TSINGHUA-PRINCETON-COMBUSTION INSTITUTE

2024 SUMMER SCHOOL ON COMBUSTION

Combustion Chemistry and Modeling

Henry Curran
University of Galway
July 07-13, 2024

Chemical Kinetic Modelling for Combustion

Prof. Henry Curran

Overview/Aims

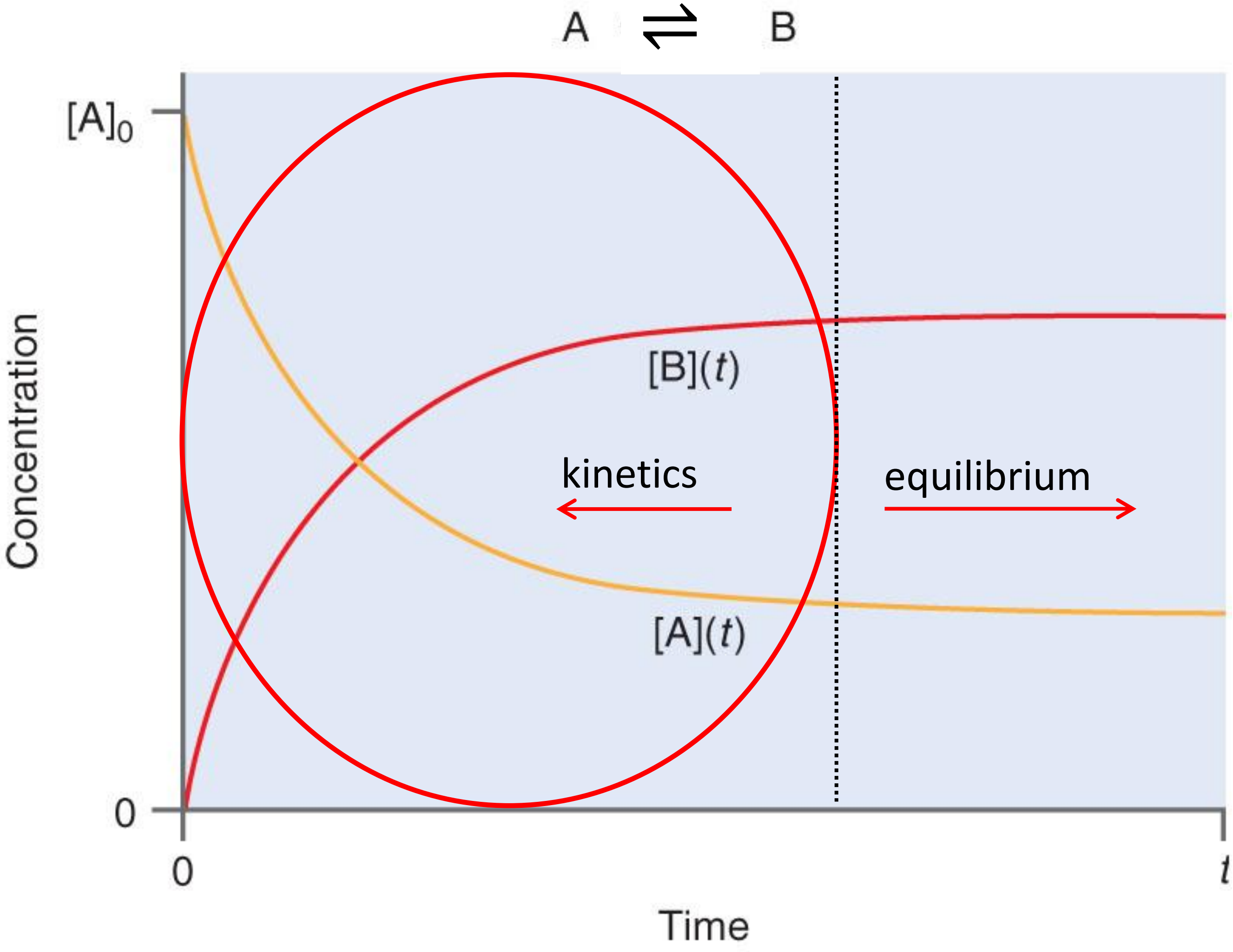
- 5 days / 15 lectures
  - Day 1
    - (1-3) Basic thermodynamic principles
  - Day 2
    - (4) Basic kinetic principles
    - (5,6) Experimental JSR, FR, RCM & ST contribution to kinetics
  - Day 3
    - (7-9) Small species mechanism development

Overview/Aims

- 5 days / 15 lectures
  - Day 4
    - (10-12) Large hydrocarbon mechanism development
  - Day 5
    - (13-15) Oxygenated hydrocarbon and ammonia mechanism development

Basic kinetic and thermodynamic principles

Kinetics and equilibrium



Thermodynamics

Properties of interest:

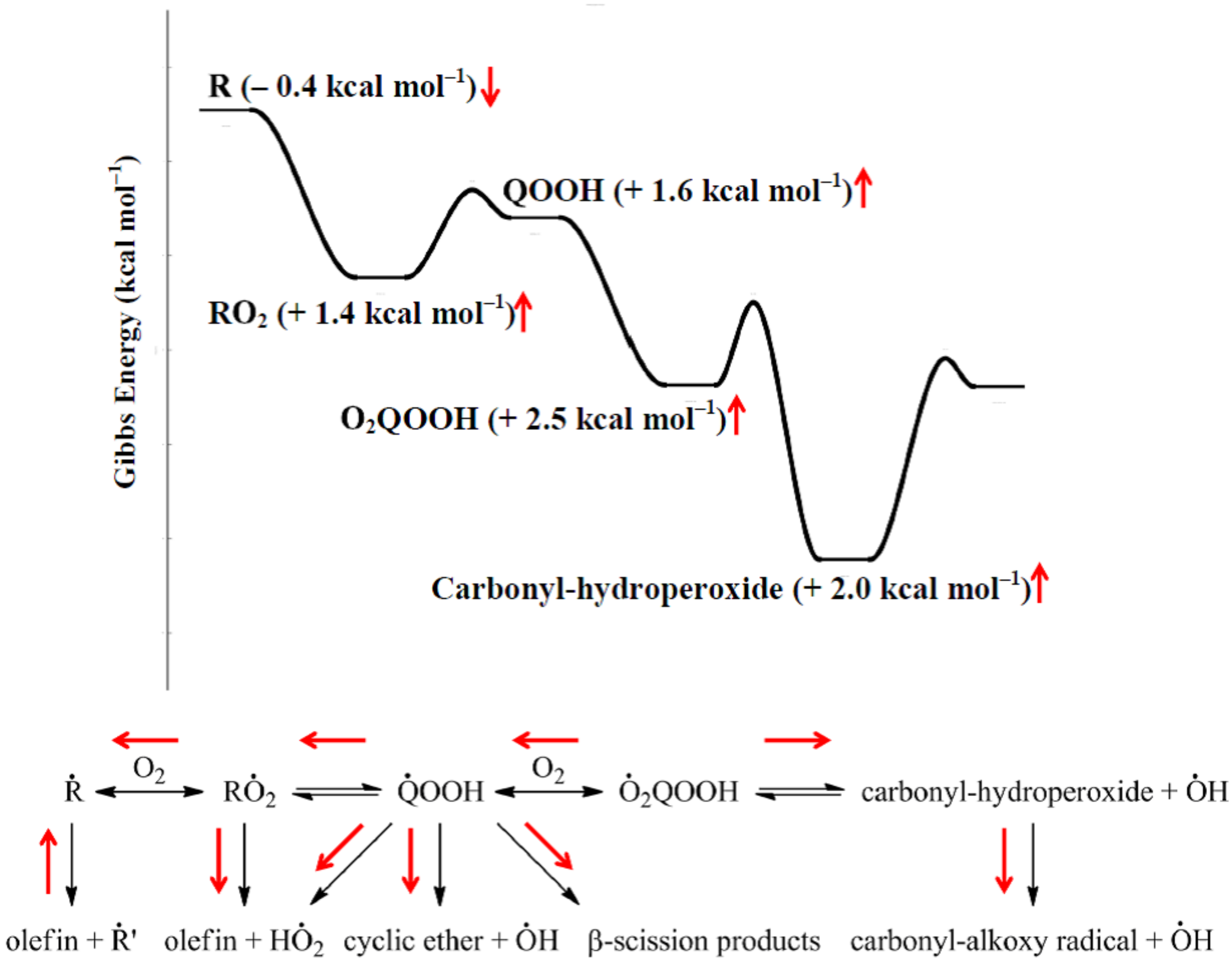
- Entropy
- Enthalpy
- Heat capacity (C_p or C_V)
  - Can be used for extrapolation of above
- Gibbs free energy: $G = H - TS$ (follows from S and H)

Why?

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

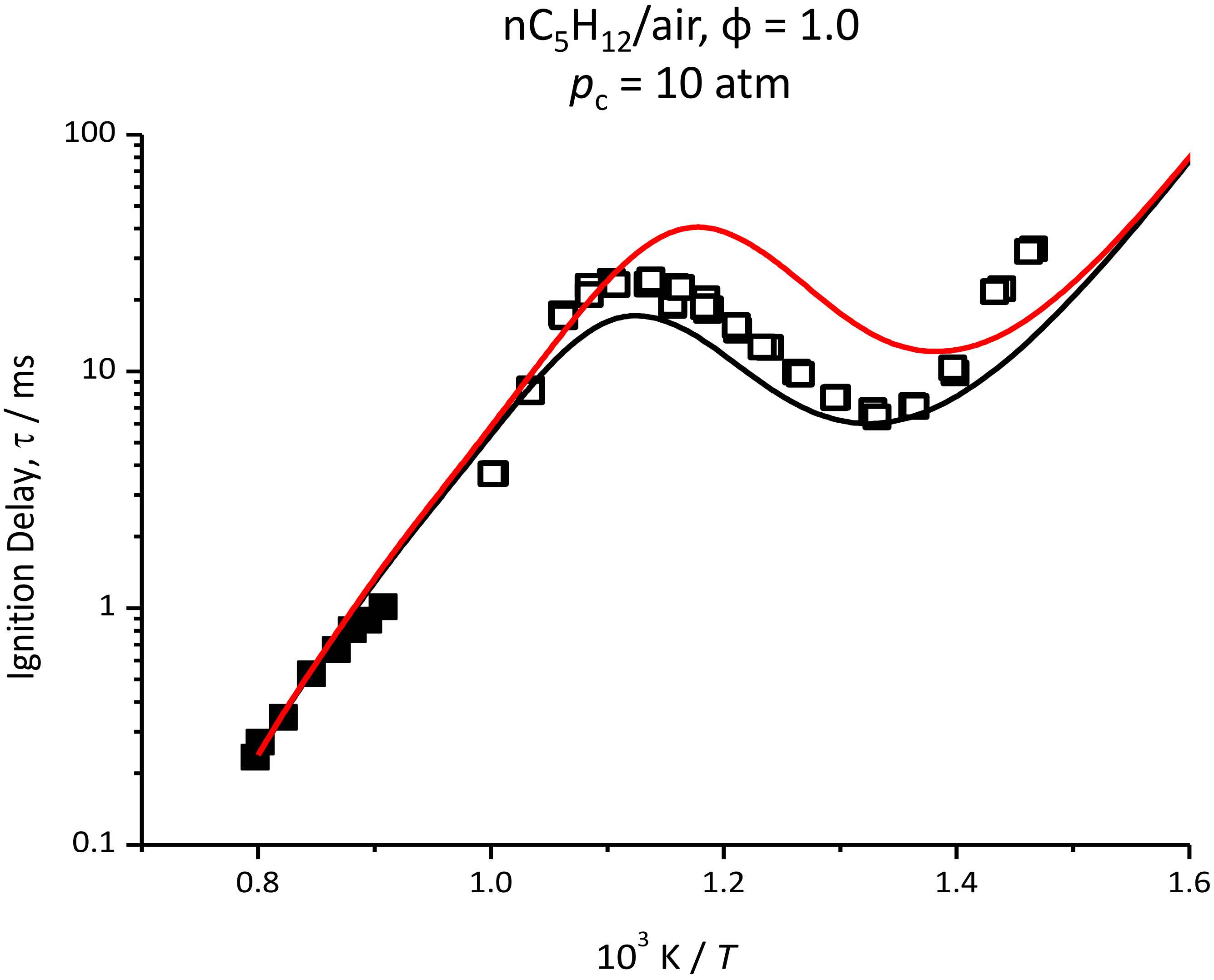
Slide courtesy of Dr. Pierre-Alexandre Glaude

Effect of thermochemistry on τ



J. Bugler et al., J. Phys. Chem. A (2015) 119(28) 7510–7527.

Effect of thermochemistry on τ



J. Bugler et al., J. Phys. Chem. A (2015) 119(28) 7510–7527.

Enthalpy of Formation

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

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

- Standard enthalpy of formation of ammonia

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

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

Slide courtesy of Dr. Pierre-Alexandre Glaude

Thermochemistry in Chemkin

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

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

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

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

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

Thermochemistry in Chemkin

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

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

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

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

Thermochemistry in Chemkin

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

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

$$\frac{H_k^o}{R} = \int_0^T \frac{C_p^o k}{R} dT = a_{1k}T + \frac{a_{2k}}{2}T^2 + \frac{a_{3k}}{3}T^3 + \frac{a_{4k}}{4}T^4 + \frac{a_{5k}}{5}T^5 + a_{6k}$$

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

e.g.: $\Delta G^o = \Delta H^o - T\Delta S^o$

Thermochemistry in Chemkin

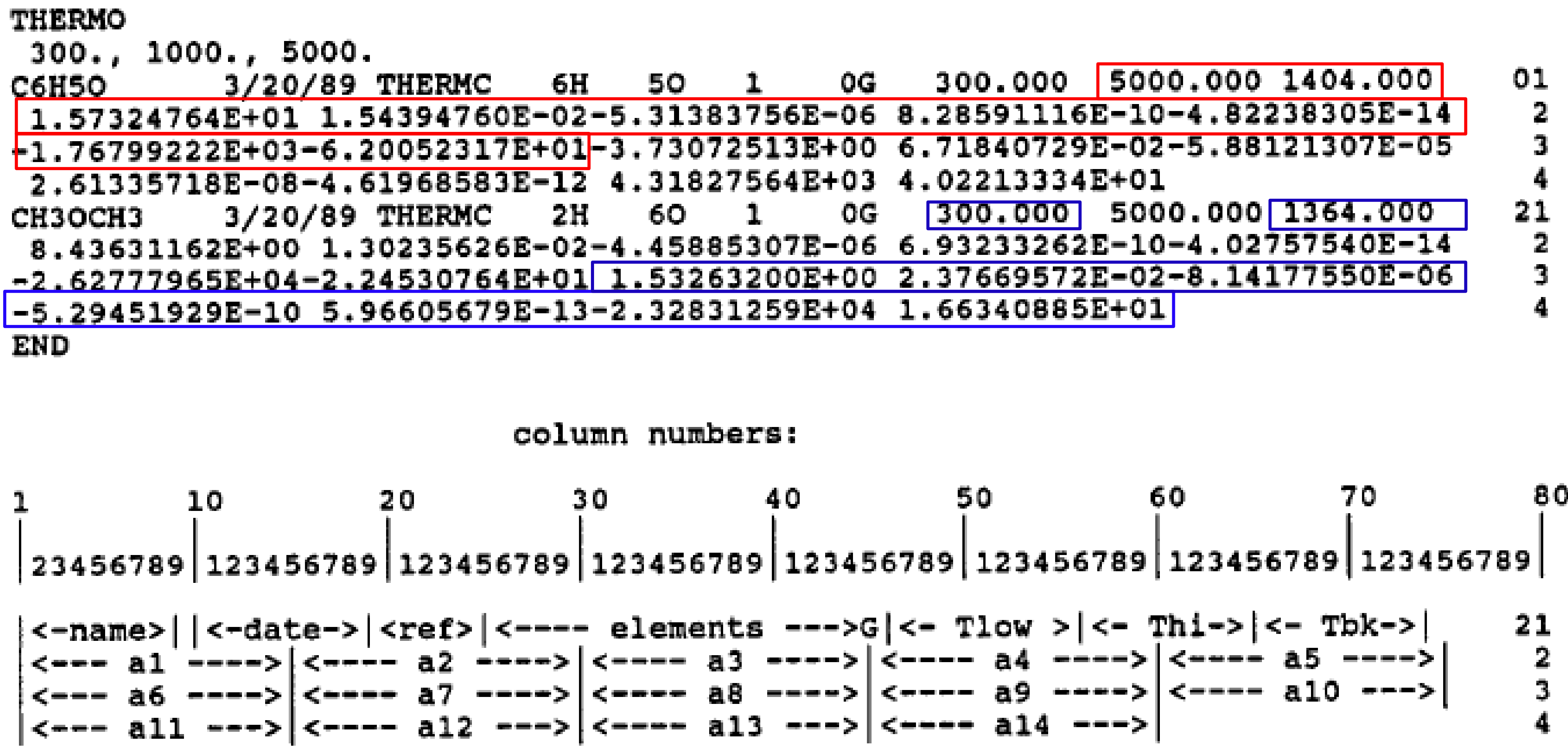
$$\frac{C_p^o k}{R} = \sum_{n=1}^{N} a_{nk} T^{(n-1)}$$

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

$$\frac{S_k^o}{R} = \int_0^T \frac{C_{p}^{o}{}_{k}}{RT} dT = a_{1k} lnT + a_{2k}T + \frac{a_{3k}}{2}T^2 + \frac{a_{4k}}{3}T^3 + \frac{a_{5k}}{4}T^4 + a_{7k}$$

