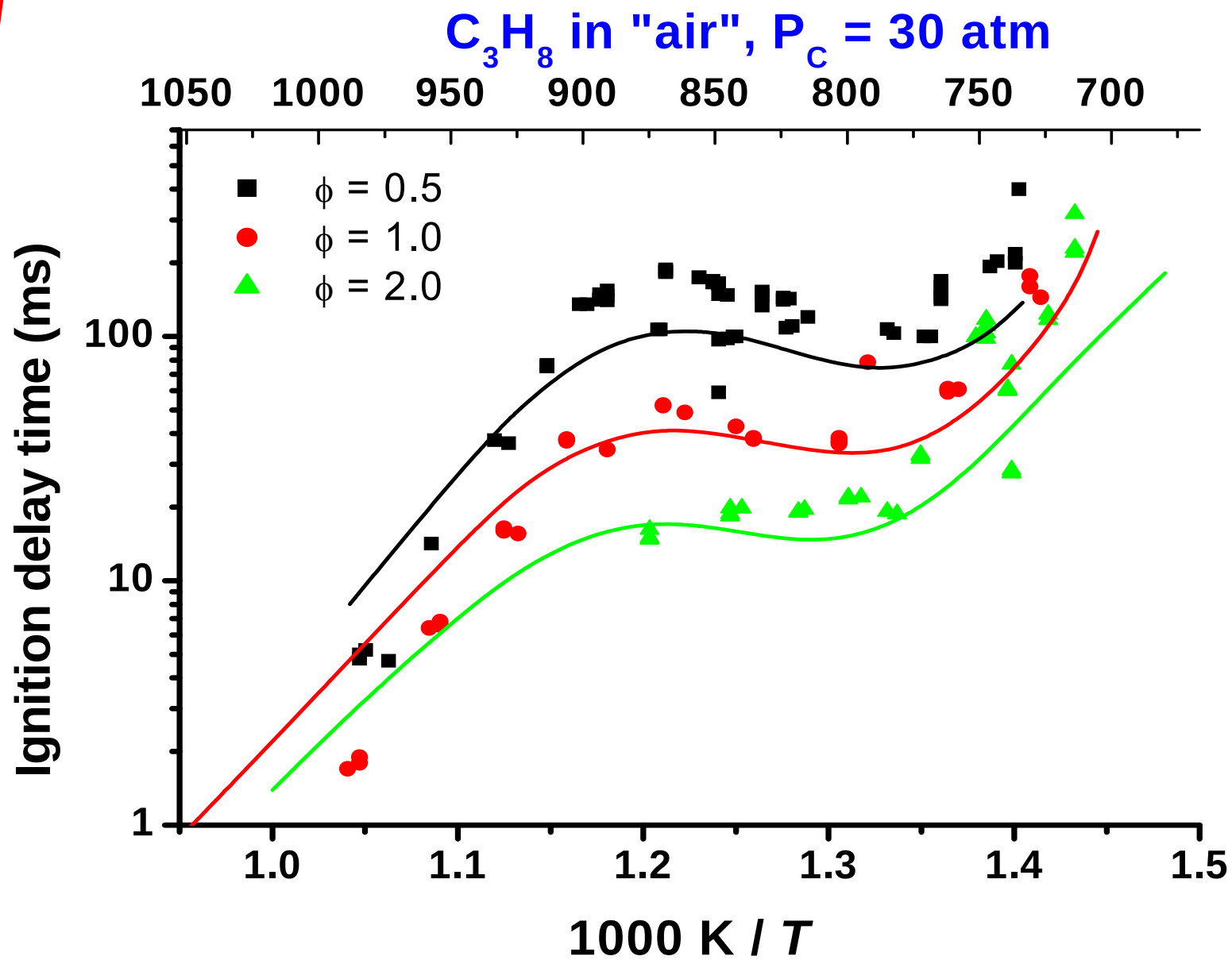
MB decomposition





Low Temperature Reaction Scheme

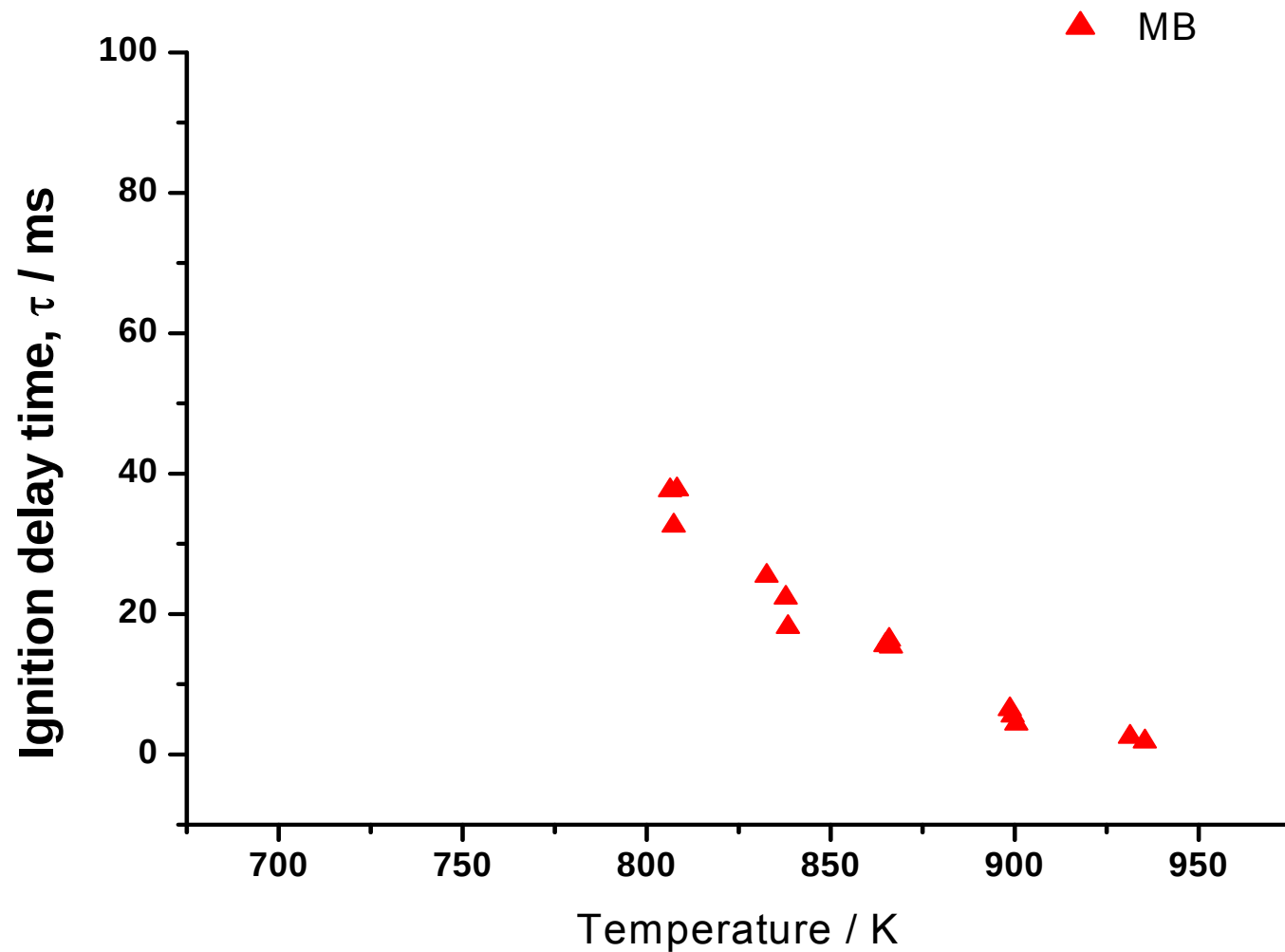