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

NASA polynomials



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

```
                          column numbers:

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

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

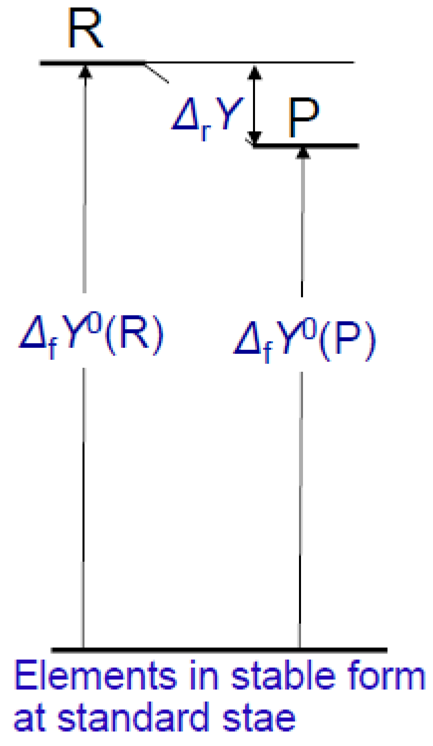
E.R. Ritter J.W. Bozzelli Intl. J. Chem. Kinet., 23 (1991) 767–778.

Thermodynamic data

$$\mathrm{R} \underset{k_{\mathrm{rev}}}{\overset{k_{\mathrm{fwd}}}{\rightleftarrows}} \mathrm{P}$$

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

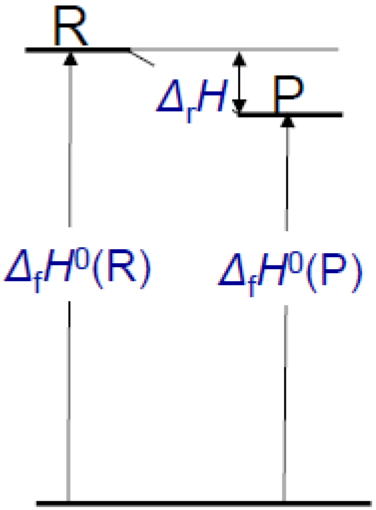
Sources of data
- Experiments
- Ab initio calculations
- Empirical schemes based on observed rules in experimental or ab initio data



$$\Delta_r Y = \Delta_f Y^0(\mathrm{P}) - \Delta_f Y^0(\mathrm{R})$$

Slide courtesy of Prof György Lendvay, Eötvös University, Budapest, Hungary

Thermodynamic data: Experimental sources

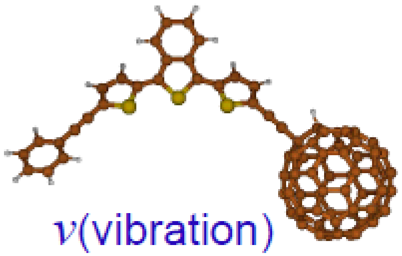


Enthalpy of formation, $\Delta_r H$
  Determine the enthalpy change of any reaction $\Delta_r H$
  Calculate enthalpy of formation from $\Delta_r H$
    and those of known reaction partners

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

Entropy of formation, $\Delta_r S$
  Rarely measured directly
    (from temperature dependence of K_r)
  Calculated from experimental molecular parameters
    using statistical thermodynamics

Specific heat capacities, C_p
  Can be measured directly for stable species
  Calculated from experimental molecular parameters
    using statistical thermodynamic



ν(vibration)
Θ(inertia)

generally simplified
formulas of statistical
thermodynamics

Slide courtesy of Prof György Lendvay, Eötvös University, Budapest, Hungary

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:

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

- Permits derivation an analytic expression as a function of *T*

Slide courtesy of Dr. Pierre-Alexandre Glaude

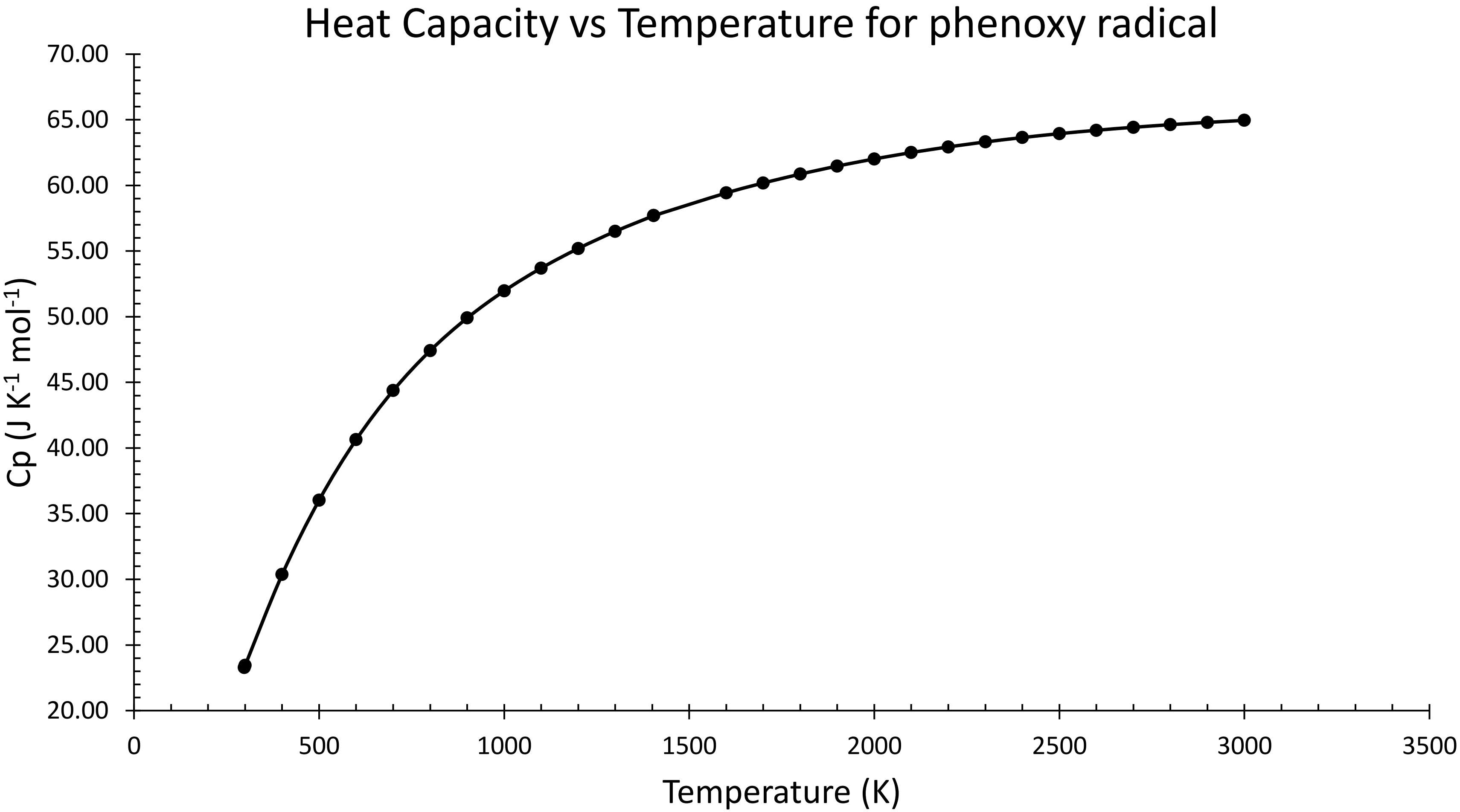
Entropy

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

$$G = H - TS$$

Slide courtesy of Dr. Pierre-Alexandre Glaude

Heat Capacity versus Temperature



Sources of thermochemical data

There is no single compendium that contains all species

Benson's Group additivity method

- ❑ THERM (Ritter and Bozzelli Int. J. Chem. Kinet. 23 (1991) 767-778.)
  - Decomposition into groups and corrections performed by user
- ❑ NIST Webbook database **Stein et al. (1991) Webbook**

  (http://webbook.nist.gov/chemistry/grp-add/)
- ❑ THERGAS **(C. Muller, V. Michel, G. Scacchi and G. M. Côme, J. Chem. Phys. 92 (1995) 1154-1177.)**
- ❑ Third Millennium Ideal Gas and Condensed Phase Database for Combustion

  Burcat and Goos (http://www.dlr.de/vt/en/desktopdefault.aspx/tabid-7603/12862_read-32379/)
- ❑ Quantum Chemistry

  Ab initio : Gaussian, Spartan, Jaguar, Molpro, ...
- ❑ Statistical rate theory
  - ChemRate, POLYRATE, Multiwell, MESS, CanTherm, MSTR

Courtesy of Dr. Pierre-Alexandre Glaude

Thermochemistry

- Active Thermochemical Tables (ATcT)[1–6] – current benchmark
  - Constructed by solving an underlying Thermochemical Network
  - Develop accurate, reliable, and internally consistent thermochemical values
  - Many experimental measurements are considered
  - Both high-level ab-initio calculations combined with ATcT approach
  - ΔH_f^0 of 348 C, N, O, and H containing species with 2σ uncertainties of ±1.0–1.5 kJ mol^{-1}
- Excellent progress for the community
- Accurate S^0 and C_p values are needed [$K_p = \exp(-\Delta G_r^0/RT)$]
- Automated comp. thermochemistry values for butane – Keceli et al.[7]
- Trade off between molecular size and accuracy of quantum calcs.
- Thus Benson's GA method still needed for larger (≥ C8) species

[1] https://atct.anl.gov/

[2] B. Ruscic et al., J. Phys. Chem. A 108 (2004) 9979–9997.

[3] B. Ruscic et al., J. Phys. Conf. Ser. 16 (2005) 561–570.

[4] B. Ruscic, Int. J. Quantum Chem. 114 (2014) 1097–1101.

[5] B. Ruscic, J. Phys. Chem. A 119 (2015) 7810–7837.

[6] S. J. Klippenstein, L. B. Harding, B. Ruscic, J. Phys. Chem. A 121 (2017) 6580–6602.

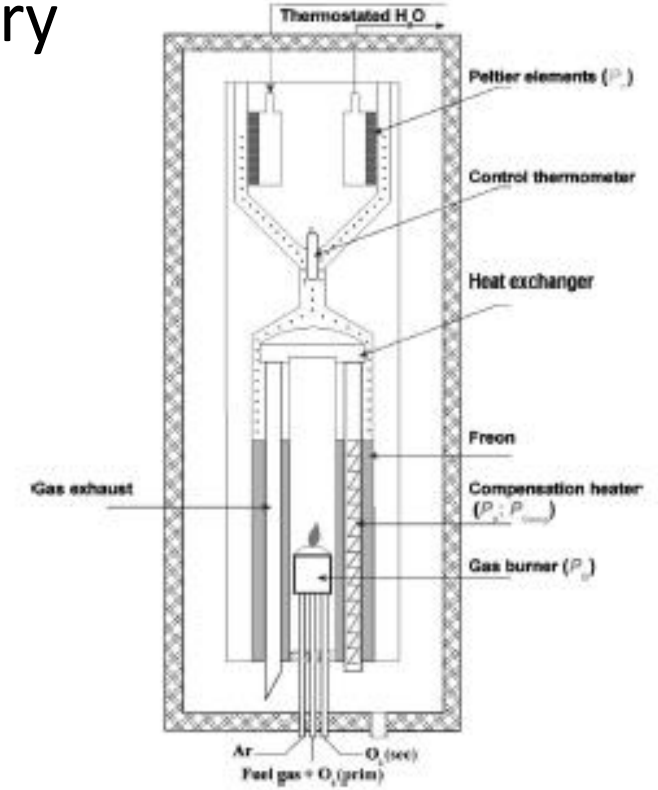
[7] M. Keçeli, S. Elliott, Y-P. Li, M.S. Johnson, C. Cavallotti, Y. Georgievskii, W.H. Green, M. Pelucchi, J.M. Wozniak, A.W. Jasper, S.J. Klippenstein, Proc. Combust. Inst. 37 (2019) 363–371.

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

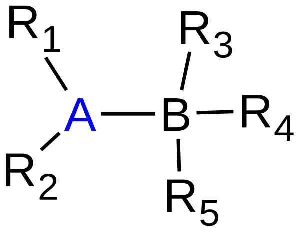
Group additivity
    within certain limits of accuracy the thermodynamic properties of properly selected groups add up to that of a molecule
    data can be borrowed from information on one or more similar molecules
    the question is the "limit of accuracy".

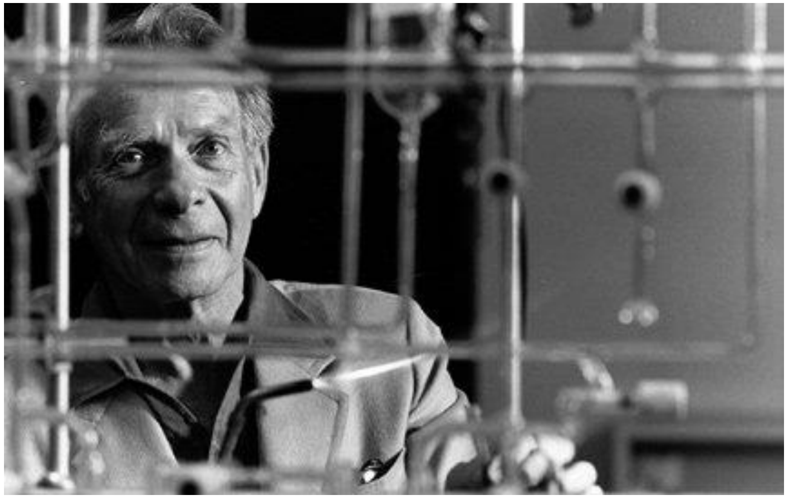
Slide courtesy of Prof György Lendvay, Eötvös University, Budapest, Hungary

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





Slide courtesy of Dr. Pierre-Alexandre Glaude

Prof. Sidney W. Benson (1918-2011)

Group Additivity

Consider Ethane:

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

$$H_3C\text{———}CH_3$$

- Thermodynamics well known
- ΔH_f^0 = –84. ± 0.4 kJ/mol (NIST)
  - Contribution of each group = –42.0 kJ/mol
- C_P 298.15 K = 52.49 J/mol (NIST)
  - Contribution of each group = 26.25 J/mol
- S^0 298.15 K = 229.28 J/mol
  - Contribution of each group.....not as simple
  - Corrections for molecular symmetry are applied

Group Additivity

Entropy calculations:

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

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

- σ = number of symmetries in the molecule = $\sigma_{ext} \times \sigma_{int}$
  - σ_{ext} number of external symmetries (rotation of molecule)
  - σ_{int} number of internal symmetries (rotations around single bonds)
- Ethane $\sigma_{ext} = 2$, $\sigma_{int} = 9$, total correction =$-$R ln(18)
- S^0 $(C/C/H3_{298.15\ K}) = (229.28 + R \ln(18))/2 = 126.65_5$ J/mol
- Similar corrections for optical isomers = +R ln(# of OI)

Group Additivity

What about free radicals?

- Estimated through definition of ‘Bond Increments’ or ‘Bond Dissociation’ values for *H, S* and C_P
- RH -> R·+ H· $\Delta_{rxn}H$ = Bond Dissociation Energy (BDE)
- $\Delta_{rxn}H\ (\mathrm{BDE}) = \Delta H_f^0(\mathrm{R}\cdot) + \Delta H_f^0(\mathrm{H}\cdot) - \Delta H_f^0(\mathrm{RH})$
- $\Delta H_f^0(\mathrm{R}\cdot) = \mathrm{BDE} + \Delta H_f^0(\mathrm{RH}) - \Delta H_f^0(\mathrm{H}\cdot)$

Varies based on type of C–H bond broken

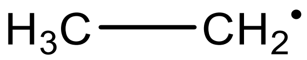
Heat of formation of ‘parent’ species

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

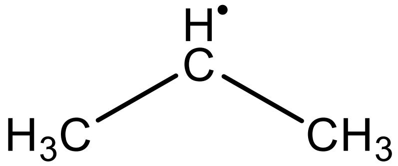
Group Additivity

BDE Groups

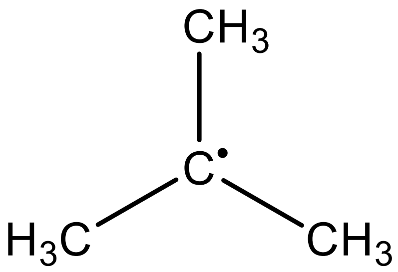
- Strength of C–H bond depends on stability of radical



Type = primary, 101.1 kcal/mol



Type = secondary, 98.45 kcal/mol

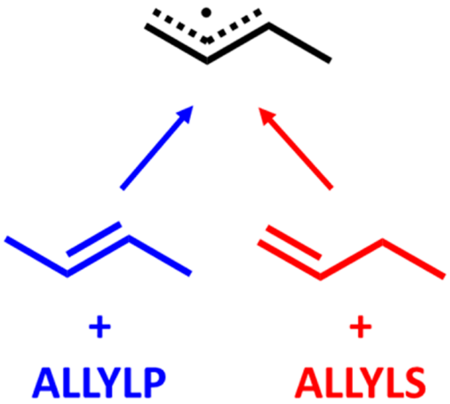


Type = tertiary, 96.50 kcal/mol

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

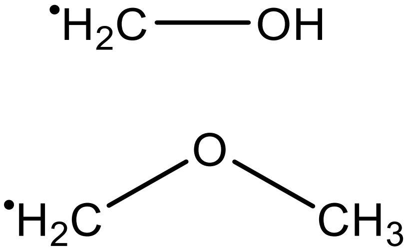
(Type = secondary allylic, 85.2 kcal/mol)

Compare with primary alkane (101.1 kcal/mol)

Group Additivity

BDE Groups

- Locally bonded electronegative atoms reduce BDE



96.2 kcal/mol

Compare with primary alkane (101.1 kcal/mol)

Group Additivity

Can be applied to:

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

Groups and super-atoms

Atom differentiation according to the type of liaison

C: sp^3 carbon atom, 4 single bonds

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

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

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

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

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

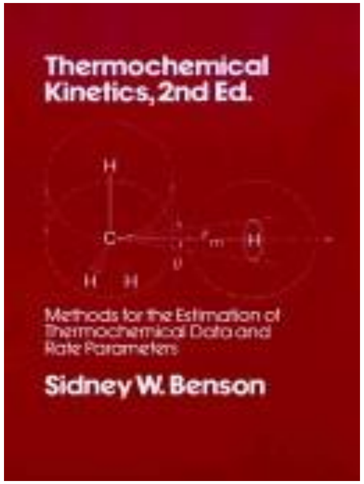
Super-atoms:

C=O, carbonyl group ≡ (CO) divalent

NO, NO_2, SO_2, PO…

Slide courtesy of Dr. Pierre-Alexandre Glaude

Benson’s groups



Thermochemical Kinetics, 2nd Ed.

Methods for the Estimation of Thermochemical Data and Rate Parameters

Sidney W. Benson

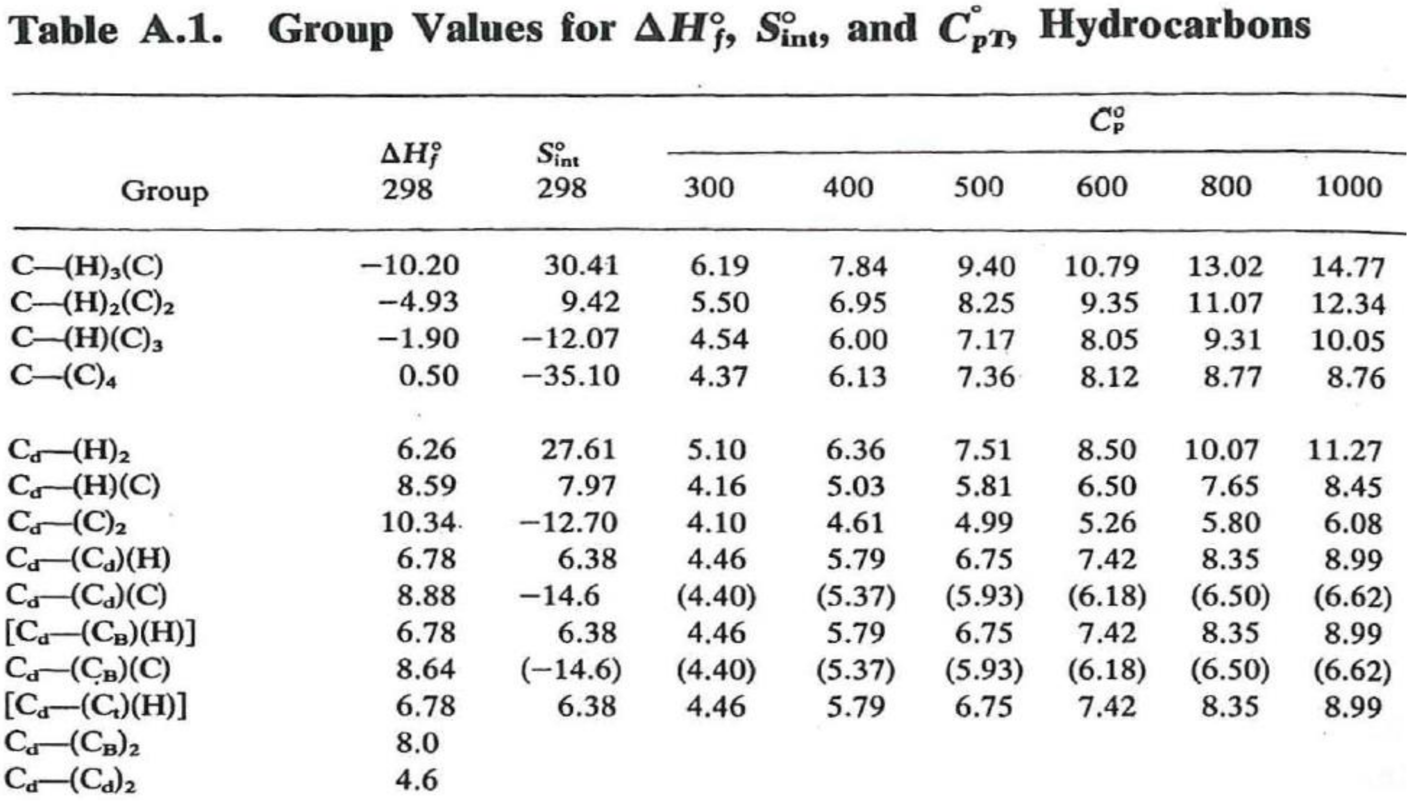
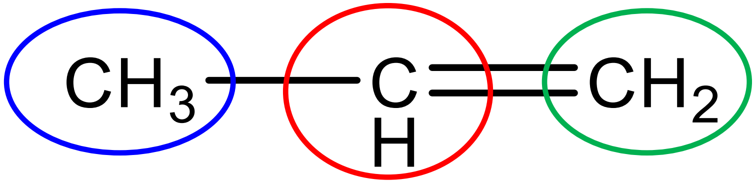


Table A.1. Group Values for ΔH°_f, S°_{int}, and C°_{pT}, Hydrocarbons

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							

Slide courtesy of Dr. Pierre-Alexandre Glaude

Propene



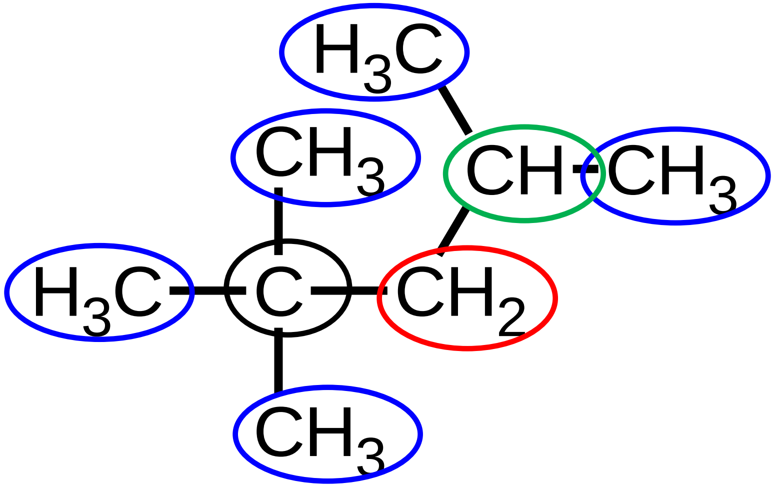
$CH_3-\underset{H}{C}=CH_2$

C/CD/H3	1 group
CD/C/H	1 group
CD/H2	1 group

Slide courtesy of Dr. Pierre-Alexandre Glaude

Group Additivity

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

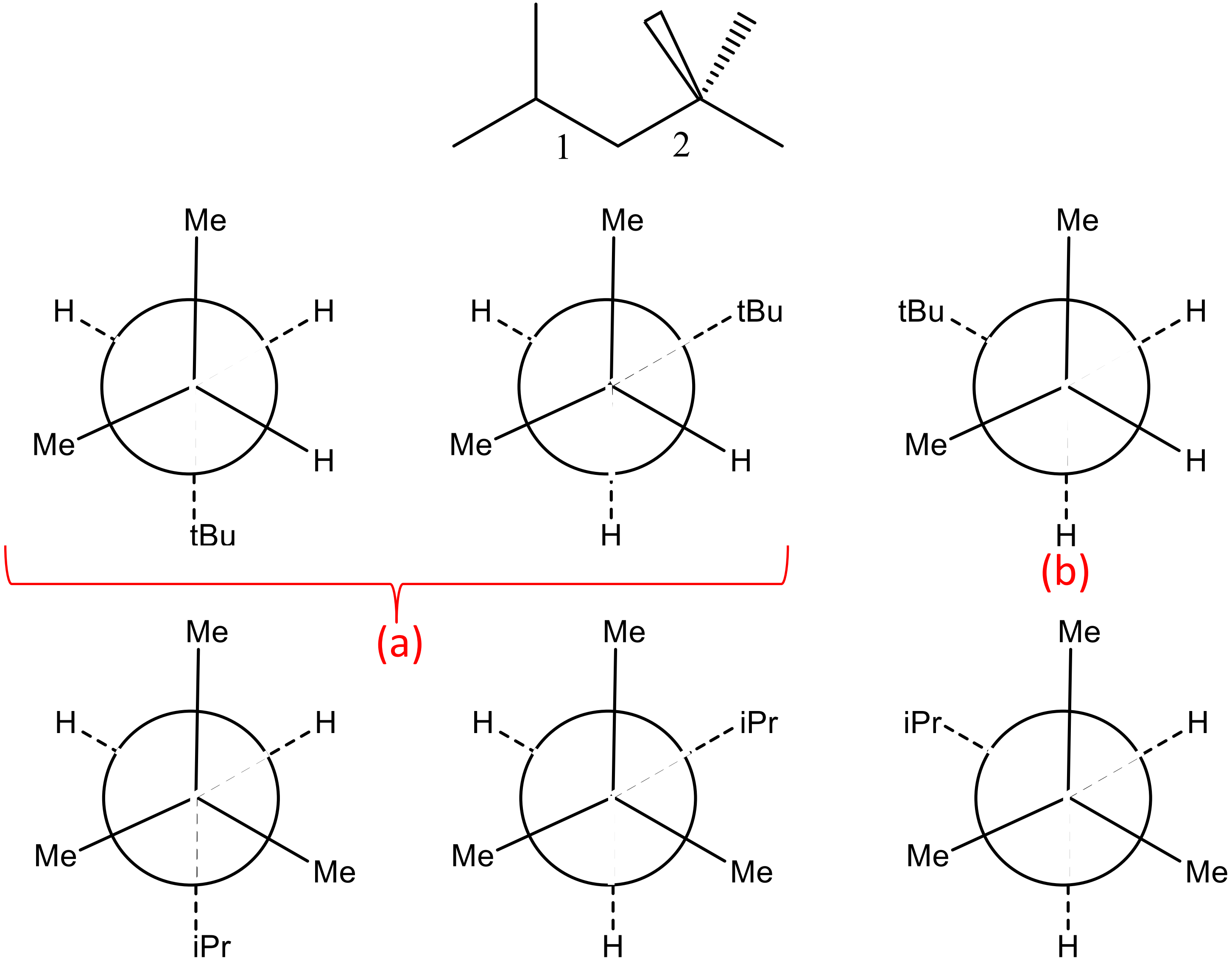


C/C/H3	5 groups
C/C2/H2	1 group
C/C3/H	1 group
C/C4	1 group

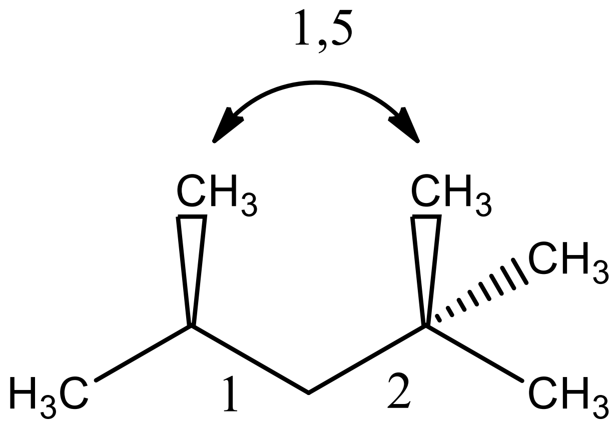
$\sigma_{ext} = 1$, $\sigma_{int} = 729$
Correction to symmetry
$-R \ln(729) = -13.1$ cal/mol/K

Slide courtesy of Dr. Pierre-Alexandre Glaude

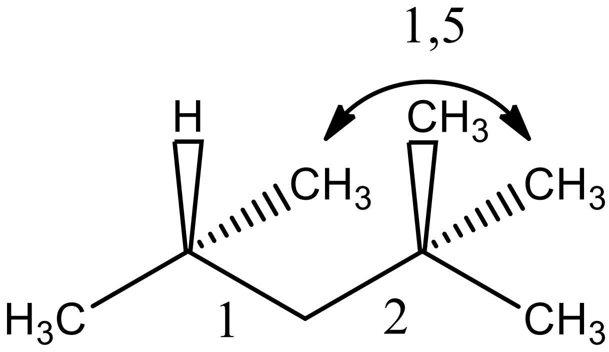
Gauche (C–C) interactions



1,5 (H–H) Interaction



or



1.5 kcal/mol

Group additivity in action

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

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

Software

Benson's Additivity Method

THERM Ritter and Bozzelli Int. J. Chem. Kinet. 23 (1991) 767-778.

Decomposition into groups and corrections done by the user

NIST database program Stein et al. (1991) Webbook

(http://webbook.nist.gov/chemistry/grp-add/)

THERGAS C. Muller, V. Michel, G. Scacchi and G. M. Côme, J. Chem. Phys. 92 (1995) 1154-1177.

CRANIUM : groups of Joback, estimation of other properties

(T_{eb}, T_{fus}, T_c, P_c...)

(http://www.molknow.com/Online/Estimation.htm)

Quantum Chemistry softwares

Semi-empirical approach: MOPAC...

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

Slide courtesy of Dr. Pierre-Alexandre Glaude

Thermochemistry in general

- Discrepancies in literature thermodynamics are large, even for foundational species
- Thermodynamics underpin kinetics
- $\Delta G = \Delta H - T\Delta S$
- Equilibrium constant linked to forward/reverse rate constant:
  - $K_{eq} = \exp(-\Delta_r G/RT) = k_f/k_r$ (be careful of Δn)
- Rate constant determined by "frequency factor" + "barrier", but:
  - $k = A\exp(-E_a/RT)$
  - $k = (k_B T/h)\exp(-\Delta^{\ddagger} G/RT)$ (Thermodynamic formulation of TST)
  - $k = (k_B T/h)\exp(\Delta^{\ddagger} S/R)\exp(-\Delta^{\ddagger} H/RT)$
  - Frequency factor *A* -> "collision factor" -> entropy factor
  - Activation Energy *Ea* -> Boltzmann factor -> enthalpy factor
  - **$k = AT^n\exp(-E_a/RT)$ -> modified Arrhenius just a fit to $k(T)$**
    - **If *n* is large, *A* and E_a are just fitting parameters**

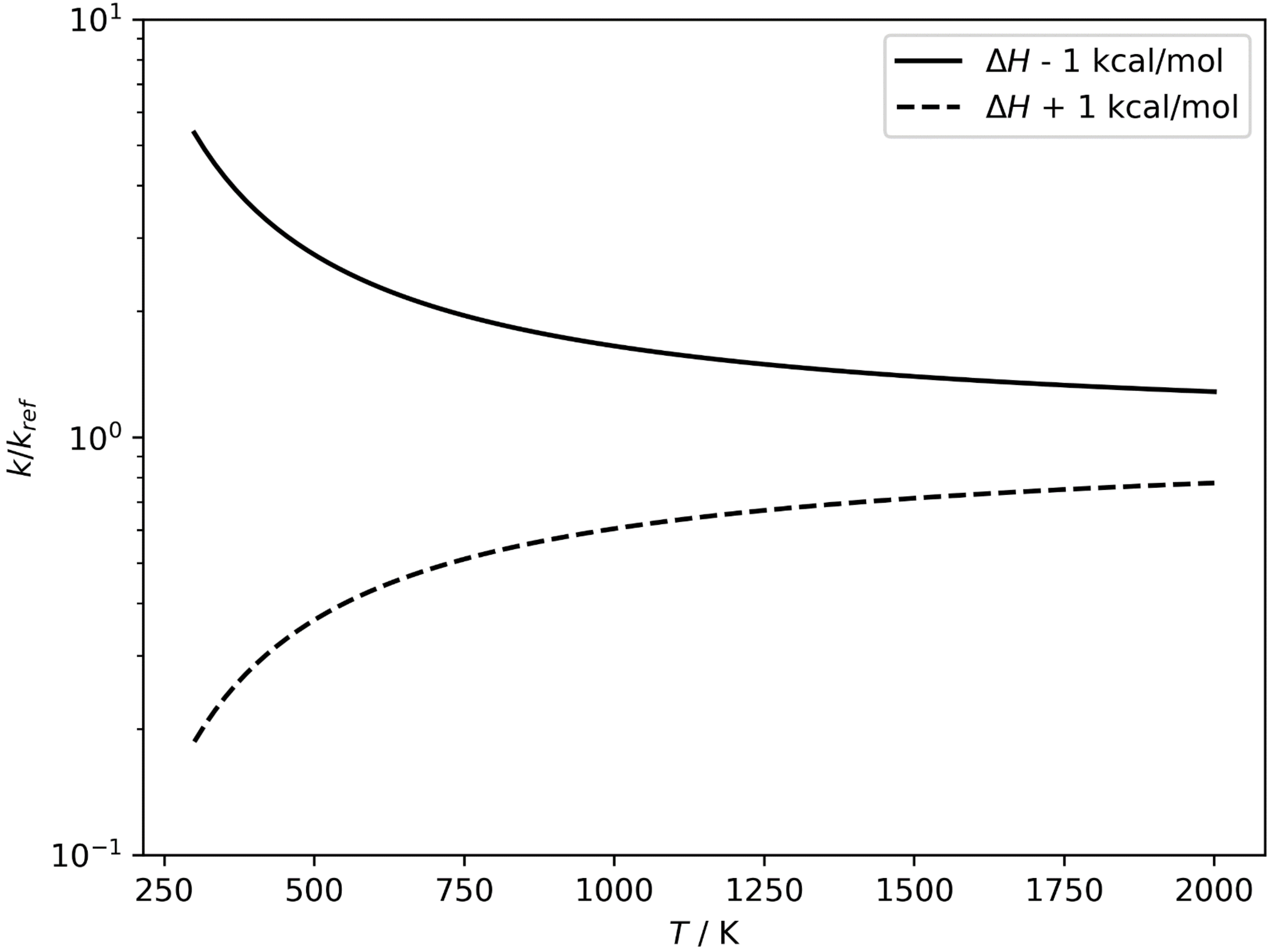
Slide courtesy of Dr. Kieran Somers

Thermochemistry in general

- $\Delta G = \Delta H - T\Delta S$ -> Gibbs changes determine spontaneity
- Enthalpy changes measured in kcal/mol
- Entropy changes measured in cal/K/mol
  - 1000 times smaller, but dependent on temperature
  - At 1000 K 1 cal/K/mol equivalent to 1 kcal/mol in ΔG
- At low temperatures ΔG dominated by enthalpy
- At high temperatures changes in ΔS dominate
- Separate the variables to test the effect:
  - Boltzmann factor = $\exp(-\Delta^{\ddagger}H/RT)$
  - Entropy factor = $\exp(\Delta^{\ddagger}S/R)$

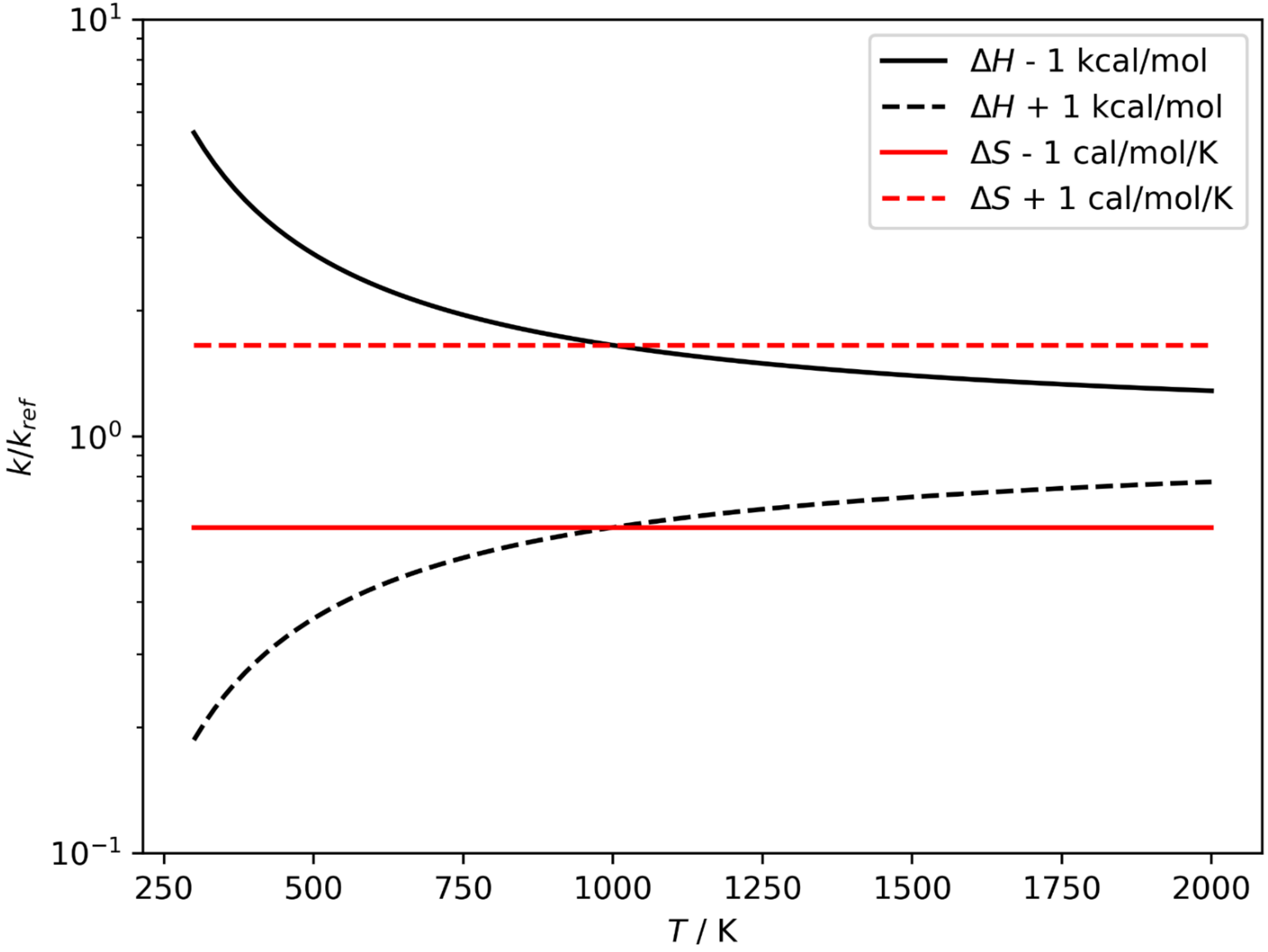
Slide courtesy of Dr. Kieran Somers

Thermochemistry in general



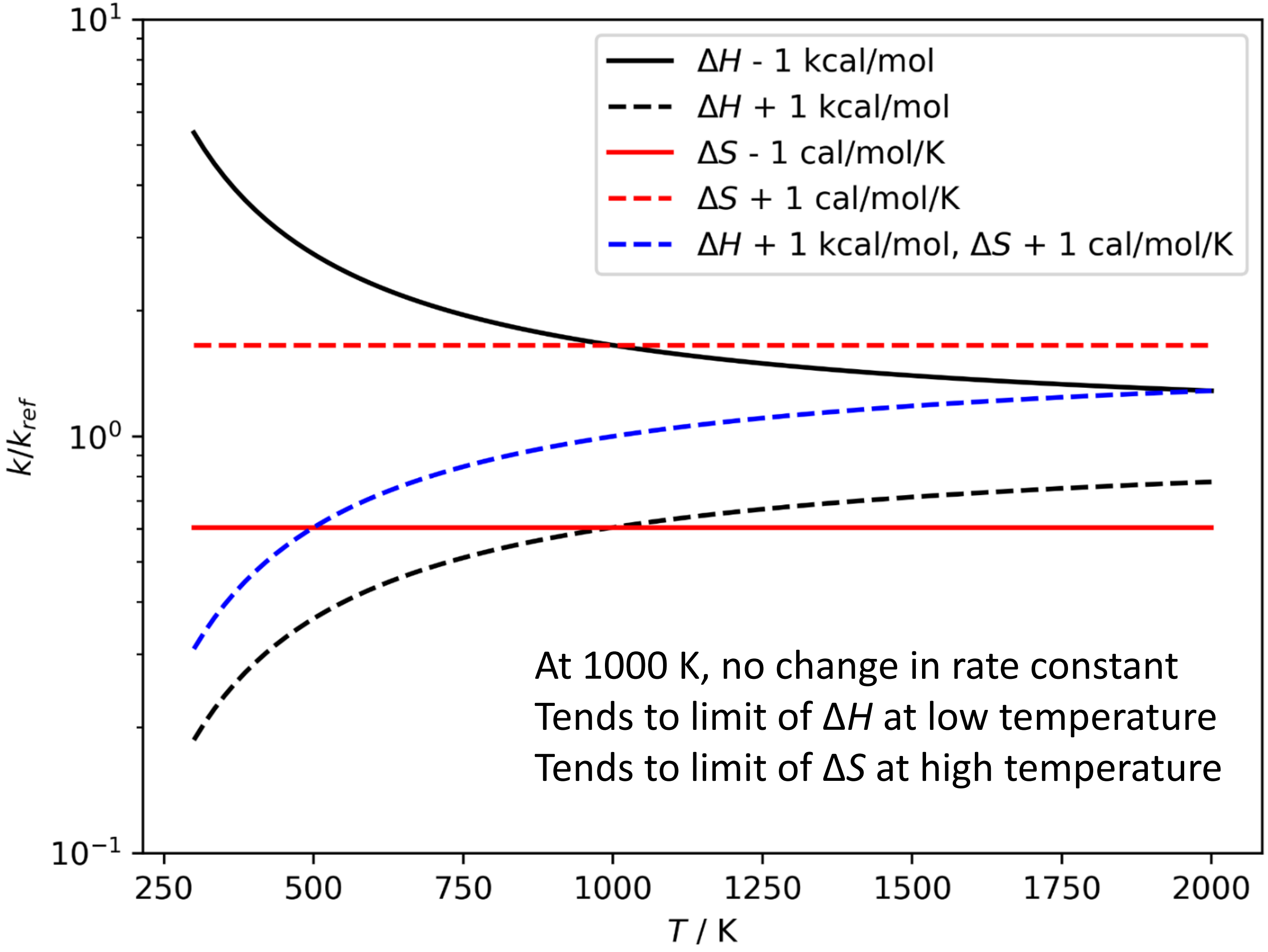
Slide courtesy of Dr. Kieran Somers

Thermochemistry in general



Slide courtesy of Dr. Kieran Somers

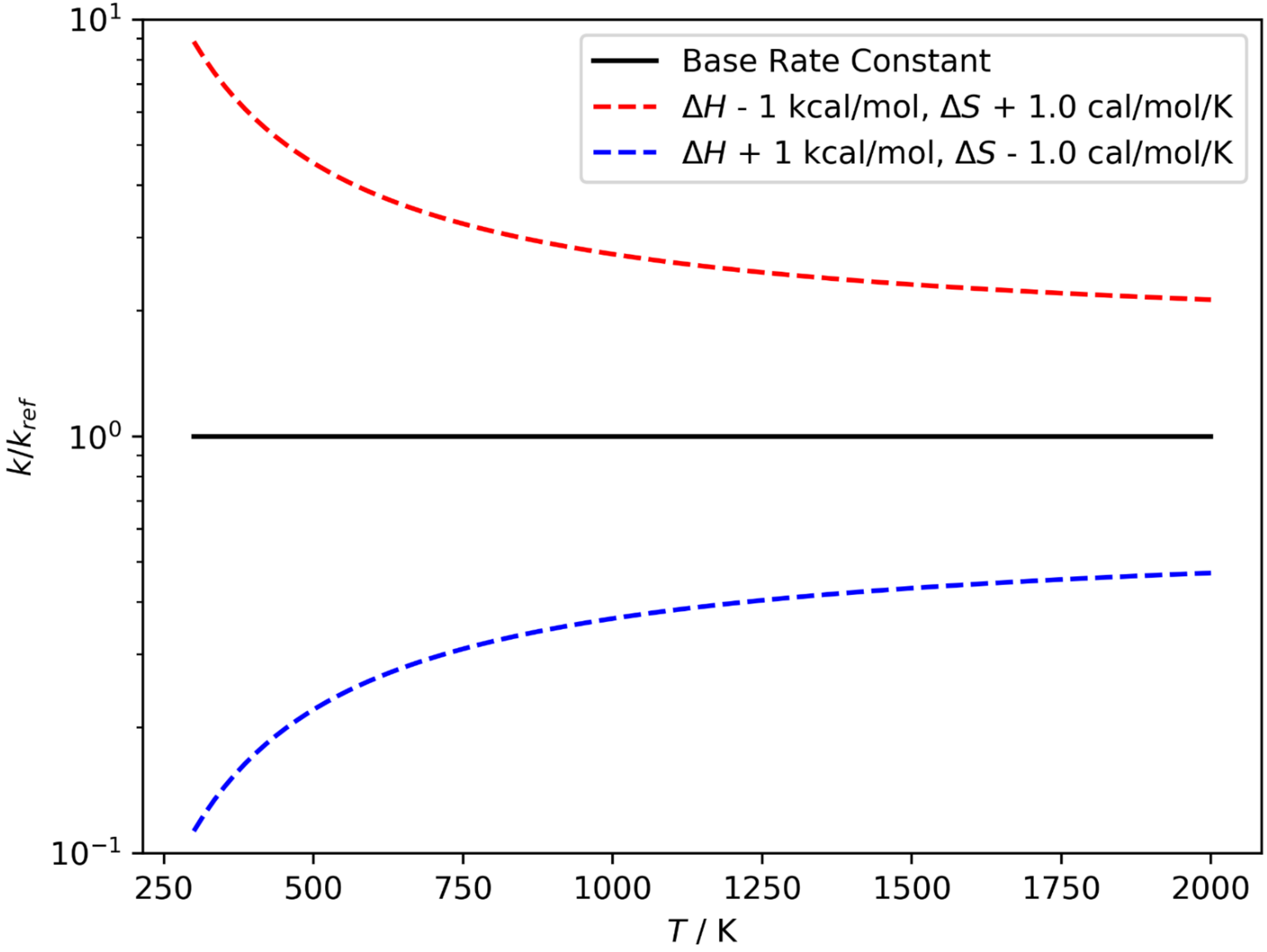
Thermochemistry in general



At 1000 K, no change in rate constant
Tends to limit of ΔH at low temperature
Tends to limit of ΔS at high temperature

Slide courtesy of Dr. Kieran Somers

Thermochemistry in general



Slide courtesy of Dr. Kieran Somers

Thermochemistry in general

- Changing species thermodynamics/rate constants effectively changes $\Delta_r G$ and K_{eq}, and/or $\Delta^{\ddagger}G$.
- Understanding which factor you are changing, and why, is crucial
- Changing E_a by a constant amount has a temperature dependent response
- Changing frequency factor by a constant factor equivalent to increasing or decreasing entropy of activation by a constant amount
- Changing both can you give temperature-dependent control
- Changing thermodynamics leads to same responses in equilibrium constant, and therefore the reverse rate constant
- Minimum uncertainties: 1 kcal/mol in enthalpy,1 cal/mol/K in entropy

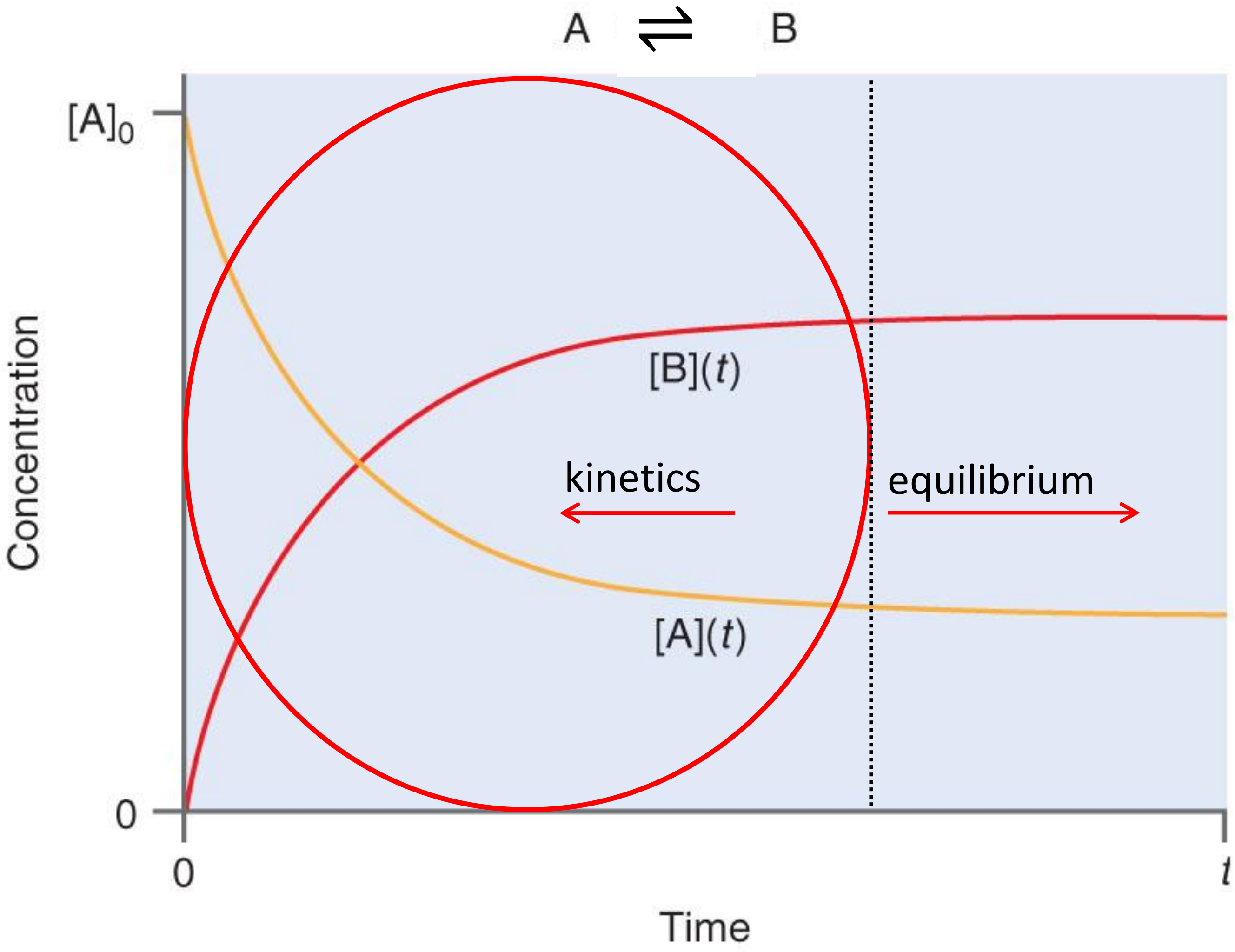
Slide courtesy of Dr. Kieran Somers

Basic Chemical Kinetic Principles I

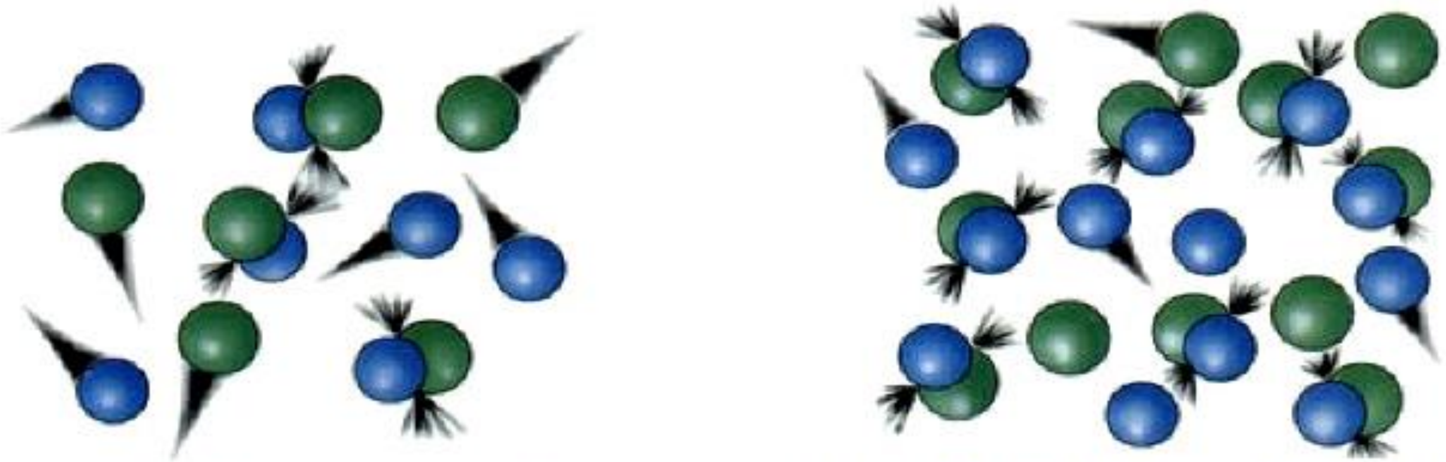
Chemical Kinetics

- 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



Rate of reaction depends on concentration of reactants



Low concentration = Few collisions High concentration = More collisions

rate $\propto$ concentration

rate = k $\times$ concentration

k: rate constant

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

$$\mathbf{5Br^- + BrO_3^- + 6H^+ = 3Br_2 + 3H_2O}$$

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

$$-(1/5)(d[Br^-]/dt) = -d[BrO_3^-]/dt = -(1/6)(d[H^+]/dt)$$

$$= (1/3)(d[Br_2]/dt) = (1/3)(d[H_2O]/dt)$$

Rate law? *Comes from experiment*

$$\text{Rate} = k\ [Br^-]^\alpha[BrO_3^-]^\beta[H^+]^\gamma$$

$$\text{Rate} = k[Br^-][BrO_3^-][H^+]^2$$

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

Rate of reaction

Stoichiometric equation

$$\mathbf{mA + nB = pX + qY}$$

$$\text{Rate} = k \times [A]^{\alpha}[B]^{\beta}$$

- **Rate = – (1/m) d[A]/dt**
- **= – (1/n) d[B]/dt**
- **= + (1/p) d[X]/dt**
- **= + (1/q) d[Y]/dt**

– Units: (concentration/time)

– in SI mol/m^3/s, more practically mol dm^{-3} s^{-1}

Rate Law

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

$$mA + nB = pX + qY$$

The Rate Law equation

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

Experimental rate laws?

$$CO + Cl_2 \rightarrow COCl_2$$

- Rate = k $[CO][Cl_2]^{1/2}$
  - Order = 1.5 or one-and-a-half order

$$H_2 + I_2 \rightarrow 2HI$$

- Rate = k $[H_2][I_2]$
  - Order = 2 or second order

$$H_2 + Br_2 \rightarrow 2HBr$$

- Rate = k $[H_2][Br_2] / (1 + k' \{[HBr]/[Br_2]\})$
  - Order = *undefined* or none

Determining the Rate Law

- **Integration**
  - Trial & error approach
  - Not suitable for multi-reactant systems
  - Most accurate
- **Initial rates**
  - Best for multi-reactant reactions
  - Lower accuracy
- **Flooding or Isolation**
  - Composite technique
  - Uses integration or initial rates methods

First-order reaction

$\mathrm{aA} \longrightarrow \text{products}$

$$-\frac{\mathrm{d[A]}}{\mathrm{dt}} \propto \mathrm{[A]^a} \quad \text{where } [A] = \frac{\mathrm{n_A}}{\mathrm{V}}\text{; assume V = 1}$$

$$-\frac{\mathrm{d[A]}}{\mathrm{dt}} = \mathrm{k\,[A]^a}$$

$$\frac{\mathrm{d[A]}}{\mathrm{[A]^1}} = -\mathrm{k\,.\,dt}$$

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

$$\mathrm{ln[A]}\Big|_{\mathrm{[A]_0}}^{\mathrm{[A]_t}} = -\mathrm{kt}$$

First-order reaction

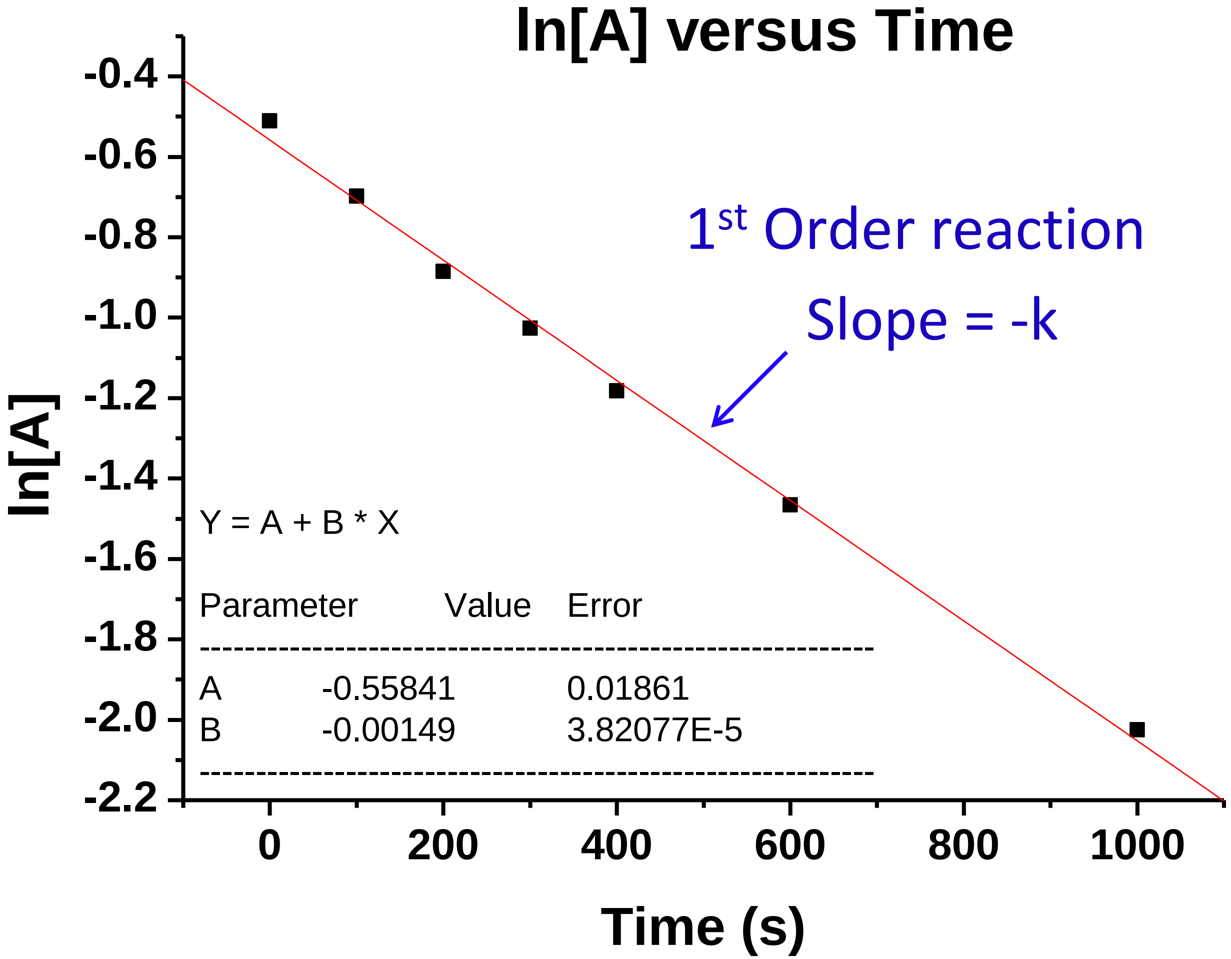
$$\ln[A]_t - \ln[A]_0 = -k_A(t - t_0)$$

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

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

Integrated rate equation

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



Y = A + B * X

Parameter	Value	Error
A	-0.55841	0.01861
B	-0.00149	3.82077E-5

1st Order reaction

Slope = -k

First-order reaction

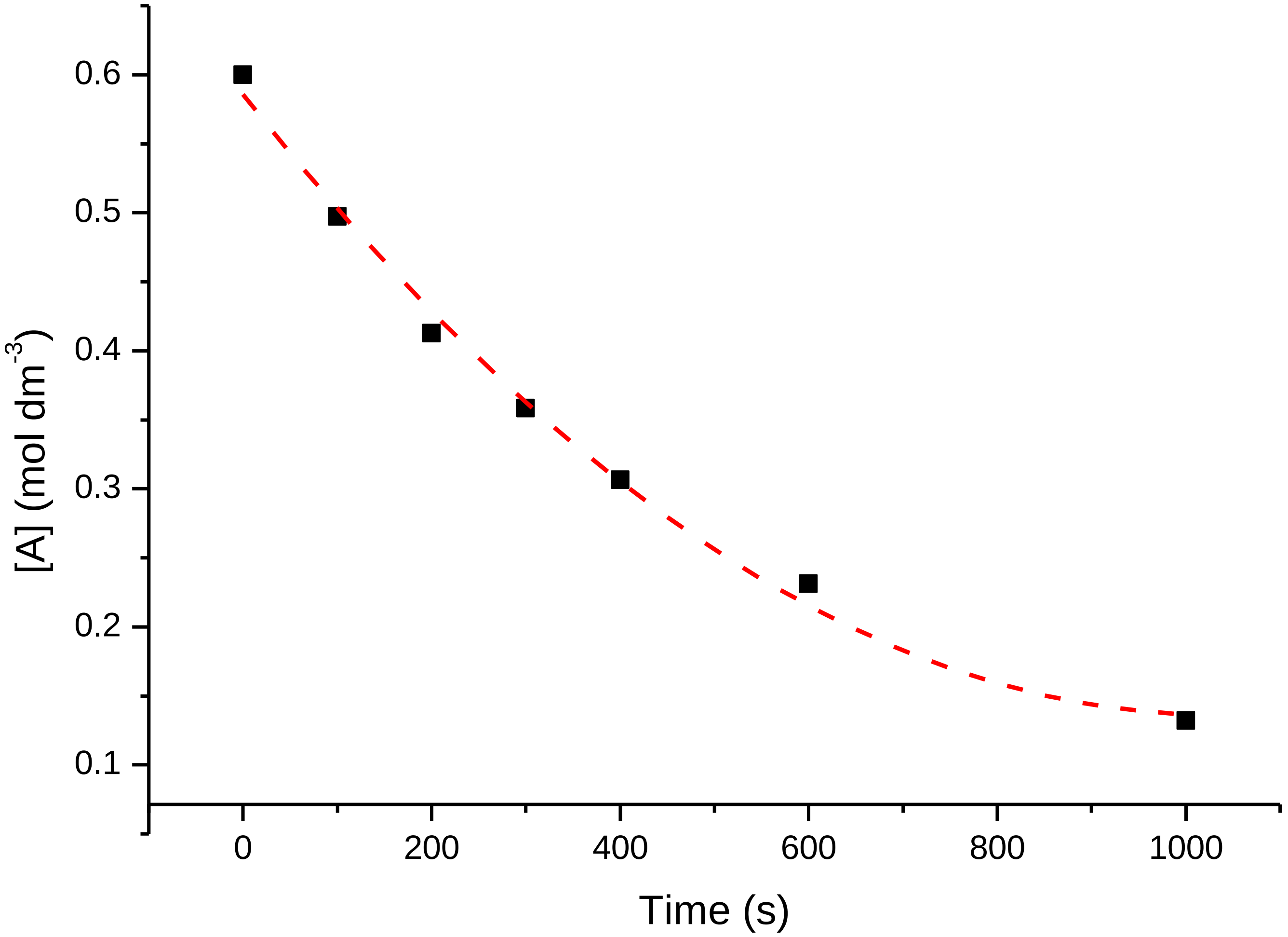
$$\ln[A]_t - \ln[A]_0 = -k_A(t - t_0)$$

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

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

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

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



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 $[A]_t = \frac{1}{2}[A]_0$ 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

aA → products

$$-\frac{d[A]}{dt} \propto [A]^a \quad \text{where } [A] = \frac{n_A}{V}\text{; assume } V = 1$$

$$-\frac{d[A]}{dt} = k\,[A]^a$$

$$\frac{d[A]}{[A]^2} = -k\,.\,dt$$

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

$$-\frac{1}{[A]}\Bigg|_{[A]_0}^{[A]_t} = -k(t - t_0)$$

Second-order reaction

$$-\frac{1}{[\mathrm{A}]_\mathrm{t}}-\left(-\frac{1}{[\mathrm{A}]_0}\right)=-\mathrm{k}(\mathrm{t}-\mathrm{t}_0)$$

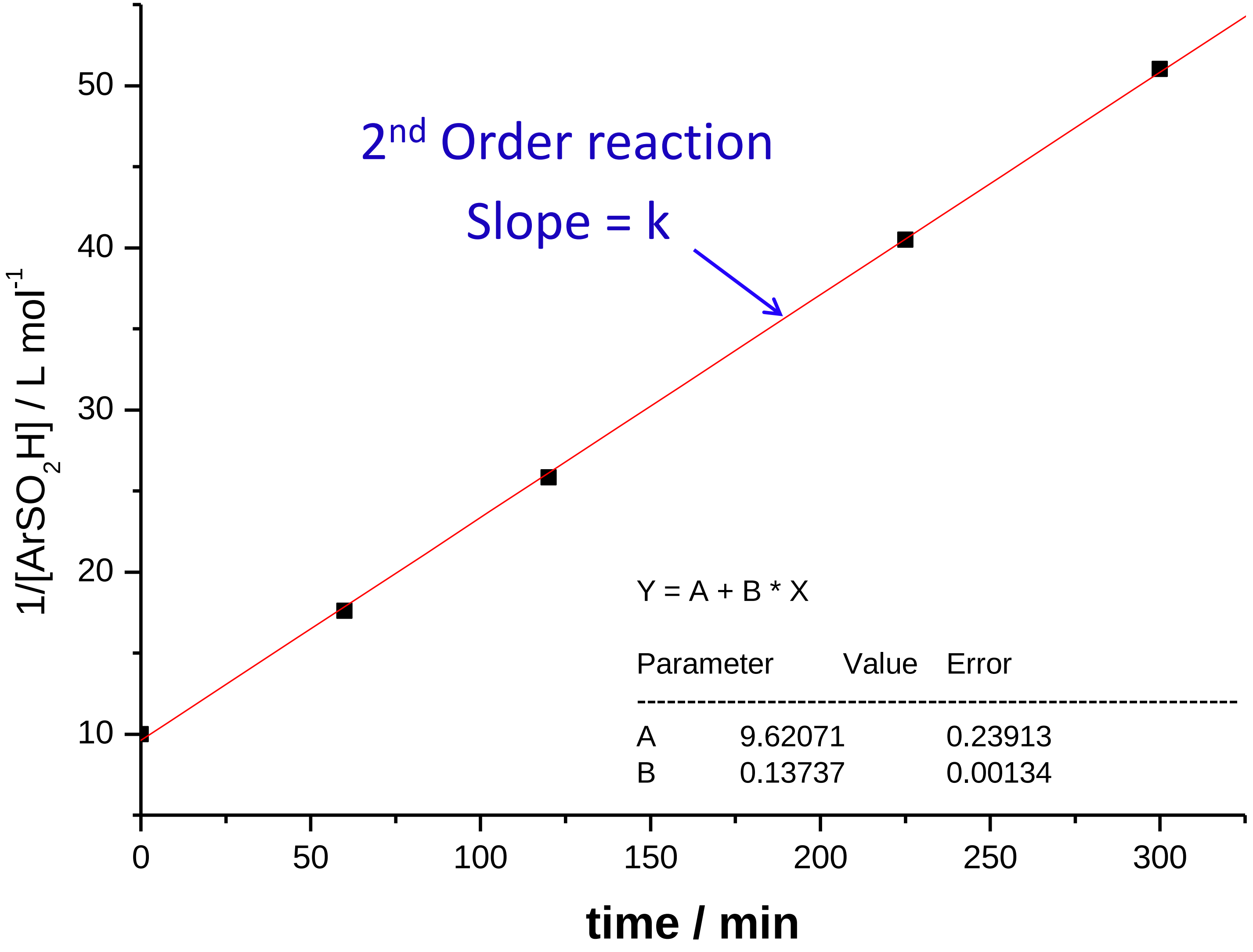
$$\frac{1}{[\mathrm{A}]_\mathrm{t}}-\frac{1}{[\mathrm{A}]_0}=\mathrm{k}(\mathrm{t}-\mathrm{t}_0)$$

$$\frac{1}{[\mathrm{A}]_\mathrm{t}}-\frac{1}{[\mathrm{A}]_0}=\mathrm{kt}$$

$$\frac{1}{[\mathrm{A}]_\mathrm{t}}=\mathrm{kt}+\frac{1}{[\mathrm{A}]_0}$$

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

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



2nd Order reaction

Slope = k

Y = A + B * X

Parameter	Value	Error
A	9.62071	0.23913
B	0.13737	0.00134

Half-life: second-order reaction

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

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

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

Initial Rate Method

$$5\mathrm{Br}^- + \mathrm{BrO_3}^- + 6\mathrm{H}^+ \rightarrow 3\mathrm{Br_2} + 3\mathrm{H_2O}$$

$$\text{Rate law:} \quad \text{rate} = k\,[\mathrm{Br}^-]^{\alpha}[\mathrm{BrO_3}^-]^{\beta}[\mathrm{H}^+]^{\gamma}$$

$$\log \text{rate} = \log k + \alpha \log[\mathrm{Br}^-]_0 + \beta \log[\mathrm{BrO_3}^-]_0 + \gamma \log[\mathrm{H}^+]_0$$

$$\log R_0 = \alpha \log[\mathrm{Br}^-]_0 + (\log k + \beta \log[\mathrm{BrO_3}^-]_0 + \gamma \log[\mathrm{H}^+]_0)$$

$$y \quad = m \;.\; x \qquad + \qquad c$$

- Do series of expts. in which all $[\mathrm{BrO_3}^-]_0$ and $[\mathrm{H}^+]_0$ etc. are constant and only $[\mathrm{Br}^-]_0$ is varied; measure R_0
- Plot log R_0 (Y-axis) *versus* log $[\mathrm{Br}^-]_0$ (X-axis)
- Slope $\Rightarrow \alpha$
- Repeat to find β by keeping $[\mathrm{Br}^-]_0$ and $[\mathrm{H}^+]_0$ constant and varying $[\mathrm{BrO_3}^-]_0$

Example: $R_0 = k[NO]^{\alpha}[H_2]^{\beta}$

$2NO + 2H_2 \rightarrow N_2 + 2H_2O$

Expt.	$[NO]_0$	$[H_2]_0$	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 H_2 and calculate k.

- *Compare* experiments #1 and #2 $\Rightarrow$ β
- *Compare* experiments #1 and #3 $\Rightarrow$ α

Now, solve for k from $k = R_0 / (\mathbf{[NO]}^{\alpha}\mathbf{[H_2]}^{\beta})$

Example: $R_0 = k[NO]^{\alpha}[H_2]^{\beta}$

- $R_0 = k[NO]^{\alpha}[H_2]^{\beta}$
- $R_1 = k[25]^{\alpha}[10]^{\beta} = 2.4 \times 10^{-3}$
- $R_2 = k[25]^{\alpha}[5]^{\beta} = 1.2 \times 10^{-3}$
- $\frac{R_1}{R_2} = \left(\frac{10}{5}\right)^{\beta} = \frac{2.4x10^{-3}}{1.2x10^{-3}}$
- $(2)^{\beta} = 2$