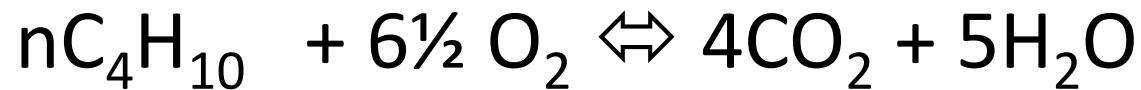
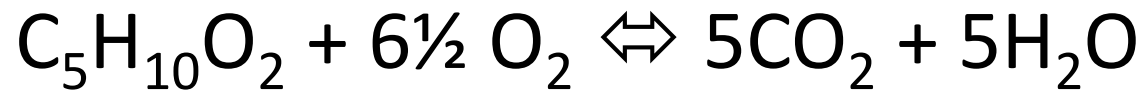
MB versus *n*-butane

RCM, Fuel/O₂/Diluent : 0.0313/0.2034/0.7653, $\phi = 1.0$ at 10 atm





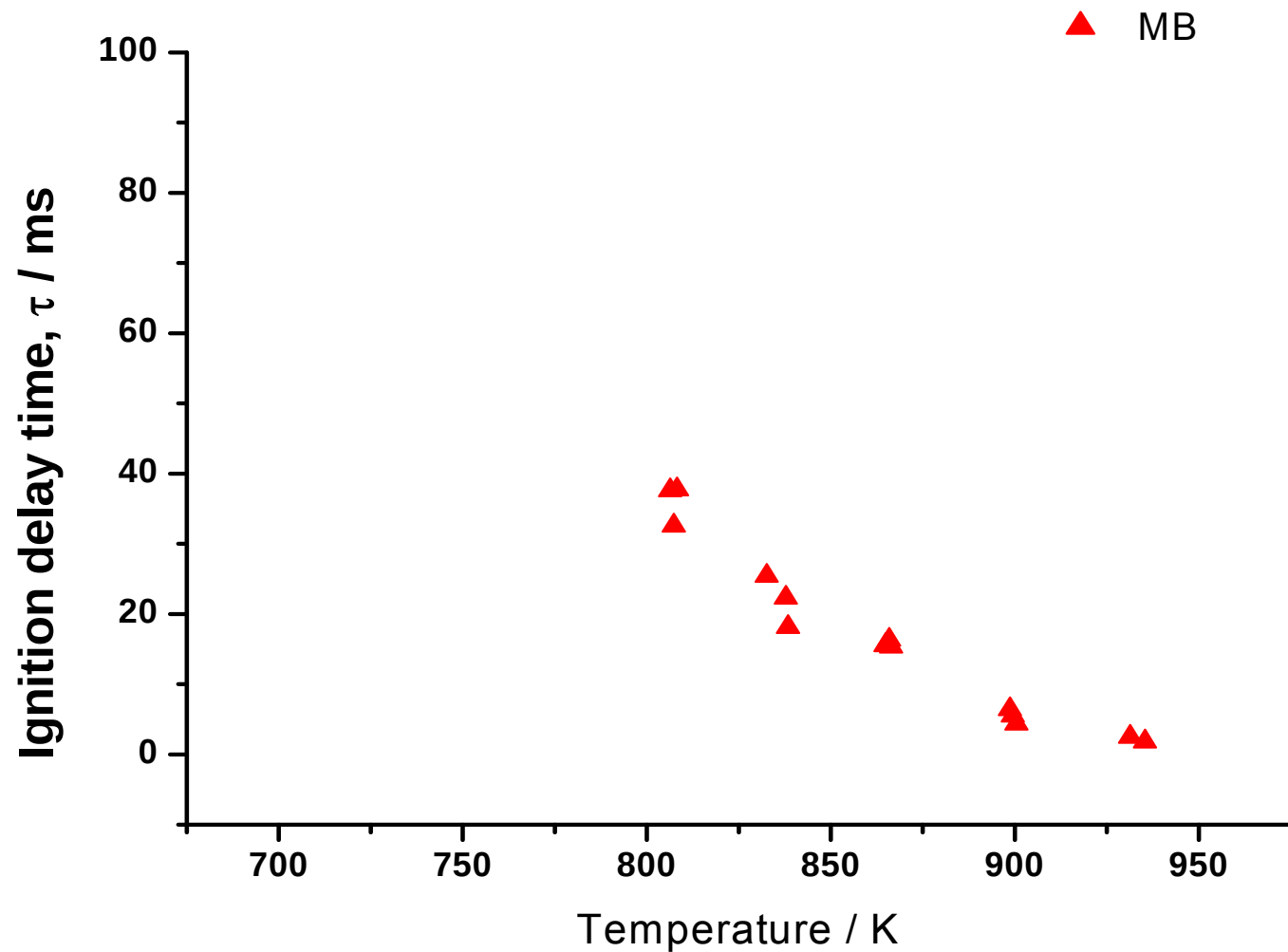
- No NTC behaviour observed for MB
- Compare to n-Butane as ϕ is common