- $\beta = 1$

- $R_0 = k[NO]^{\alpha}[H_2]^{\beta}$
- $R_1 = k[25]^{\alpha}[10]^{\beta} = 2.4 \times 10^{-3}$
- $R_3 = k[12.5]^{\alpha}[10]^{\beta} = 0.6 \times 10^{-3}$
- $\frac{R_1}{R_3} = \left(\frac{25}{12.5}\right)^{\alpha} = \frac{2.4x10^{-3}}{0.6x10^{-3}}$
- $(2)^{\alpha} = 4$
- $\alpha = 2$

$k_1 = R_0 / ([NO]^{\alpha}[H_2]^{\beta})$
$k_1 = 2.4 \times 10^{-3}/((25)^2(10)^1)$
$k_1 = 3.84 \times 10^{-7}\ \mathrm{dm^6\ mol^{-2}\ s^{-1}}$

$k_2 = R_0 / ([NO]^{\alpha}[H_2]^{\beta})$
$k_2 = 1.2 \times 10^{-3}/((25)^2(5)^1)$
$k_2 = 3.84 \times 10^{-7}\ \mathrm{dm^6\ mol^{-2}\ s^{-1}}$

$k_3 = R_0 / ([NO]^{\alpha}[H_2]^{\beta})$
$k_3 = 0.6 \times 10^{-3}/((12.5)^2(10)^1)$
$k_3 = 3.84 \times 10^{-7}\ \mathrm{dm^6\ mol^{-2}\ s^{-1}}$

How to measure initial rate?

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

	A + B + …		→	P + Q + …		
t=0	100	100	→	0	0	mol m^{-3}
10 s	99	99	→	1	1	ditto

- Rate?

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

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

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

Isolation / flooding

$$IO_3^- + 8\ I^- + 6\ H^+ \rightarrow 3\ I_3^- + 3\ H_2O$$

- **Rate = k $[IO_3^-]^\alpha\ [I^-]^\beta\ [H^+]^\gamma$**
  - **Add excess iodate to reaction mix**
  - **Hence $[IO_3^-]$ is *effectively* constant**
  - **Rate = k′$[I^-]^\beta[H^+]^\gamma$ …where k′= k $[IO_3^-]^\alpha$**
  - **Add excess acid**
  - **Therefore $[H^+]$ is *effectively* constant**
- **Rate ≈ k″ $[I^-]^\beta$ (where k″= k $[IO_3^-]^\alpha\ [H^+]^\gamma$)**
- Use integral or initial rate methods *as desired*

Rate law for elementary reaction

- Law of Mass Action applies:
  - **rate of rxn ∝ 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 = $k_3 [A]^2 [B]^1$**

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.***

$CO + Cl_2 \not\rightarrow COCl_2$

- Experimental rate law: **$-(d[CO]/dt) = k\,[CO]\,[Cl_2]^{1/2}$**
  - Conclusion?: reaction does *not* proceed as written
  - “Elementary” reactions; rxns. that proceed as written at the *molecular level*.

$Cl_2 \rightarrow Cl + Cl$	(1)	decay
$Cl + CO \rightarrow COCl$	(2)	collisional
$COCl + Cl_2 \rightarrow COCl_2 + Cl$	(3)	collisional
$Cl + Cl \rightarrow Cl_2$	(4)	collisional

- Steps 1 thru 4 comprise the “mechanism” of the reaction.

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

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

then, $Cl_2 \rightleftharpoons 2Cl$ or $K = [Cl]^2 / [Cl_2]$

So $[Cl] = \sqrt{K} \times [Cl_2]^{1/2}$

Hence:

$$-(d[CO]/dt) = k_2[Cl]^1[CO]^1$$

$$-(d[CO]/dt) = k_2 \times \sqrt{K} \times [Cl_2]^{1/2} \times [CO]$$

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

Complex (non-elementary) rxns

Chain reactions

$CH_3CHO \rightarrow CH_4 + CO$ in over 90% yield

Traces of C_2H_6, H_2, CH_3COCH_3, etc.

Rate law rate = $k[CH_3CHO]^{3/2}$

Possible mechanism?

- $CH_3CHO \rightarrow \dot{C}H_3 + H\dot{C}O$ initiation
- $\dot{C}H_3 + CH_3CHO \rightarrow CH_4 + CH_3\dot{C}O$ propagation
- $CH_3\dot{C}O \rightarrow \dot{C}H_3 + CO$ propagation
- $\dot{C}H_3 + \dot{C}H_3\ (+M) \rightarrow C_2H_6\ (+M)$ termination

Basic Chemical Kinetic Principles II

Temperature dependence?

$$C_2H_5Cl \rightarrow C_2H_4 + HCl$$

$$\text{rate} = k[C_2H_5Cl]^1$$

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

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

Details of T dependence

Hood (1878)

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

Arrhenius (1889)

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

A pre-exponential factor

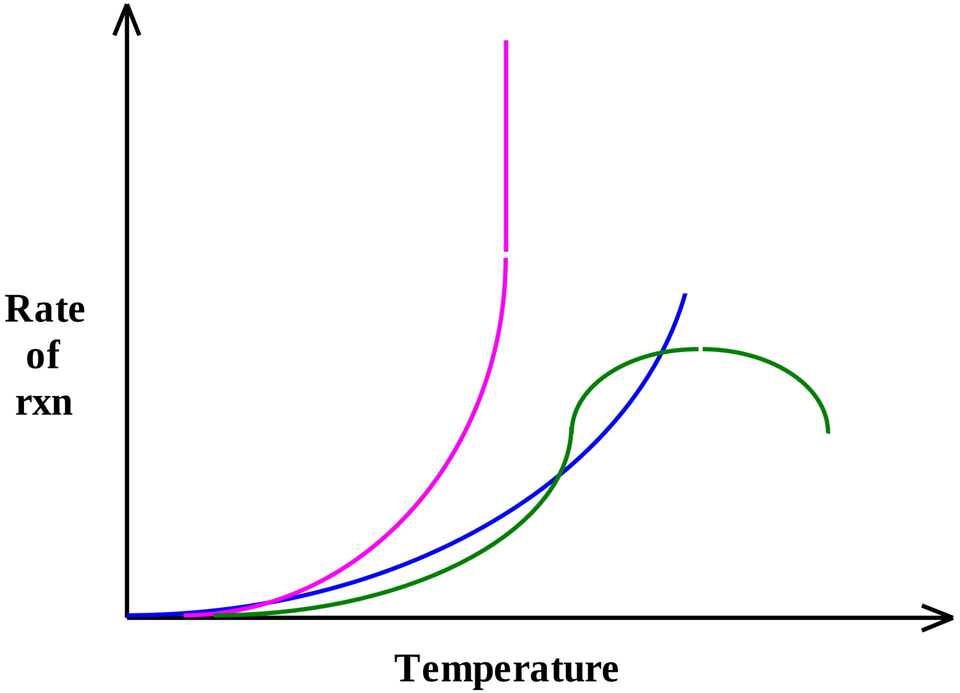
orA-factor

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

E activation energy

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

R gas constant.



http://en.wikipedia.org/wiki/Cherry_blossom_front#Forecasts

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

Svante Arrhenius
(Swedish scientist)

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 $= \ln A$

Temperature dependence?

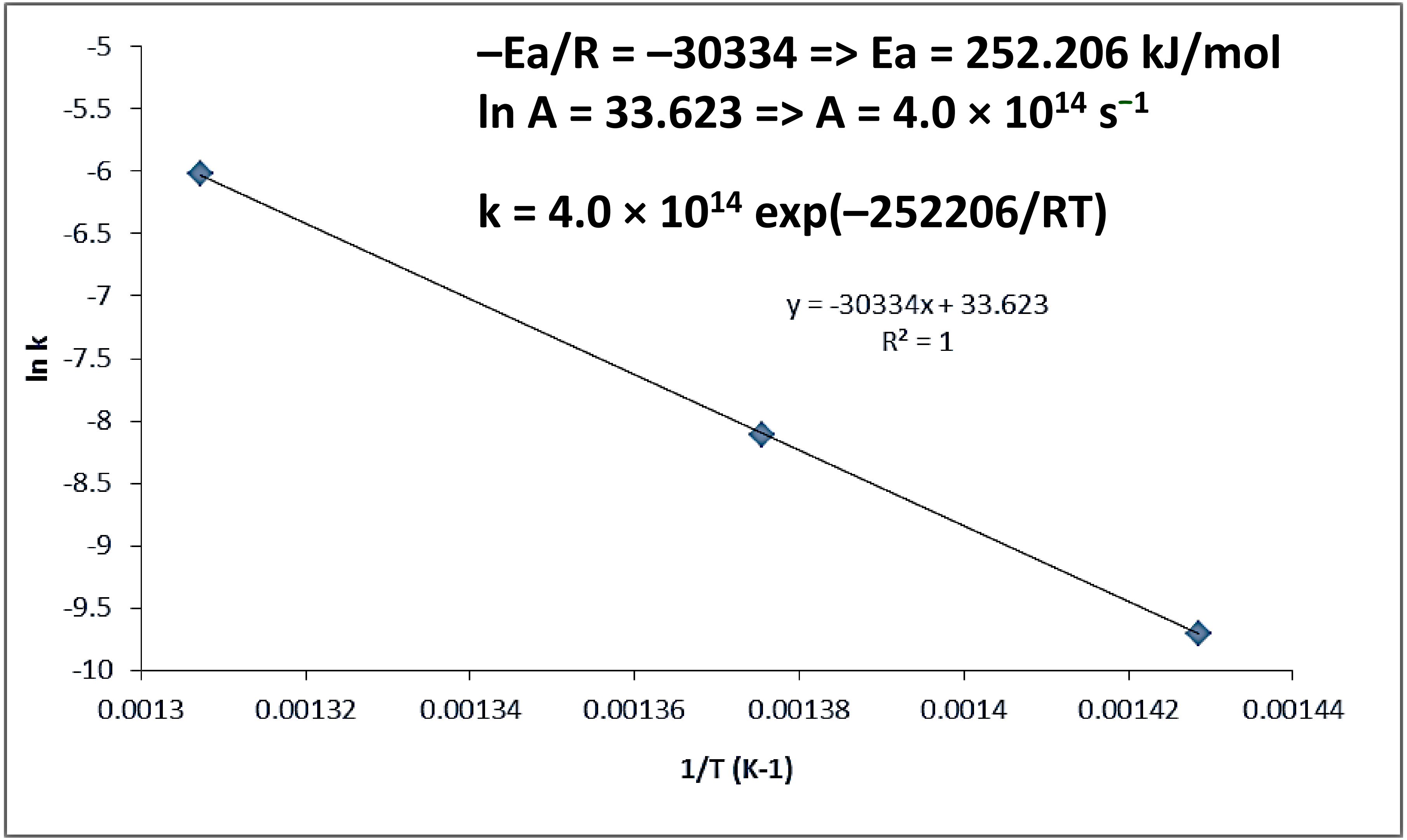
$$C_2H_5Cl \rightarrow C_2H_4 + HCl$$

$$\text{rate} = k[C_2H_5Cl]^1$$

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

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

Temperature dependence?



$-E_a/R = -30334 \Rightarrow E_a = 252.206$ kJ/mol

$\ln A = 33.623 \Rightarrow A = 4.0 \times 10^{14}\ \text{s}^{-1}$

$k = 4.0 \times 10^{14} \exp(-252206/RT)$

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

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

Examples:

– $\dot{H} + HCl \rightarrow H_2 + \dot{Cl}$	19 kJ mol^{-1}
– $\dot{H} + HF \rightarrow H_2 + F\cdot$	139 kJ mol^{-1}
– $C_2H_5I \rightarrow C_2H_4 + HI$	209 kJ mol^{-1}
– $C_2H_6 \rightarrow 2\dot{C}H_3$	368 kJ mol^{-1}

Problem

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

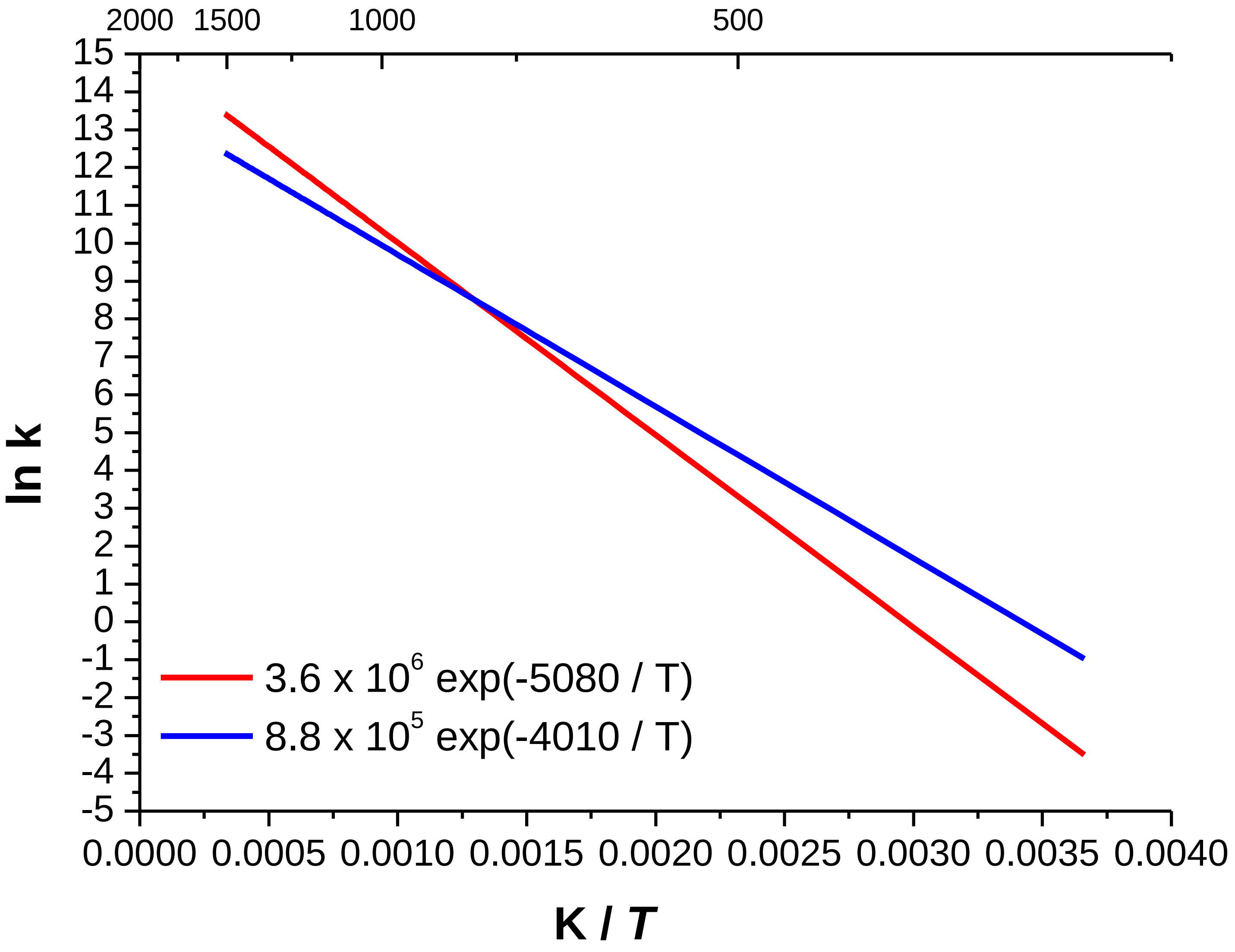
$DA \rightarrow B \rightarrow P$ The Arrhenius equations are:

first step: **$3.6\times10^{6}\ \exp\{-5{,}080/T\}\ s^{-1}$**

second step: **$8.8\times10^{5}\ \exp\{-4{,}010/T\}$** 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?

$$k = A\exp\left(\frac{-E_A}{RT}\right) \qquad \frac{exp\left(\frac{-E_A}{RT_1}\right)}{exp\left(\frac{-E_A}{RT_2}\right)} = exp\left[\left(\frac{-E_A}{RT_1}\right) - \left(\frac{-E_A}{RT_2}\right)\right]$$

$$\frac{k_1}{k_2} = \frac{A}{A}\exp\left(\frac{(-E_A)}{RT_1} - \frac{(-E_A)}{RT_2}\right) \qquad \ln\left(\frac{1}{2}\right) = \left(\frac{-E_A}{8.314}\right)\left(\frac{1}{293.15} - \frac{1}{303.15}\right)$$

$$\frac{k_1}{k_2} = \exp\left(\frac{-E_A}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad -0.693 = \left(\frac{-E_A}{8.314}\right)\left(1.12526\times10^{-4}\right)$$

$$\ln\left(\frac{k_1}{k_2}\right) = \left(\frac{-E_A}{R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad -6158.58 = \left(\frac{-E_A}{8.314}\right) \Rightarrow E_A = 51.202\ \text{kJ mol}^{-1}$$

Pressure-dependent fall-off reactions

- ☐ In some reactions a “third body” is required for the reaction to occur:

$$A + M \longrightarrow B + C + M$$

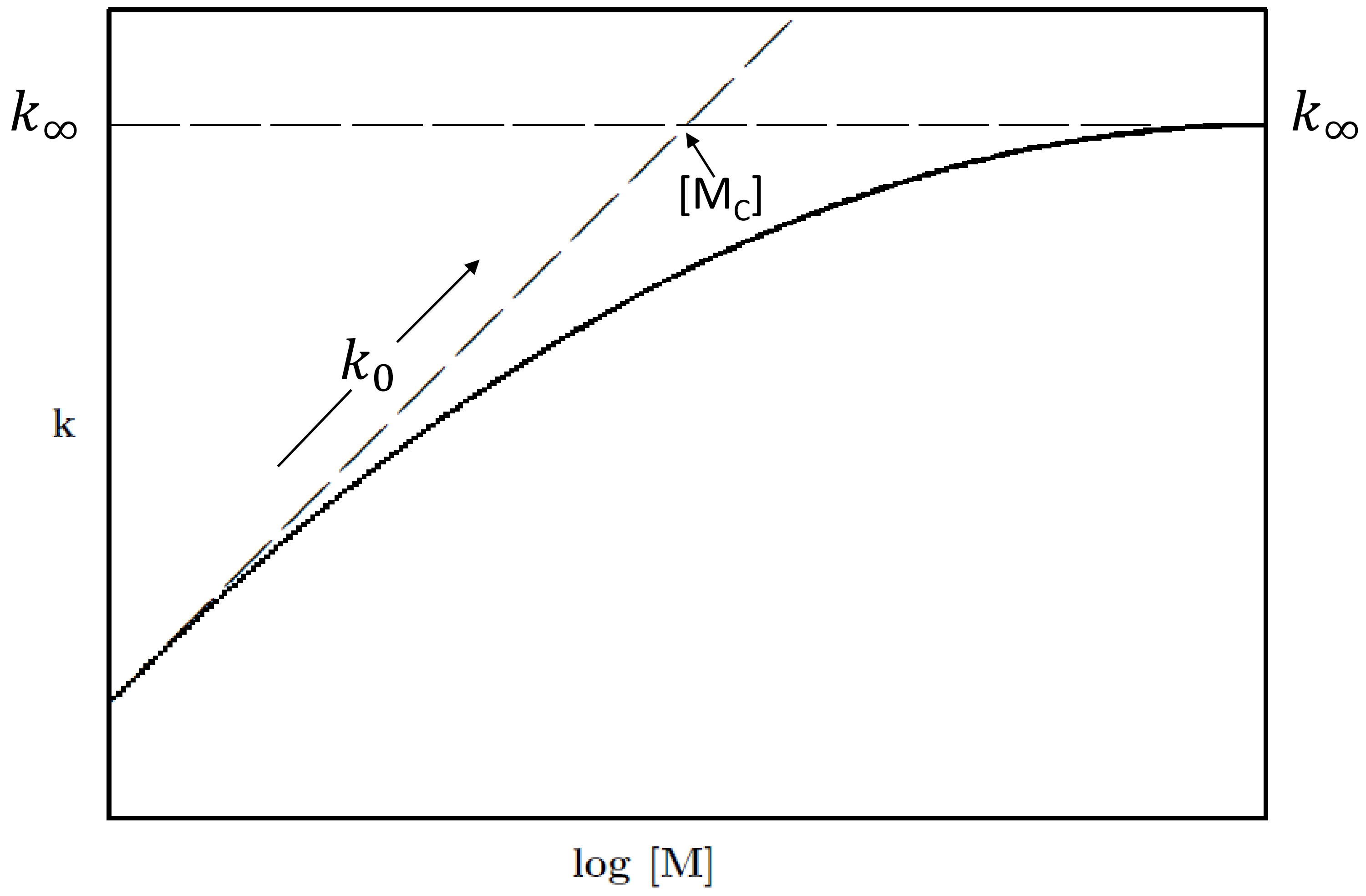
M represents collectively, all of the atoms and molecules of the reacting gas,

and is given by: $[M] = p/RT$

Some colliders may react more efficiently as third bodies than others:

Collision Partner	Relative Rate Coefficient
CO	1.0
H_2	1.3
CO_2	2.0
H_2O	6.0

Pressure-dependent fall-off reactions



Pressure-dependent fall-off reactions

❑ A dissociation reaction involves three steps;

1. Collisional activation to form excited molecules
2. Collisional deactivation
3. Unimolecular fragmentation

$$AB + M \xrightarrow{k_1} AB^* + M$$

$$AB^* + M \xrightarrow{k_{-1}} AB + M$$

$$AB^* \xrightarrow{k_2} A + B$$

$$A + B \xrightarrow{k_{-2}} AB^*$$

These reactions involve an energy-rich intermediate species, denoted AB*

Pressure-dependent fall-off reactions

$$k_{diss} \equiv -\frac{1}{[\mathrm{AB}]}\frac{d[\mathrm{AB}]}{dt}$$

$$k_{rec} \equiv +\frac{1}{[\mathrm{A}][\mathrm{B}]}\frac{d[\mathrm{AB}]}{dt}$$

Applying the steady-state approximation *d*[AB*]/*dt* = 0 to [AB*] we can show that:

$$k_{diss} = k_1[\mathrm{M}]\left(\frac{k_2}{k_2+k_{-1}[\mathrm{M}]}\right)$$

$$k_{rec} = k_{-2}\left(\frac{k_{-1}[\mathrm{M}]}{k_2+k_{-1}[\mathrm{M}]}\right)$$

then:

$$\frac{k_{diss}}{k_{rec}} = \frac{k_1}{k_{-1}}\frac{k_2}{k_{-2}} = \left(\frac{[\mathrm{A}][\mathrm{B}]}{[\mathrm{AB}]}\right)_{eq} = K_c$$

Pressure-dependent fall-off reactions

❑ Given that:

$$k_{diss} = k_1[\mathrm{M}]\left(\frac{k_2}{k_2+k_{-1}[\mathrm{M}]}\right)$$

$$k_{rec} = k_{-2}\left(\frac{k_{-1}[\mathrm{M}]}{k_2+k_{-1}[\mathrm{M}]}\right)$$

The limiting rate coefficients are:

- low-pressure limit:

$$\lim_{[\mathrm{M}]\to 0} k_{diss} \equiv k_{0,\,diss} = k_1[\mathrm{M}]$$

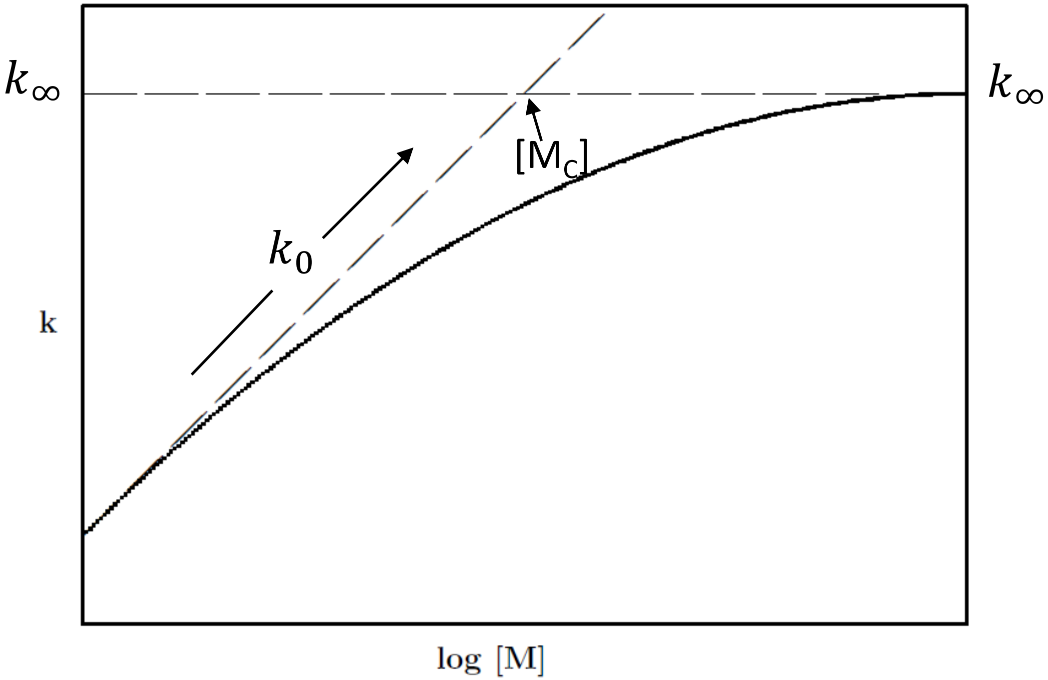
$$\lim_{[\mathrm{M}]\to 0} k_{rec} \equiv k_{0,\,rec} = \frac{k_{-2}}{k_2}k_{-1}[\mathrm{M}]$$

Pressure-dependent fall-off reactions

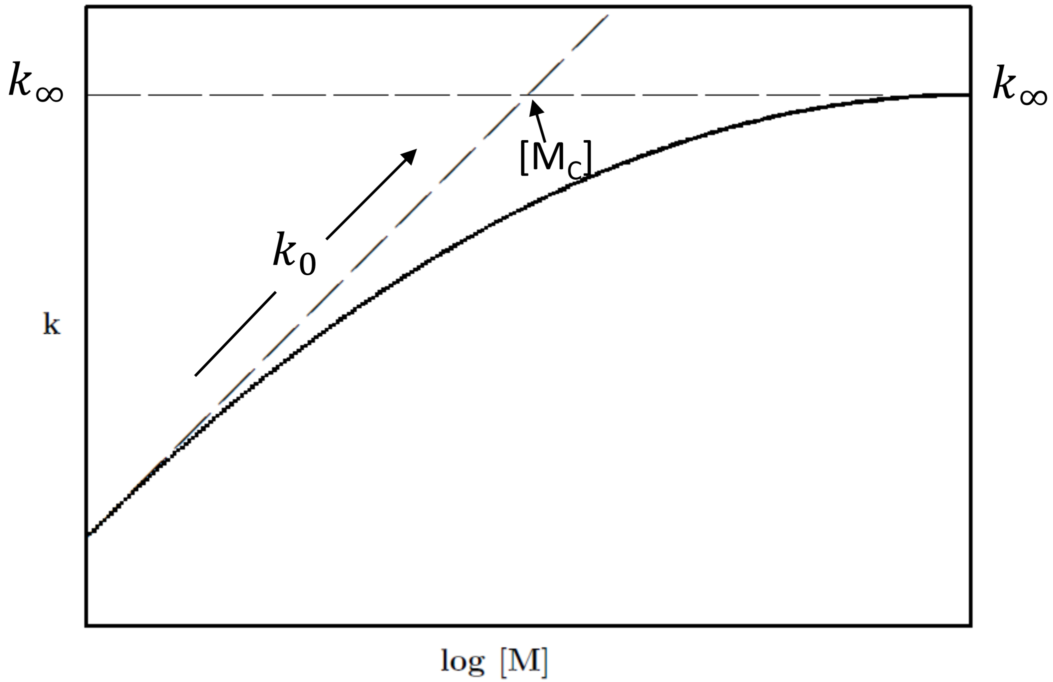
- high-pressure limit:

$$\lim_{[\mathrm{M}]\to\infty} k_{diss} \equiv k_{\infty,\,diss} = \frac{k_1}{k_{-1}} k_2$$

$$\lim_{[\mathrm{M}]\to\infty} k_{rec} \equiv k_{\infty,\,rec} = k_{-2}$$



Pressure-dependent fall-off reactions



$$\frac{[\mathrm{M}]}{[\mathrm{M_C}]} = \left(\frac{k_0[\mathrm{M}]}{k_\infty}\right) = x$$

$$\frac{k}{k_\infty} = \frac{k_0/k_\infty}{1+k_0/k_\infty} = \frac{[\mathrm{M}]/[\mathrm{M_C}]}{1+[\mathrm{M}]/[\mathrm{M_C}]} = \frac{x}{1+x}$$

Pressure-dependent fall-off reactions

- ❑ Recombination of Ḣ atom with $\dot{C}H_3$ radicals
  - ❑ High-pressure limit: $\dot{C}H_3 + \dot{H} \rightleftarrows CH_4$ $\qquad k_\infty = A_\infty T^{n_\infty} \exp(-E_\infty/RT)$
  - ❑ Low-pressure limit: $\dot{C}H_3 + \dot{H} + M \rightleftarrows CH_4 + M$ $\qquad k_0 = A_0 T^{n_0} \exp(-E_0/RT)$
  - ❑ Between the limits: $\dot{C}H_3 + \dot{H}\ (+M) \rightleftarrows CH_4\ (+M)$ $\qquad$????

Lindemann format:

$$k = k_\infty\left(\frac{P_r}{1+Pr}\right)F$$

where:

$$P_r = \frac{k_0[M]}{k_\infty}$$

(P_r = reduced pressure)

If *F* (broaden factor) is unity then this is the Lindemann form[1]

[1] F. Lindemann, Trans. Faraday Soc. 17 (1922) 598.

Pressure-dependent fall-off reactions

- ☐ Troe[1] format:

F (broaden factor) is given by:

$$\log F = \left[1 + \left(\frac{\log P_r + c}{n - d(\log P_r + c)}\right)^2\right]^{-1} \log F_{\text{cent}}$$

where

$$c = -0.4 - 0.67 \log F_{\text{cent}}$$

$$n = 0.75 - 1.27 \log F_{\text{cent}}$$

$$d = 0.14$$

and

$$F_{\text{cent}} = (1 - a) \exp(-T/T^{***}) + a \exp(-T/T^{*}) + \exp(-T^{**}/T)$$

The four parameters a, T^{***}, T^{*} and T^{**} must be specified in the input

Can sometimes lead to unnecessary inaccuracies

[1] J. Troe, J. Phys. Chem. 83 (1979) 114–126.

Pressure-dependent fall-off reactions

- ☐ Generalized polynomial PLOG format[1]

Rate constants generalized over a range of pressures ($p = p_1, p_2, \ldots, p_N$)

$$k_u(T, P_i) = \sum_{j=1}^{M} A_{ij}\, T^{n_{ij}} exp(-E_o^{ij}/RT), i \;=\; 1, \ldots, N, M \geq \; 1$$

Extrapolation is bounded by two pressure p_1 and p_N

To calculate k_u (T, p) for any pressure log k_u interpolated as linear function of log p

If p is between p_i and p_{i+1} for any temperature, a rate constant can be found via:

$$log\ k_u(T, p_i) = log\ k_{u,i} + (log\ p - \log p_i)\frac{log\ k_{u,i+1} - log\ k_{u,i}}{log p_{i+1} - log p_i}$$

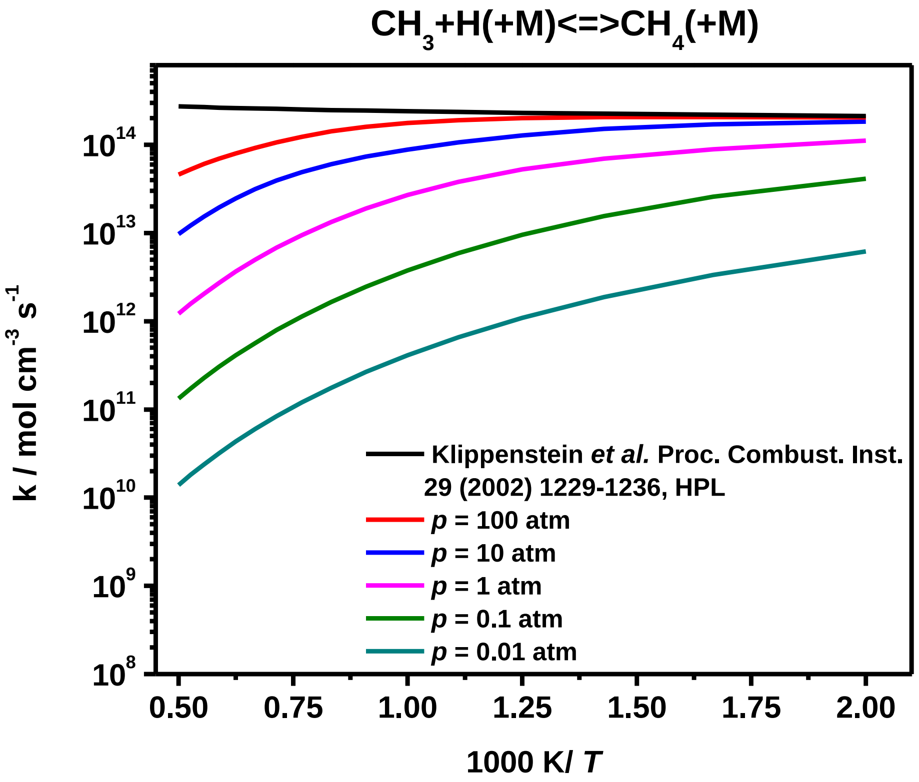
Generally more accurate than the TROE formalism

---

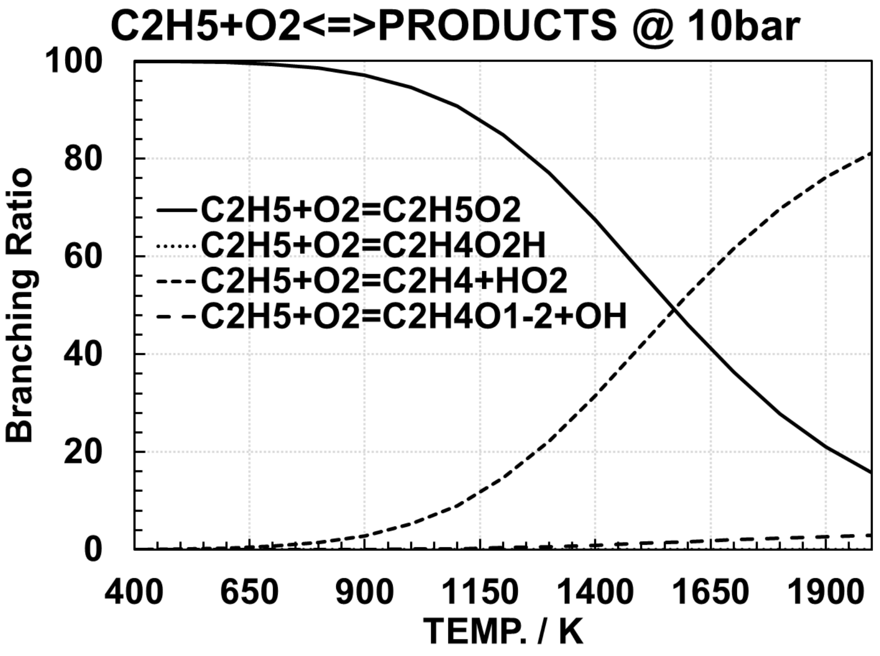
[1] J. Miller and A. Lutz 2003 Personal Communication

Pressure-dependent fall-off reactions

Troe formalism, produces good fit for **single well** systems



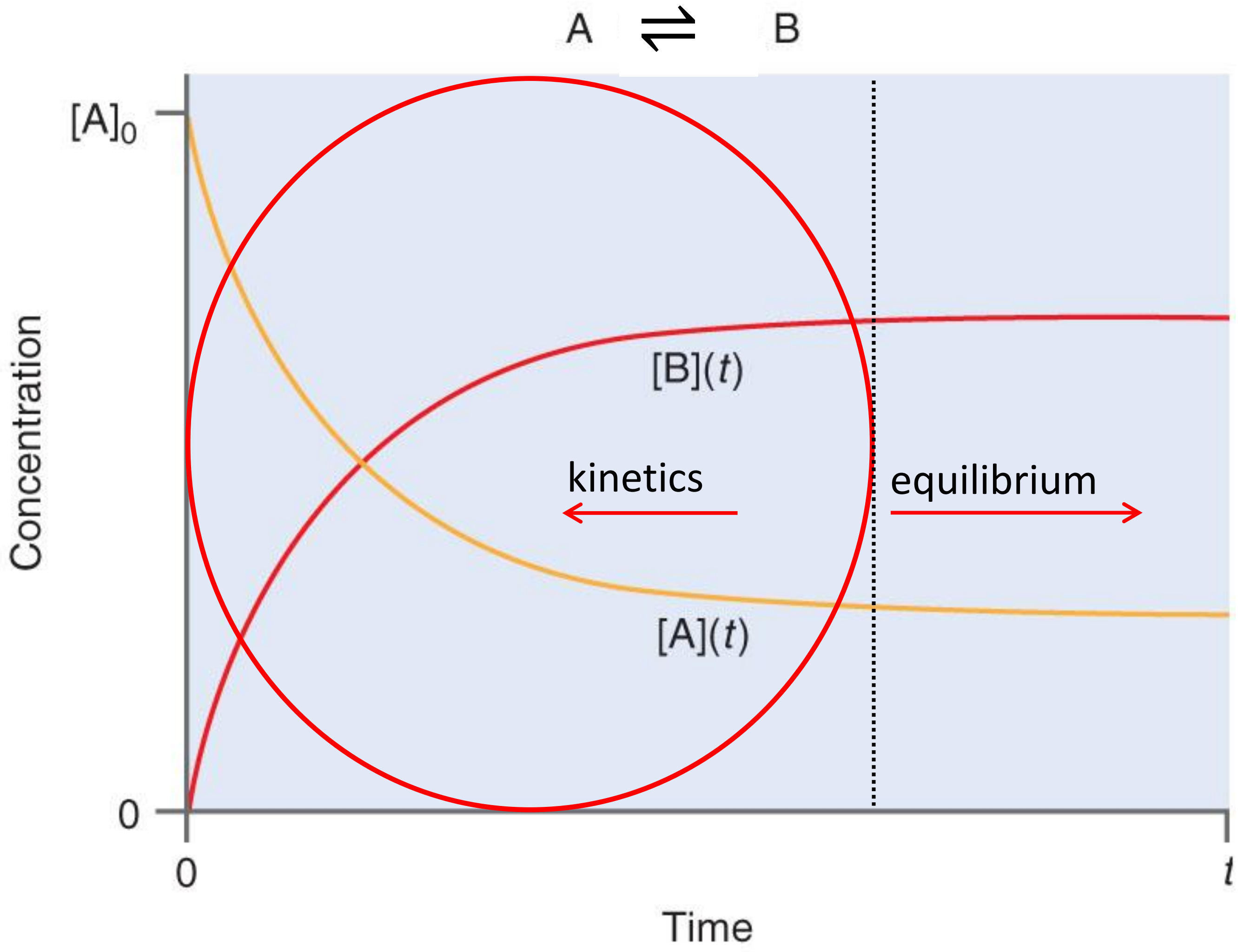
For complex **multiple well** systems it is easier to use explicit 'PLOG' Arrhenius fits



S.J. Klippenstein, Proc. Combust. Inst. 36 (2017) 77-111

Slide courtesy of Dr Ultan Burke

Kinetics and equilibrium



$$A \rightleftharpoons B$$

Kinetics Rate in forward direction: $k_f[A]$

Rate in reverse direction: $k_r[B]$

@ equilibrium: $k_f [A]_e = k_r[B]_e$

$$k_f/k_r = [B]_e/[A]_e = K_p$$

($K_p = K_C$ as $\Delta n = 0$)

$$k_f = A_f \exp(-E_f/RT) \text{ and } k_r = A_r \exp(-E_r/RT)$$

$$k_f/k_r = K_p = (A_f/\mathbf{A_r}) \times \exp[-(\mathbf{E_f} - E_r)/RT]$$

Thermodynamics $K_p = \exp(-\Delta G_r^0/RT)$

$$= \exp(\Delta S_r^0/R) \times \exp(-\Delta H_r^0/RT)$$

$=$

Problem

For the rxn trans → cis perfluorobut-2-ene

- measured $\mathbf{k_F=3.16\times10^{13}\ exp\{-31{,}030/T\}\ s^{-1}}$
- Given that $\mathbf{\Delta H^0=+3.42}$ kJ mol^{-1} and
- $\mathbf{\Delta S^0=-2.03}$ J K^{-1} mol^{-1}
- Calculate $\mathbf{k_R}$ at 750 K.

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

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

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

$E_F = 258._0$ kJ mol^{-1} $\Rightarrow E_R = 254._6$ kJ mol^{-1}

$$(A_f/A_r) * \exp((E_f - E_r)/RT) = k_f/k_r = \exp(\Delta S/R)*\{ \exp(-\Delta H/RT)\} / (RT/p_o)^{\Delta n}$$

$$\mathrm{A\ (+M)} \leftrightarrow \mathrm{B + C\ (+M)}$$

$$\exp(\Delta S/R)$$

$$= \exp[(S_B+S_C - S_A)/R]$$

$$= \exp\ [\{(S_{B,gr} - R*\ln(\sigma_B)) + (S_{C,gr} - R\ln(\sigma_C)) - (S_{A,gr} - R\ln(\sigma_A))\}/R]$$

$$= \exp\ [(S_{B,gr} + S_{C,gr} - S_{A,gr})/R - (\ln(\sigma_B) + \ln(\sigma_C) - \ln(\sigma_A))]$$

$$= \exp[(\Delta S_{,gr}/R) * \exp(\ln(\sigma_A / \sigma_B / \sigma_C)]$$

$$= \exp[(\Delta S_{,gr}/R)*(\sigma_A/(\sigma_B.\sigma_C)]$$

GROUP VALUE FACTOR

SYMMETRY NUMBER FACTOR

Reaction profile diagram

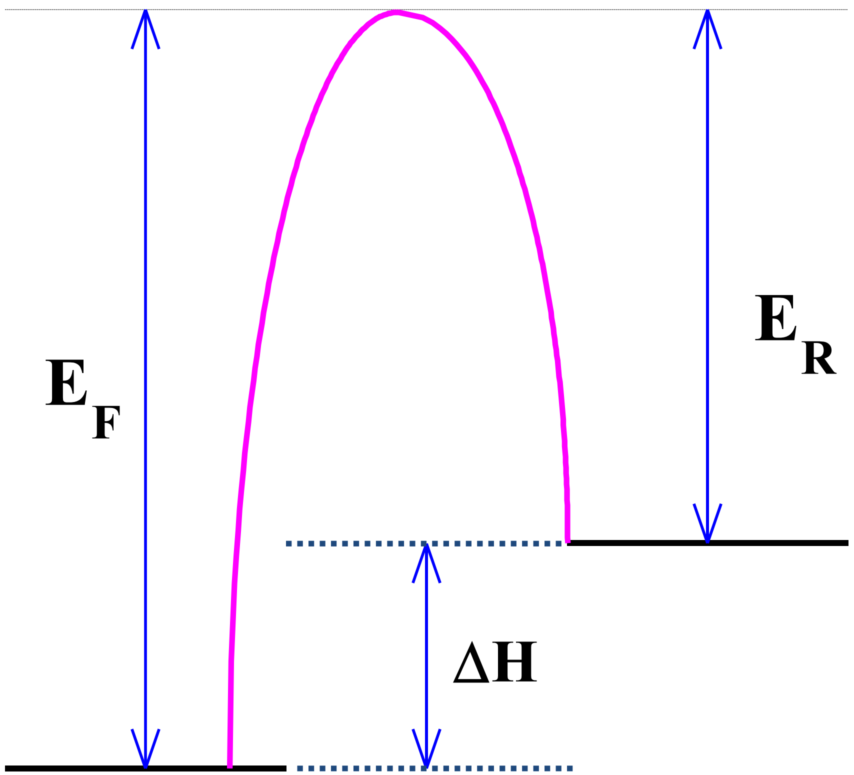
- **Y-axis?**
  - Energy
  - common path via TS
- **X-axis?**

Time?

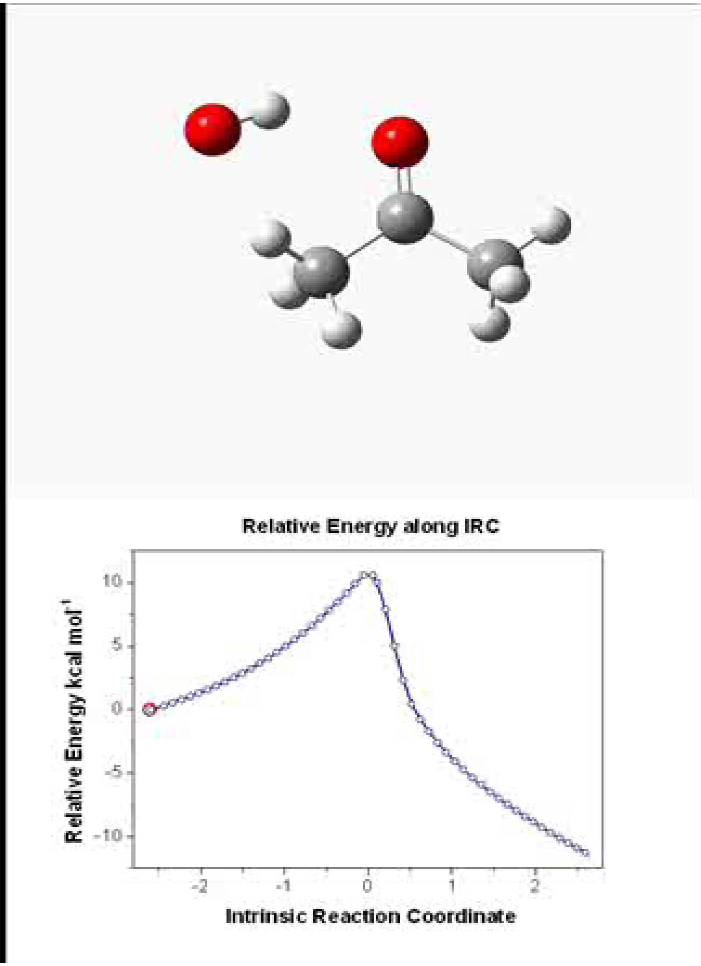
Reactant-product identity

Multi-dimensional

- *Reaction co-ordinate*
- Schematic diagram
  - **Concept of energy barrier to rxn**



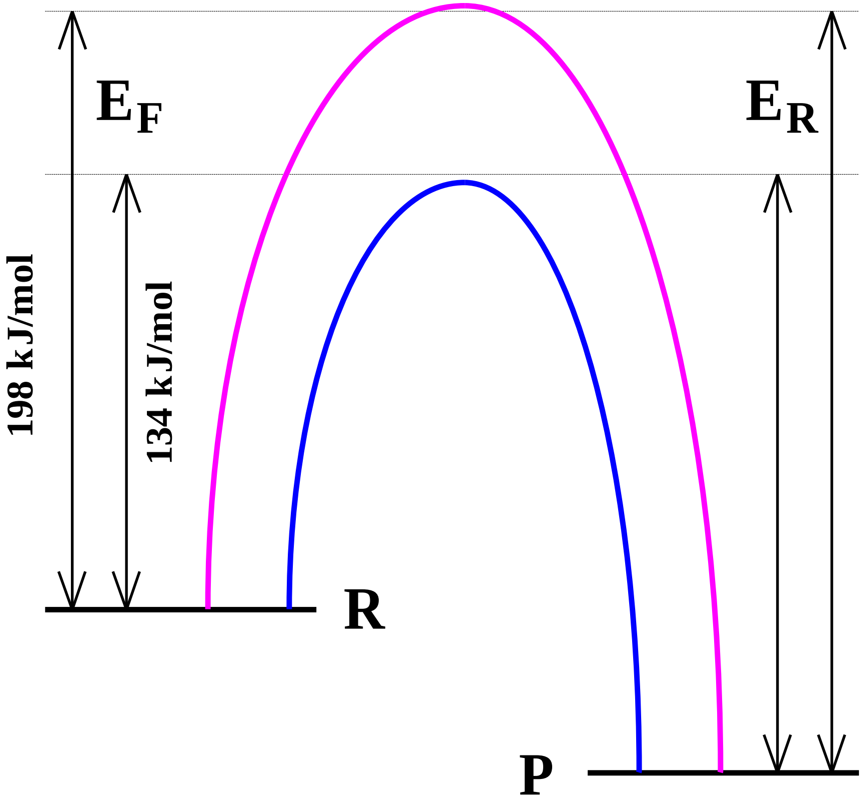
DMK + OH in plane H-abstraction



Reaction profile diagram

$CH_3CHO \rightarrow CH_4 + CO$

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



Thermochemistry from kinetics

$$C_2H_6 \rightarrow 2\dot{C}H_3 \quad 368\ \text{kJ mol}^{-1}$$

- $E_F = 368$ kJ mol^{-1} $E_R = 0$ kJ mol^{-1}

$\Delta H_{RXN} = E_F - E_R = +368$ kJ mol^{-1}

$= 2\Delta H_f(\dot{C}H_3) - \Delta H_f(C_2H_6)$

$\Delta H_f(\dot{C}H_3) = [\Delta H_{RXN} + \Delta H_f(C_2H_6)]/2$

But $\Delta H_f(C_2H_6) = -85$ kJ mol^{-1}

- $\Delta H_f(\dot{C}H_3) = (368 - 85)/2 = +141_{.5}$ kJ mol^{-1}

ΔH_{RXN} = Energy of bond broken = **$\Delta(H_3C\text{–}CH_3)$**

⇒ *Tables of bond dissociation energies*

Common mathematical functions

Kinetics, Arrhenius

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

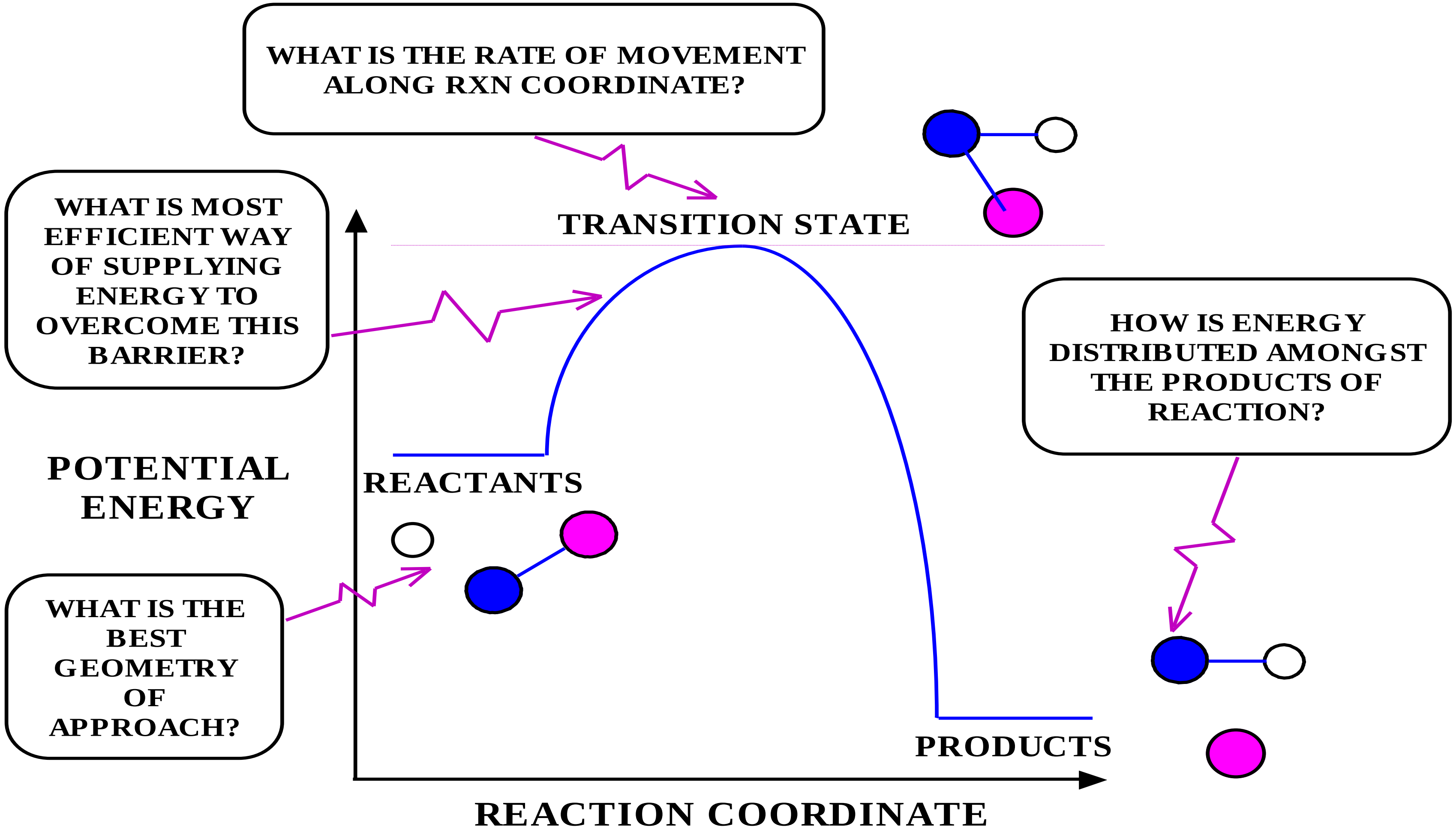
Vapour pressure, Clausius-Clayperon

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

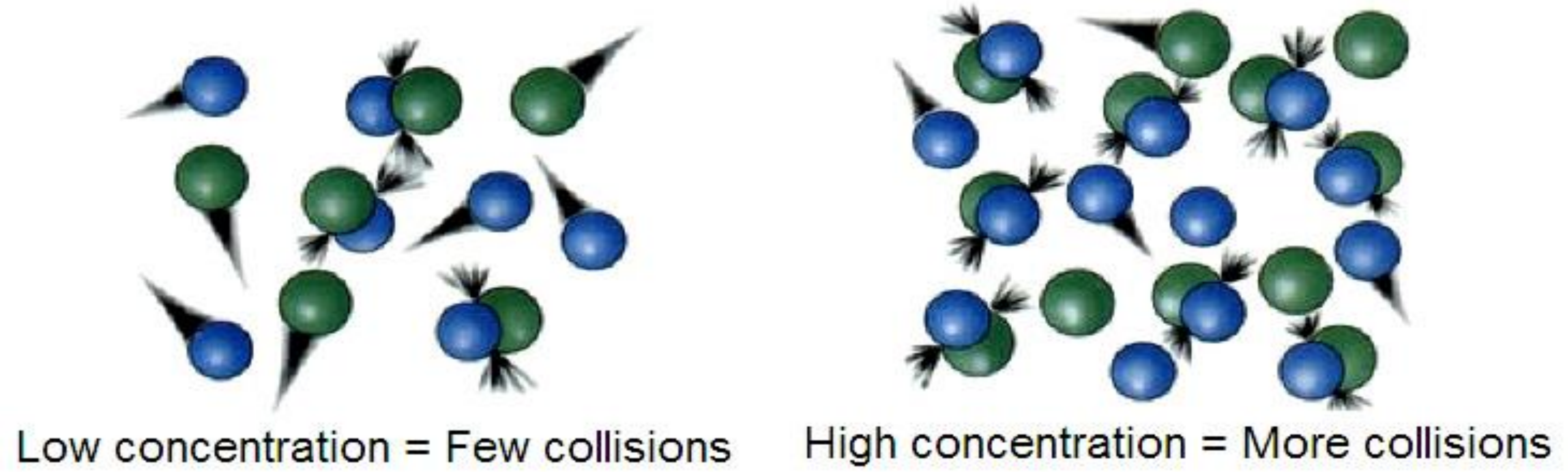
Viscosity, Andrade

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

Questions?


WHAT IS THE RATE OF MOVEMENT ALONG RXN COORDINATE?
WHAT IS MOST EFFICIENT WAY OF SUPPLYING ENERGY TO OVERCOME THIS BARRIER?
TRANSITION STATE
HOW IS ENERGY DISTRIBUTED AMONGST THE PRODUCTS OF REACTION?
POTENTIAL ENERGY
REACTANTS
WHAT IS THE BEST GEOMETRY OF APPROACH?
PRODUCTS
REACTION COORDINATE

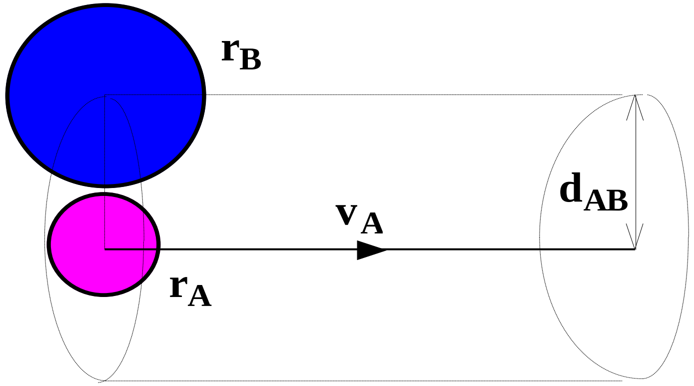
Collision theory



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 ⟶ products



Assumptions?

- molecules hard-spheres
- every collision is reactive

Calculate rate of collision ⇒ rate of reaction

- In 1 s a typical A travels a distance $d = \nu_A t$ & will collide with all B's within collision cylinder of volume = $\pi(r_A+r_B)^2\nu_A$ m^3 *so* $n_B \times \pi(r_A+r_B)^2\nu_A$ single collision of A with B per second ⇒ collision frequency $\mathbf{z_A}$
- Total collision rate $Z_{AB} = n_A n_B \times \pi(r_A+r_B)^2\nu_{AB}$ m^{-3} s^{-1}

SCT

Reaction rate = $k_2\, n_A n_B$

Collision rate = $\pi(r_A+r_B)^2\, \nu_{AB} \times n_A n_B$ "collision density"

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

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

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

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

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

with $\boldsymbol{M}_x$ in kg mol^{-1} & $\boldsymbol{T}$ 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}.

$\sigma_{AA} = \pi d^2 = 2.64\times10^{-19}$ m^2

$\nu_{\mathbf{AA}} = 563.67$ m s^{-1} (*NB twice* the speed of sound)

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

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

$\mathbf{z}_{AA} = \mathbf{n_A}\, \sigma_{AA} \times \nu_{AA} = 3.57\times10^{9}$ molecules s^{-1} $\Rightarrow$

$t_C = (1/Z_{AA}) = 280$ ps

Test of SCT

$$\dot{C}H_3 + \dot{C}H_3 \rightarrow C_2H_6$$

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

d (methyl) ≈ 0.308 nm

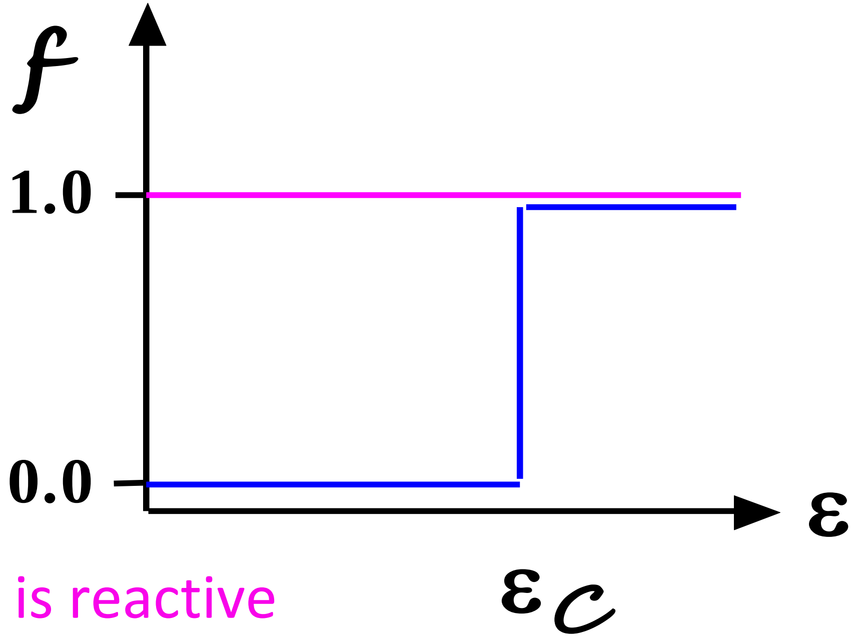
$\Rightarrow k_2 = \sigma_{AA}\nu_{AA} = 2.980\times10^{-19} \times 920.25 = 2.745 \times 10^{-16}$ m^3 molecule^{-1} s^{-1}

convert to cm^3 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 ε(coll) $\geq$ critical value ε_c then rxn occurs otherwise not
- What fraction, **f**, of collisions have $\varepsilon \geq \varepsilon_c$? M-B

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

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

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

Comparison with Arrhenius

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

- Does $E_C = E_A$?

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

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

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

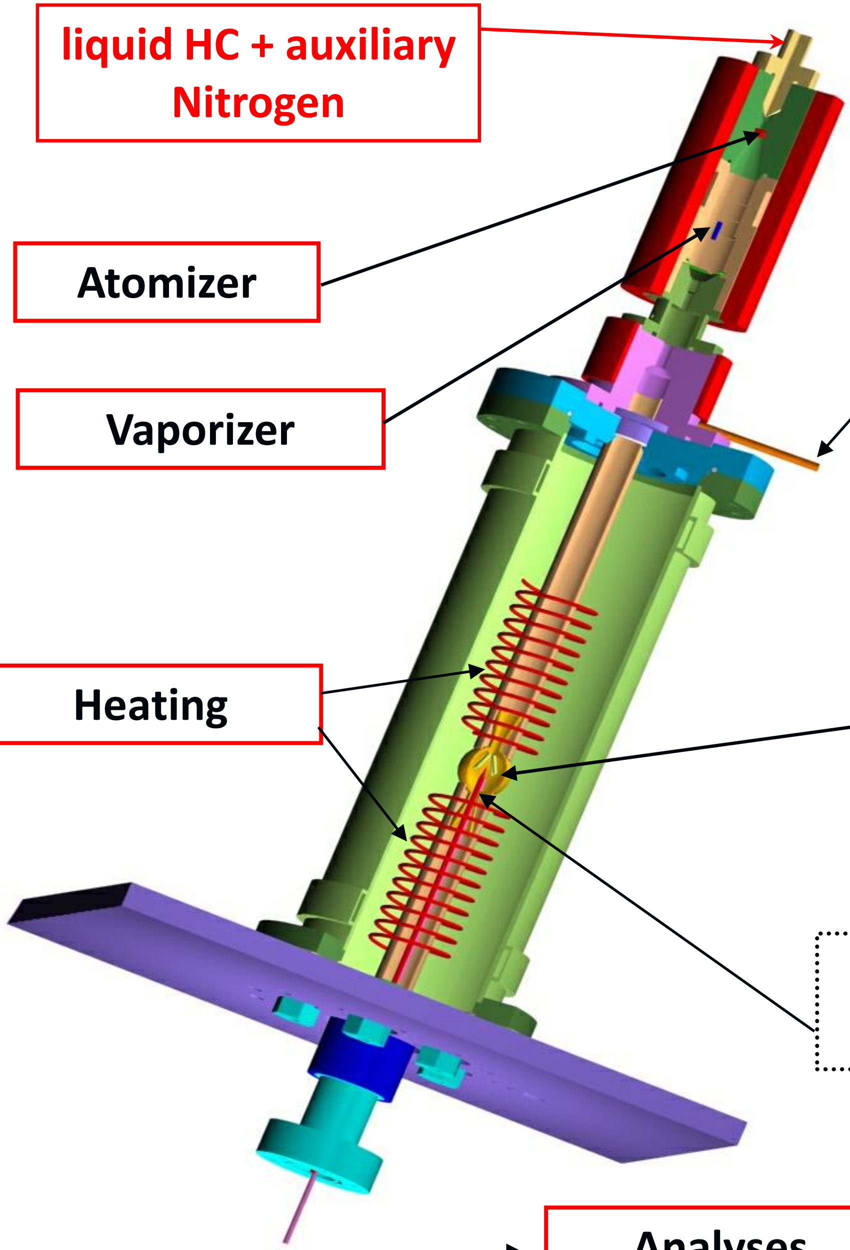
$\ln k = -(1/2) \ln (1/T) - (E_C/R)(1/T) + \ln Y$

- $d(\ln k)/d(1/T) = -(1/2)T - (E_C/R) = -(E_A/R)$
- $E_C = E_A - RT/2$ (**NB RT** is *small* in cf. with most E_A's)

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

JSRs and Flow Reactors

Jet Stirred Reactor (JSR)



liquid HC + auxiliary Nitrogen

Atomizer

Vaporizer

Heating

Oxygen + Nitrogen

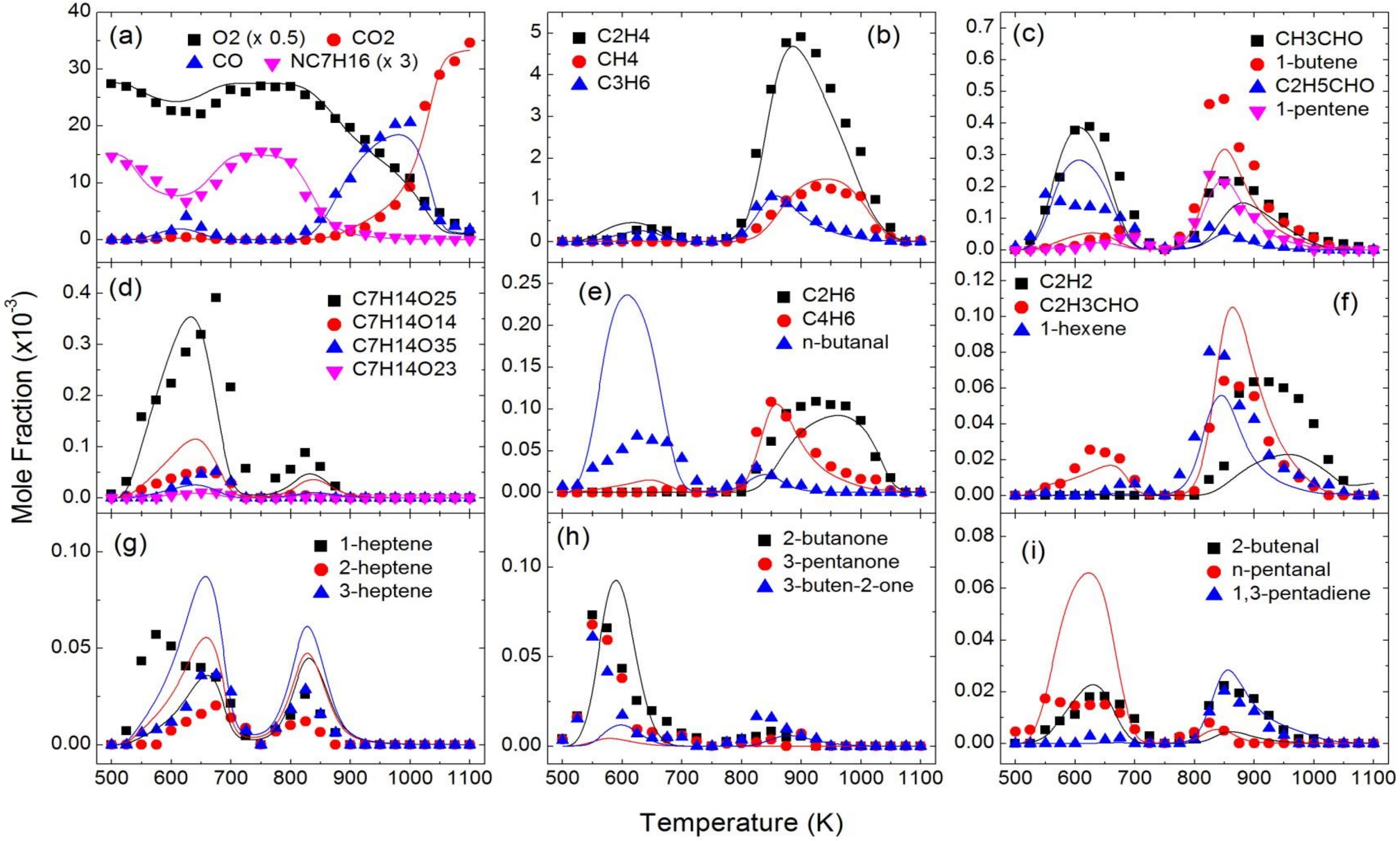
Nozzles

Fused silica reactor

Probe sampling + Thermocouple

Analyses

Example data: n-Heptane



φ = 1.0, τ = 2.0 s, 1.06 bar, 0.5% fuel
Herbinet et al., Combust. Flame, 159 (2012), 3455-3471

Proper rate of reaction

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

where ν_i is a stoichiometric coefficient

+ve for products, – ve for reactants

Example: $2H_2 + O_2 = 2H_2O$

- $\nu(H_2) = -2$, $\nu(O_2) = -1$ and $\nu(H_2O) = +2$
- At constant volume: $[A] = n/V$ *or* $n = V \times [A]$

So: $(dn_A/dt) = V. (d[A]/dt)$

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**

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

'Plug' flow; no mixing at all at all

- *cylindrical* shape of volume **V**

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

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

A 'residence' or 'contact' time

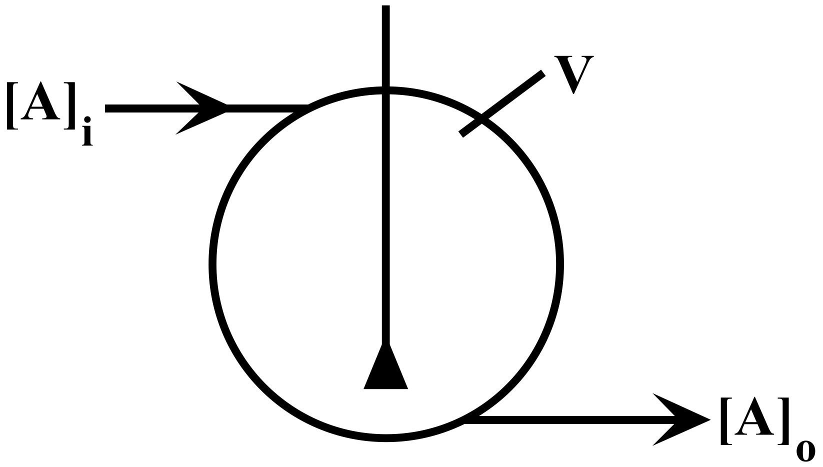
Stirred flow; 1st order

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

- inflow = outflow + reaction

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

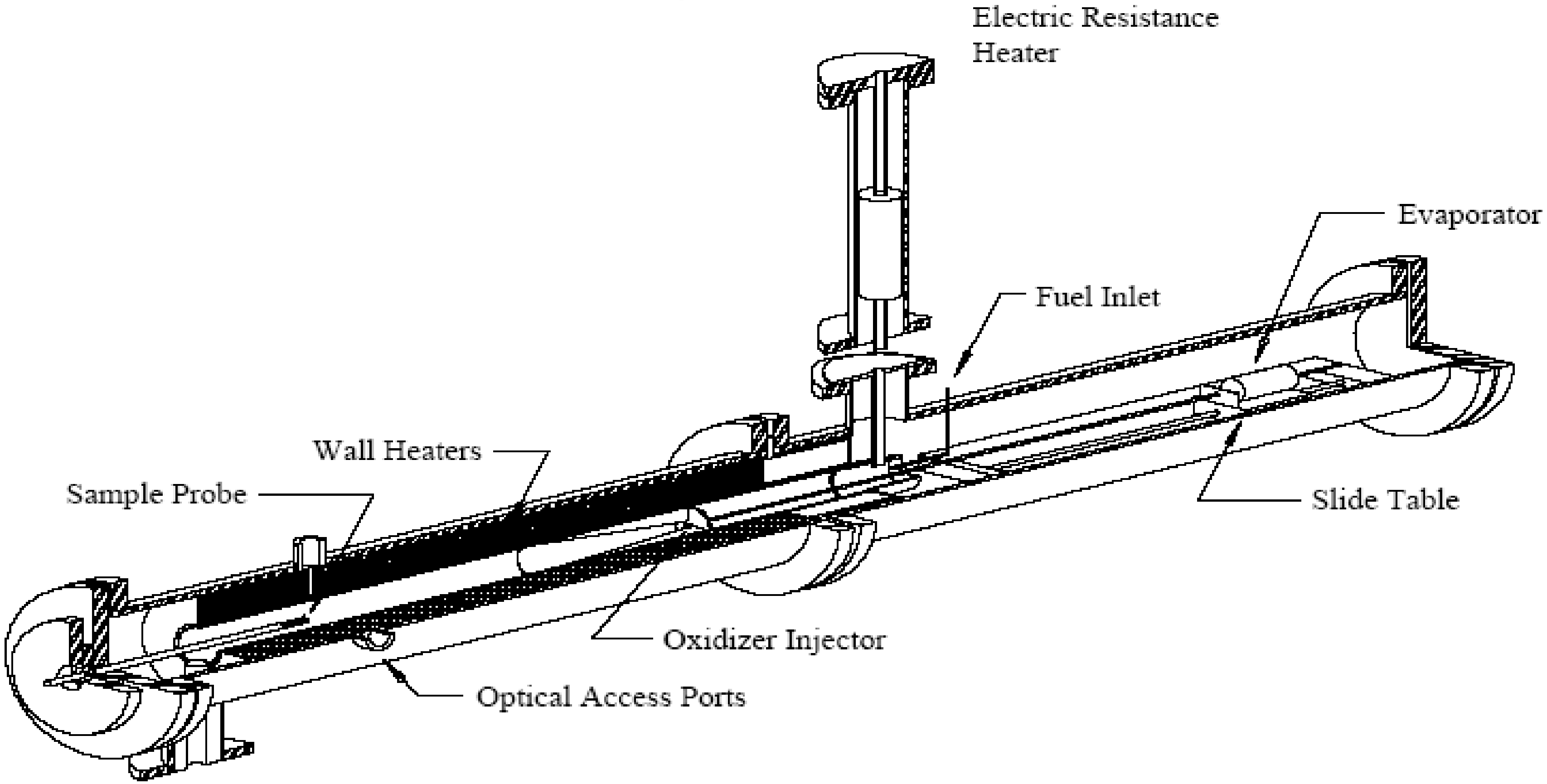
- $\nu[A]_i = \nu[A]_o - (dn_A/dt)$
- $\nu[A]_i = \nu[A]_o + k\, V\, [A]_o$
- $[A]_i = [A]_o + (k\, V\, [A]_o)/\nu$
- $[A]_i/[A]_o = 1 + k\, (V/\nu)$
- $[A]_o = [A]_i \,/\, \{1 + k(V/\nu)\}$



Test? vary ν, measure $[A]_o$ & $[A]_i$, is k the same?

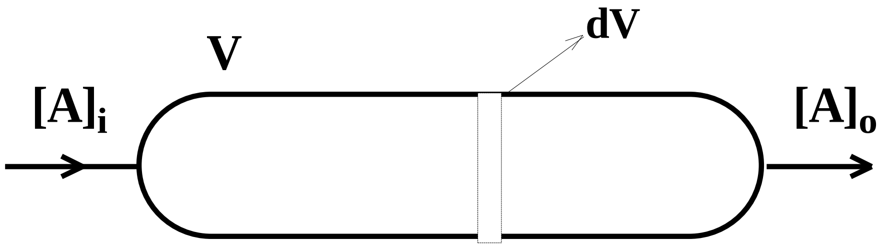
Variable Pressure Flow reactor