MB versus *n*-butane

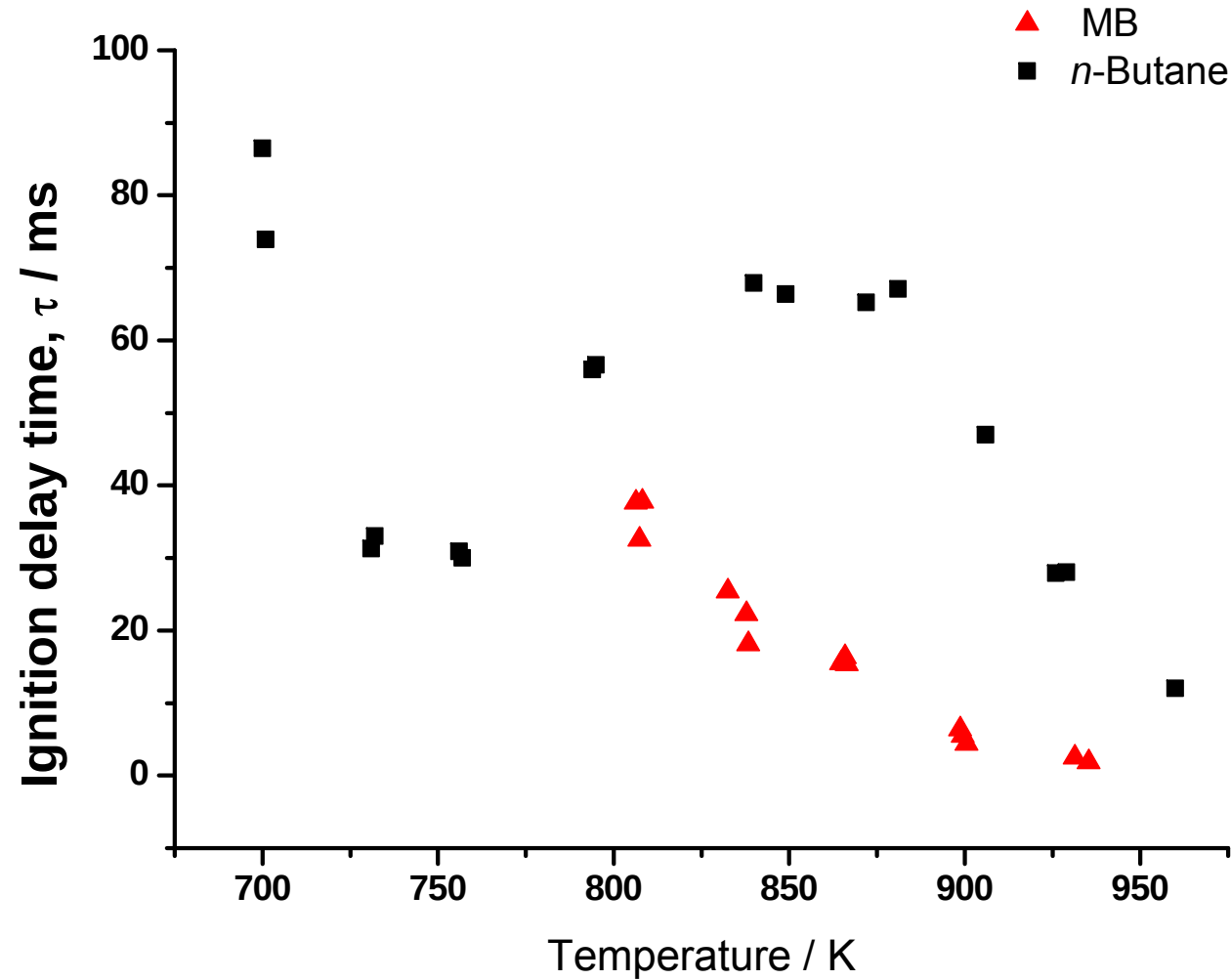
RCM, Fuel/O₂/Diluent : 0.0313/0.2034/0.7653, $\phi = 1.0$ at 10 atm





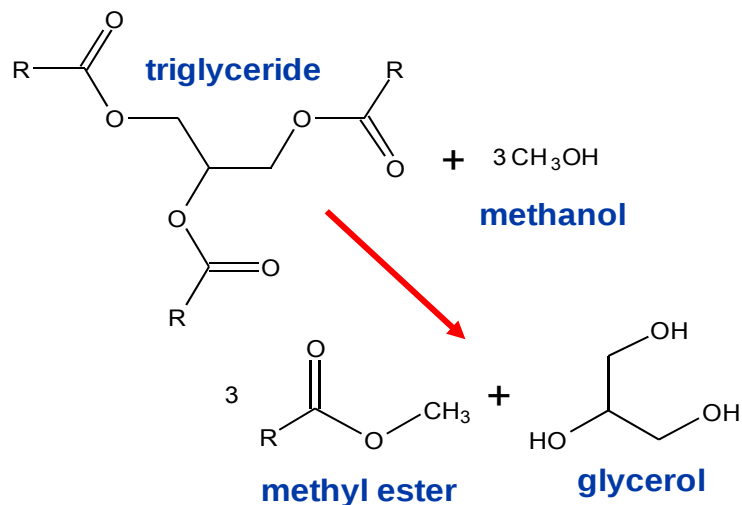
MB versus *n*-butane

RCM, Fuel/O₂/Diluent : 0.0313/0.2034/0.7653, $\phi = 1.0$ at 10 atm



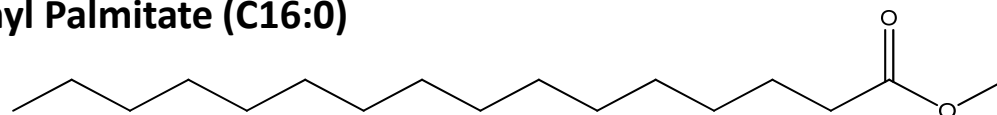


Soybean and rapeseed derived biodiesels have only 5 principal components

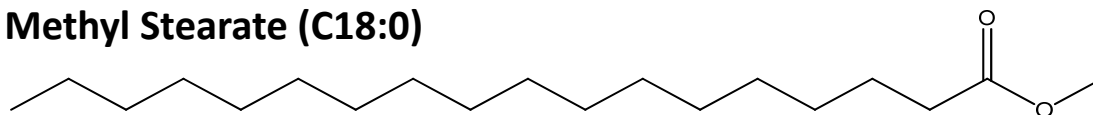


Fatty acid methyl esters (FAMES):

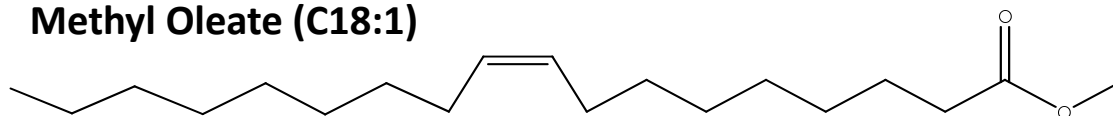
Methyl Palmitate (C16:0)



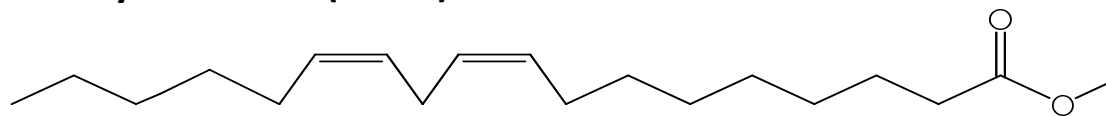
Methyl Stearate (C18:0)