(Princeton U.)



Plug flow; 1st order rxn

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



inflow = outflow + reaction

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

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

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

$$-\nu\delta[A] = k\,\delta V\,[A]$$

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

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

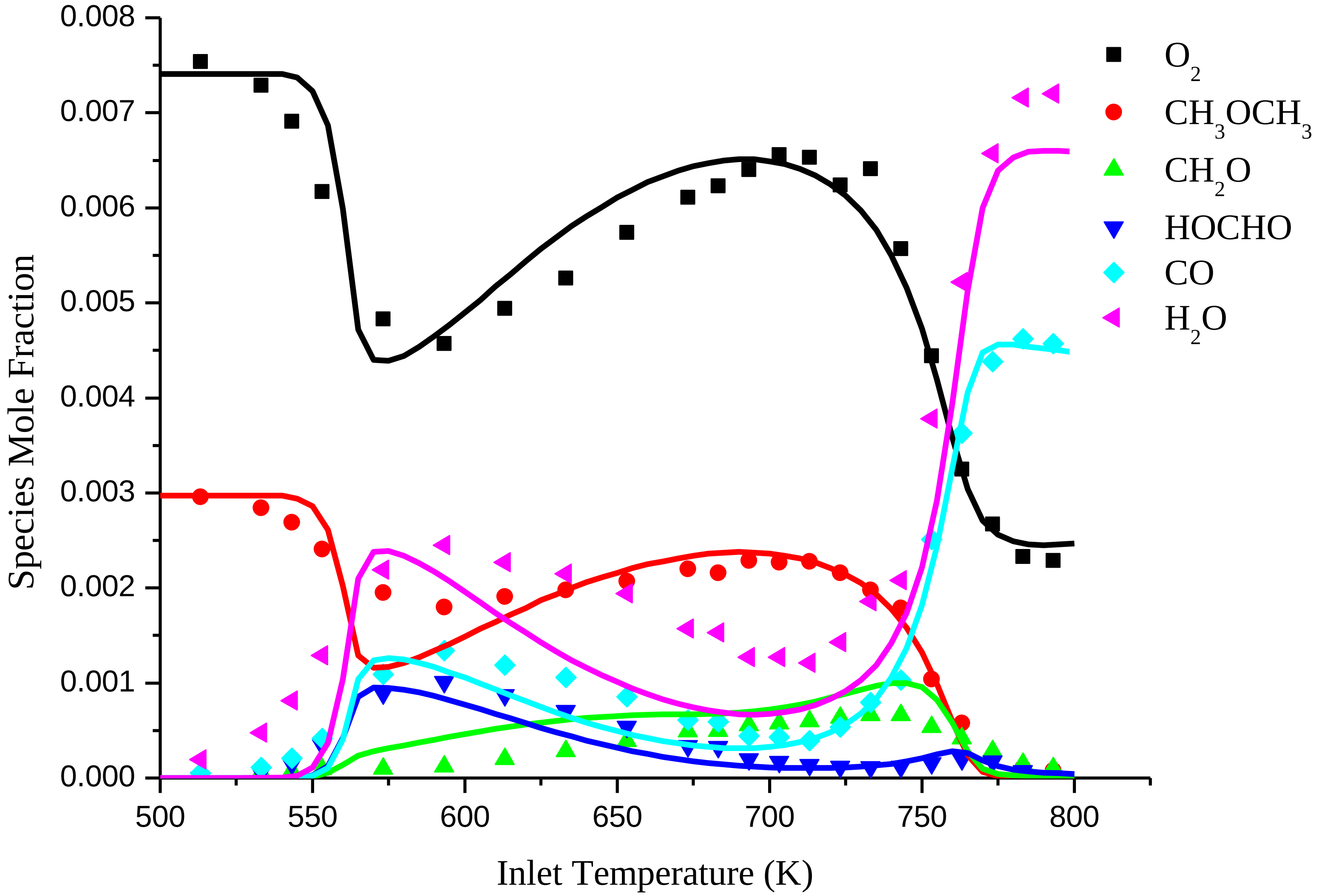
$$\int_{[A]_i}^{[A]_o} \frac{\delta[A]}{[A]} = -k/\nu\int_0^V \delta V$$

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

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

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

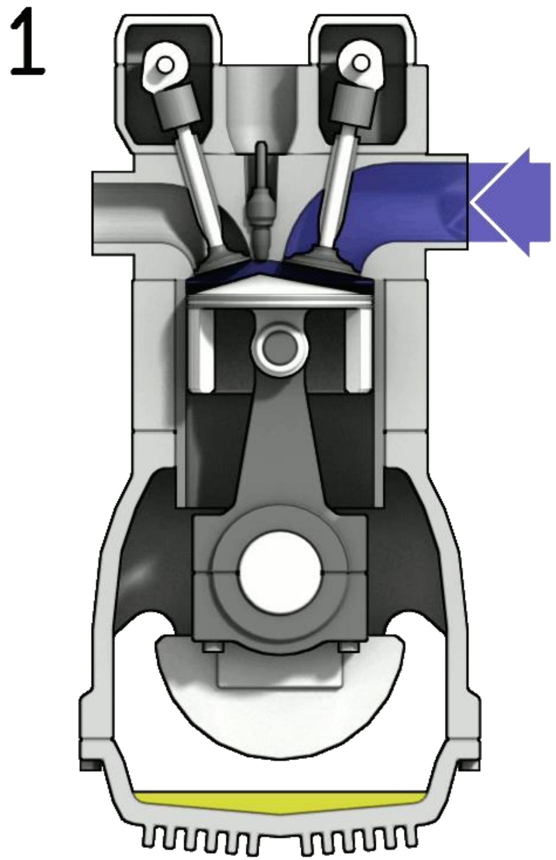
3030 ppm DME, ϕ = 1.19, *p* = 12.5 atm, τ = 1.8 s.



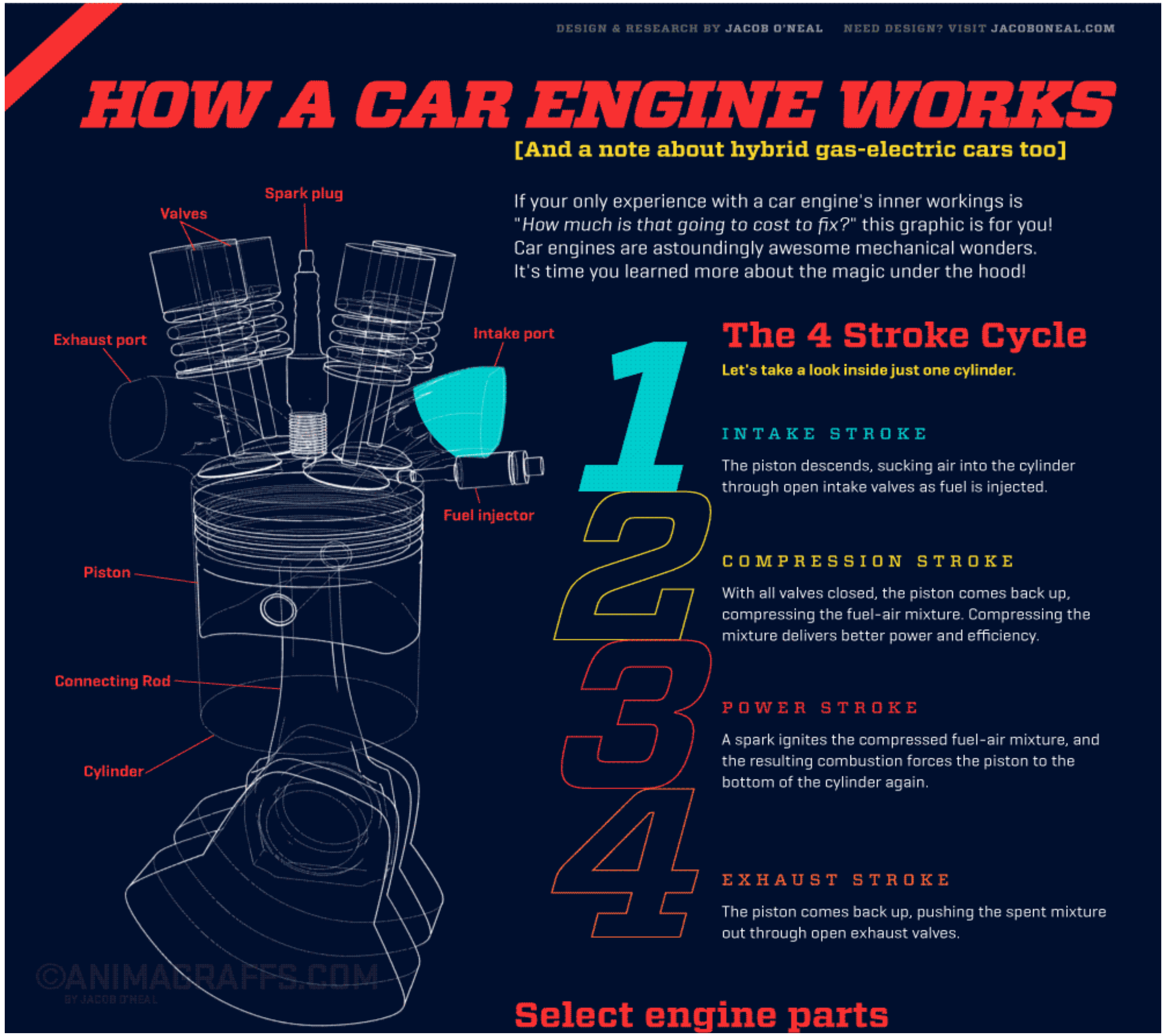
ST and RCM contribution to mechanism generation and validation

Introduction

- Intake stroke: the piston descends, sucking air into the cylinder through open air intake valves as fuel is injected
- Compression stroke: with all valves closed, the piston comes back up, compressing the fuel-air mixture to TDC. Compressing the mixture delivers better power and efficiency.
- Power stroke: A spark ignites the compressed fuel-air mixture and the resulting gas expansion forces the piston to BDC again.
- Expansion stoke: The piston comes back up, pushing the exhaust gases out through the exhaust valves.



4-Stroke Engine



DESIGN & RESEARCH BY **JACOB O'NEAL** NEED DESIGN? VISIT **JACOBONEAL.COM**

HOW A CAR ENGINE WORKS

[And a note about hybrid gas-electric cars too]

If your only experience with a car engine's inner workings is "*How much is that going to cost to fix?*" this graphic is for you! Car engines are astoundingly awesome mechanical wonders. It's time you learned more about the magic under the hood!

The 4 Stroke Cycle

Let's take a look inside just one cylinder.

INTAKE STROKE

The piston descends, sucking air into the cylinder through open intake valves as fuel is injected.

COMPRESSION STROKE

With all valves closed, the piston comes back up, compressing the fuel-air mixture. Compressing the mixture delivers better power and efficiency.

POWER STROKE

A spark ignites the compressed fuel-air mixture, and the resulting combustion forces the piston to the bottom of the cylinder again.

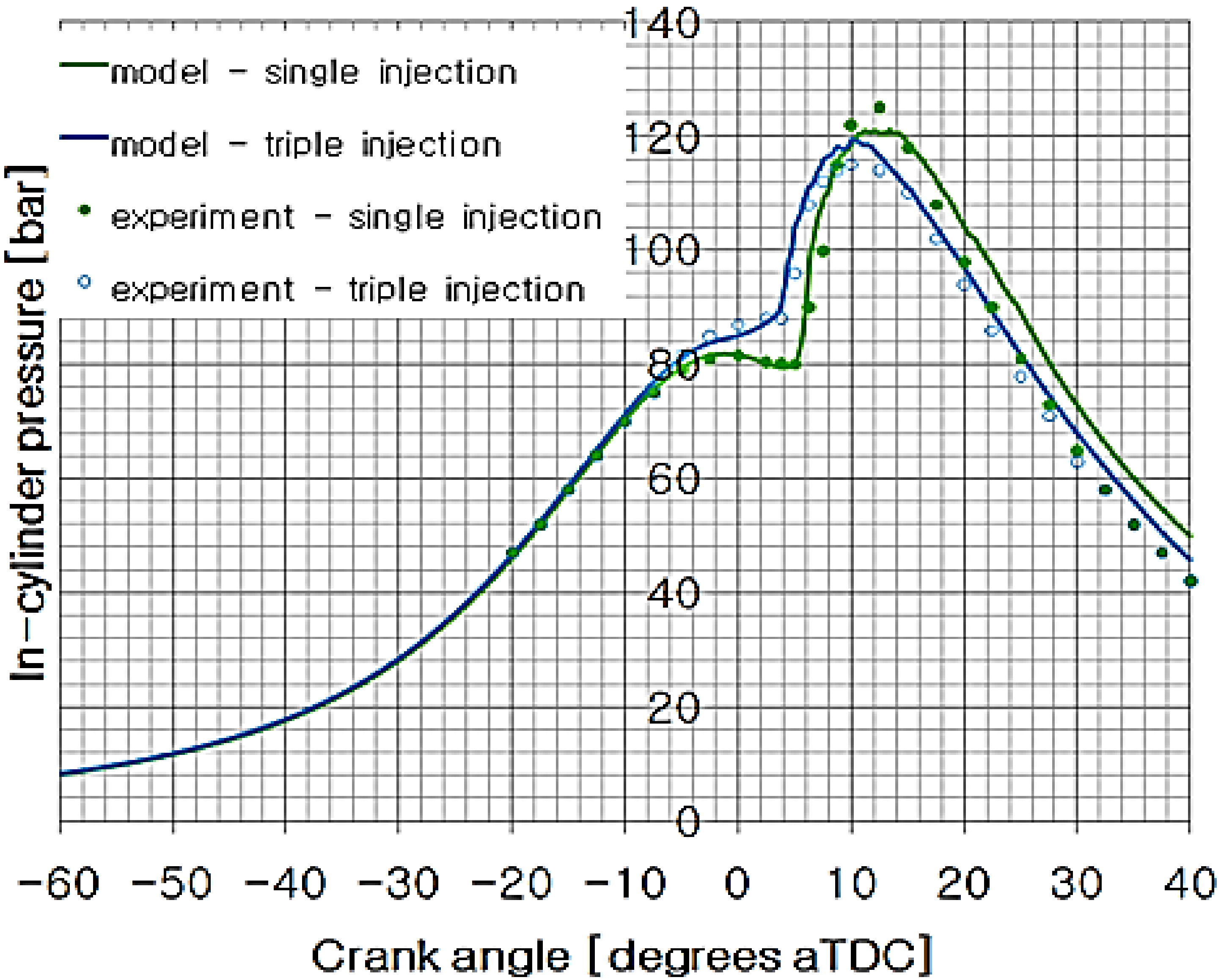
EXHAUST STROKE

The piston comes back up, pushing the spent mixture out through open exhaust valves.

Select engine parts

Source: *https://giphy.com/gifs/car-works-engine-TMAJKmJj3ys2k*

Pressure vs CAD in an engine

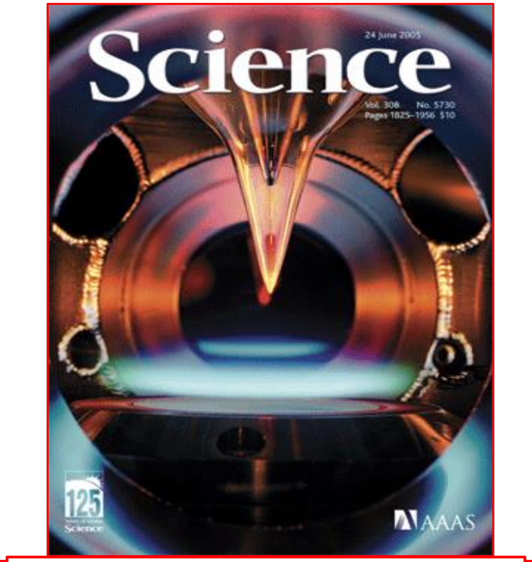


Experimental Studies: Engine Relevant

Rapid Compression Machine

Shock Tube

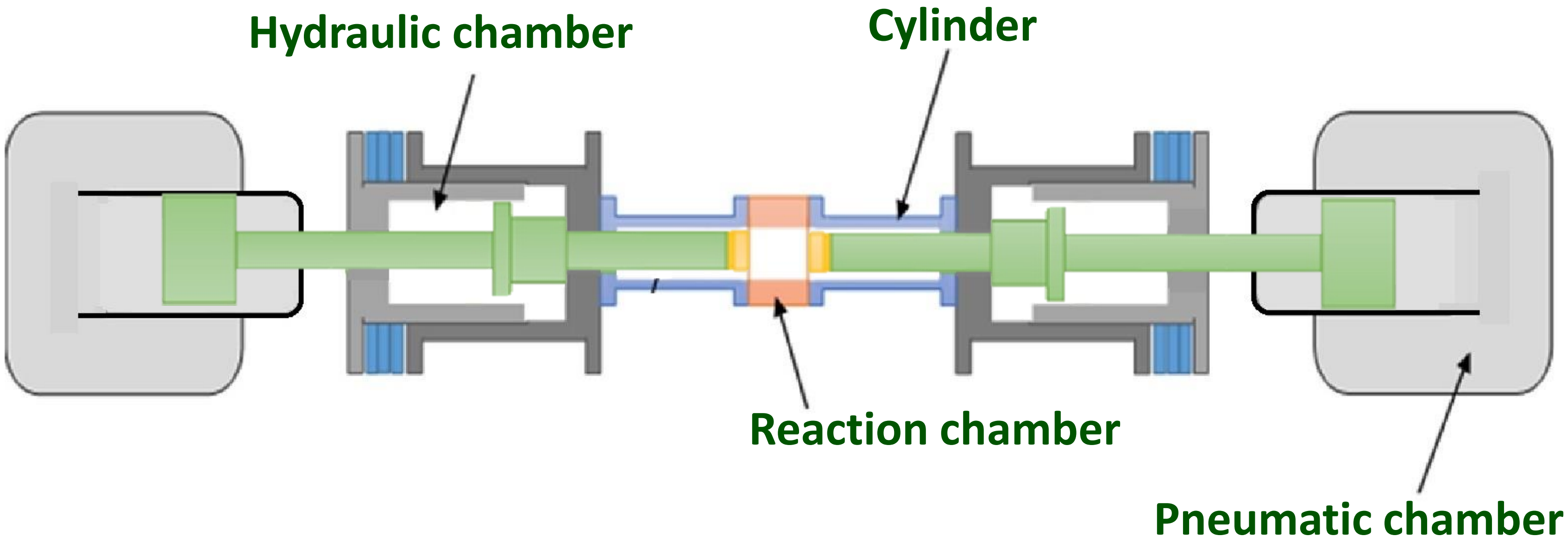
Jet Stirred Reactor



Flat Flame Burner

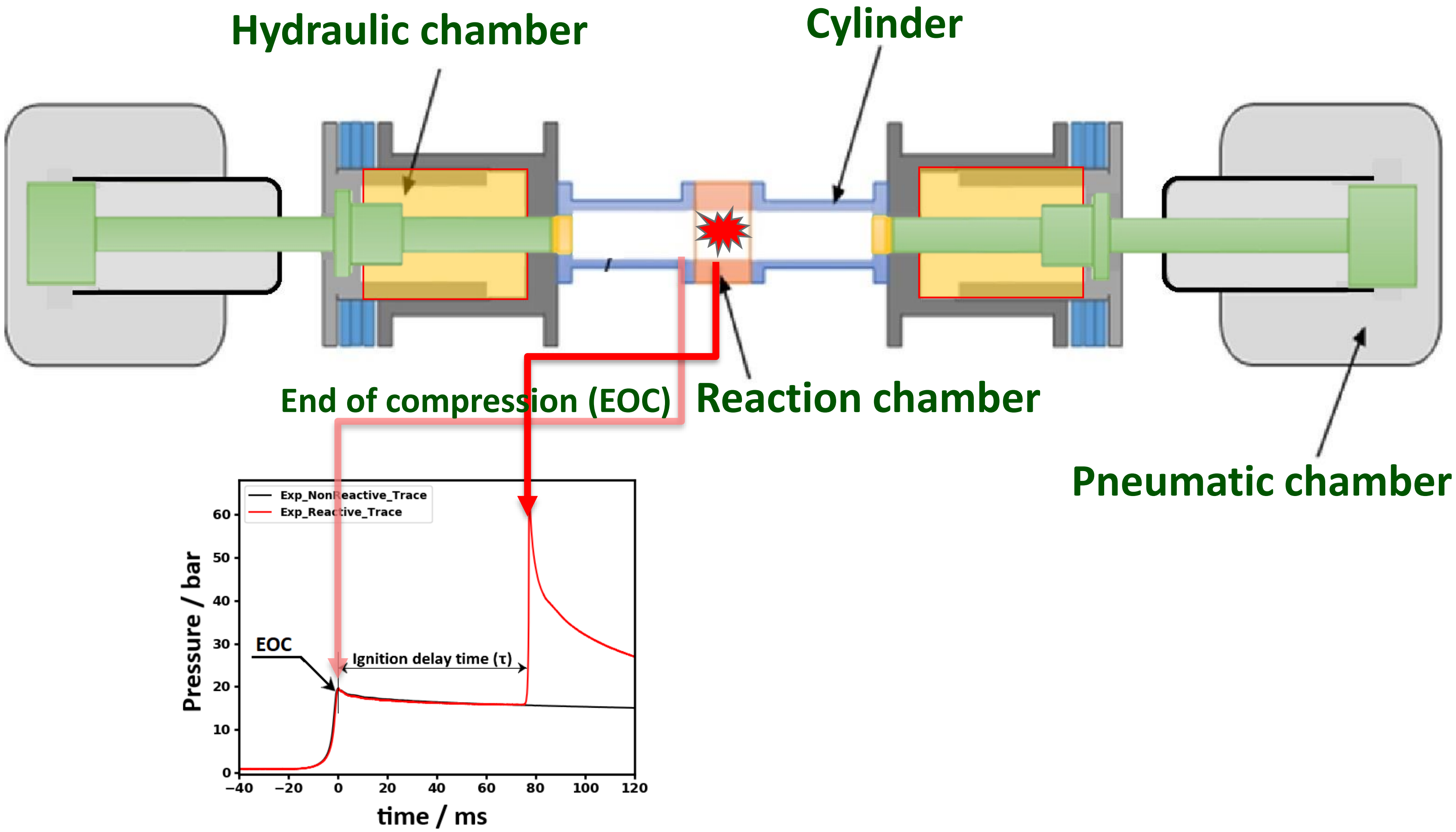
Rapid Compression Machine

Rapid Compression Machine



Source: C. Dumitrache et al. A study of laser induced ignition of methane-air mixtures inside a Rapid Compression Machine. Proc Combust Inst 2017;36:3431–9. doi:10.1016/j.proci.2016.05.033.

Rapid Compression Machine


Hydraulic chamber

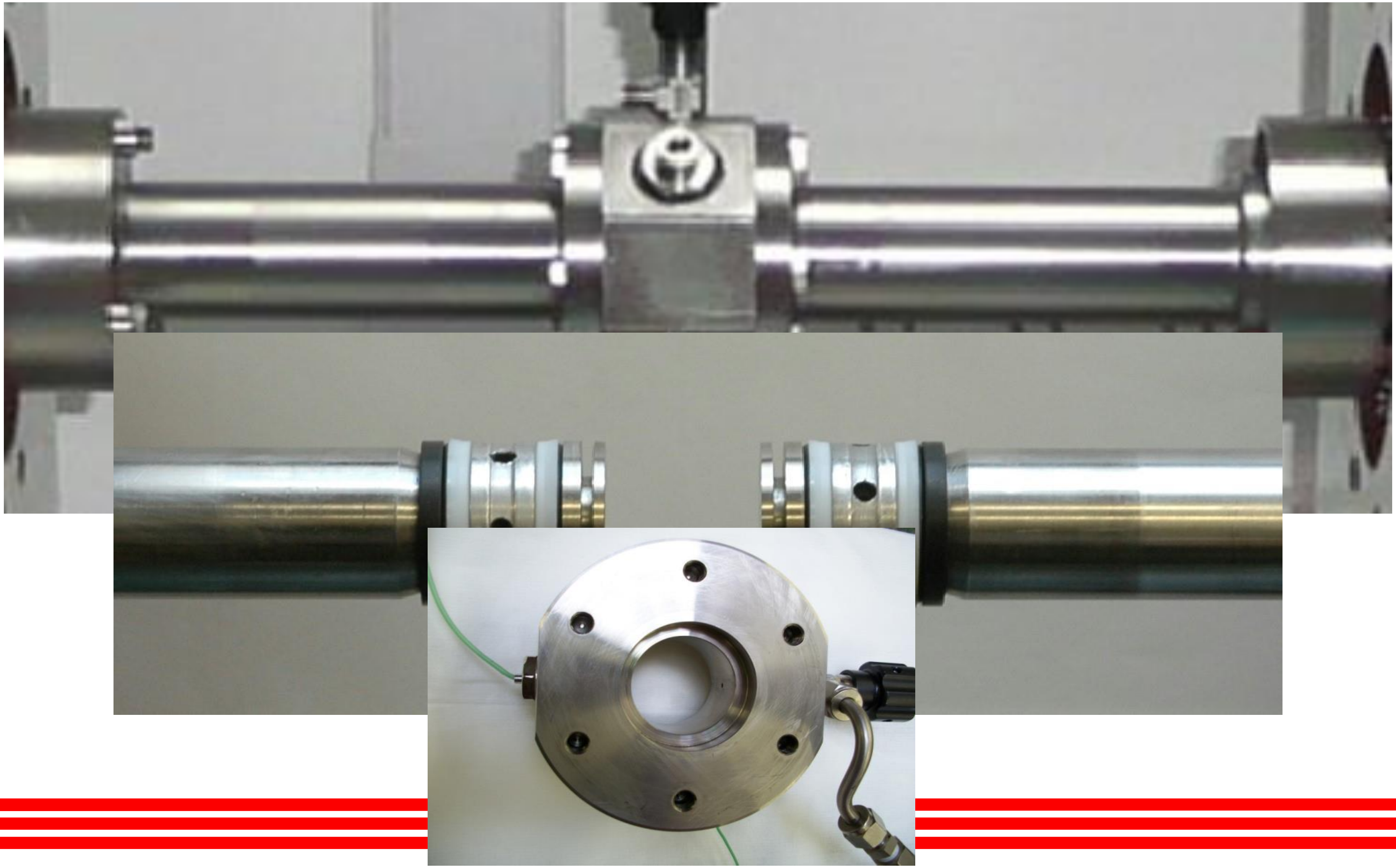
Cylinder

End of compression (EOC)

Reaction chamber

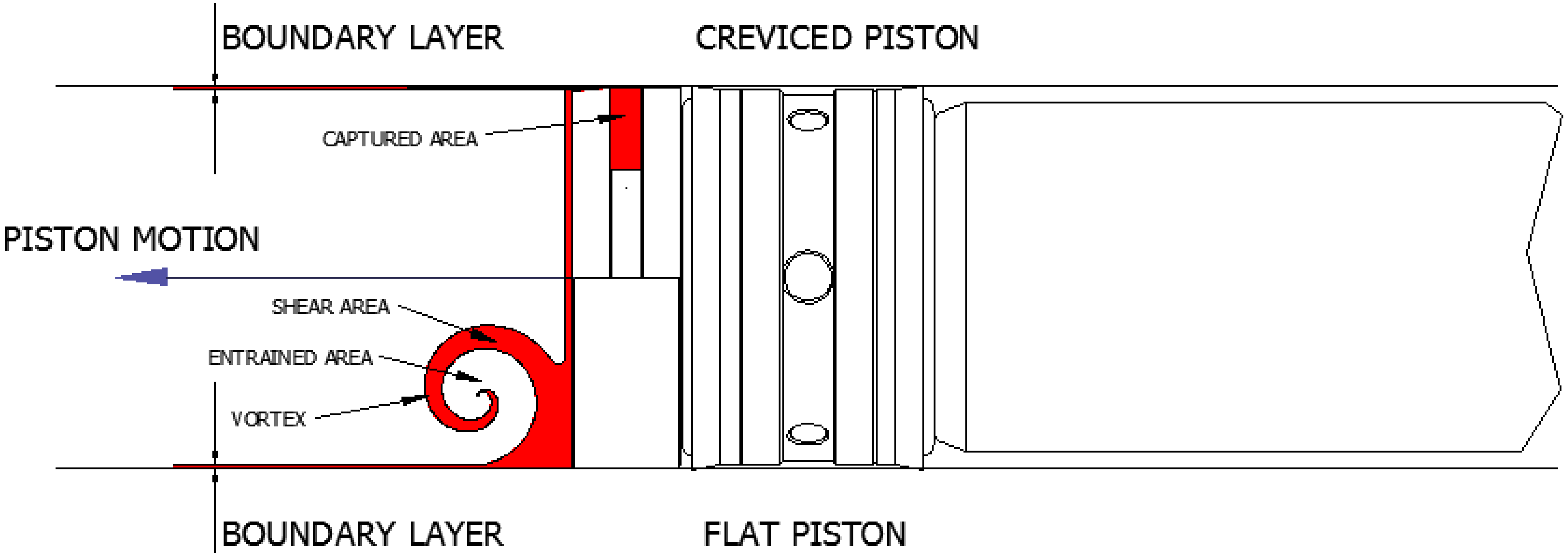
Pneumatic chamber

Rapid Compression Machine



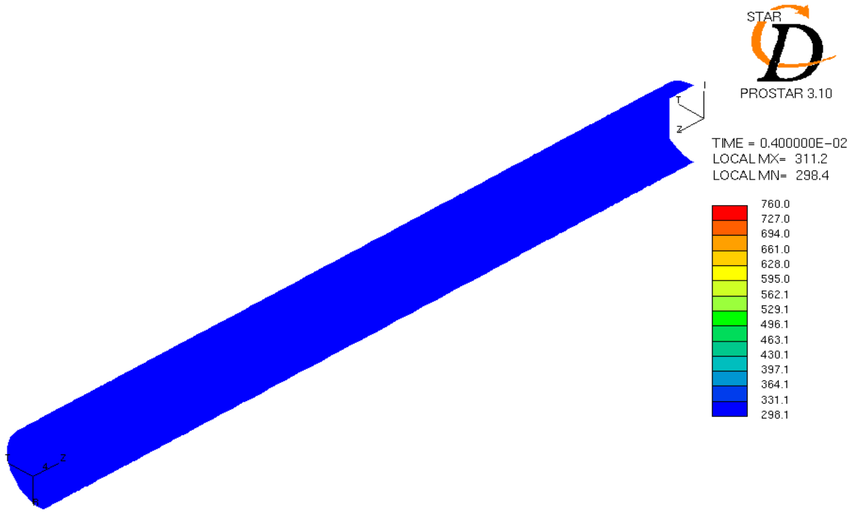
Roll up vortex

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

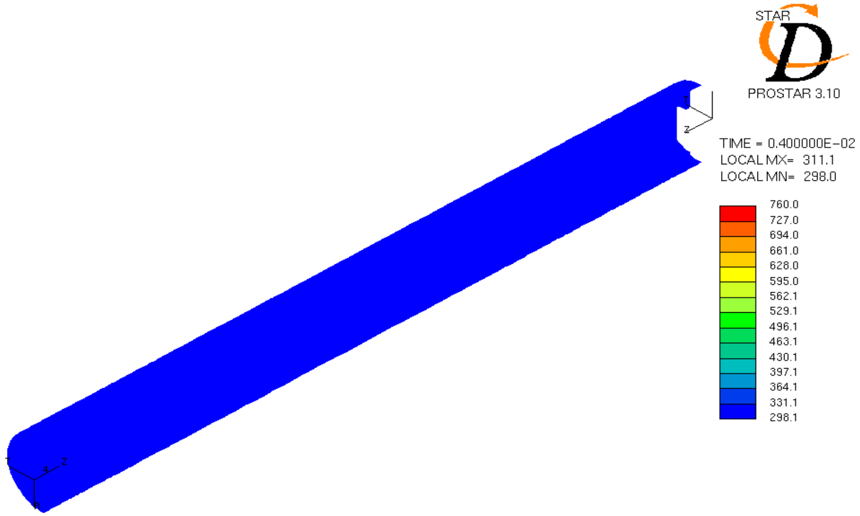


Piston heads: flat versus creviced

Flat piston

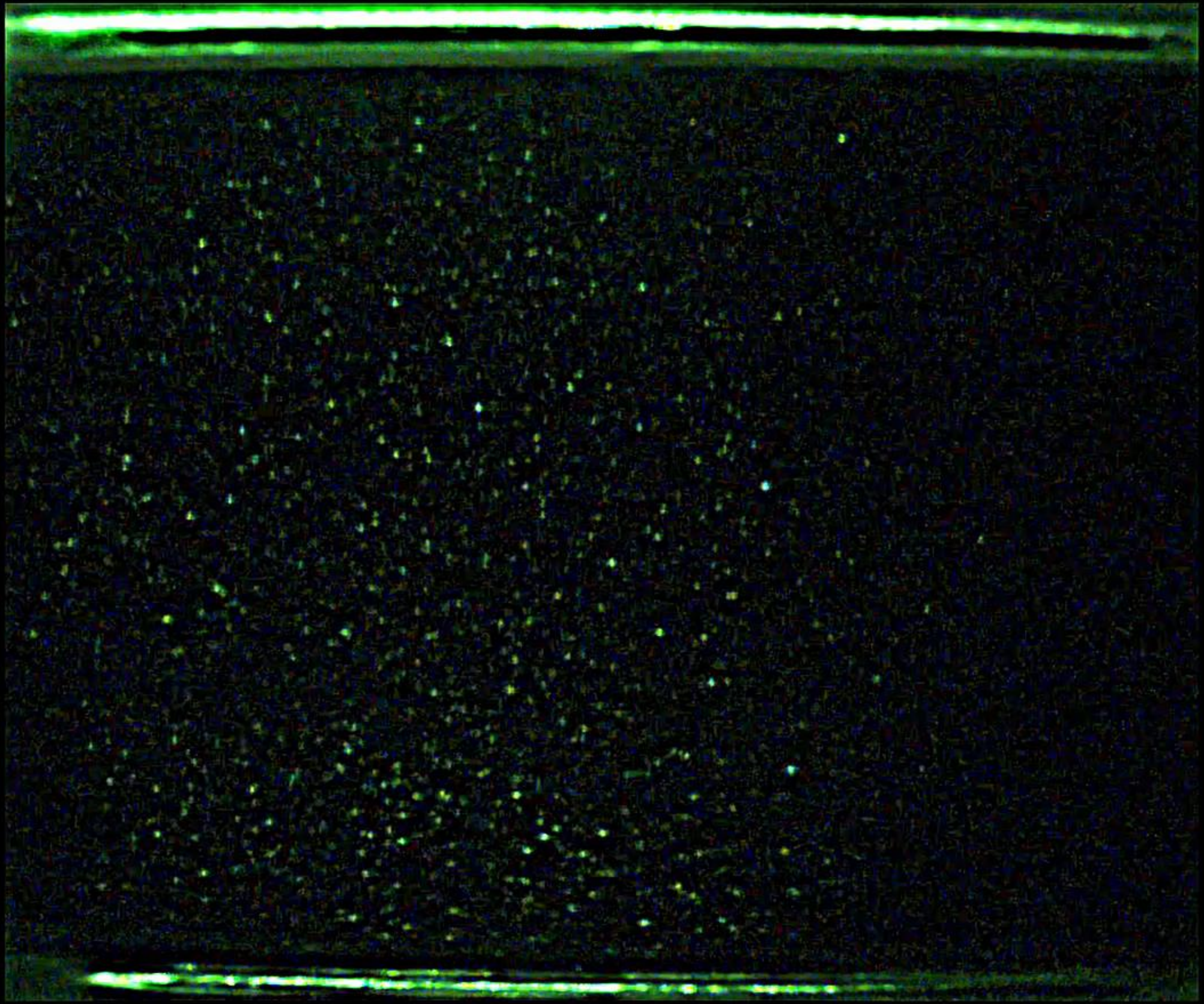


Creviced piston

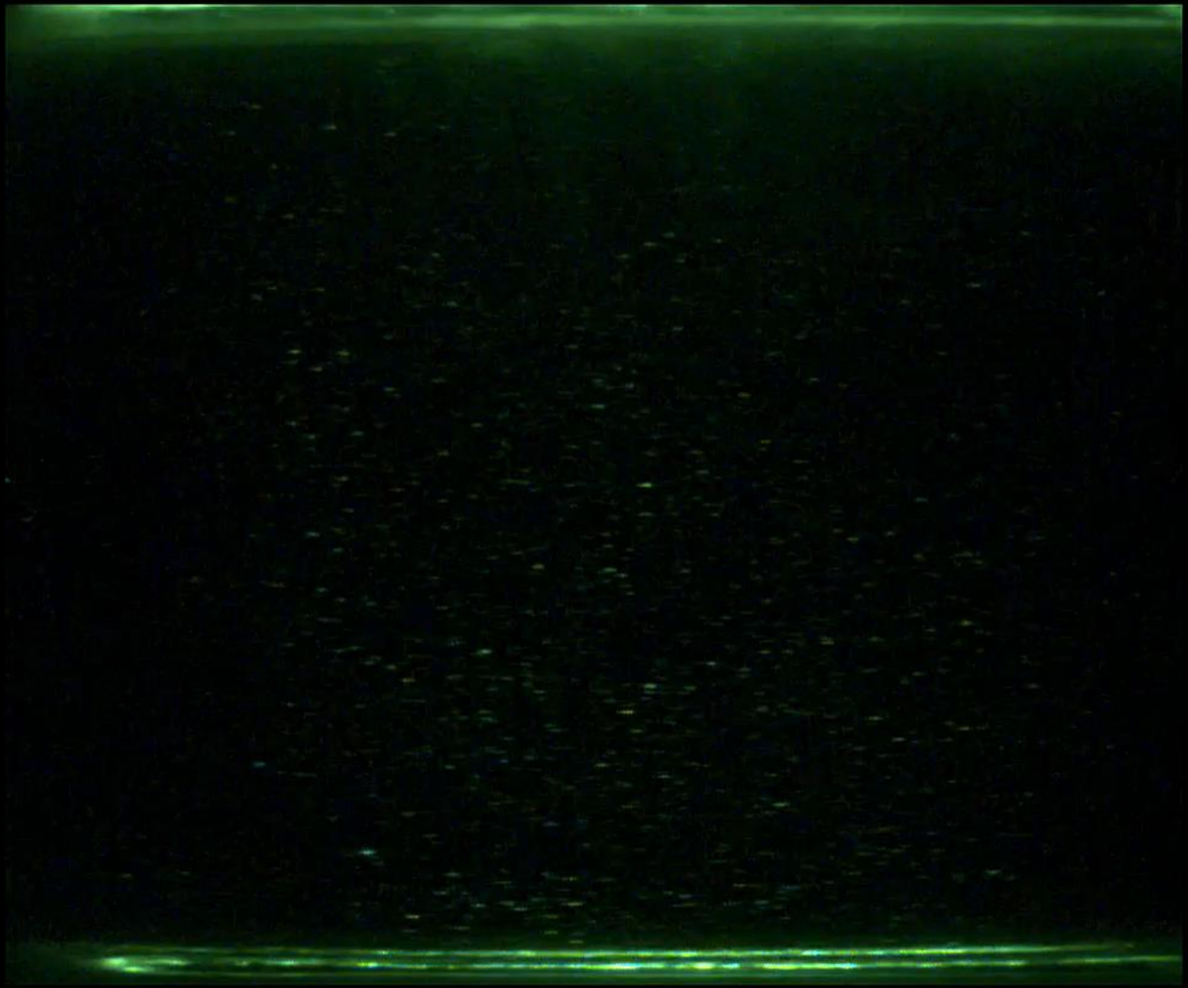


Würmel and Simmie, Combust. Flame, 141 (2005), 417-430.

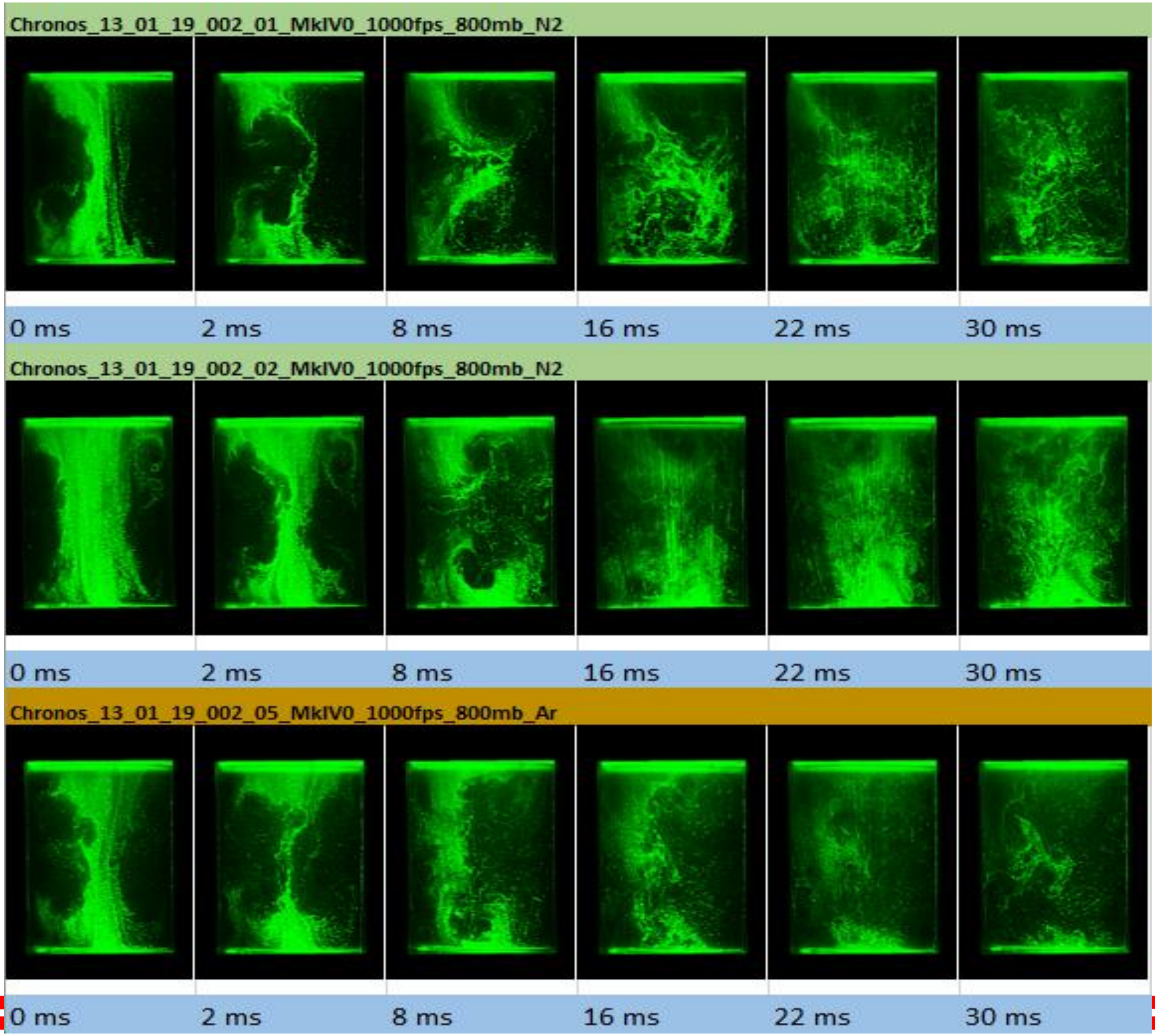
PIV using flat piston heads



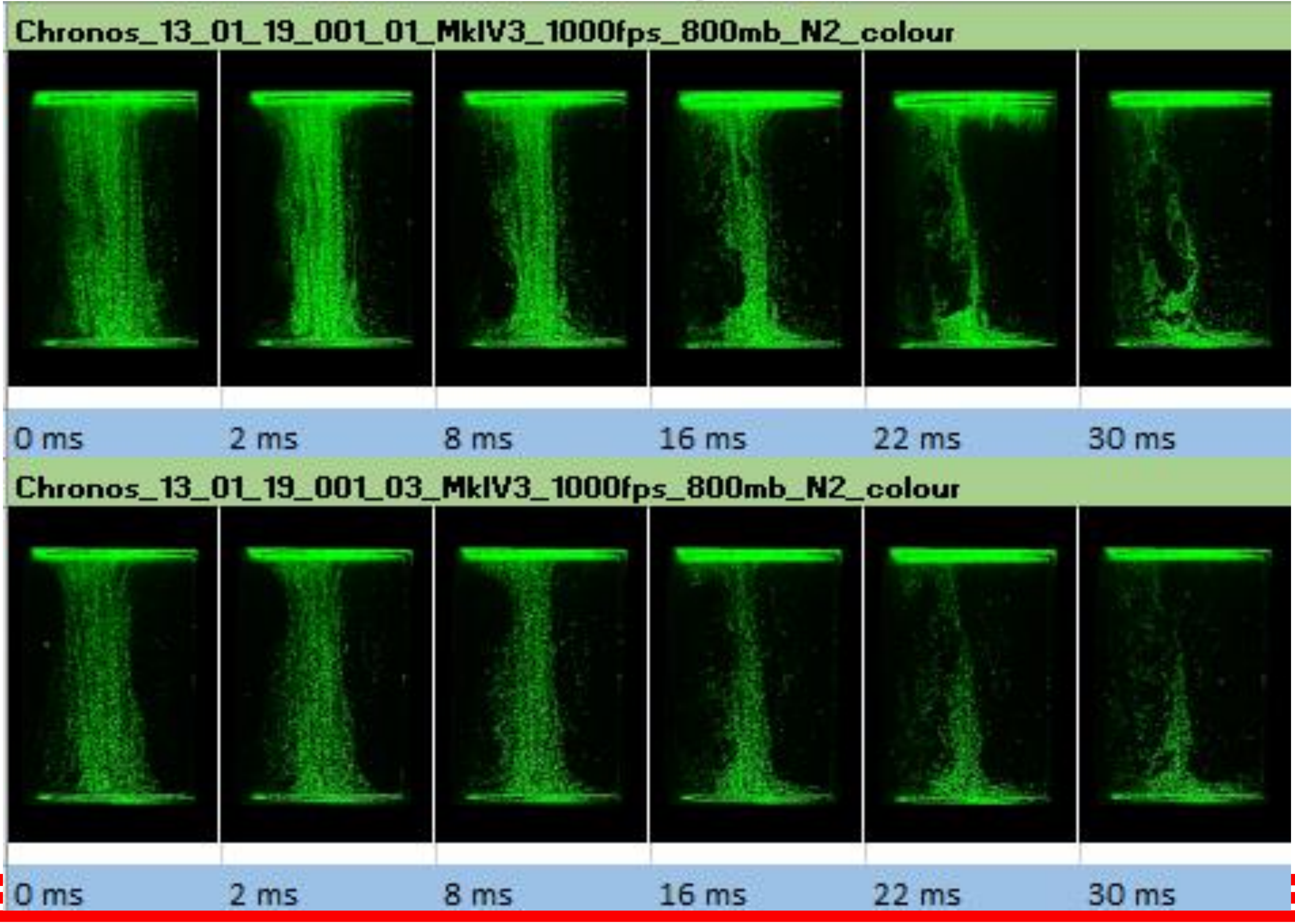
PIV using creviced piston heads



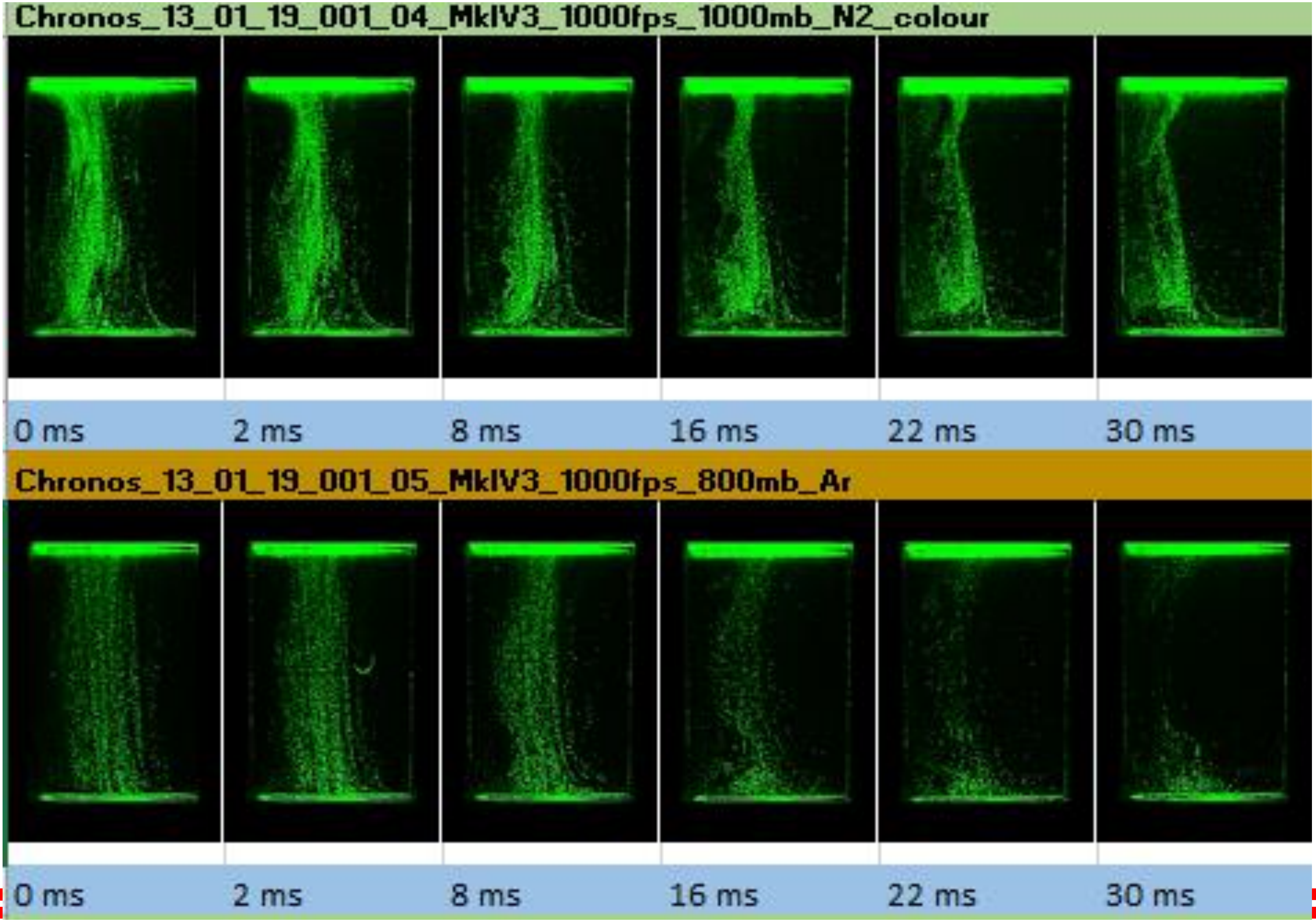
Pistons heads: flat PIV experimental measurements



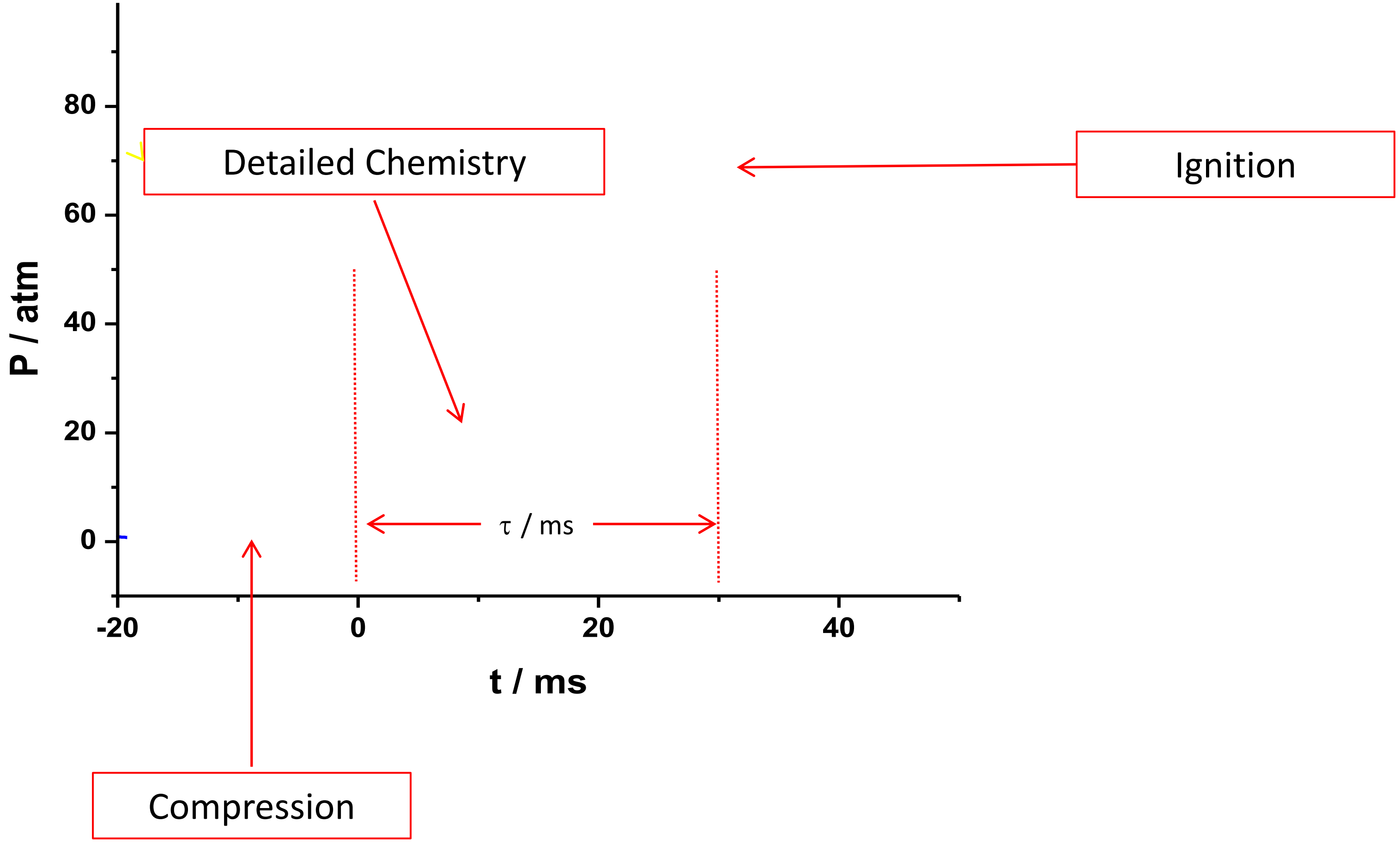
Pistons heads: creviced PIV experimental measurements



Pistons heads: creviced PIV experimental measurements



RCM Engine Relevant Studies



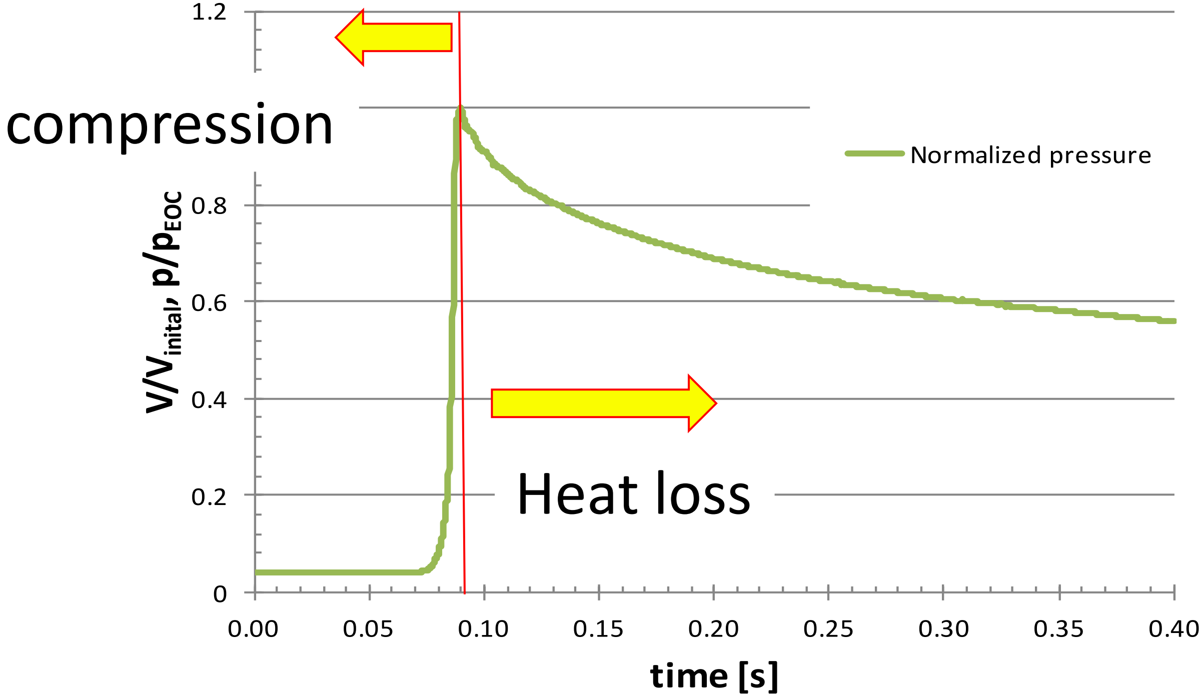
Detailed Chemistry

Ignition

Compression

Data processing for RCM simulation

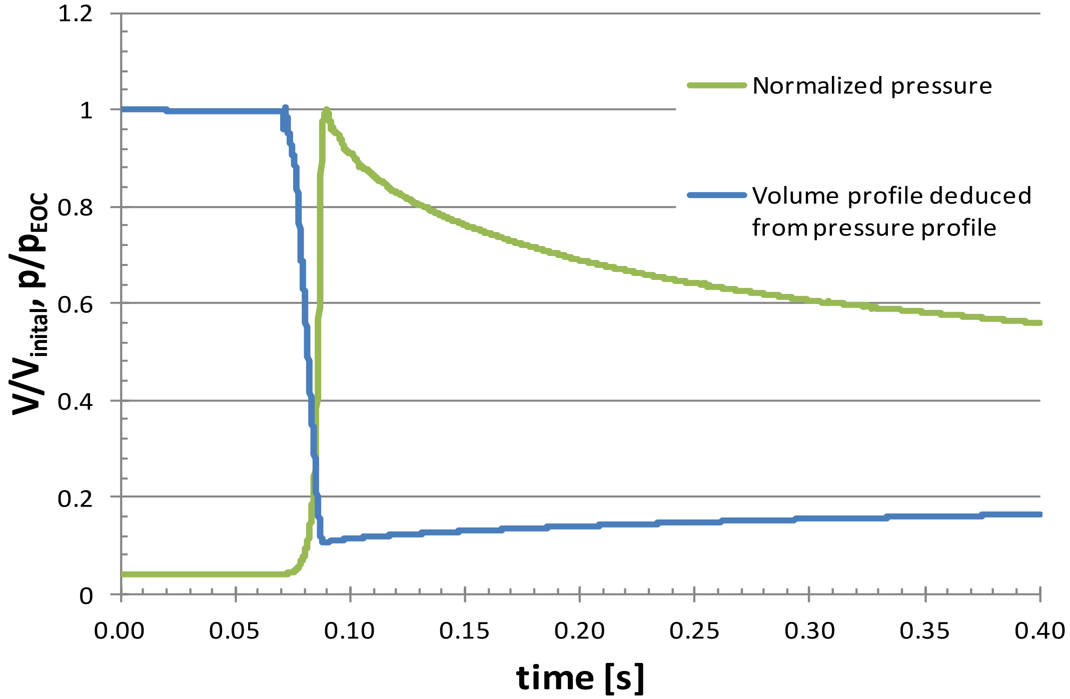
Step 1: Non-reactive experiment



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

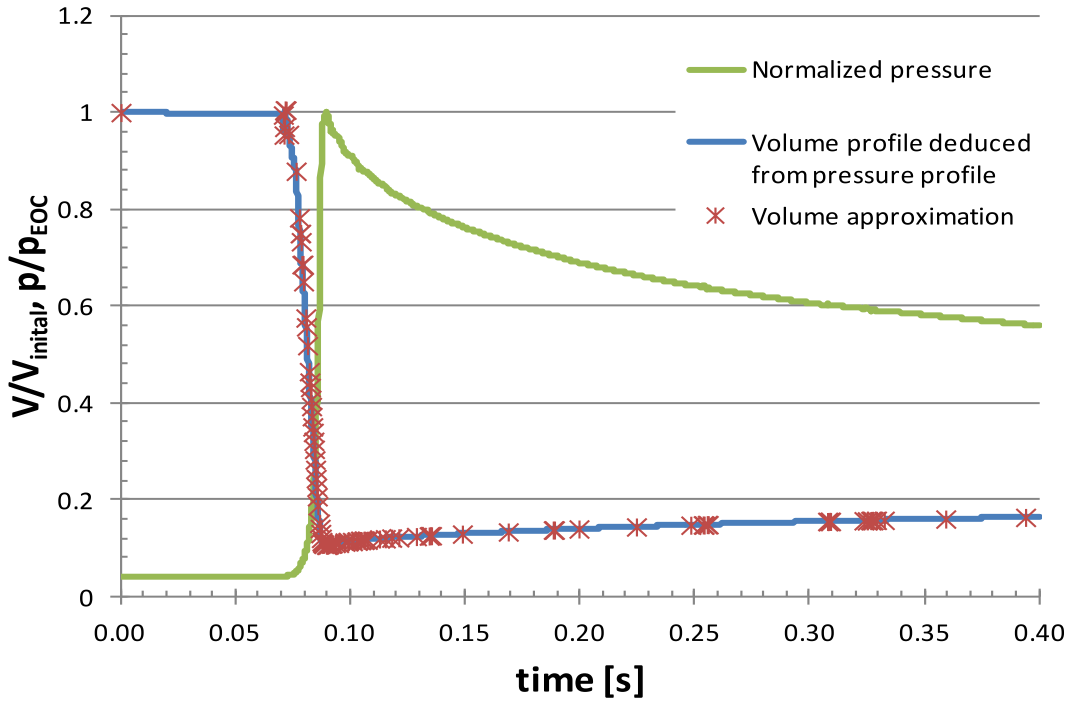


$$\frac{p_2}{p_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

- 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

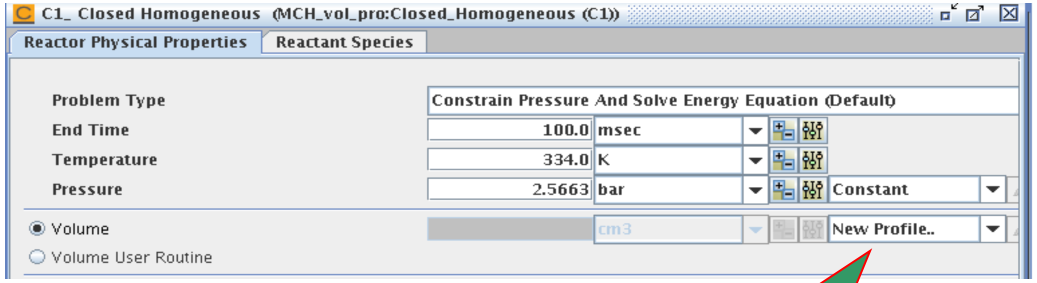


- Reduction in # of data points to reduce simulation time for reactive simulations.
- Non-uniform distribution of data points => accurate reproduction of volume profile.

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 and Cantera
  - Better agreement with experimental pressure profiles

We want to make the life of modelers easy!



Problem Type: Constrain Pressure And Solve Energy Equation (Default)
End Time: 100.0 msec
Temperature: 334.0 K
Pressure: 2.5663 bar, Constant
● Volume: cm3, New Profile..
○ Volume User Routine

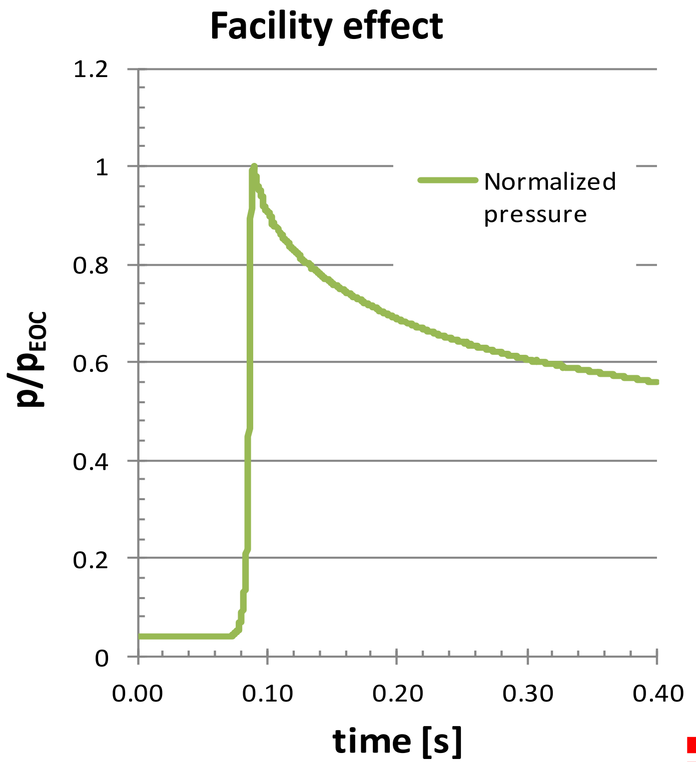
CHEMKIN-Pro and Cantera Volume Profile Input

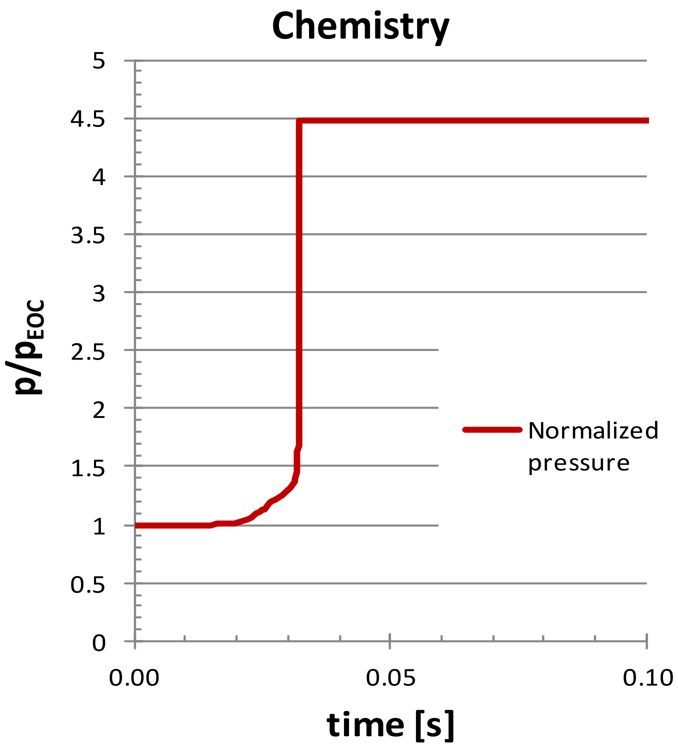
Data processing for RCM simulation

Step 4: Simulating reactive experiment

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

➡ Perturbation of the constant volume reactor by the given volume profile


Facility effect


Chemistry

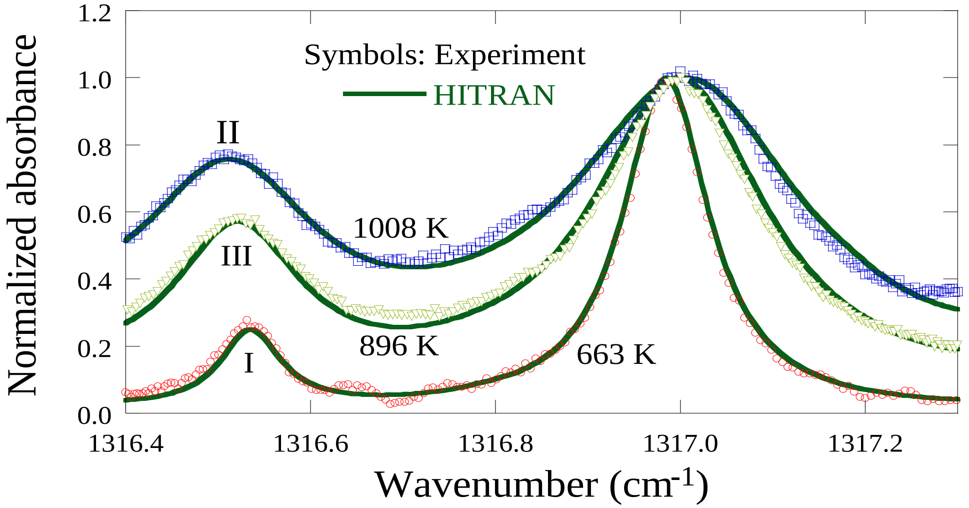
Early pressure rise used to estimate Temp rise

Assume Temperature and Pressure are Related by:

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

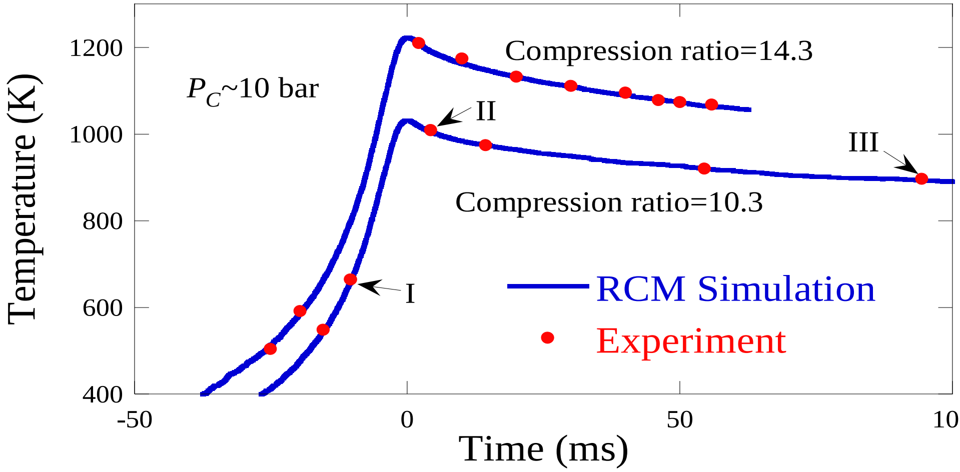
Two-Line Thermometry and H_2O Measurements in RCM using laser absorption at 7.6 μm

Line ratio comparison for three representative cases



Non-Reactive Mixtures

Comparison of experimental and calculated temperatures



- Mixture of Ar with 2.87%H_2O 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).

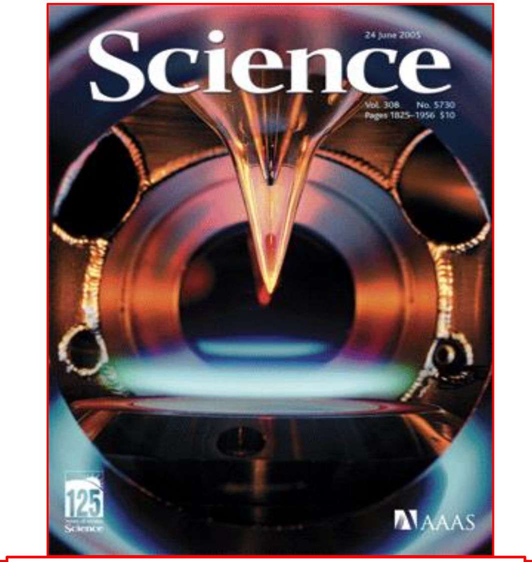
A.K. Das, M. Uddi, C-J. Sung
Combust. Flame, 159 (2012) 3493–3501.

Experimental Studies: Engine Relevant

Rapid Compression Machine

Shock Tube

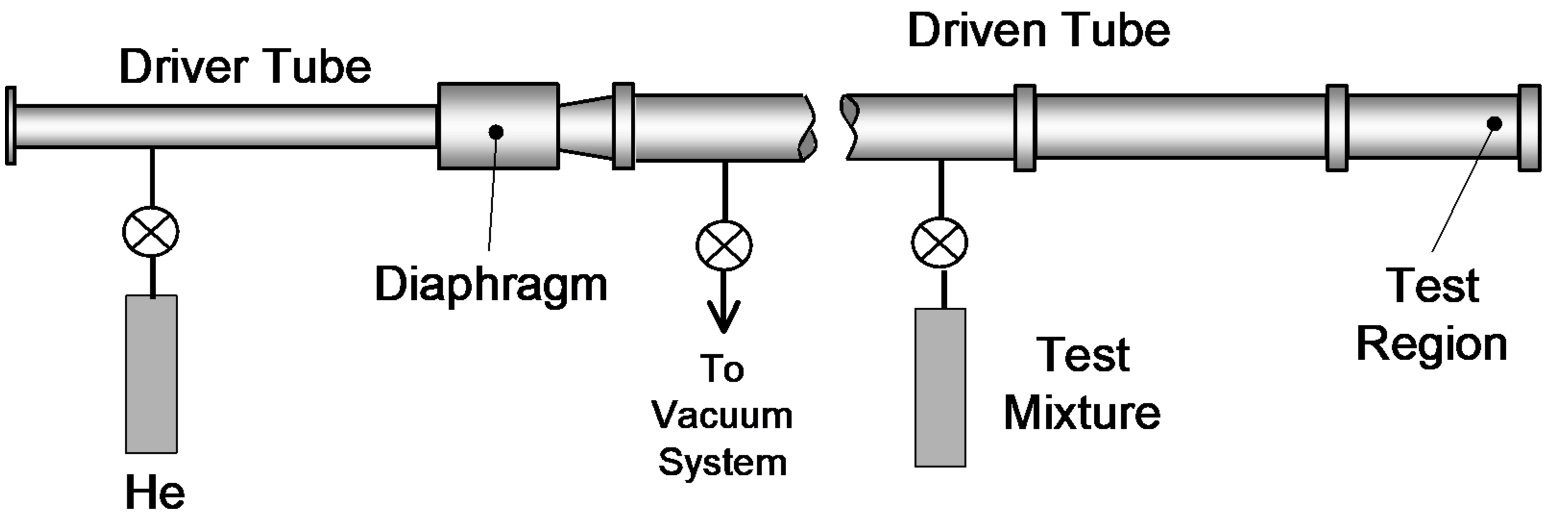
Jet Stirred Reactor



Flat Flame Burner

ST and RCM contribution to mechanism generation and validation

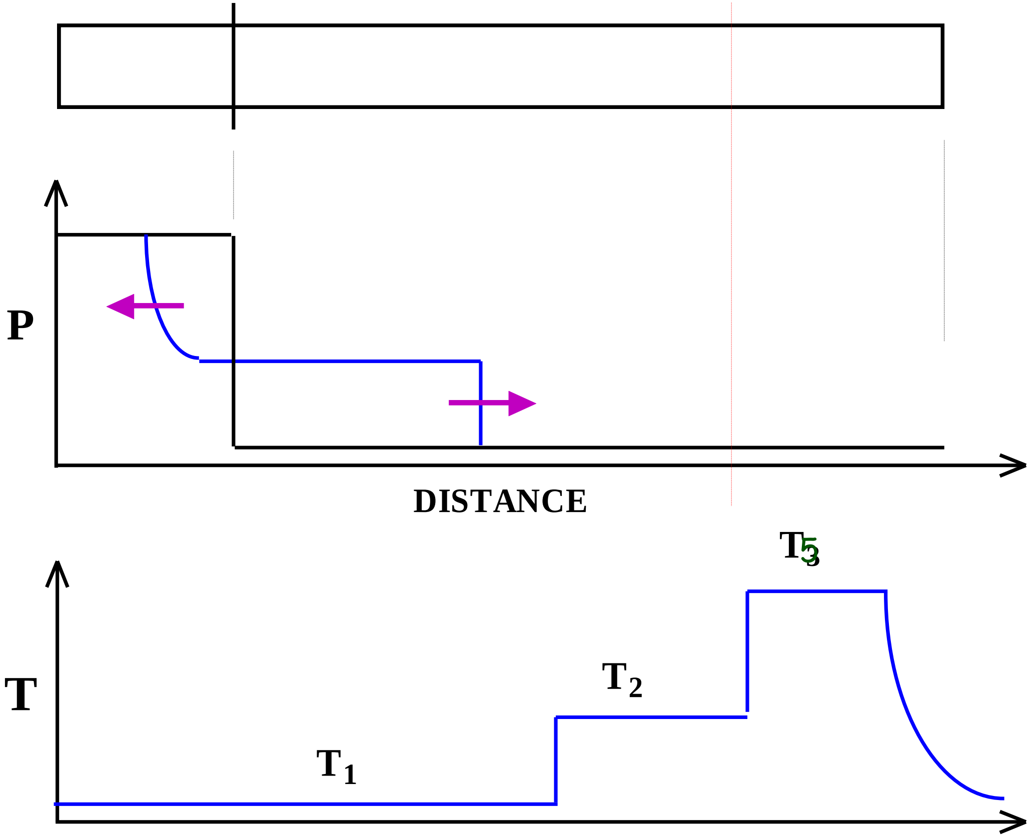
Reactions in shock waves



- 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: $\mathbf{C_6H_5CHO \rightarrow CO^* + C_6H_6}$
- Energy transfer rxns.: $\mathbf{CO_2 + M \rightarrow CO_2^* + M}$
- Relative rates, use standard rxn as "clock"

Mode of action of shock tube

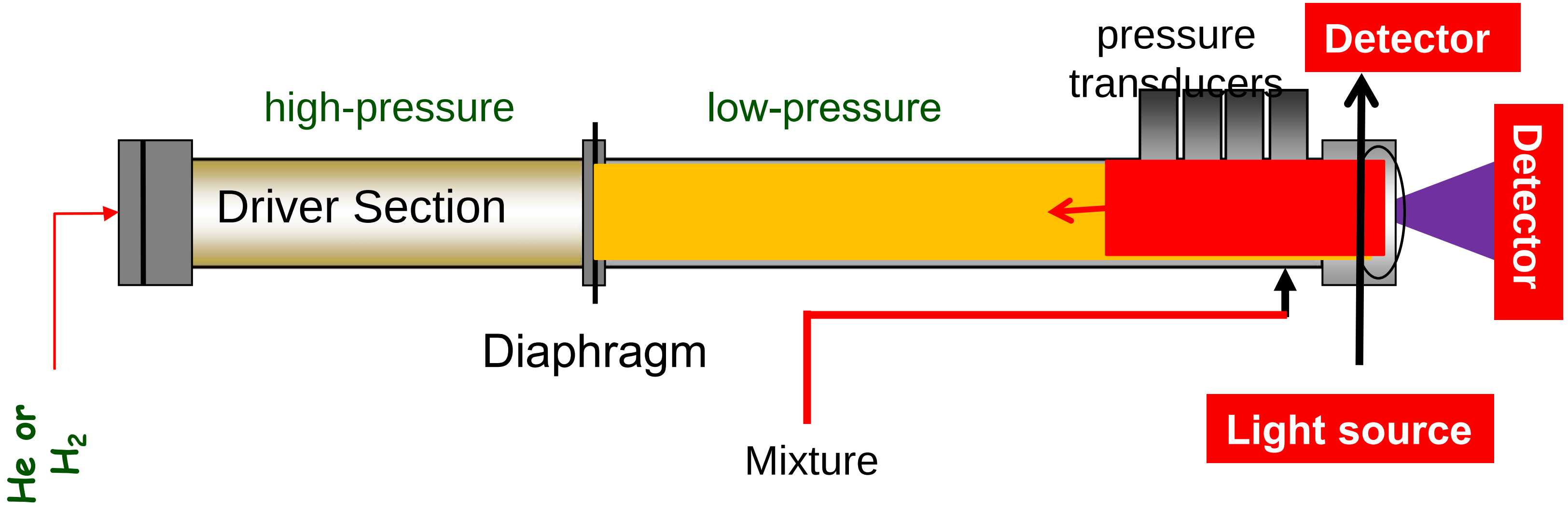
- Fast bunsen-burner (ns)
- Shock wave acts as a piston compressing & heating the gas ahead of it
- Study rxns behind incident shock wave or reflected shock wave (ms-ms times)
- Non-invasive techniques
- ***T*** & ***p*** by computation from measured shock velocity



How does a shock tube work?

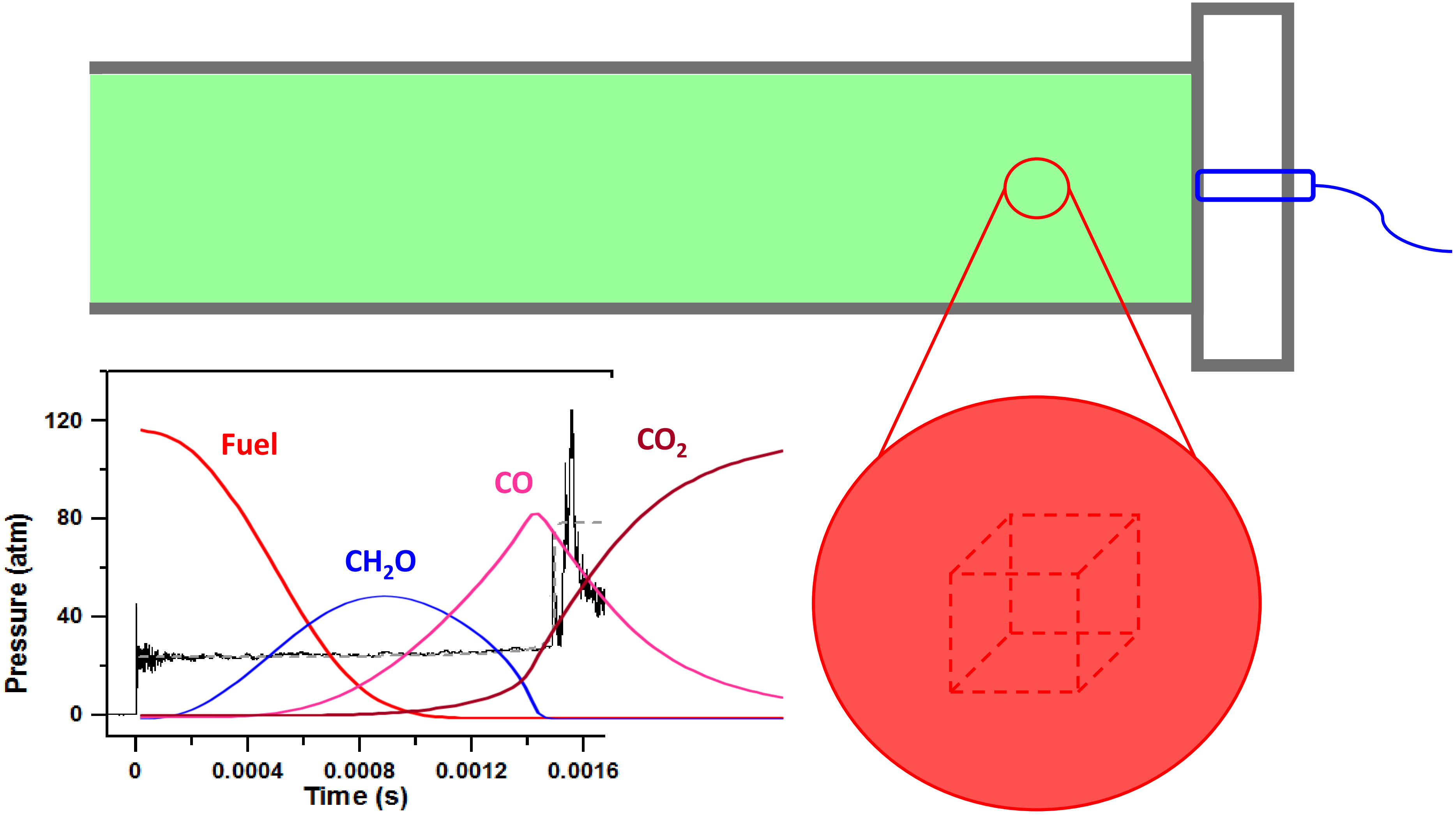
Source: https://www.nist.gov/video/dynamic-pressure-sensing-shock-tube

Shock Tube Operation



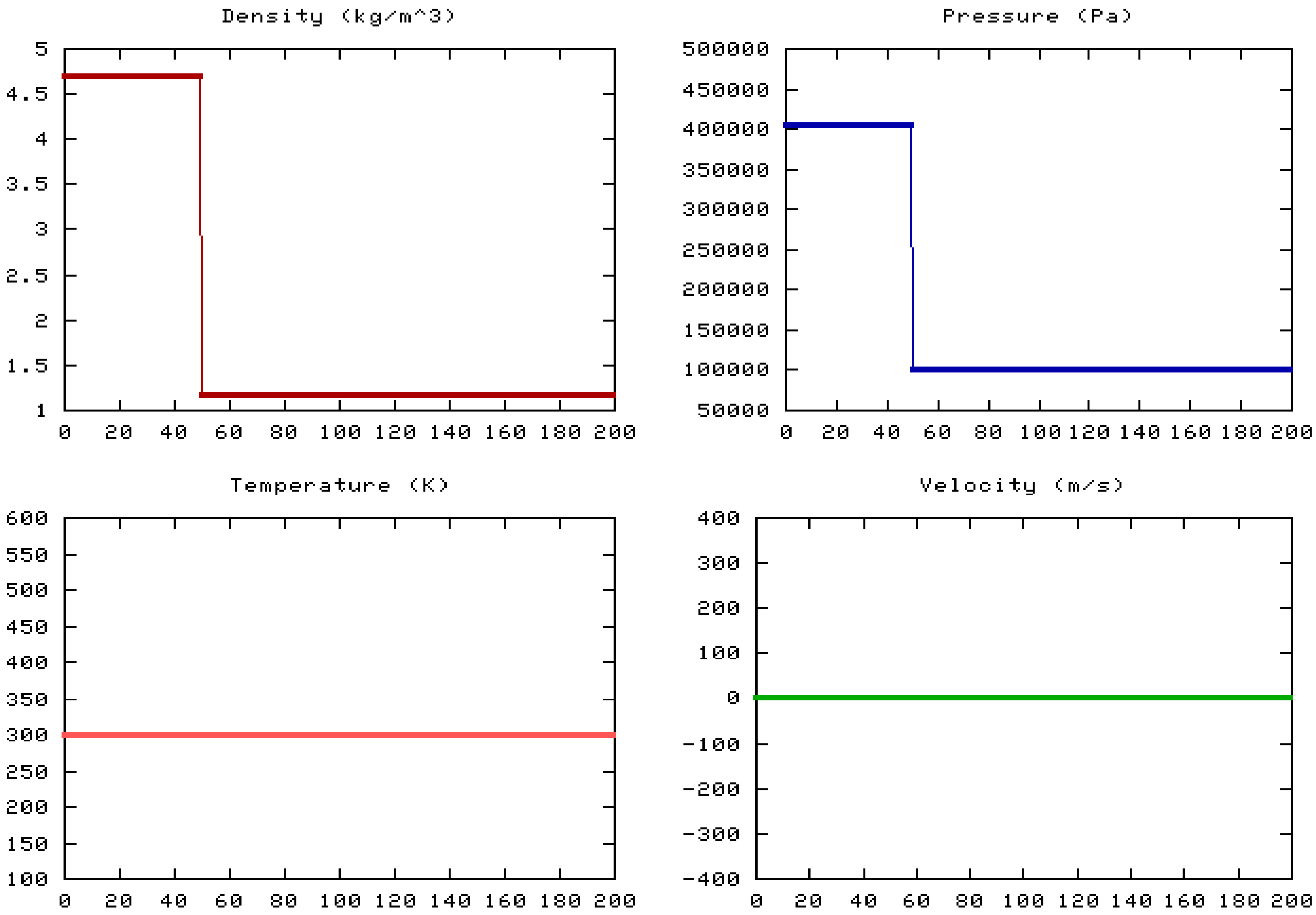
Slide courtesy of: Siavash Zabeti, Stephan Faust, Thomas Dreier, Oliver Welz, Mustapha Fikri, Christof Schulz, University of Duisburg, Essen

Shock tube

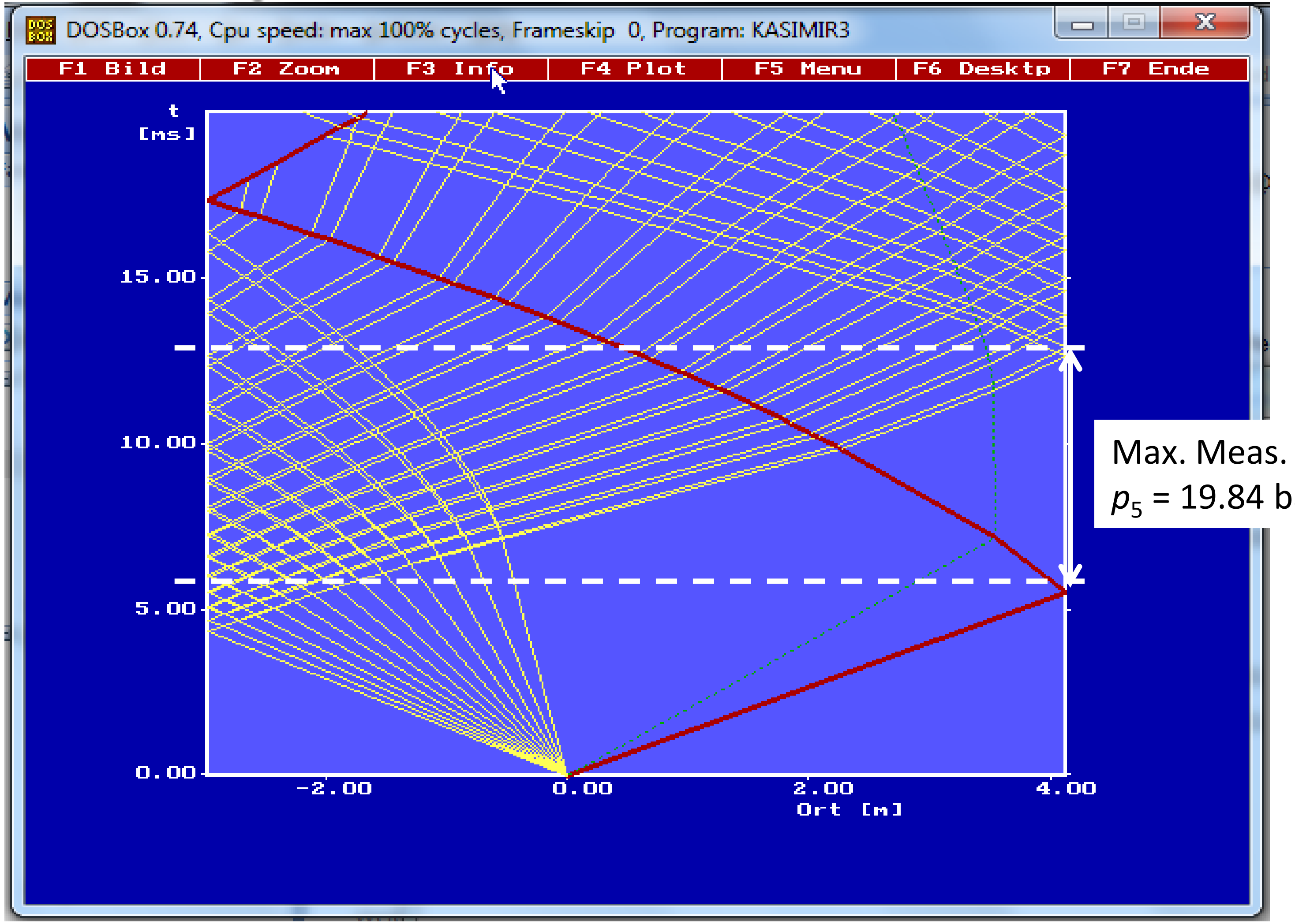


120
80
40
0
Pressure (atm)
0
0.0004
0.0008
0.0012
0.0016
Time (s)
Fuel
CH_2O
CO
CO_2

Shock Tube Simulation



Shock position vs time available in ST



Max. Meas. Time ≈ 7 ms

p_5 = 19.84 bar, T_5= 806 K

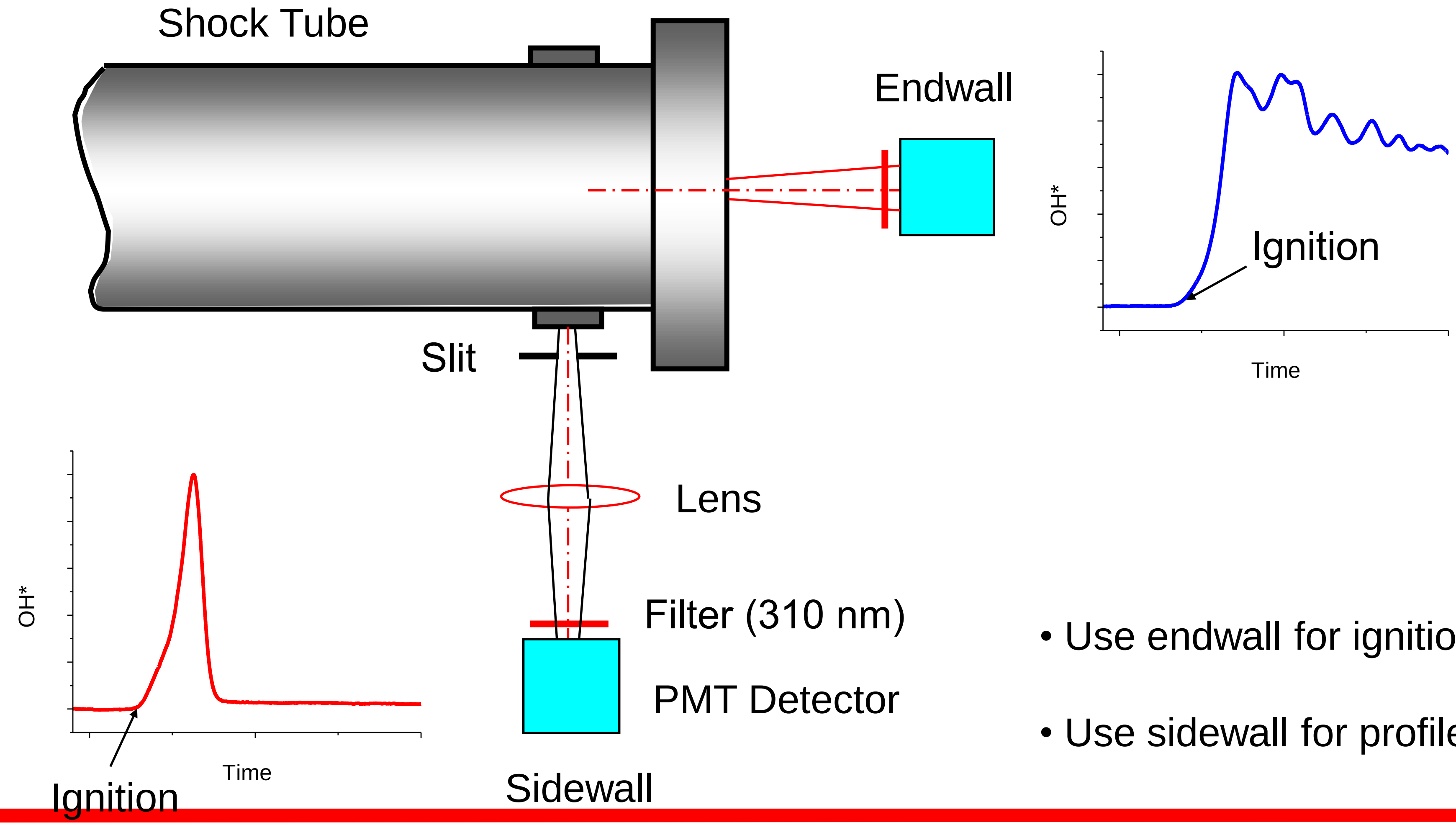
Driver gas: 10% Ar / 90% He Driven gas: air

p_4 = 20 bar, p_1 = 1 bar

Real available measuring time around 5.3 ms (estimation)

Ignition delay times

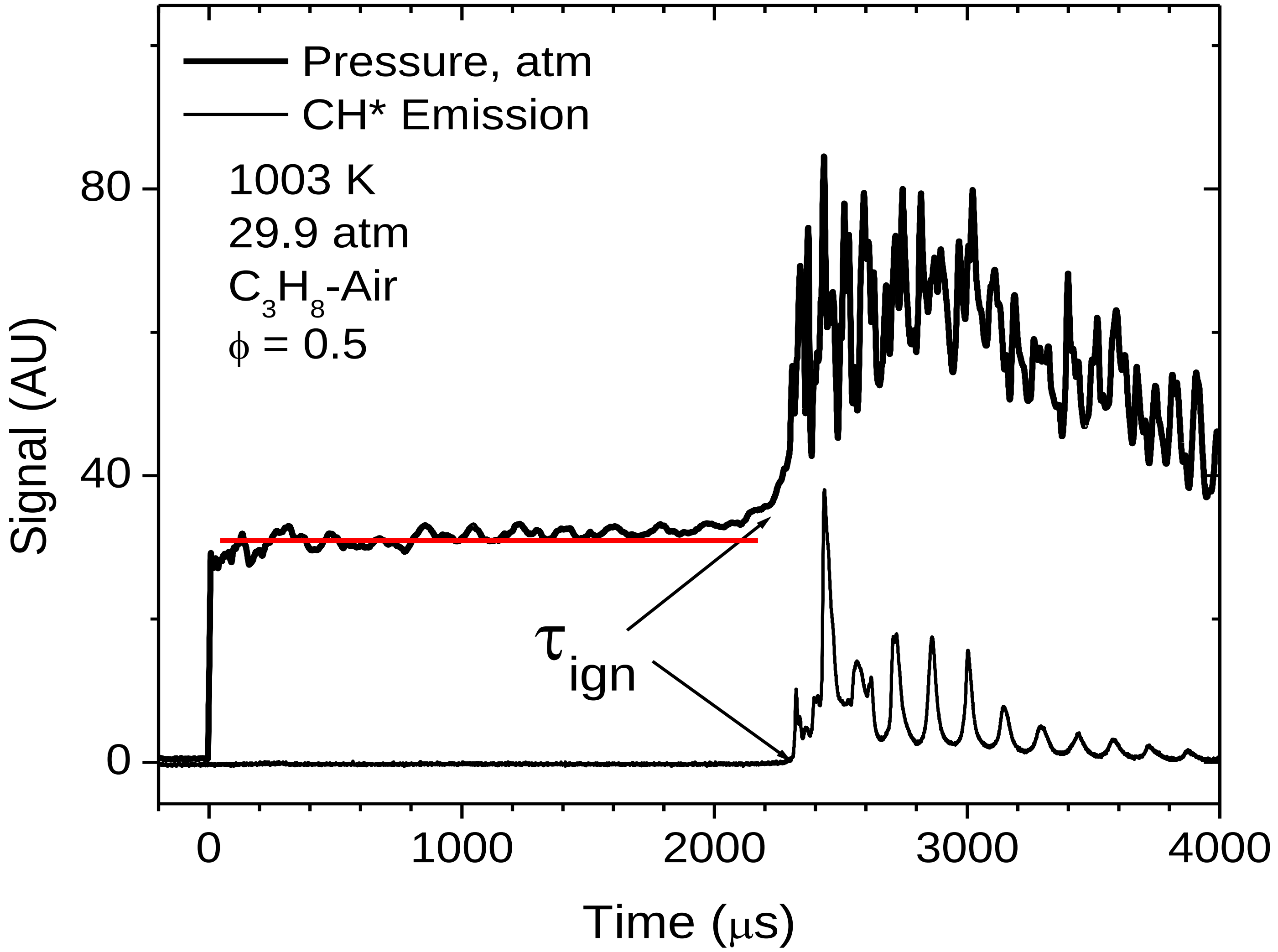
CH **Chemiluminescence (431 nm)** Detected at Endwall and Sidewall*



- Use endwall for ignition
- Use sidewall for profiles

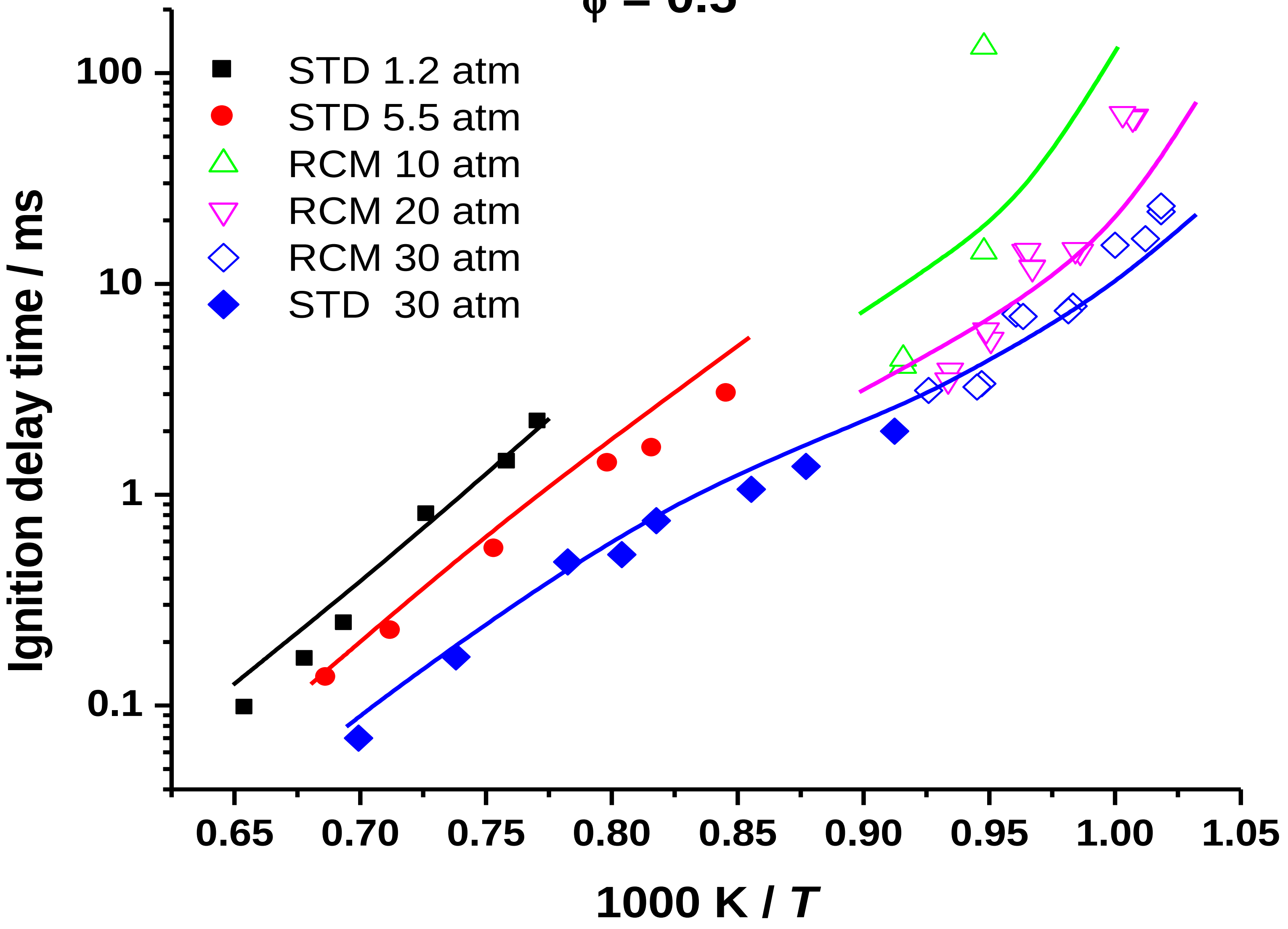
Slide courtesy of Prof. E. Petersen

Typical ST experimental record



Slide courtesy of Prof. E. Petersen

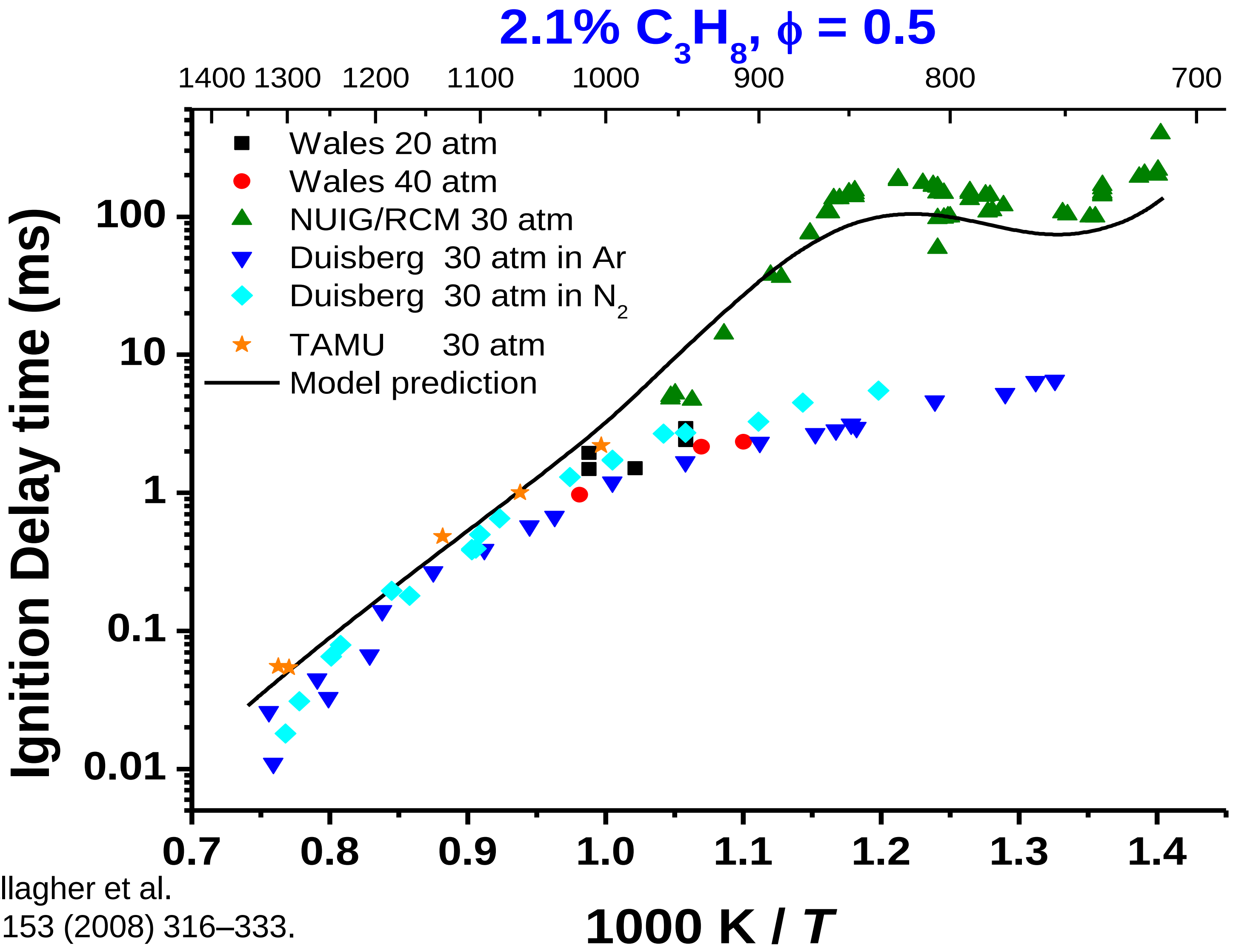
90% CH_4, 6.6% C_2H_6, 3.3% C_3H_8
$\phi = 0.5$



Ignition delay times

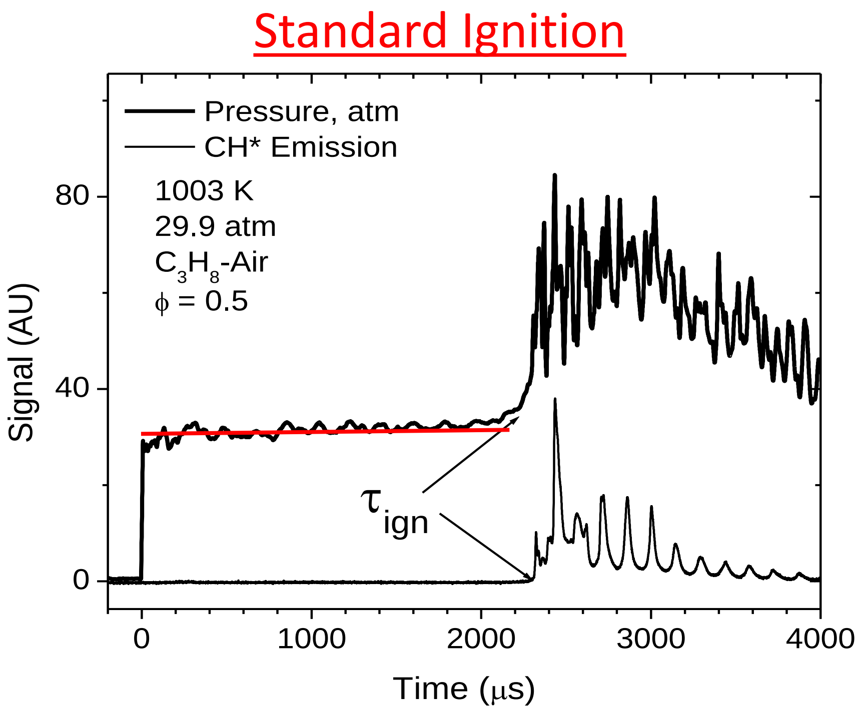
- Important indicator of fuel reactivity
  - *T*, *p*, ϕ, dilution
    - RCM: 600—1100 K, ST: 1100—2000 K
    - based on time available
  - Problems at intermediate *T*, High *p*

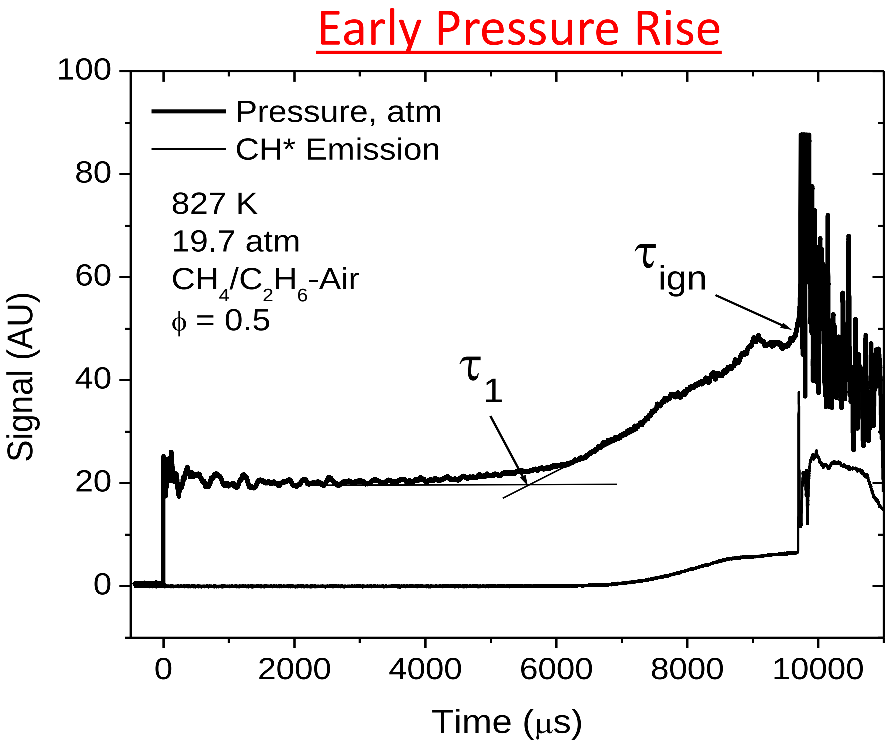
Propane Results Show Discrepancy between RCM and Shock Tube



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

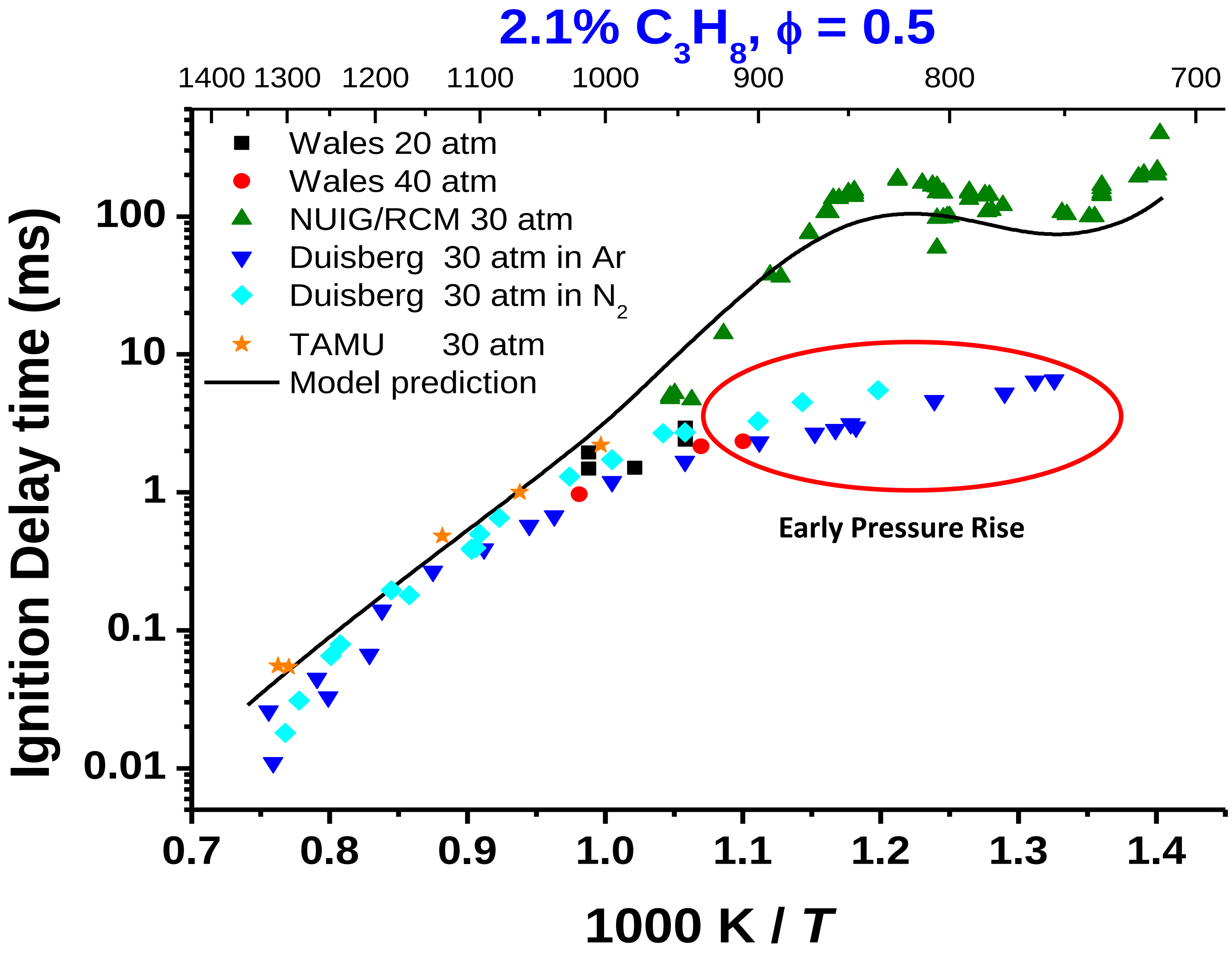
Lower-Temp Runs Exhibit Early Pressure Rise



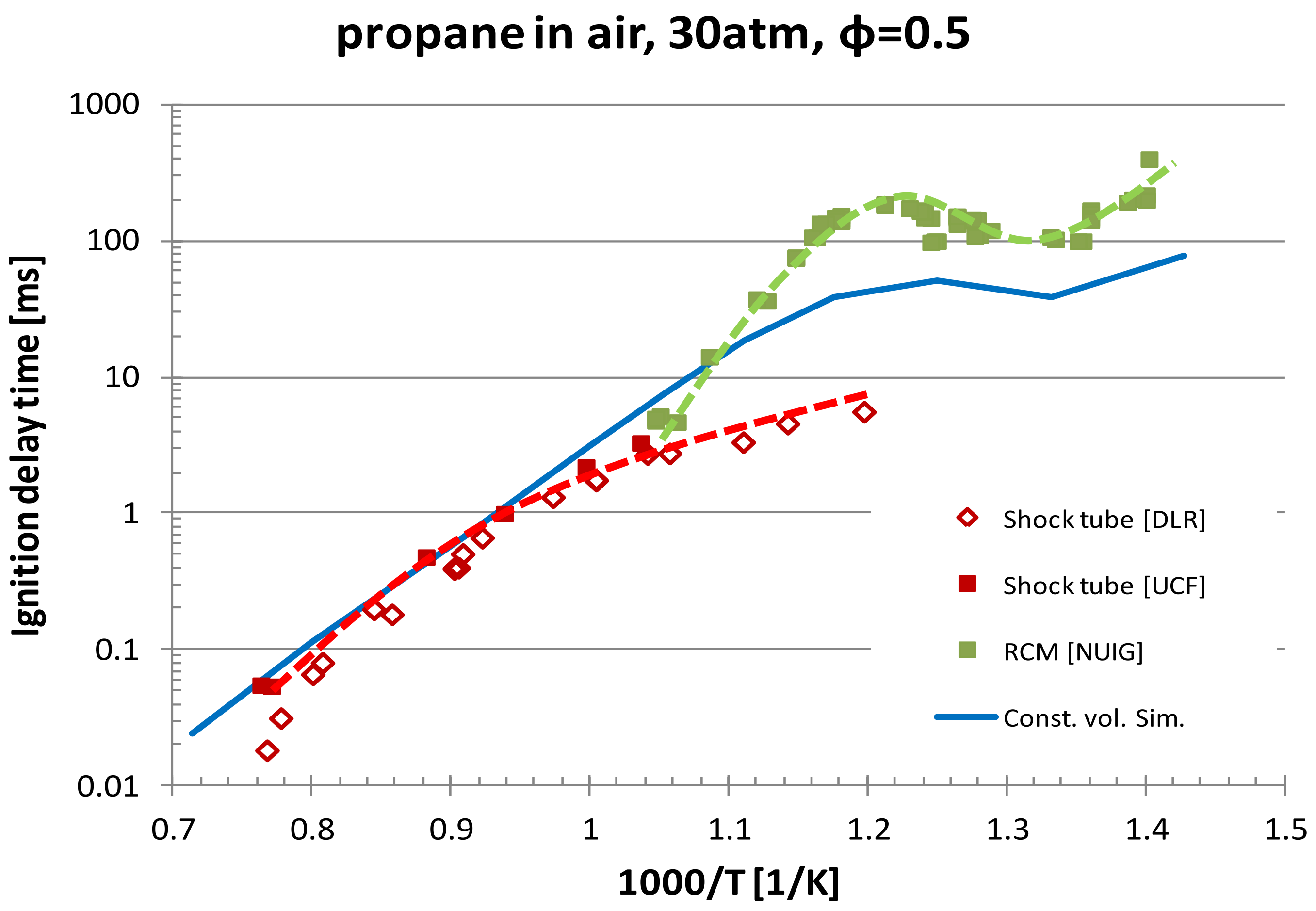


Slide courtesy of Prof. E. Petersen

Lower-Temp Runs Exhibit Early Pressure Rise



Typical data



H_2 / O_2 in Ar

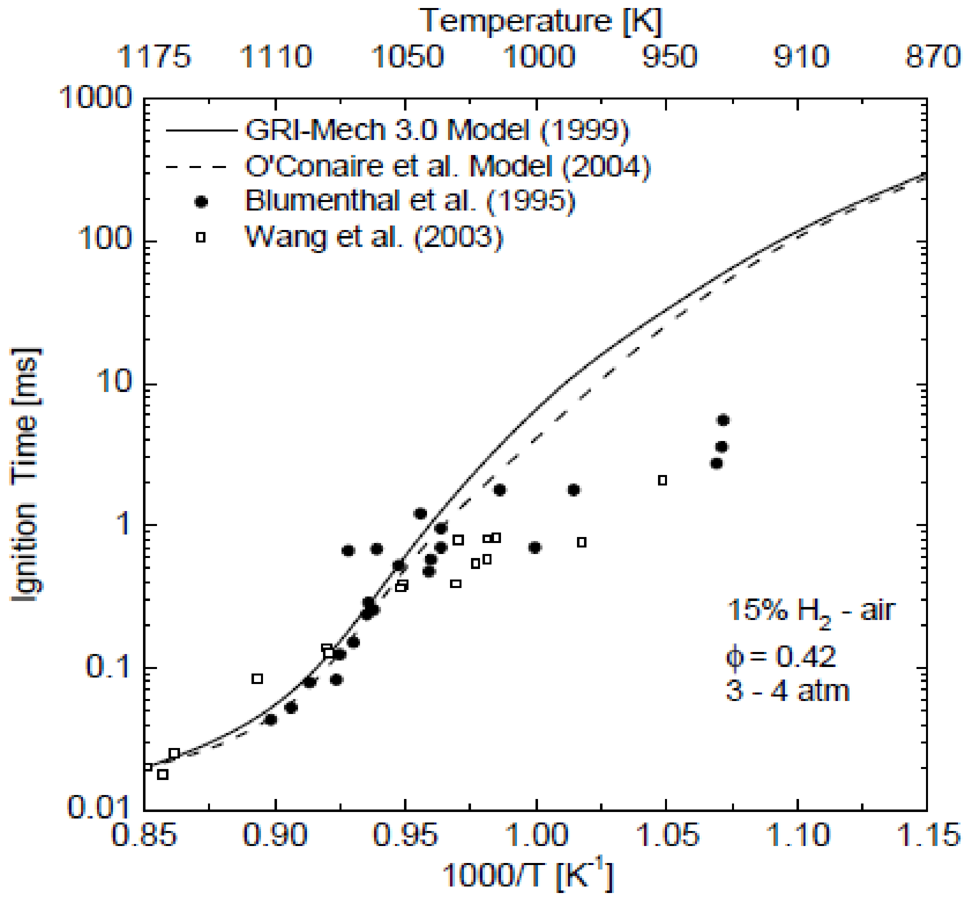


Fig. 1. Reflected-shock ignition delay time data compared to current kinetic models.

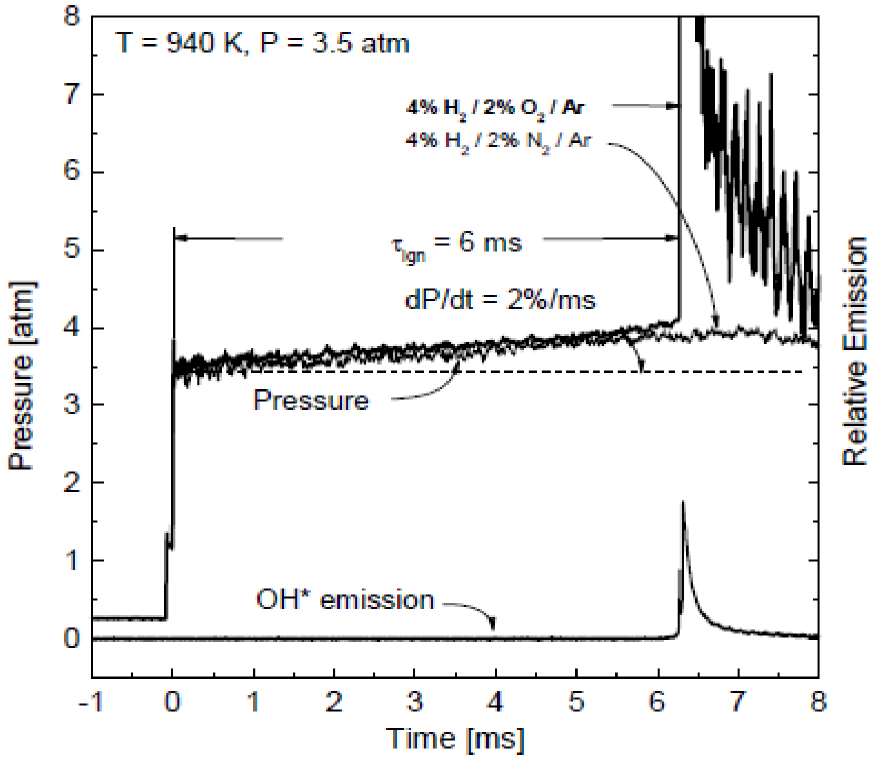


Fig. 2. Experimental data for a 4% H_2/2% O_2/Ar test gas mixture at initial post-shock conditions of 940 K and 3.5 atm for reactive and inert mixtures.

G.A. Pang, D.F. Davidson and R.K. Hanson *Proc. Combust. Inst.*, 32 (2009) 181–188.

Early pressure rise used to estimate Temp rise

Assume Temperature and Pressure are Related by:

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

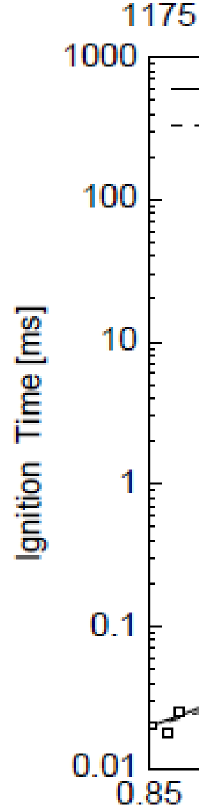
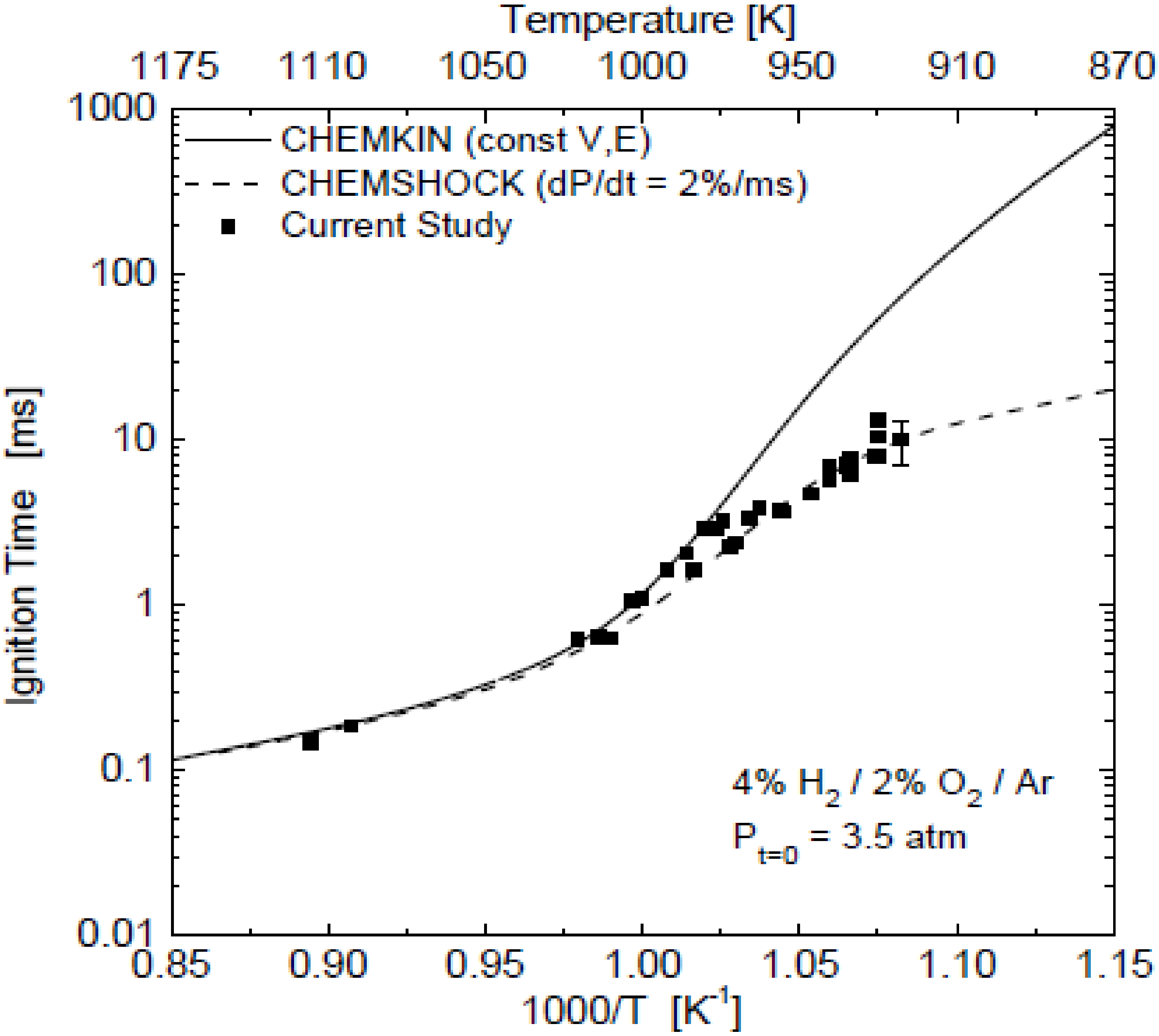
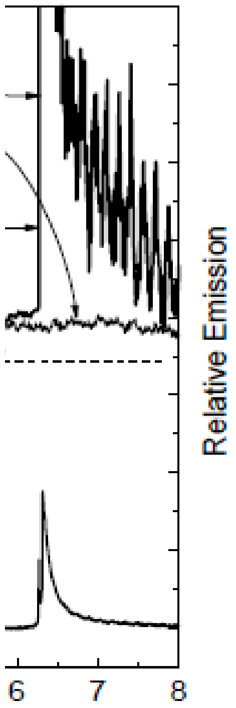


Fig. 1. Ref
pared to cu





/2% O_2/Ar test
ns of 940 K and

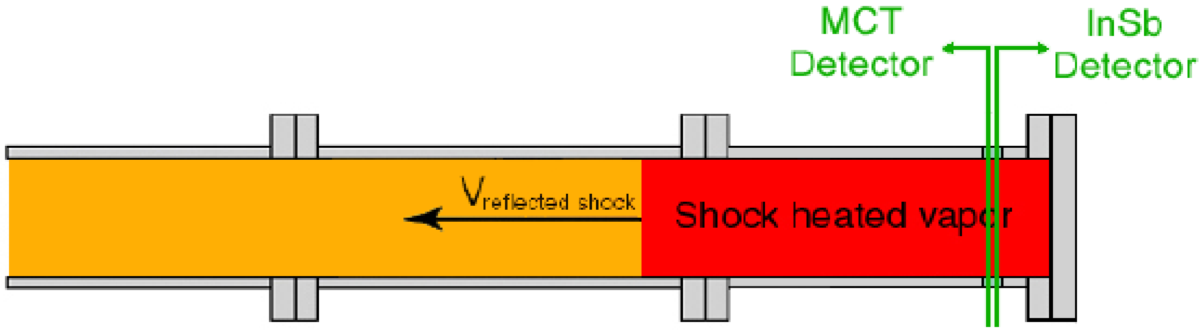
Fig. 3. Reflected-shock ignition delay times for a 4% H_2/2% O_2/Ar mixture. Experimental data and calculated

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:

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

- I and I_o are the transmitted and incident beam intensities
- k_ν 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



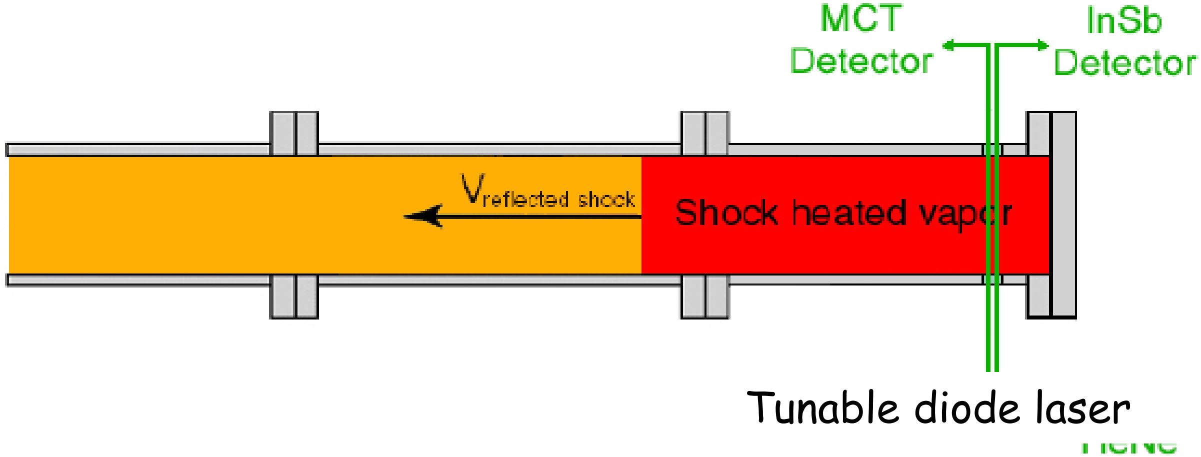
613.4 nm using
Spectra Physics
380 ring Dye laser

Laser absorption measurements

- CO_2 measured at 2752.5 nm
- H_2O measured at 2550.96 nm
- Concentration calculated using Beer's law:

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

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



Laser absorption measurements

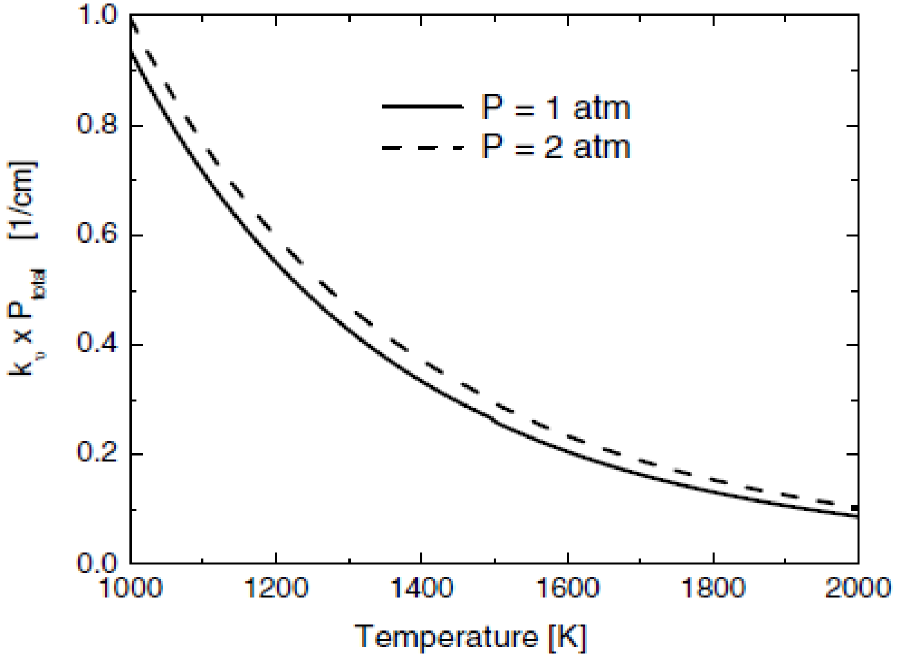


Fig. 1. Absorption coefficient × pressure product, $k_\nu \times P_{\text{total}}$ [cm^{-1}] for the R(28) CO_2 transition near 3633.08 cm^{-1} (2752.5 nm) at $P = 1$ and 2 atm.

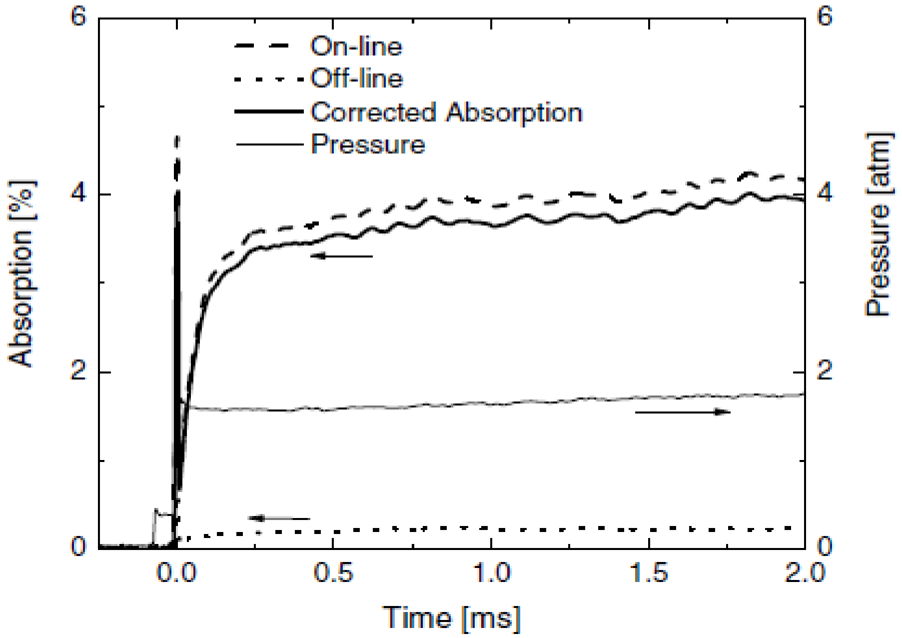


Fig. 2. Example on-line and off-line absorption measurement in 2% MB/Argon. Reflected shock conditions: $T_5 = 1426$ K, $P_5 = 1.58$ atm. On-line wavenumber = 3633.08 cm^{-1}; Off-line wavenumber = 3633.25 cm^{-1}.

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

Laser absorption measurements

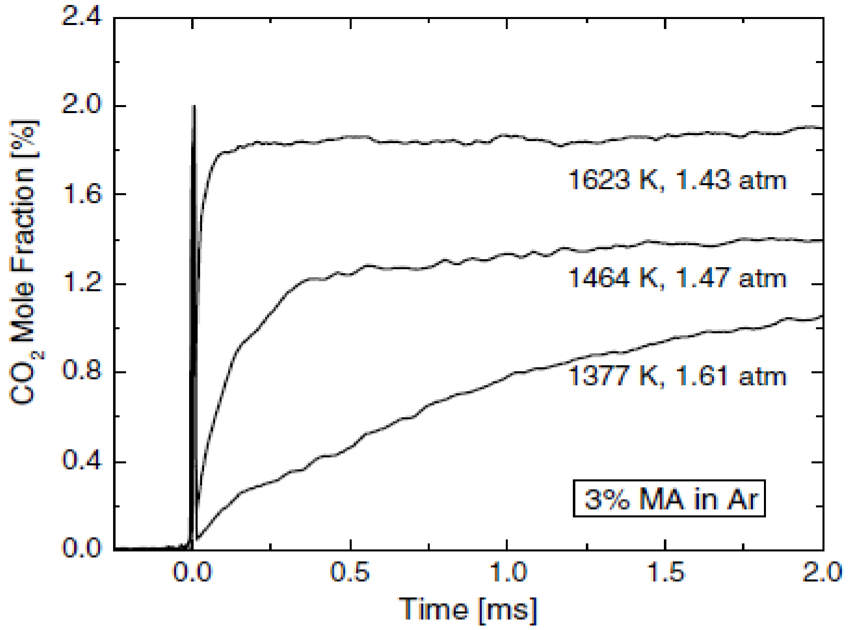


Fig. 3. Measured CO_2 time-histories behind reflected shock waves (T_5, P_5 shown) for methyl acetate pyrolysis (3% MA in Ar).

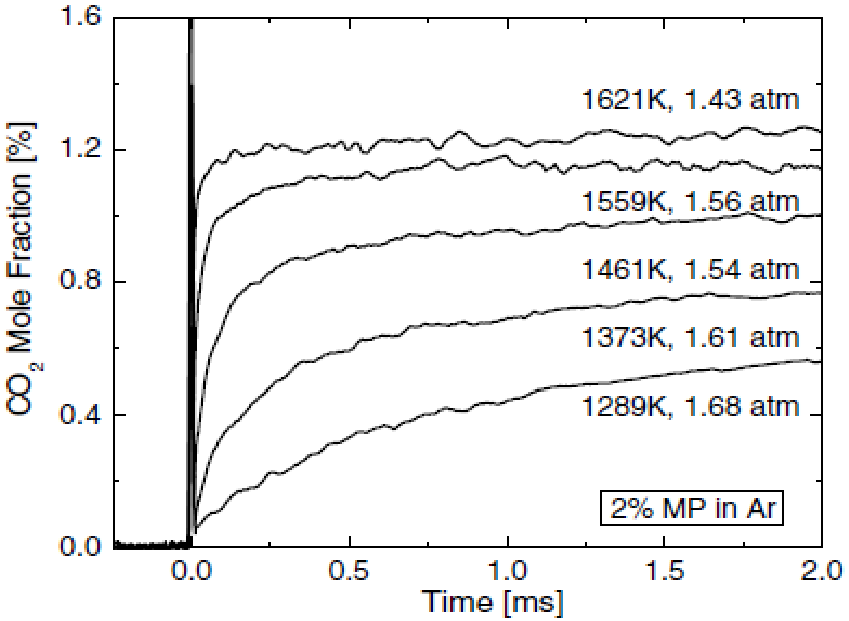
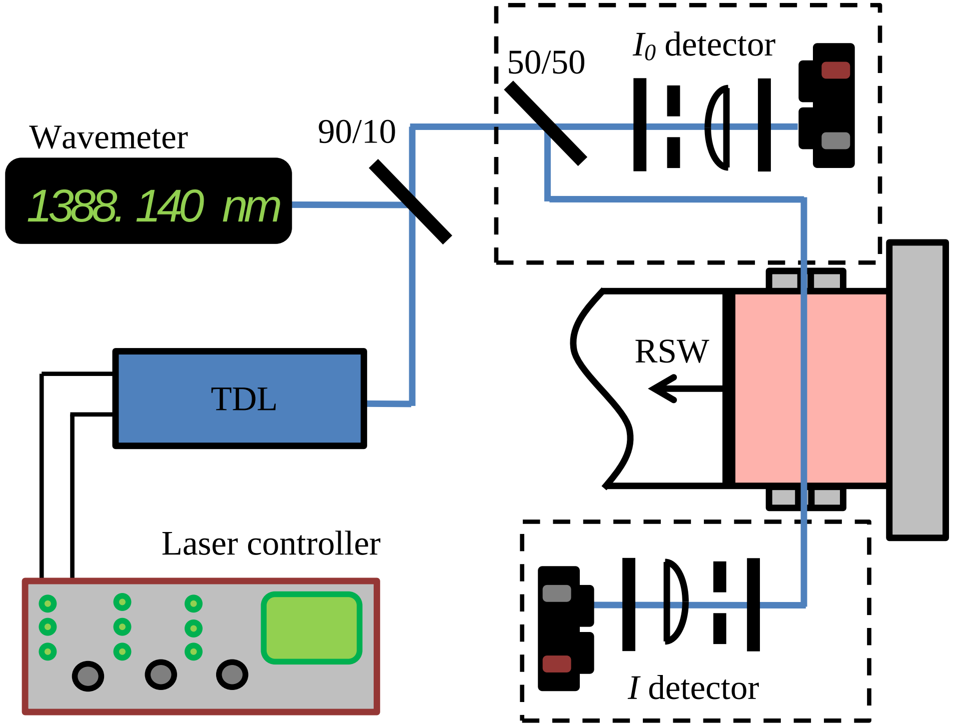


Fig. 4. Measured CO_2 time-histories behind reflected shock waves (T_5, P_5 shown) for methyl propionate pyrolysis (2% MP in Ar).

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

Setup: H_2O Diagnostic

- **Tunable diode laser (TDL)**
  - Temperature- and current-controlled
  - Typically 20.8°C and 96 mA
- **InGaAs photodetectors**
  - Common-mode rejection
  - 150-kHz bandwidth
- **Lexan enclosures**
  - Purged by N_2
  - < 0.1% relative humidity



TURBOMACHINERY LABORATORY
TEXAS A&M ENGINEERING EXPERIMENT STATION

Slide courtesy of Prof. E. Petersen

Theory: Absorption Spectroscopy

- Attenuation of monochromatic light can give species concentrations

$$\frac{I}{I_0} = \exp(-k_\nu L P X_i)$$

- k_ν can be calculated at different conditions

$$k_\nu = \underbrace{S}_{\substack{\text{Linestrength}\\ f(T)}} \times \underbrace{\phi(\nu - \nu_0)}_{\substack{\text{Lineshape}\\ f(T,P,\nu)}}$$

- By measuring remaining parameters, X_i can be backed out

- Attenuation of monochromatic light can give species concentrations

$$\frac{I}{I_0} = \exp(-k_\nu L P X_i)$$

- k_ν can be calculated at different conditions

$$k_\nu = S \times \phi(\nu - \nu_0)$$

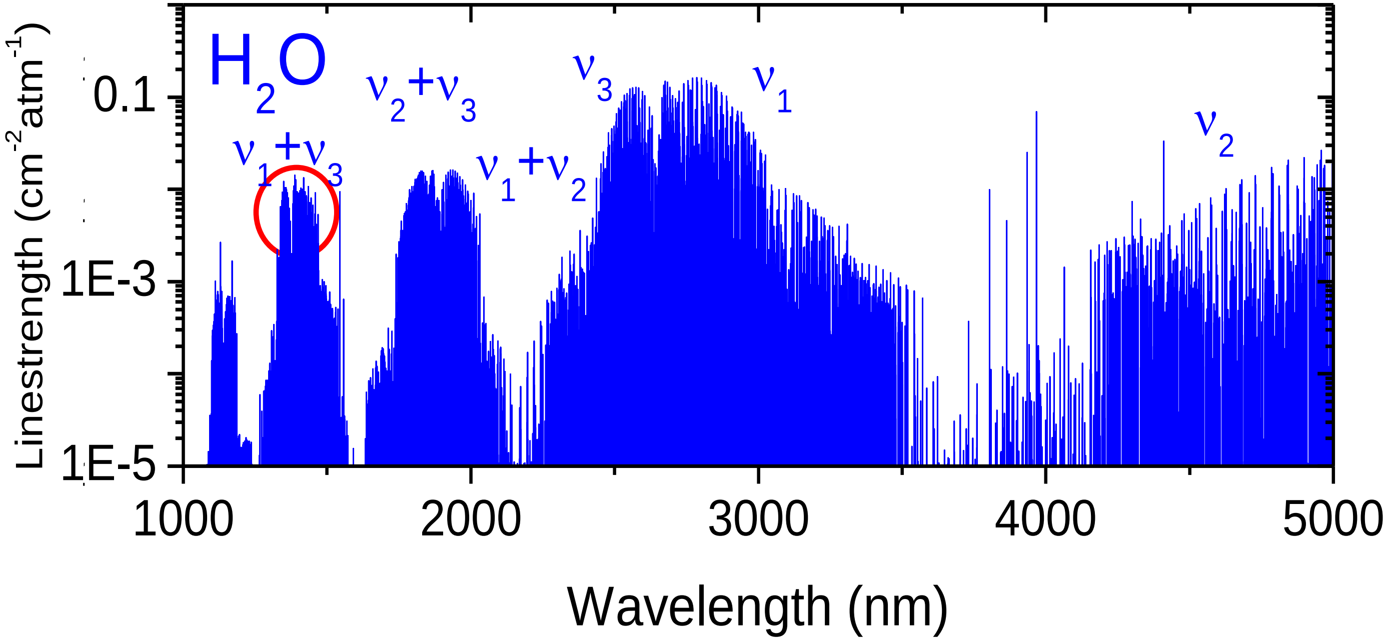
Linestrength $f(T)$ Lineshape $f(T,P,\nu)$

- By measuring remaining parameters, X_i can be backed out

Slide courtesy of Prof. E. Petersen

Theory: Spectral Line Selection

- Accessed the fundamental $\nu_1 + \nu_3$ combination H_2O band
  - $5_{5,1} \leftarrow 5_{5,0}$ transition at 1388.139 nm

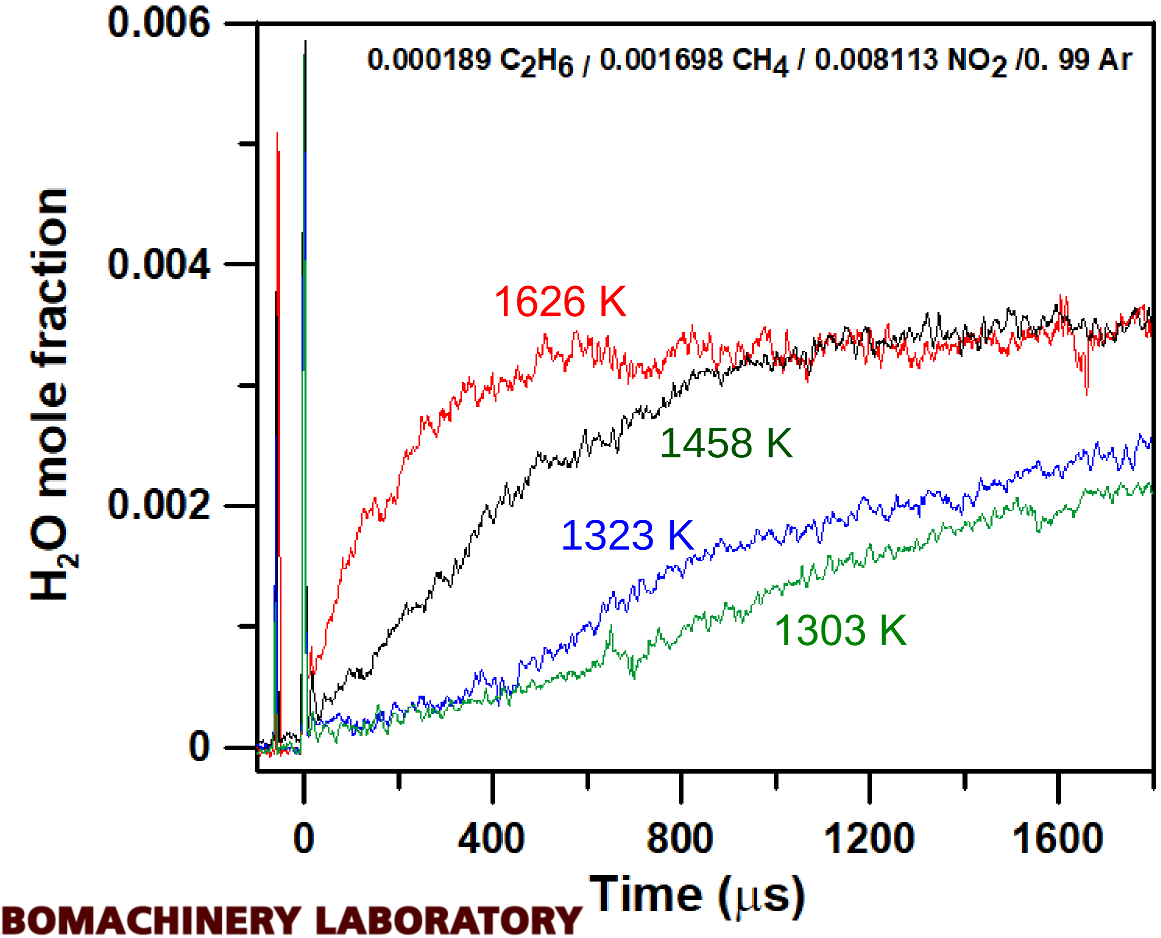


TURBOMACHINERY LABORATORY
TEXAS A&M ENGINEERING EXPERIMENT STATION

Slide courtesy of Prof. E. Petersen

Results – H_2O measurements

Temperature affects the slope of H_2O formation

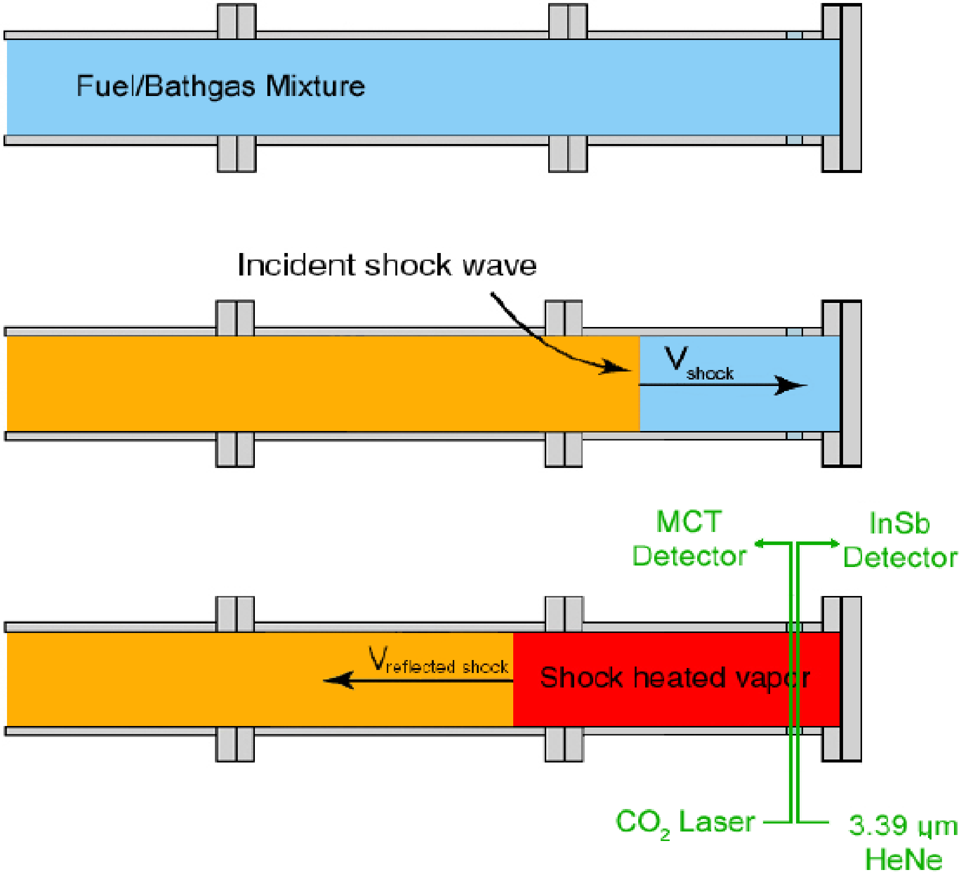


TURBOMACHINERY LABORATORY
TEXAS A&M ENGINEERING EXPERIMENT STATION

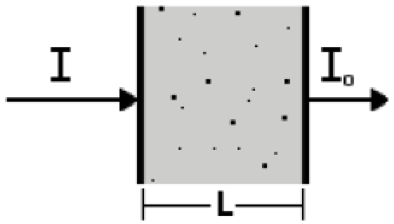
O. Mathieu, C. Mulvihill, E.L. Petersen, H.J. Curran Paper # GT2018-75874, ASME Turbo Expo 2018, June 11—15 2018, Lillestrøm , Norway.

Laser absorption measurements

- Fuel measurement at 3.39 μm
- C_2H_4 measurement at 10.5 μm



Beer's Law

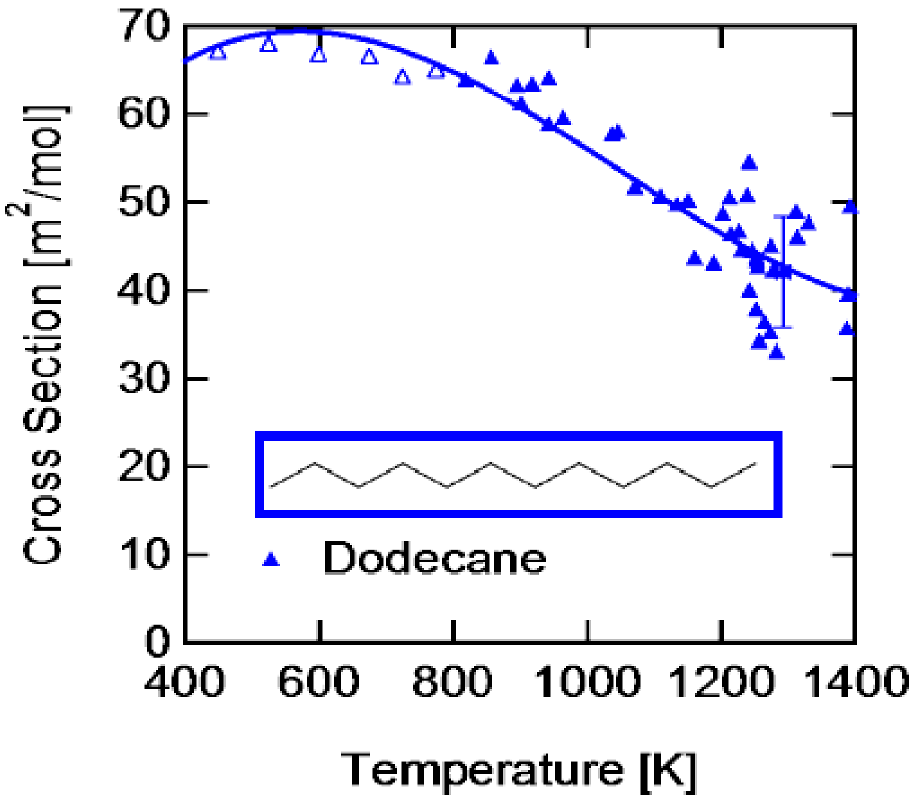


$$\frac{I}{I_o} = \exp(-\sigma N L)$$

Absorption cross section

IR Fuel Diagnostic (3.39 μm)

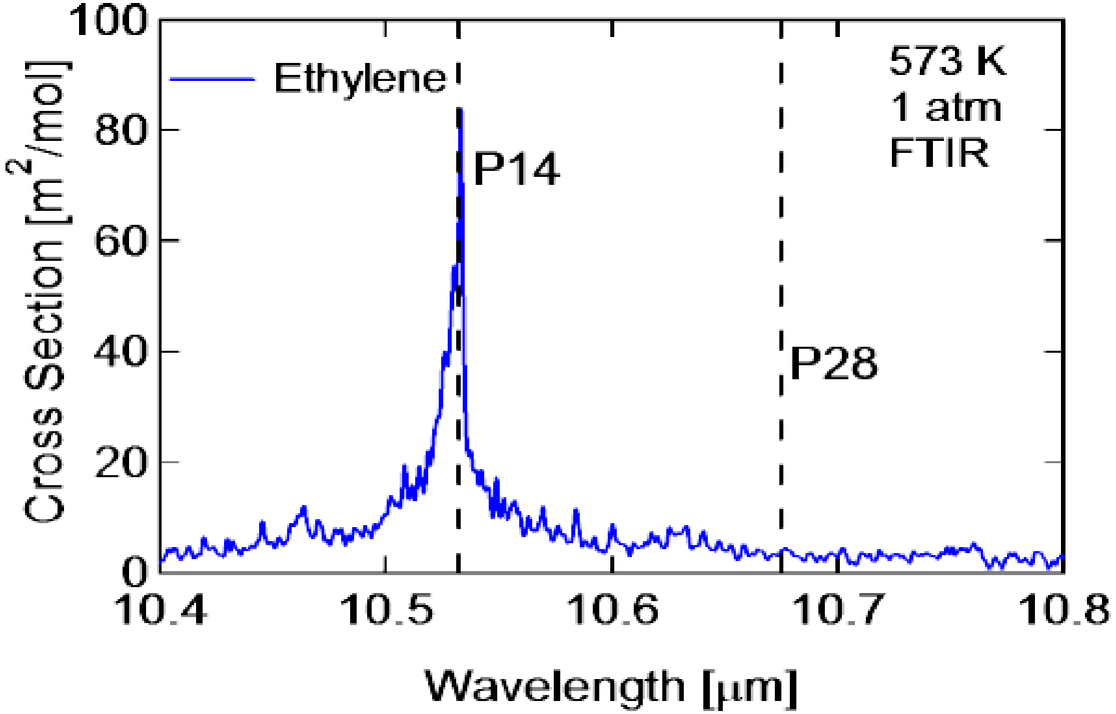
- 3.39 μm strongly absorbed by all HC fuels
- Beer's Law + Absorption cross sections → Fuel mole fraction
- **Need fuel cross section at 3.39 μm**



MacDonald et al., J. Prop. Power, 2011

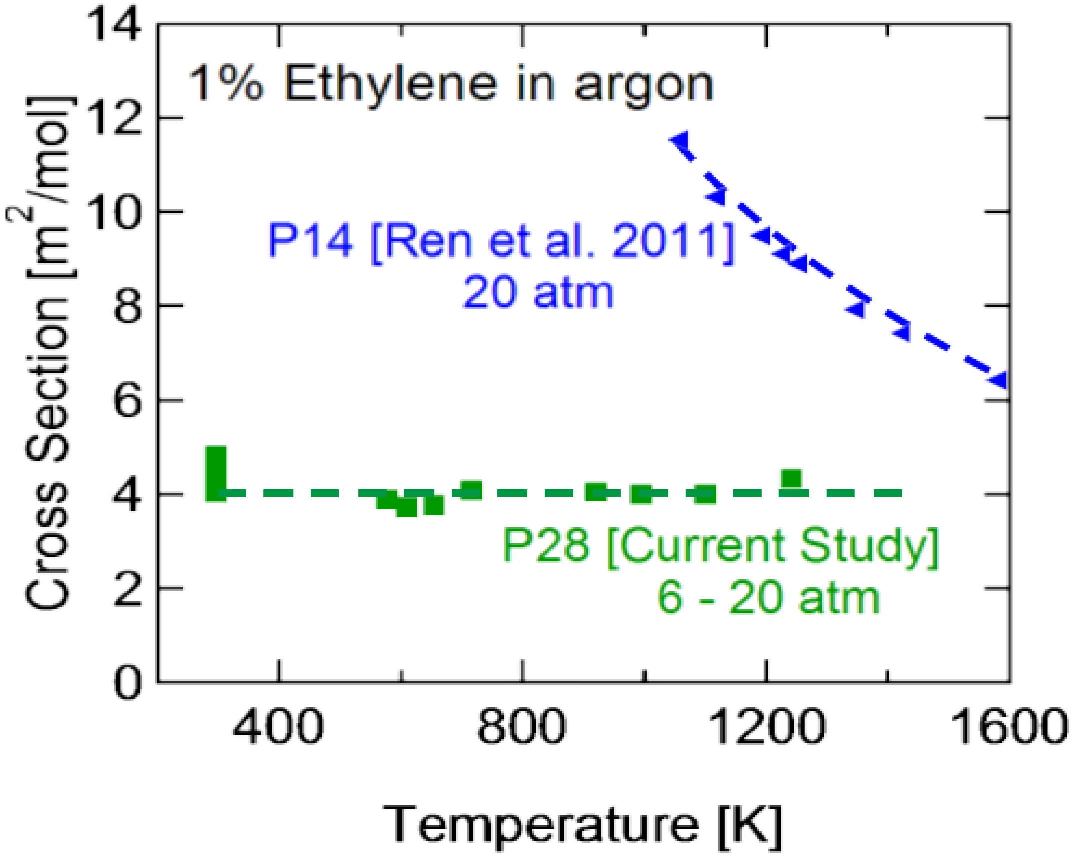
IR Ethylene Diagnostic (10.5 μm)

- 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)

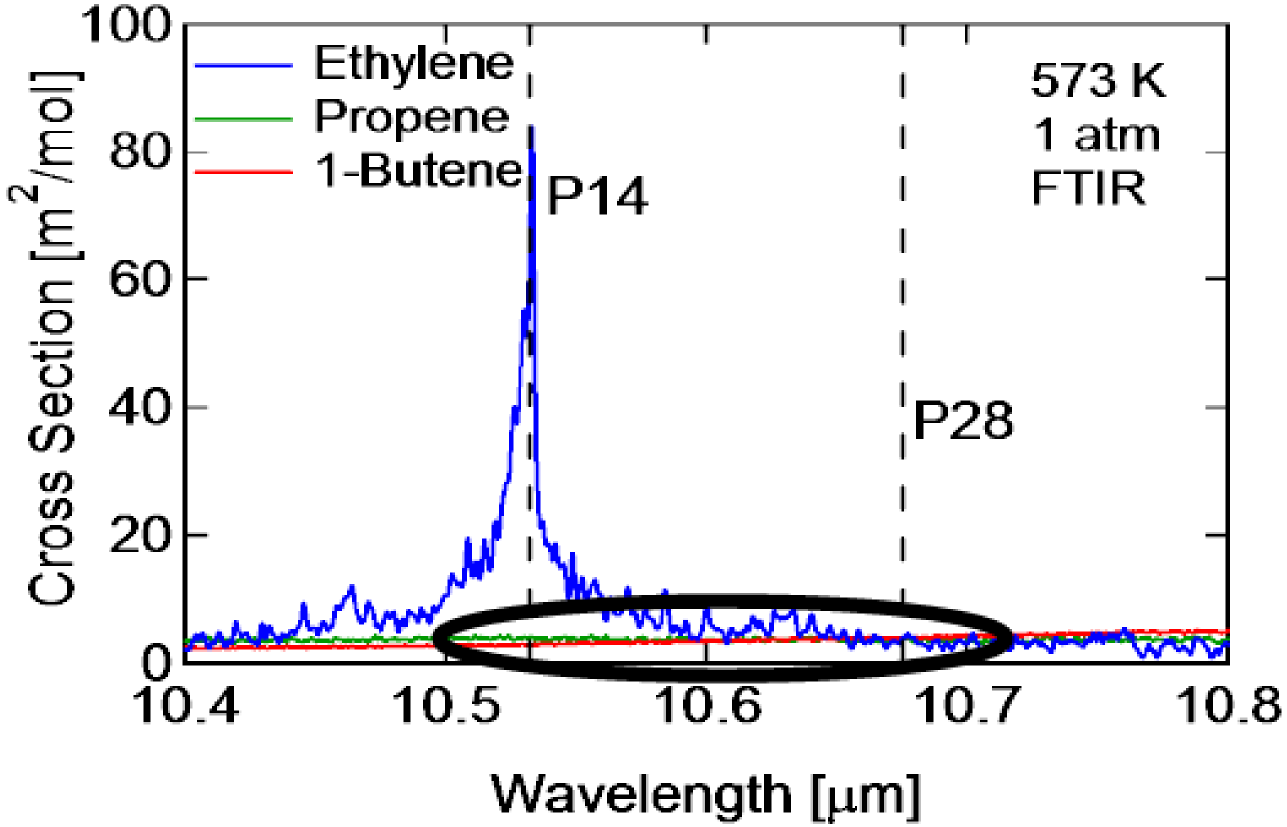
- **Need ethylene cross sections at both lines**
- Other alkenes absorb at 10.5 μm
- Interfering species have a constant cross section
- Differential absorption at 2 wavelengths permits isolation of C_2H_4 absorption



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

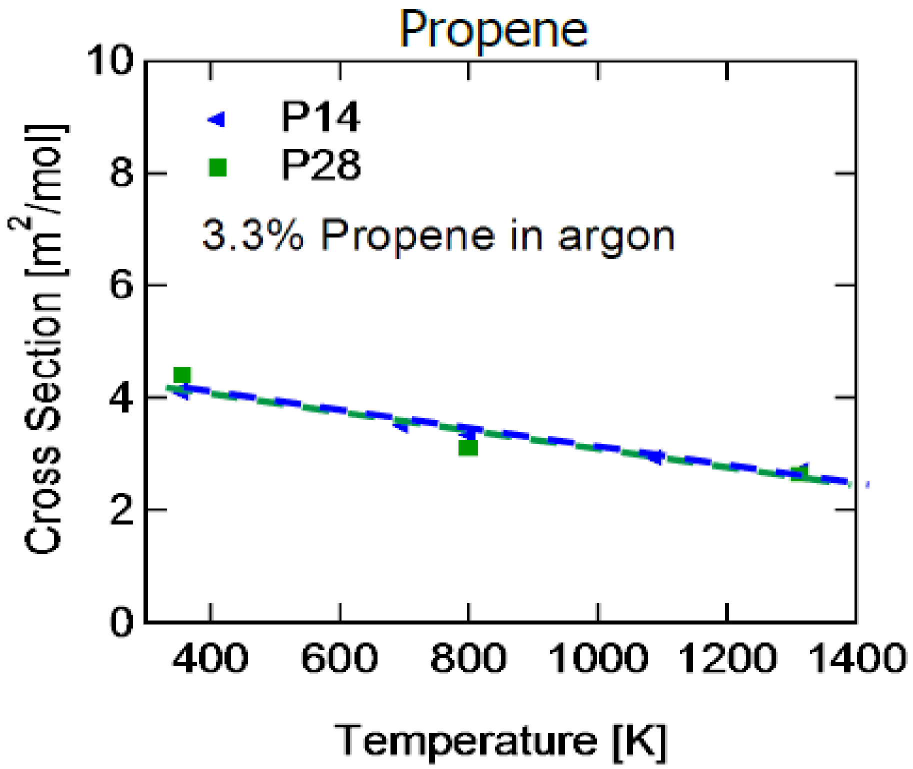
Cross sections of interfering species

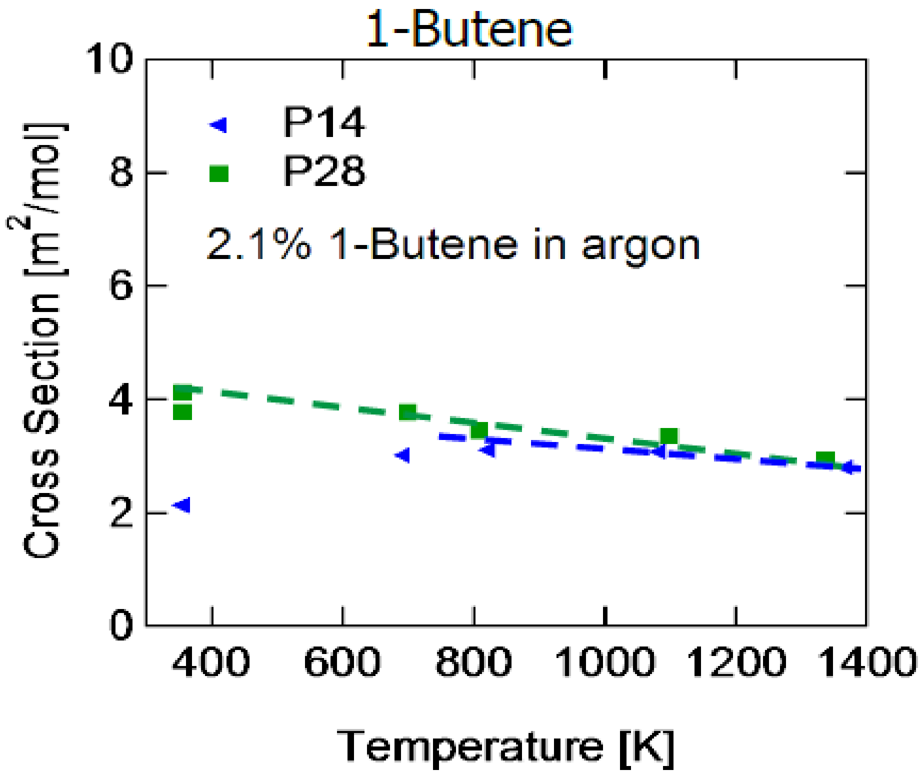
- Small absorption by propene and 1-butene



Cross sections of interfering species

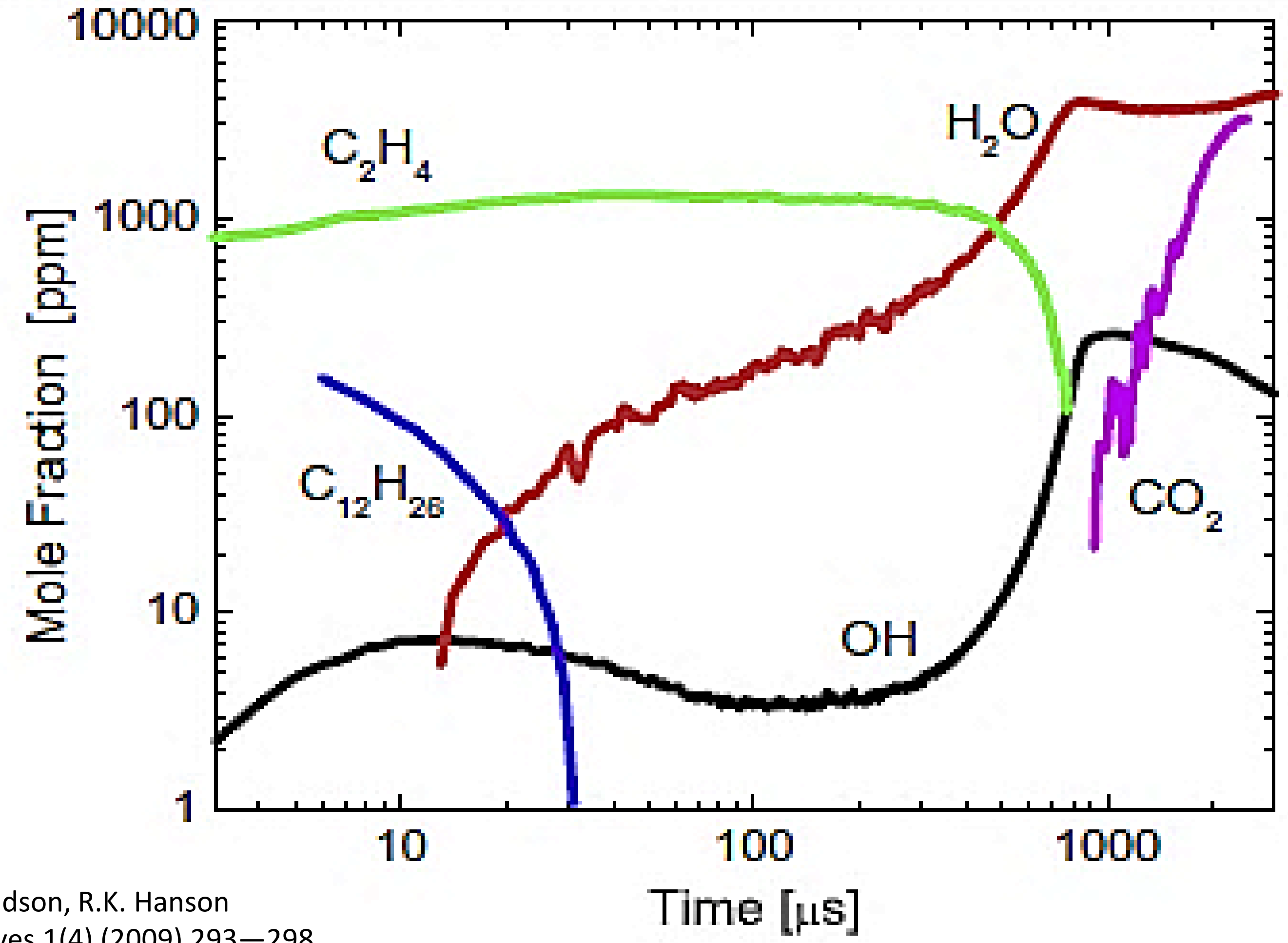
- Small absorption by propene and 1-butene with nearly constant cross-sections at P14 and P28





Species time-history measurements

457 ppm *n*-Dodecane/O_2/Argon
ϕ = 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 Prof. Aamir Farooq’s laboratory:

Species	Laser	Wavelength
OH	Ring-Dye w/ external doubling	306 nm
CH_2O	Difference-frequency-generation laser	3.6 μm
CO_2	Quantum-cascade laser (QCL)	4.3 μm
N_2O	Quantum-cascade laser (QCL)	4.5 μm
CO	Quantum-cascade laser (QCL)	4.6 μm
H_2O	Quantum-cascade laser (QCL)	7.6 μm
H_2O_2	Quantum-cascade laser (QCL)	7.7 μm
CH_4	Quantum-cascade laser (QCL)	7.7 μm
C_2H_2	Quantum-cascade laser (QCL)	7.8 μm
NH_3	Quantum-cascade laser (QCL)	9.0 μm
C_2H_4	Quantum-cascade laser (QCL)	10.5 μm
C_2H_2	Quantum-cascade laser (QCL)	13.3 μm

Laser absorption measurements

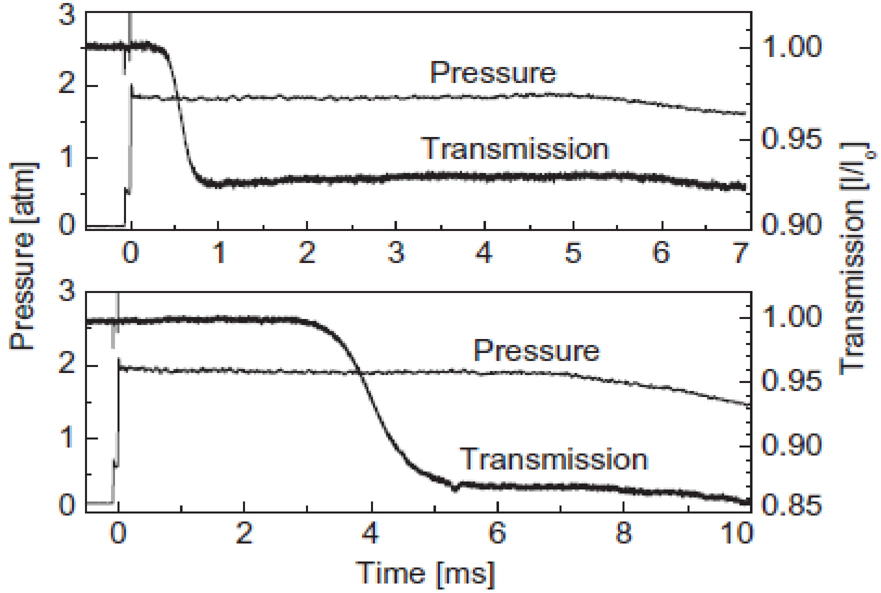


Fig. 1. Typical pressure and laser transmission histories in reflected-shock experiments: (a. upper) 0.1% O_2, 0.9% H_2, 99% Ar, 1472 K, 1.83 atm; (b. lower) 0.1% O_2, 2.9% H_2, 97% Ar, 1100 K, 1.95 atm.

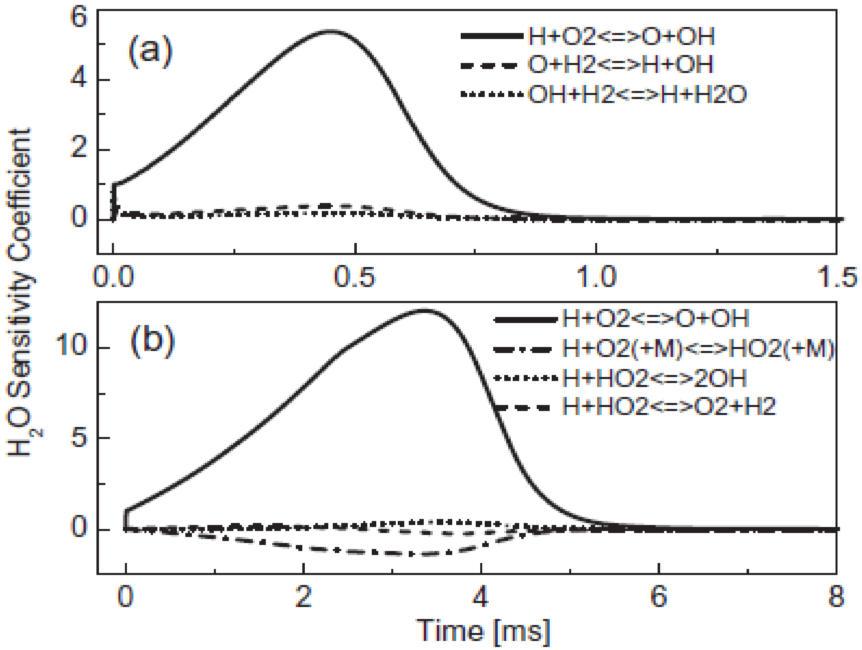


Fig. 2. H_2O sensitivity plot at conditions of the corresponding panels of Fig. 1.

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

Laser absorption measurements

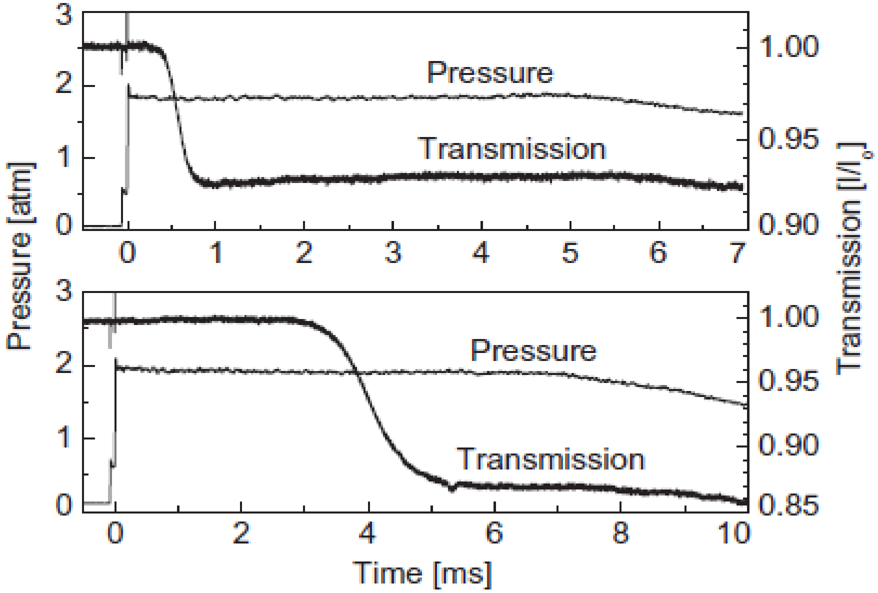


Fig. 1. Typical pressure and laser transmission histories in reflected-shock experiments: (a. upper) 0.1% O_2, 0.9% H_2, 99% Ar, 1472 K, 1.83 atm; (b. lower) 0.1% O_2, 2.9% H_2, 97% Ar, 1100 K, 1.95 atm.

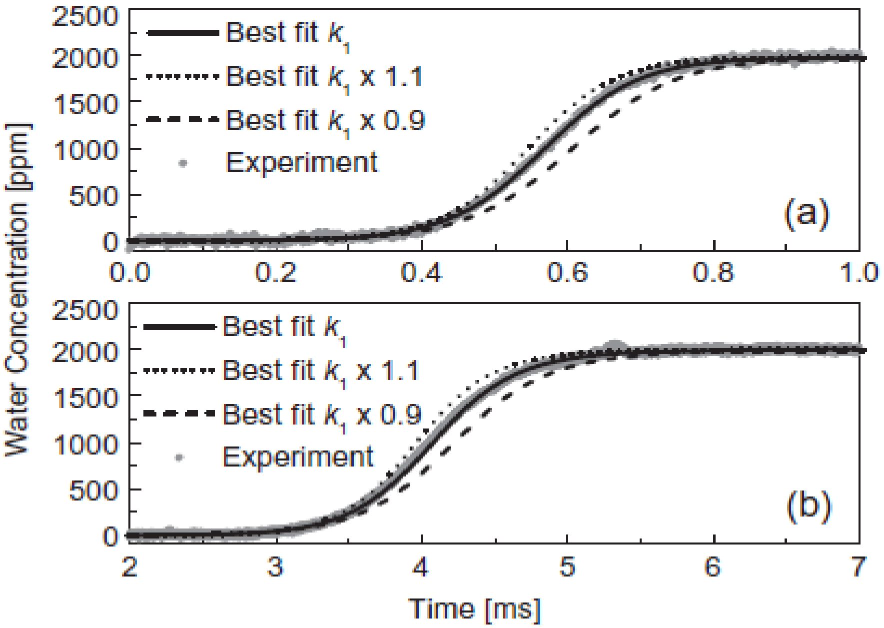
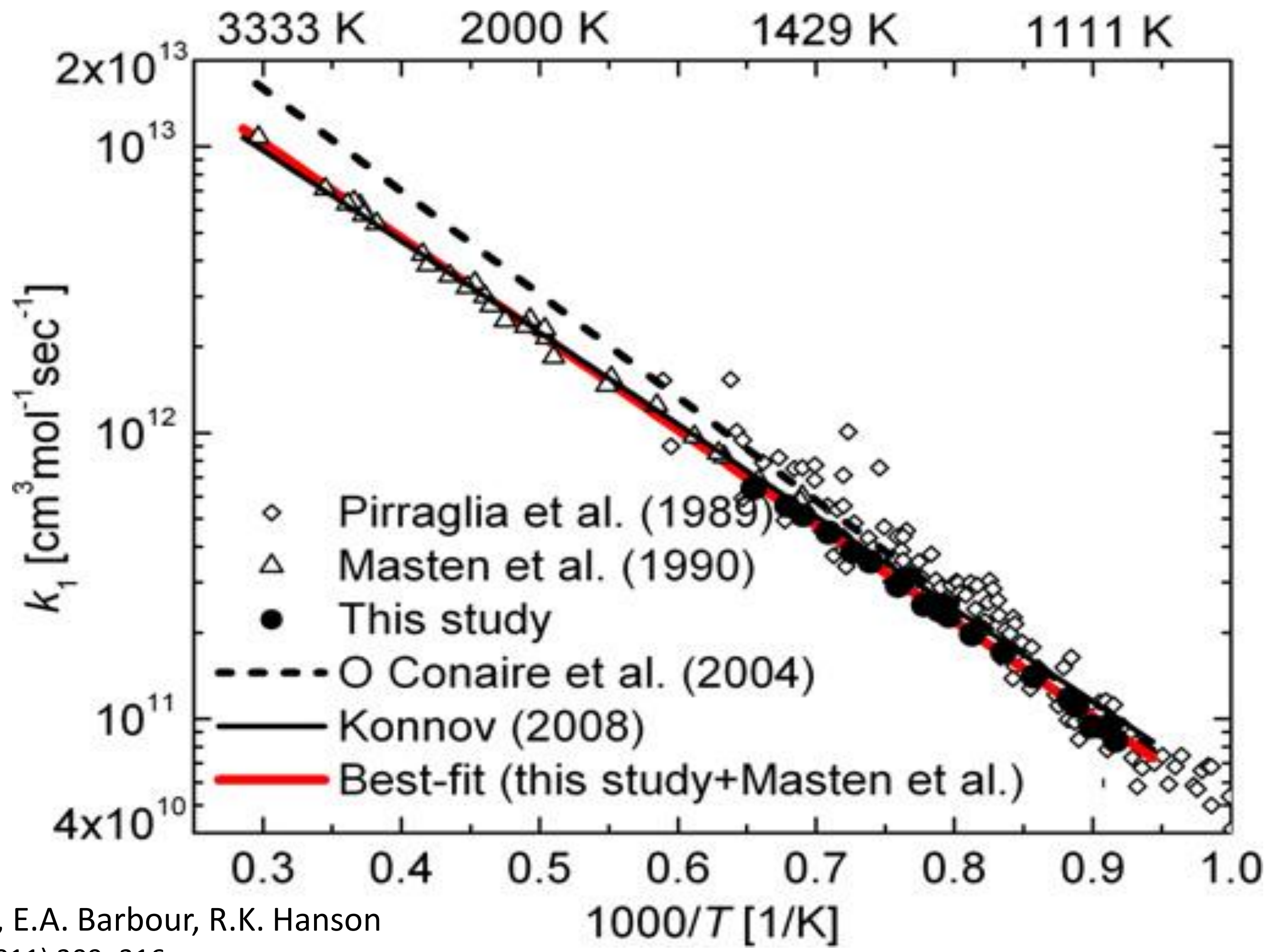


Fig. 3. Comparison of experimental and Senkin calculated H_2O profiles using best-fit k_1 with effect of ±10% variation on k_1 at conditions of the corresponding panels of Fig. 1.

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

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



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

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

Conclusions

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

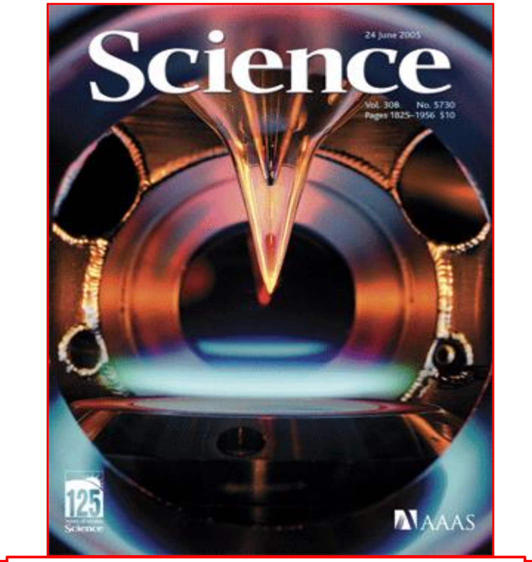
Generation of Detailed Chemical Kinetic Models for C_0–C_2 Hydrocarbon and Oxygenated Fuels

Experimental Studies: Engine Relevant

Rapid Compression Machine

Shock Tube

Jet Stirred Reactor



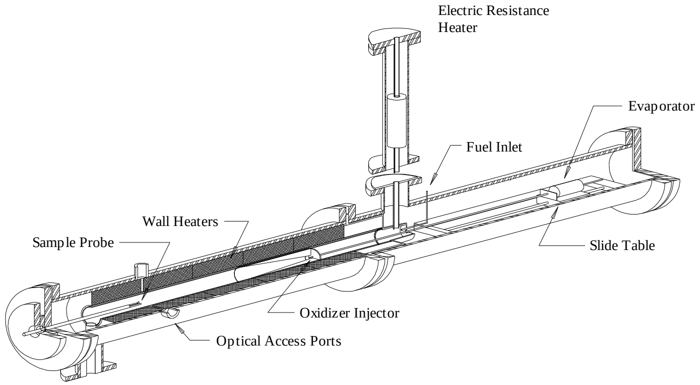
Flat Flame Burner

Quantitative Combustion Modelling

Ignition Delay Time Measurements

Species FR/JSR
Flames
Laminar Flame Speeds

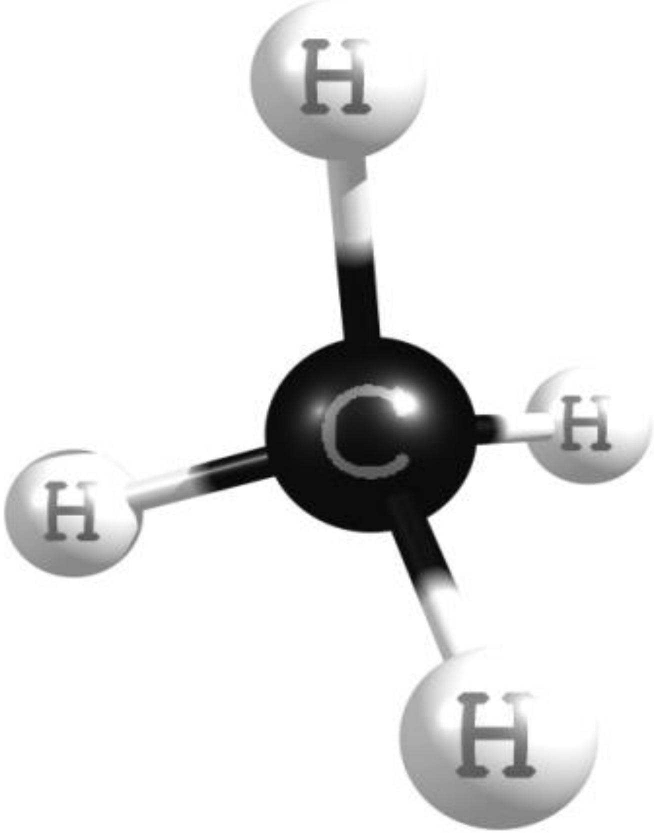
Chemical Kinetic Modelling



Ab-initio Thermochemistry / Kinetics

Chemical Modeling

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



Visualization of fuel consumption

Hierarchical structure

H_2-O_2

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

What does a mechanism look like?

Hydrogen

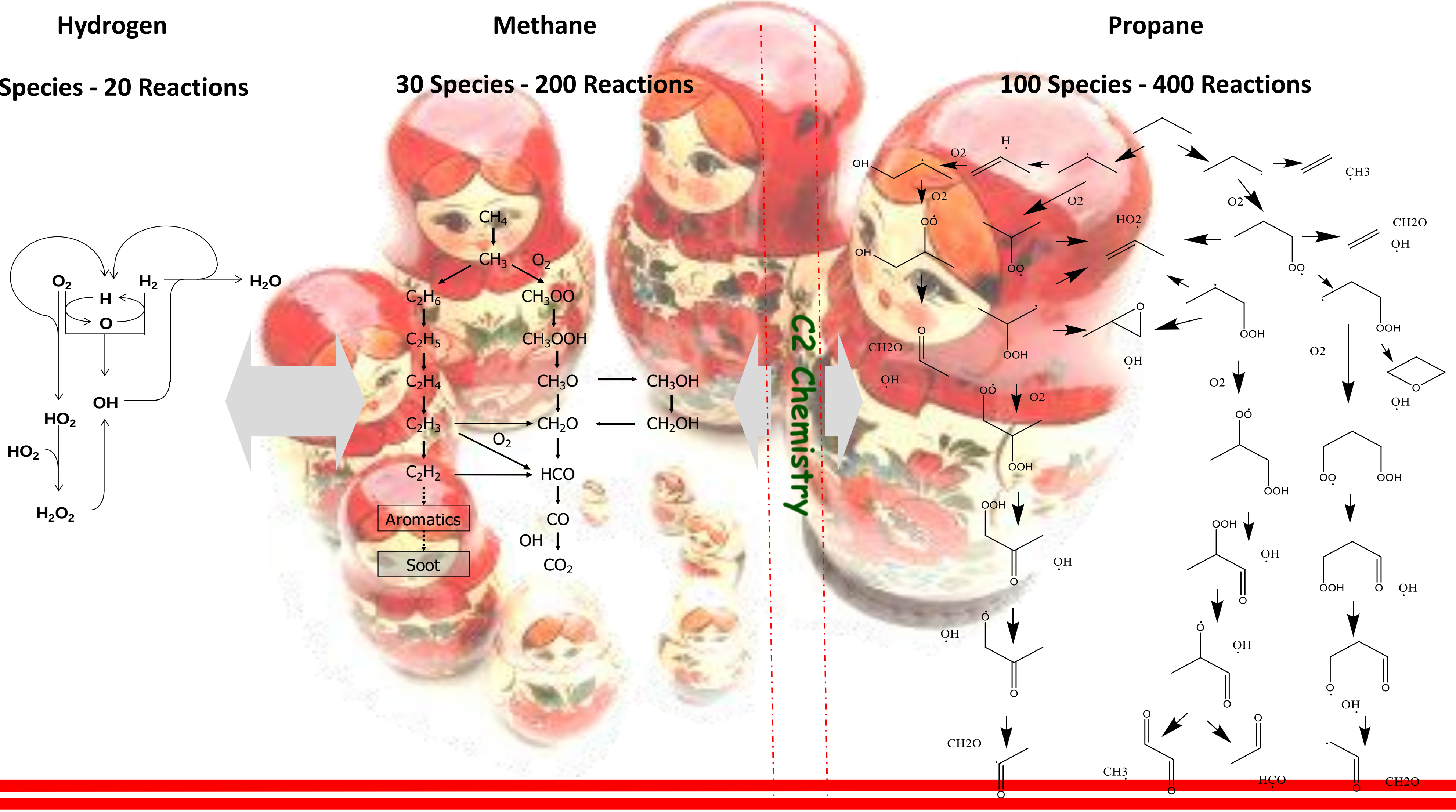
8 Species - 20 Reactions

Methane

30 Species - 200 Reactions

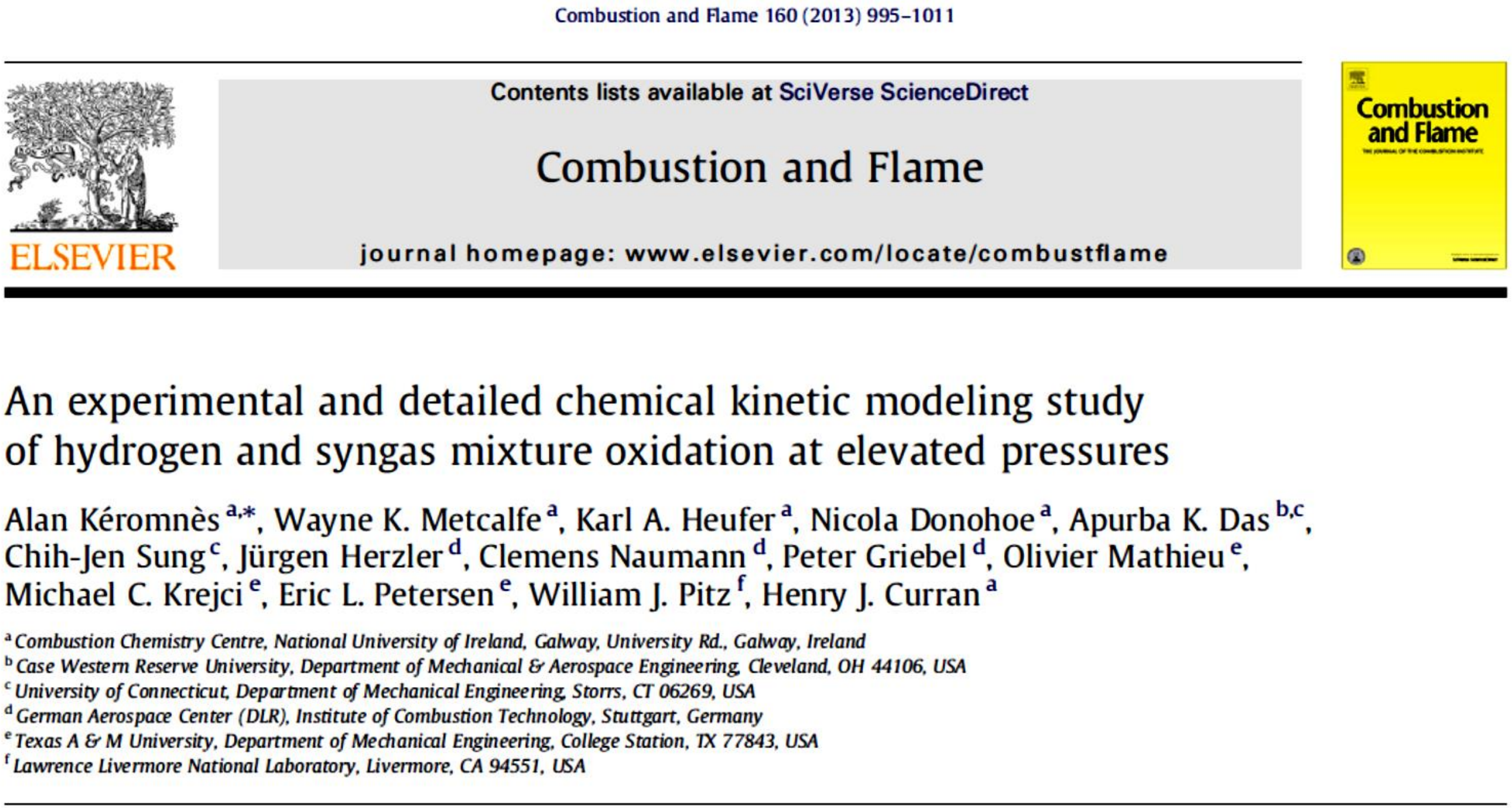
Propane

100 Species - 400 Reactions



Courtesy of William Pitz, Lawrence Livermore National Laboratory

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

Alan Kéromnès [a,*], Wayne K. Metcalfe [a], Karl A. Heufer [a], Nicola Donohoe [a], Apurba K. Das [b,c], Chih-Jen Sung [c], Jürgen Herzler [d], Clemens Naumann [d], Peter Griebel [d], Olivier Mathieu [e], Michael C. Krejci [e], Eric L. Petersen [e], William J. Pitz [f], Henry J. Curran [a]

[a] *Combustion Chemistry Centre, National University of Ireland, Galway, University Rd., Galway, Ireland*
[b] *Case Western Reserve University, Department of Mechanical & Aerospace Engineering, Cleveland, OH 44106, USA*
[c] *University of Connecticut, Department of Mechanical Engineering, Storrs, CT 06269, USA*
[d] *German Aerospace Center (DLR), Institute of Combustion Technology, Stuttgart, Germany*
[e] *Texas A & M University, Department of Mechanical Engineering, College Station, TX 77843, USA*
[f] *Lawrence Livermore National Laboratory, Livermore, CA 94551, USA*

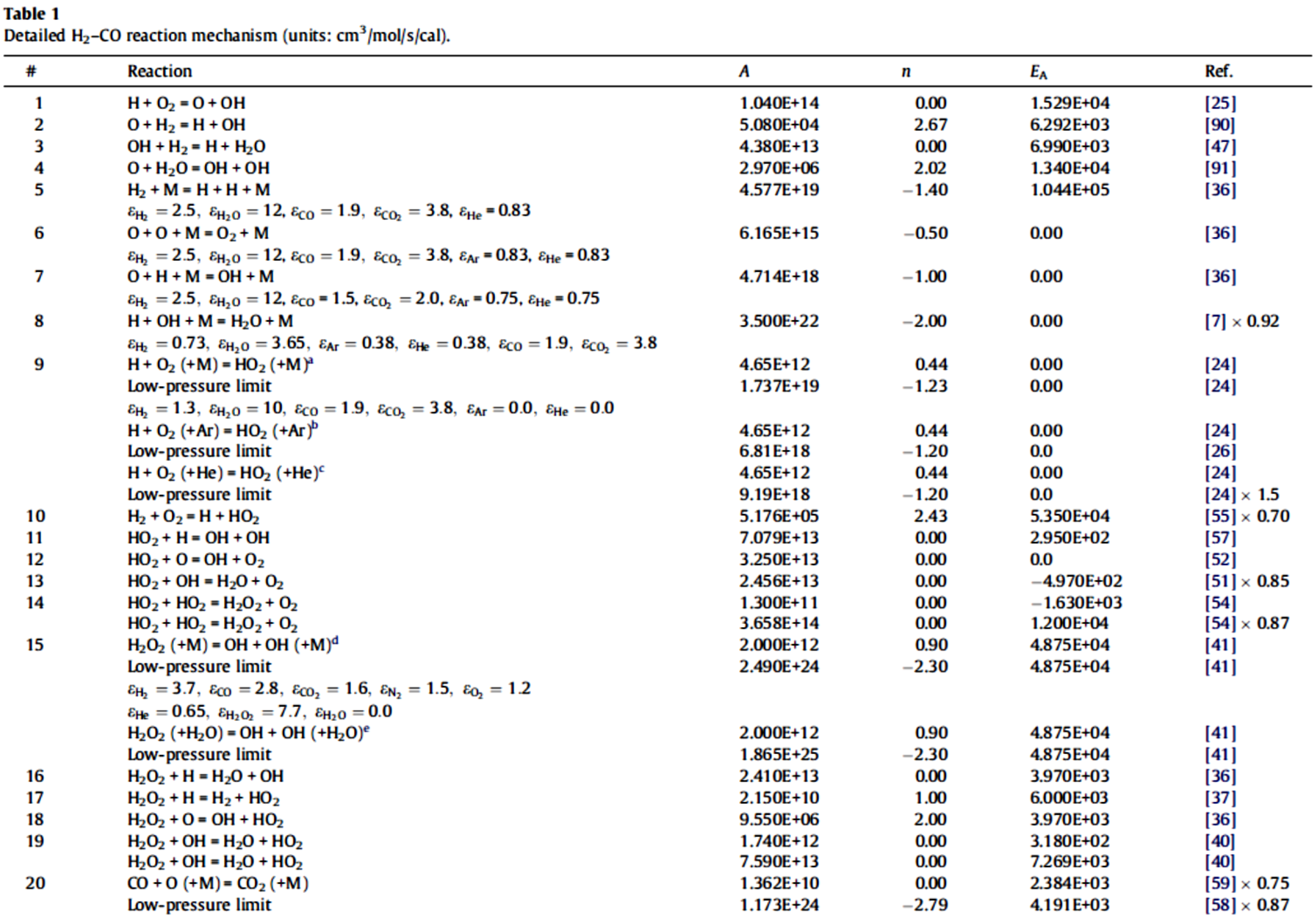
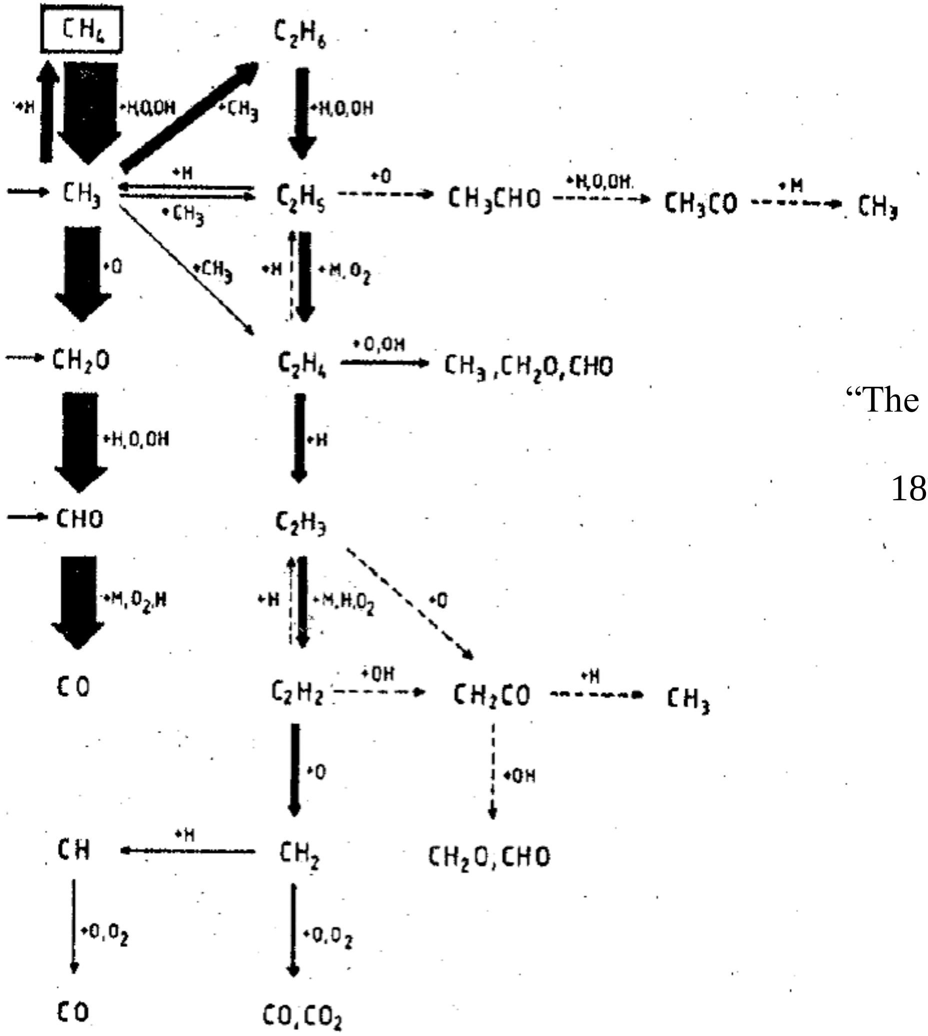


Table 1