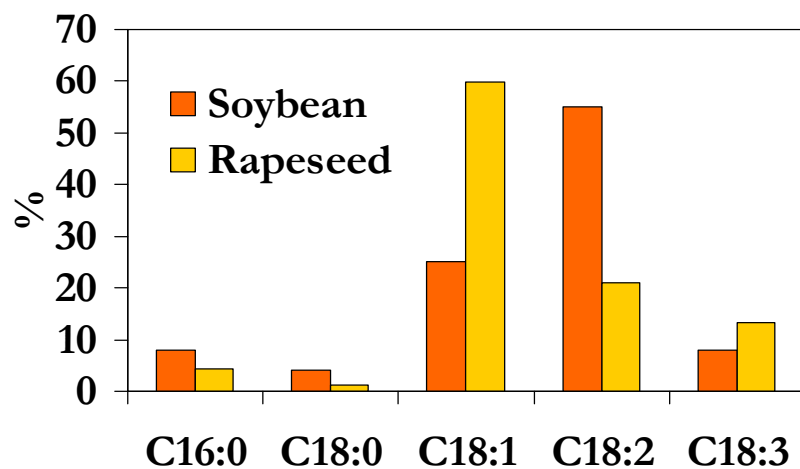
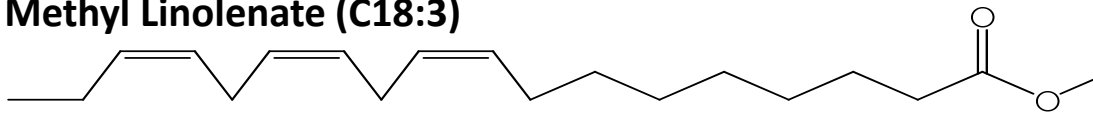
Methyl Oleate (C18:1)



Methyl Linoleate (C18:2)

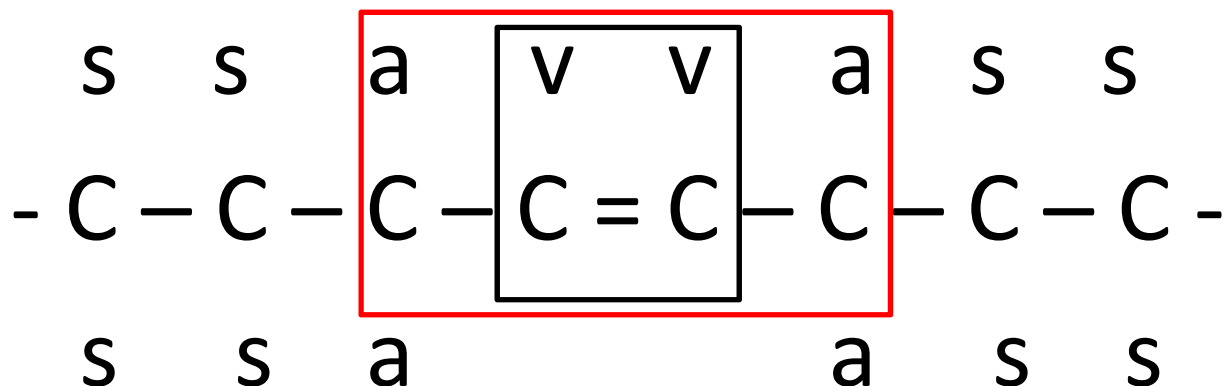


Methyl Linolenate (C18:3)





C = C double bonds reduce low T reactivity



- Inserting one C=C double bonds changes the reactivity of 4 carbons atoms in the C chain
- Allylic C – H bond sites are weaker than most others
- Therefore they are preferentially abstracted by radicals
- O₂ is also very weakly bound at allylic sites and falls off rapidly, inhibiting low T reactivity



Two double bonds make a huge difference