Detailed H_2–CO reaction mechanism (units: cm^3/mol/s/cal).

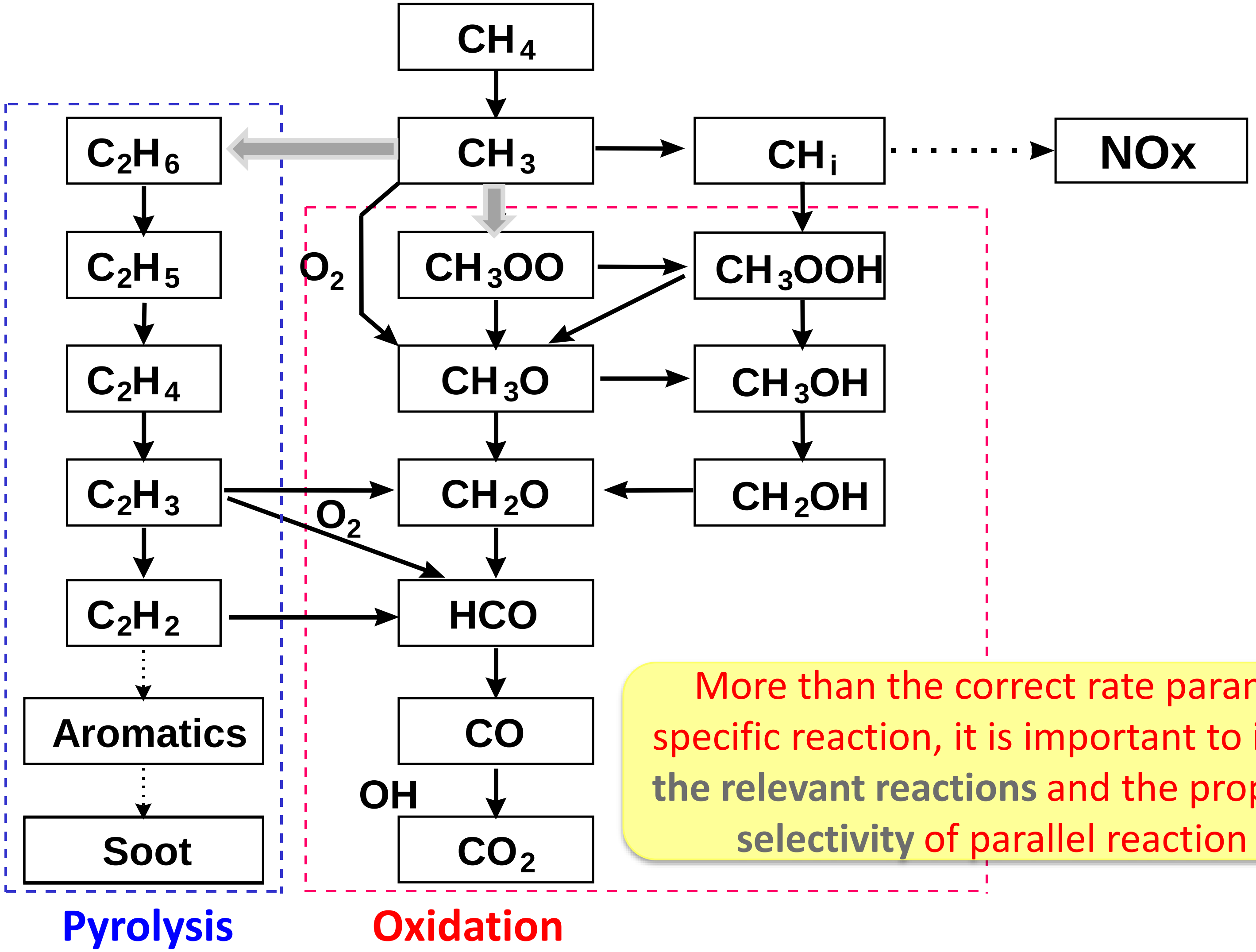
#	Reaction	*A*	*n*	E_A	Ref.
1	$H + O_2 = O + OH$	1.040E+14	0.00	1.529E+04	[25]
2	$O + H_2 = H + OH$	5.080E+04	2.67	6.292E+03	[90]
3	$OH + H_2 = H + H_2O$	4.380E+13	0.00	6.990E+03	[47]
4	$O + H_2O = OH + OH$	2.970E+06	2.02	1.340E+04	[91]
5	$H_2 + M = H + H + M$	4.577E+19	−1.40	1.044E+05	[36]
	$\varepsilon_{H_2} = 2.5,\ \varepsilon_{H_2O} = 12,\ \varepsilon_{CO} = 1.9,\ \varepsilon_{CO_2} = 3.8,\ \varepsilon_{He} = 0.83$				
6	$O + O + M = O_2 + M$	6.165E+15	−0.50	0.00	[36]
	$\varepsilon_{H_2} = 2.5,\ \varepsilon_{H_2O} = 12,\ \varepsilon_{CO} = 1.9,\ \varepsilon_{CO_2} = 3.8,\ \varepsilon_{Ar} = 0.83,\ \varepsilon_{He} = 0.83$				
7	$O + H + M = OH + M$	4.714E+18	−1.00	0.00	[36]
	$\varepsilon_{H_2} = 2.5,\ \varepsilon_{H_2O} = 12,\ \varepsilon_{CO} = 1.5,\ \varepsilon_{CO_2} = 2.0,\ \varepsilon_{Ar} = 0.75,\ \varepsilon_{He} = 0.75$				
8	$H + OH + M = H_2O + M$	3.500E+22	−2.00	0.00	[7] × 0.92
	$\varepsilon_{H_2} = 0.73,\ \varepsilon_{H_2O} = 3.65,\ \varepsilon_{Ar} = 0.38,\ \varepsilon_{He} = 0.38,\ \varepsilon_{CO} = 1.9,\ \varepsilon_{CO_2} = 3.8$				
9	$H + O_2\ (+M) = HO_2\ (+M)^a$	4.65E+12	0.44	0.00	[24]
	Low-pressure limit	1.737E+19	−1.23	0.00	[24]
	$\varepsilon_{H_2} = 1.3,\ \varepsilon_{H_2O} = 10,\ \varepsilon_{CO} = 1.9,\ \varepsilon_{CO_2} = 3.8,\ \varepsilon_{Ar} = 0.0,\ \varepsilon_{He} = 0.0$				
	$H + O_2\ (+Ar) = HO_2\ (+Ar)^b$	4.65E+12	0.44	0.00	[24]
	Low-pressure limit	6.81E+18	−1.20	0.0	[26]
	$H + O_2\ (+He) = HO_2\ (+He)^c$	4.65E+12	0.44	0.00	[24]
	Low-pressure limit	9.19E+18	−1.20	0.0	[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	$HO_2 + OH = H_2O + O_2$	2.456E+13	0.00	−4.970E+02	[51] × 0.85
14	$HO_2 + HO_2 = H_2O_2 + O_2$	1.300E+11	0.00	−1.630E+03	[54]
	$HO_2 + HO_2 = H_2O_2 + O_2$	3.658E+14	0.00	1.200E+04	[54] × 0.87
15	$H_2O_2\ (+M) = OH + OH\ (+M)^d$	2.000E+12	0.90	4.875E+04	[41]
	Low-pressure limit	2.490E+24	−2.30	4.875E+04	[41]
	$\varepsilon_{H_2} = 3.7,\ \varepsilon_{CO} = 2.8,\ \varepsilon_{CO_2} = 1.6,\ \varepsilon_{N_2} = 1.5,\ \varepsilon_{O_2} = 1.2$				
	$\varepsilon_{He} = 0.65,\ \varepsilon_{H_2O_2} = 7.7,\ \varepsilon_{H_2O} = 0.0$				
	$H_2O_2\ (+H_2O) = OH + OH\ (+H_2O)^e$	2.000E+12	0.90	4.875E+04	[41]
	Low-pressure limit	1.865E+25	−2.30	4.875E+04	[41]
16	$H_2O_2 + H = H_2O + OH$	2.410E+13	0.00	3.970E+03	[36]
17	$H_2O_2 + H = H_2 + HO_2$	2.150E+10	1.00	6.000E+03	[37]
18	$H_2O_2 + O = OH + HO_2$	9.550E+06	2.00	3.970E+03	[36]
19	$H_2O_2 + OH = H_2O + HO_2$	1.740E+12	0.00	3.180E+02	[40]
	$H_2O_2 + OH = H_2O + HO_2$	7.590E+13	0.00	7.269E+03	[40]
20	$CO + O\ (+M) = CO_2\ (+M)$	1.362E+10	0.00	2.384E+03	[59] × 0.75
	Low-pressure limit	1.173E+24	−2.79	4.191E+03	[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



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

Slide courtesy of Prof. E. Ranzi

Reaction mechanism

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

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

Rate constant

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

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

Slide courtesy of Dr. Pierre-Alexandre Glaude

Databases

- **On-line databases**

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

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

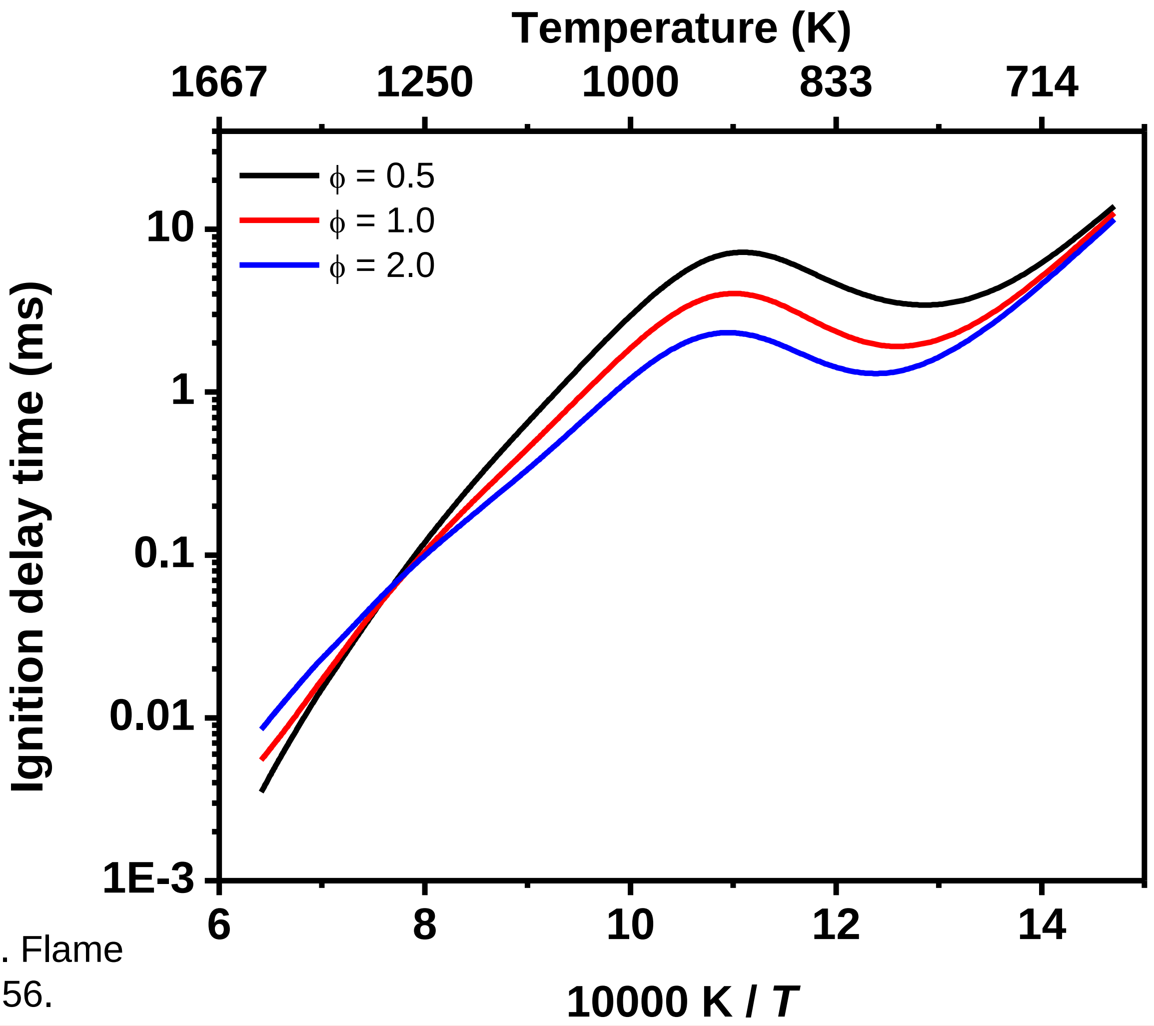
- **On-line mechanisms:**
  - **Estimated rate constants for most reactions, to handle and mix carefully**
  - **GRI-mech, LLNL, Leeds, Konnov, NUIG, POLIMI, Jet-Surf, UCSD…**

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

Slide courtesy of Dr. Pierre-Alexandre Glaude

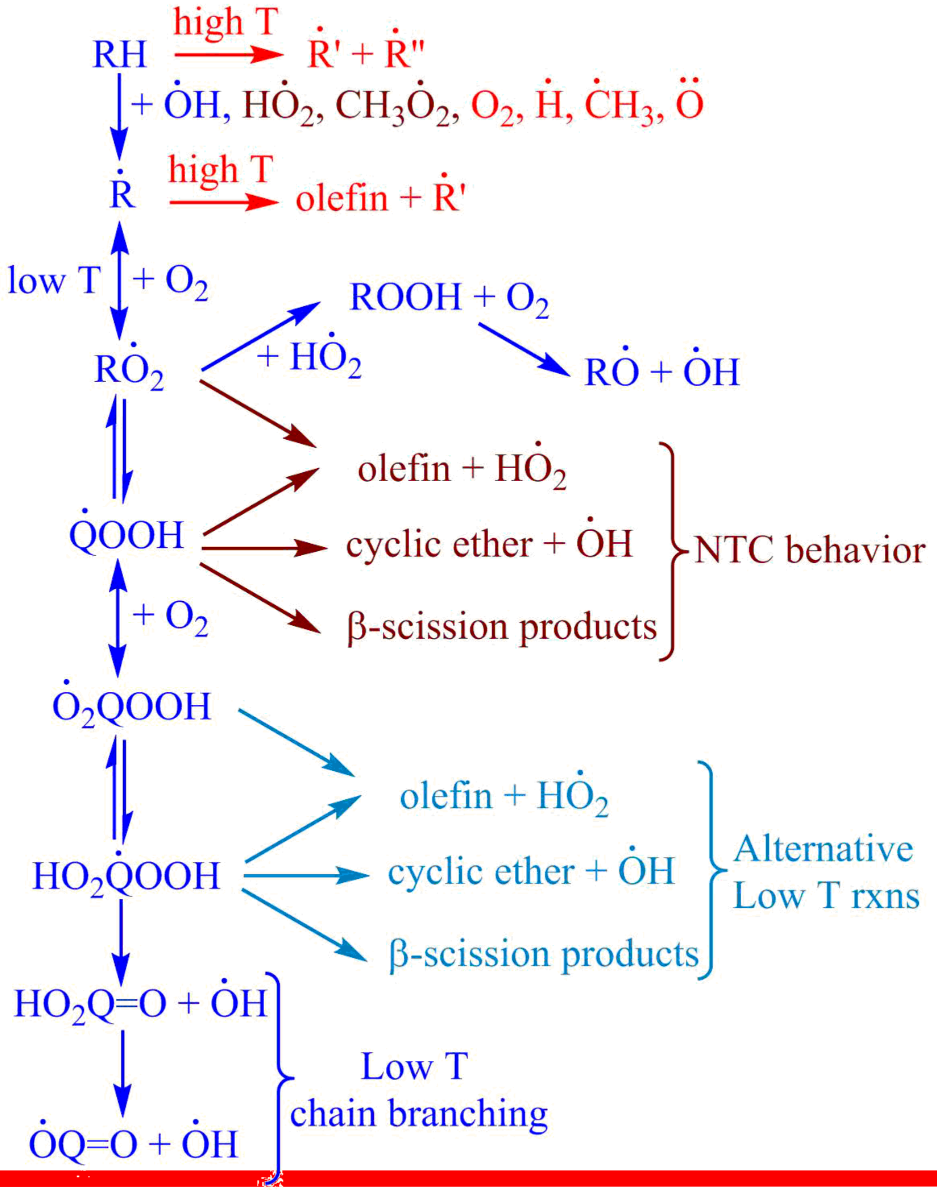
Three distinct temperature regimes

nC_5H_{12} in air, *p* = 20 atm



J. Bugler et al., Combust. Flame 163(1) (2016) 138–156.

Three distinct temperature regimes



$RH \xrightarrow{\text{high T}} \dot{R}' + \dot{R}''$

$+\ \dot{O}H,\ H\dot{O}_2,\ CH_3\dot{O}_2,\ O_2,\ \dot{H},\ \dot{C}H_3,\ \ddot{O}$

$\dot{R} \xrightarrow{\text{high T}} \text{olefin} + \dot{R}'$

low T $+\ O_2$

$R\dot{O}_2 \xrightarrow{+\ H\dot{O}_2} ROOH + O_2 \rightarrow R\dot{O} + \dot{O}H$

$\dot{Q}OOH$

olefin + $H\dot{O}_2$

cyclic ether + $\dot{O}H$

β-scission products

NTC behavior

$+\ O_2$

$\dot{O}_2QOOH$

$HO_2\dot{Q}OOH$

olefin + $H\dot{O}_2$

cyclic ether + $\dot{O}H$

β-scission products

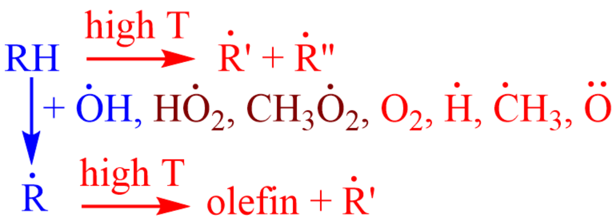
Alternative
Low T rxns

$HO_2Q{=}O + \dot{O}H$

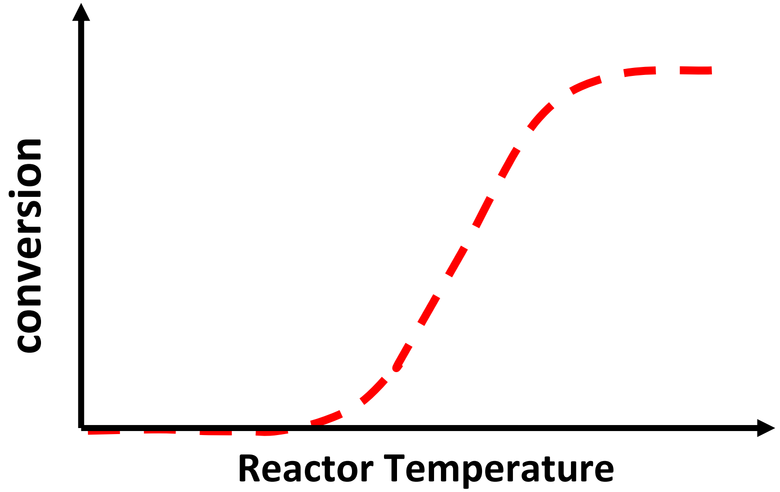
$\dot{O}Q{=}O + \dot{O}H$

Low T
chain branching

Three distinct temperature regimes



$$\begin{tikzcd} RH \arrow[r, "\text{high T}"] \arrow[d, "+\ \dot{O}H,\ H\dot{O}_2,\ CH_3\dot{O}_2,\ O_2,\ \dot{H},\ \dot{C}H_3,\ \ddot{O}"] & \dot{R}' + \dot{R}'' \\ \dot{R} \arrow[r, "\text{high T}"] & \text{olefin} + \dot{R}' \end{tikzcd}$$



$$\cancel{\dot{H}} + O_2 \rightarrow \cancel{\ddot{O}} + \dot{O}H$$

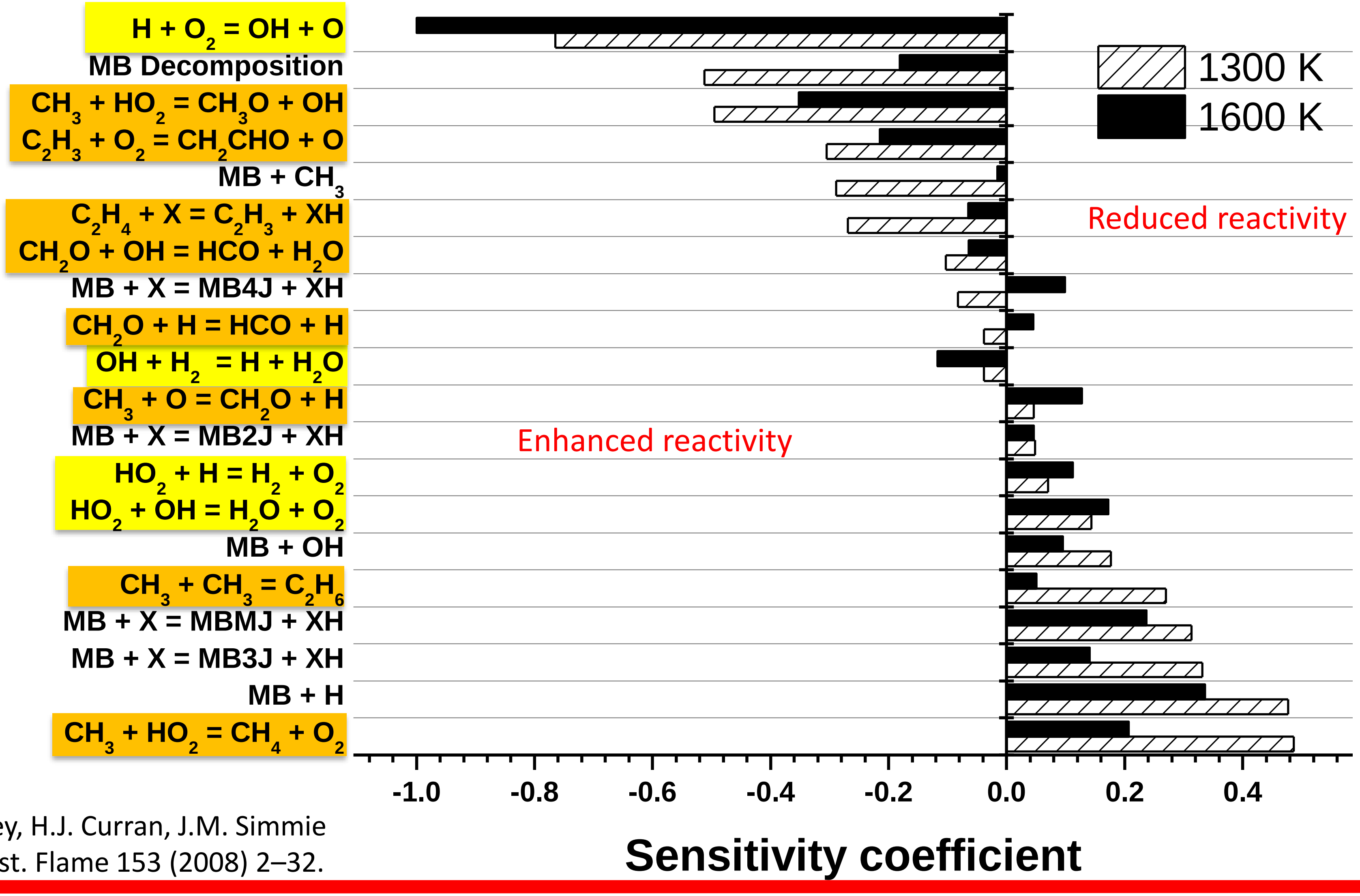
$$\cancel{\ddot{O}} + H_2 \rightarrow \cancel{\dot{H}} + \cancel{\dot{O}H}$$

$$\underline{\cancel{\dot{O}H} + H_2 \rightarrow H_2O + \dot{H}}$$

$$\text{Net: } 2H_2 + O_2 \rightarrow \dot{O}H + \dot{H} + H_2O$$

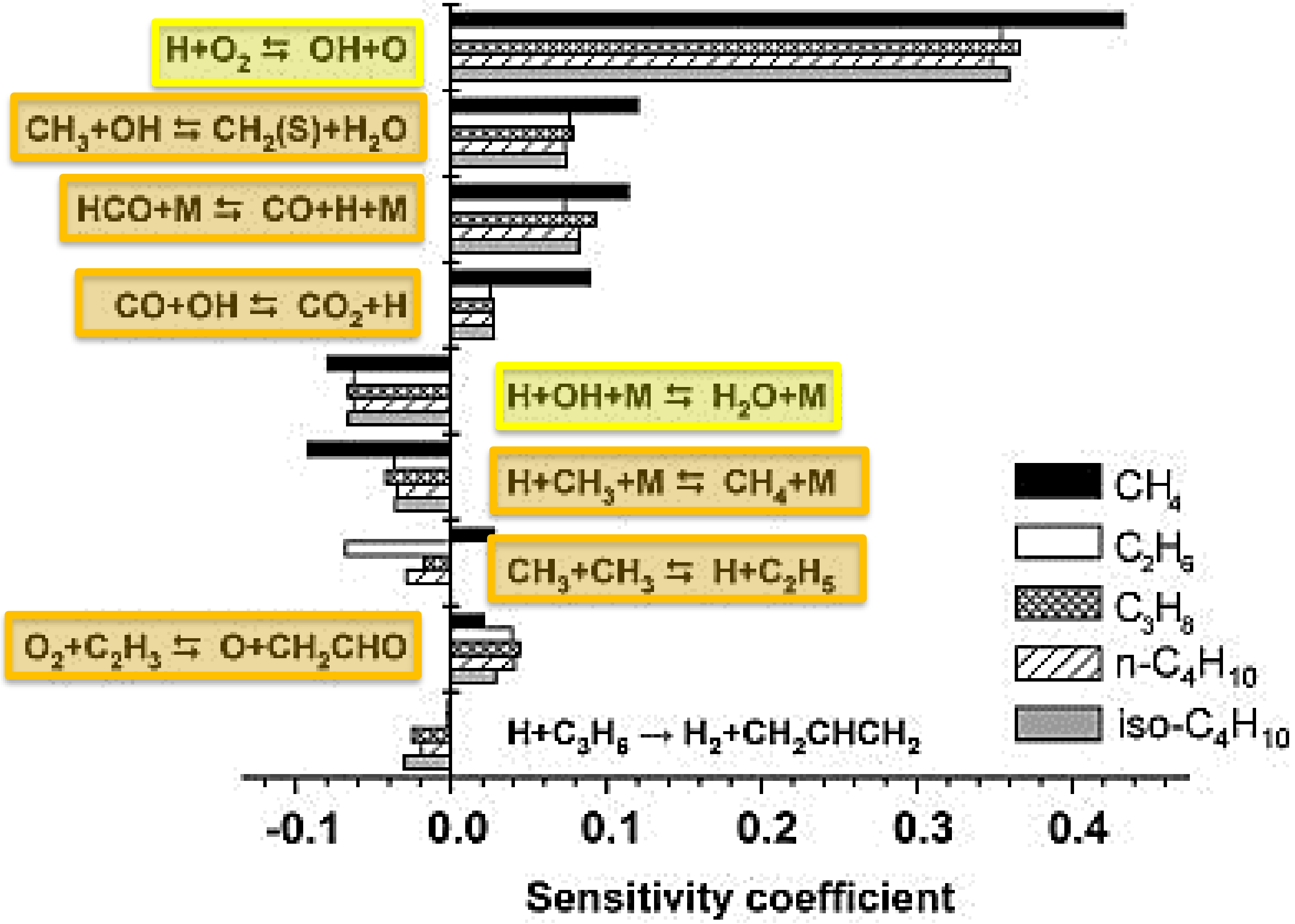
Sensitivity to ignition delay time at low *p* / high *T*

1% MB ($C_5H_{10}O_2$) oxidation, φ = 1.0 in Ar, *p* = 1 atm



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

Sensitivity to flame speed at *p* = 1 atm, *T* = 298 K, $\phi = 1.0$



E. Ranzi, A. Frassoldati, R. Grana, A. Cuoci, T. Faravelli, A.P. Kelley, C.K. Law, Prog. Energy Combust. Sci., 38(4) (2012) 468–501.

Small molecule kinetic mechanisms

- In small molecule kinetics, each elementary reaction is treated individually
- Many of the elementary reactions are rather idiosyncratic or unusual
- Extensive validation experiments usually exist
- Principal reactions are usually:
  - $\dot{H} + O_2 = \ddot{O} + \dot{O}H$
  - $\dot{H} + O_2\ (+M) = H\dot{O}_2\ (+M)$
  - $CO + \dot{O}H = CO_2 + \dot{H}$

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

Three distinct chain branching pathways

1) $\dot{H} + O_2 \rightarrow \ddot{O} + \dot{O}H$

$\ddot{O} + H_2 \rightarrow \dot{H} + \dot{O}H$ High T

$\underline{\dot{O}H + H_2 \rightarrow H_2O + \dot{H}}$

Net: $2H_2 + O_2 \rightarrow \dot{O}H + \dot{H} + H_2O$

2) $\dot{H} + O_2\ (+M) \rightarrow H\dot{O}_2\ (+M)$ Intermediate T

$RH + H\dot{O}_2 \rightarrow \dot{R} + H_2O_2$

$H_2O_2\ (+M) \rightarrow \dot{O}H + \dot{O}H\ (+M)$ chain branching

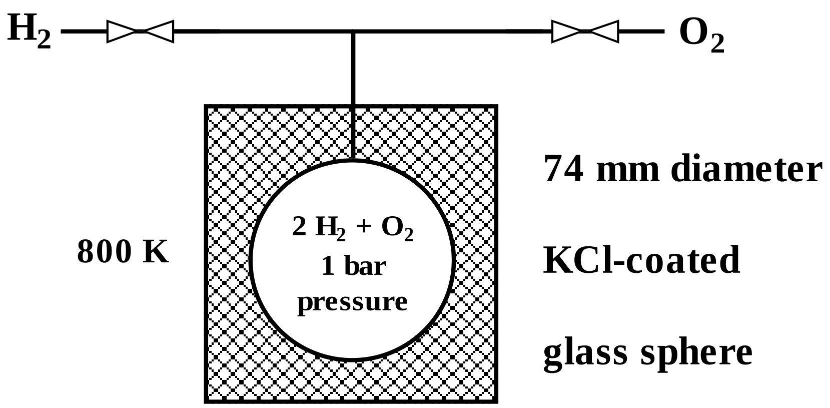
$\dot{R} + O_2 \leftrightarrow R\dot{O}_2$

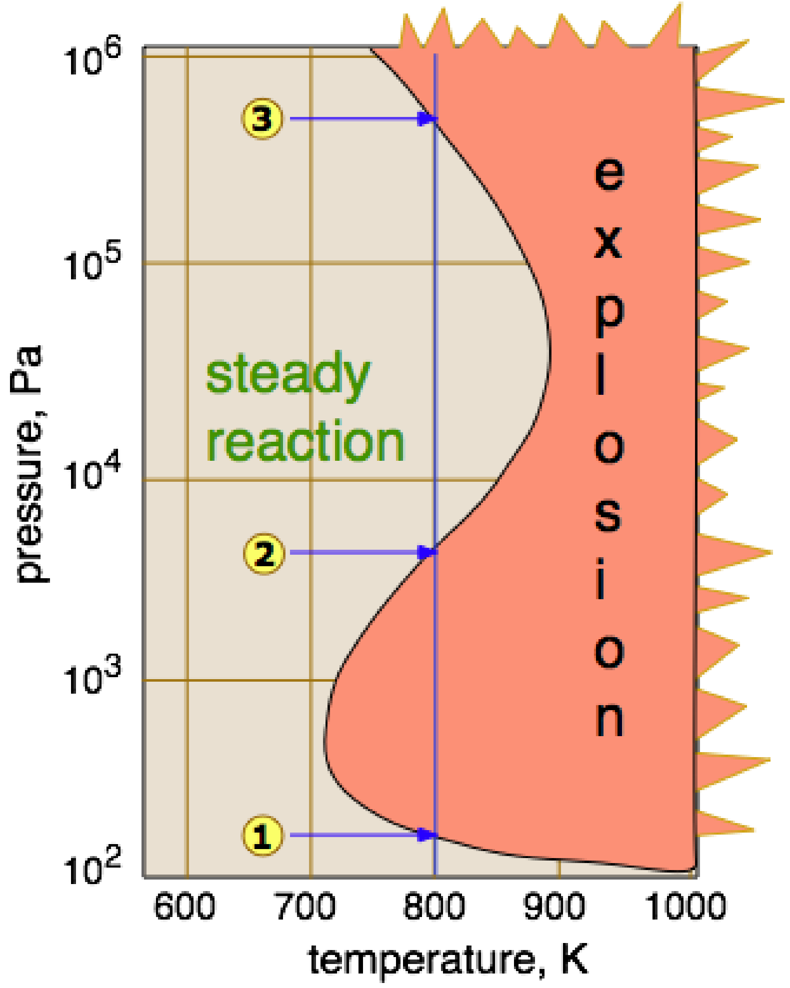
$R\dot{O}_2 \rightarrow \text{olefin} + H\dot{O}_2$

3) $\dot{R} + O_2 \leftrightarrow R\dot{O}_2$ Low T

$R\dot{O}_2 \rightleftharpoons \dot{Q}OOH \leftrightarrow \dot{O}_2QOOH \rightleftharpoons R\dot{O} + \dot{O}H + \dot{O}H$

Hydrogen – three explosion limits

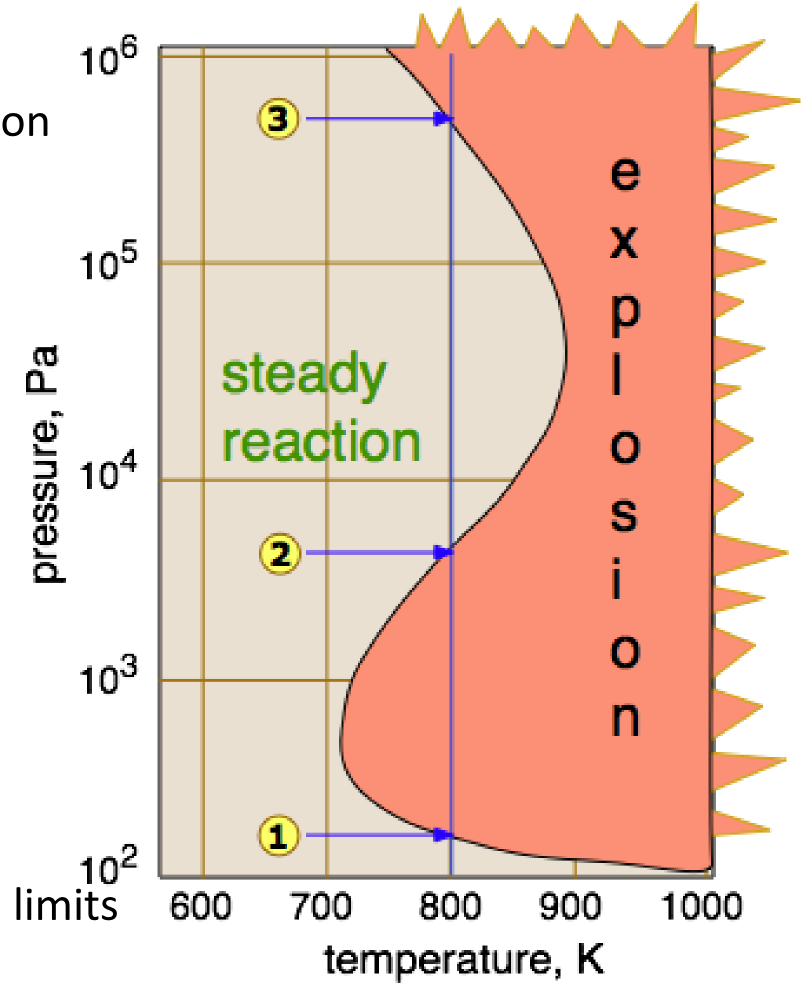




☐ $H_2 + O_2 = H\dot{O}_2 + \dot{H}$	initiation
☐ $H_2 + H\dot{O}_2 = H_2O + \dot{O}H$	propagation
☐ $H_2 + \dot{O}H + = H_2O + \dot{H}$	propagation
☐ $\dot{H} + O_2\ (+M) = H\dot{O}_2\ (+M)$	propagation
☐ $\dot{H} + O_2 = \ddot{O} + \dot{O}H$	branching
☐ $\dot{H} \Rightarrow$ *diffuses to wall*	termination

W. Liang, C.K. Law, Phys. Chem. Chem. Phys. 20 (2018) 742–751.

Hydrogen – three explosion limits



- ❑ 1st Explosion Limit (sensitive to surface, vessel shape)

Low pressure (≤ 160 Pa) controlled by rate of Ḣ atom diffusion to walls ($R_{\dot{H} + O2} < R_{diffusion}$ => no rxn)

- ❑ 2nd Explosion Limit (insensitive to surface, vessel shape)

Intermediate pressure (160 – 5000 Pa) controlled

by rate of $\dot{H} + O_2 = \ddot{O} + \dot{O}H$

- ❑ 3rd Explosion Limit (sensitive to vessel shape/size)

High pressure (> 5000 Pa) rate of $\dot{H} + O_2$ (+M) = $H\dot{O}_2$ (+M) competes with $\dot{H} + O_2 = \ddot{O} + \dot{O}H$. Limit at ~ 5 bar

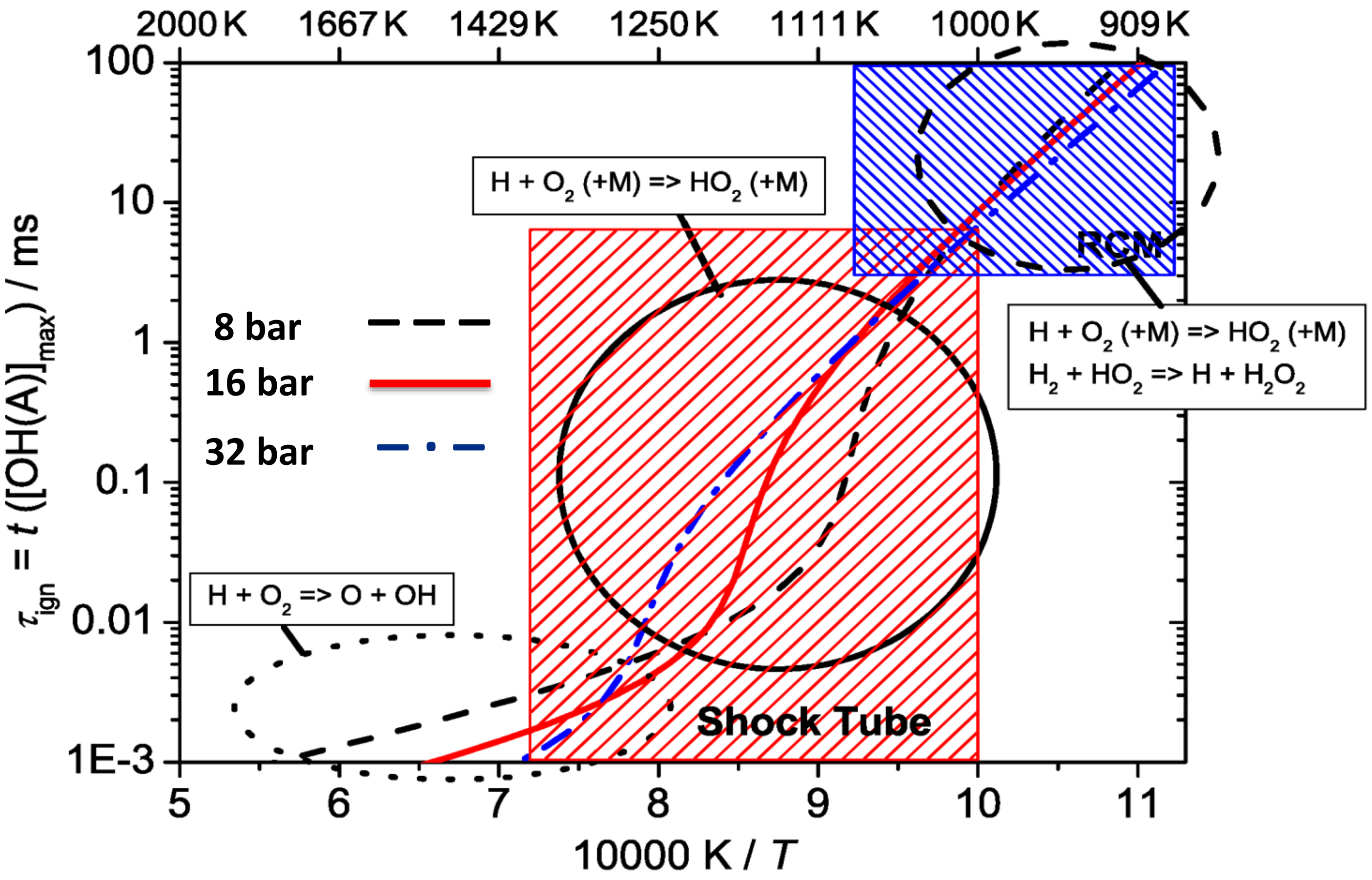
Controlled by competition between gas phase chemistry of $H\dot{O}_2$ and H_2O_2 competing with reactor wall deactivation

$H\dot{O}_2$ controlling at the turning point between the 2nd and 3rd limits

H_2O_2 controlling at high pressures of 3rd limit

W. Liang, C.K. Law, Phys. Chem. Chem. Phys. 20 (2018) 742–751.

Hydrogen ignition delay times



A. Kéromnès et al. Combust. Flame 160 (2013) 995–1011.

Simulated using mechanism from: J. Li, Z. Zhao, A. Kazakov, F.L. Dryer, Int. J. Chem. Kinet. 36 (2004) 566–575.

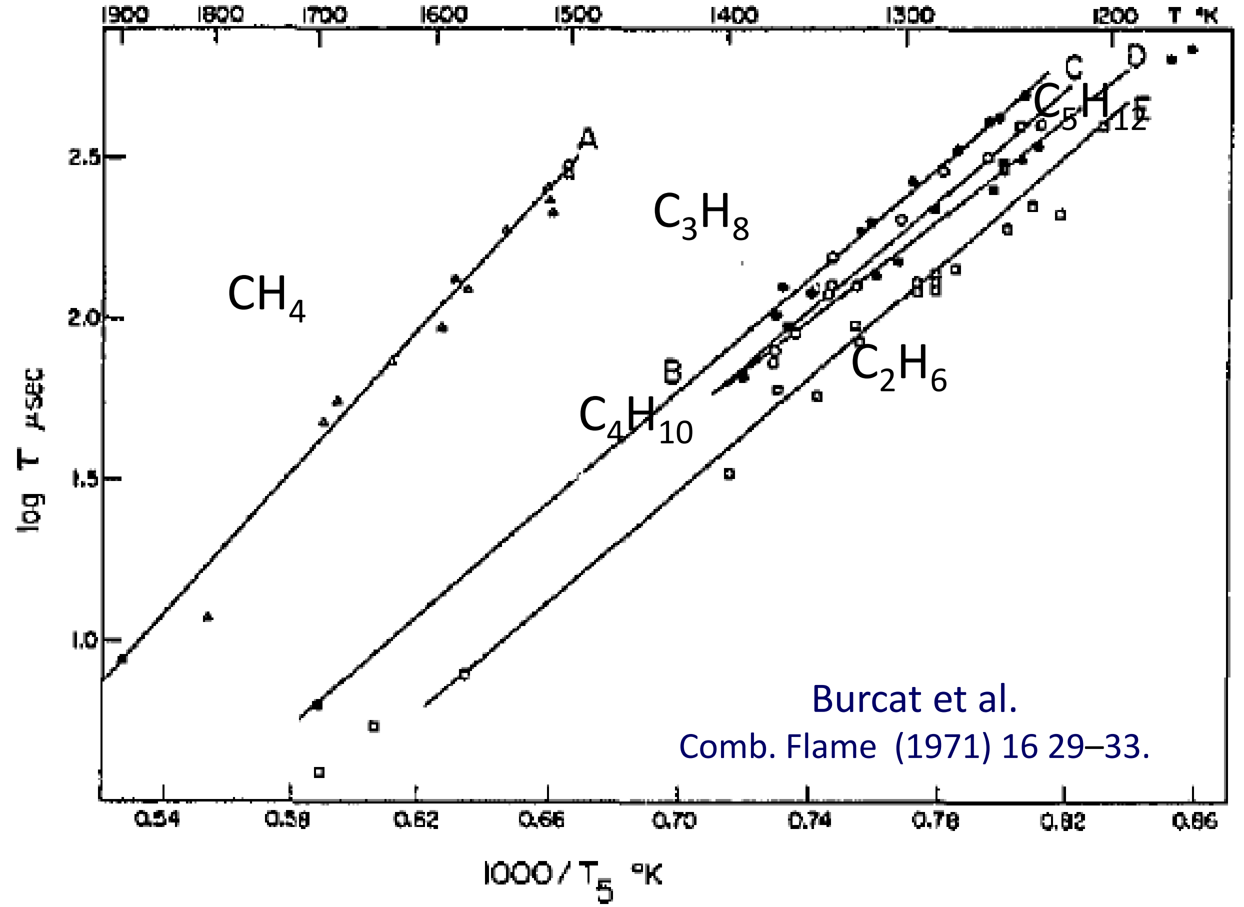
Chain Branching at High Temperatures

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

The most important reaction in combustion

- Activation energy is relatively high (16.44 kcal/mol)
- $\dot{H}$ atoms produced by thermal decomposition of radicals (e.g. $H\dot{C}O$, $\dot{C}_2H_3$, $\dot{C}_2H_5$, $i\dot{C}_3H_7$ etc.) activation energy relatively high (~ 30 kcal/mol)
- Therefore this sequence requires High T
- Illustrated best by shock tube experiments

Relative reactivity of fuels



Burcat et al.
Comb. Flame (1971) 16 29–33.

Figure 1. A plot of log τ 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

$$\cancel{\dot{H}} + O_2 \rightarrow \cancel{\ddot{O}} + \dot{O}H$$

$$\cancel{\ddot{O}} + H_2 \rightarrow \cancel{\dot{H}} + \cancel{\dot{O}H}$$

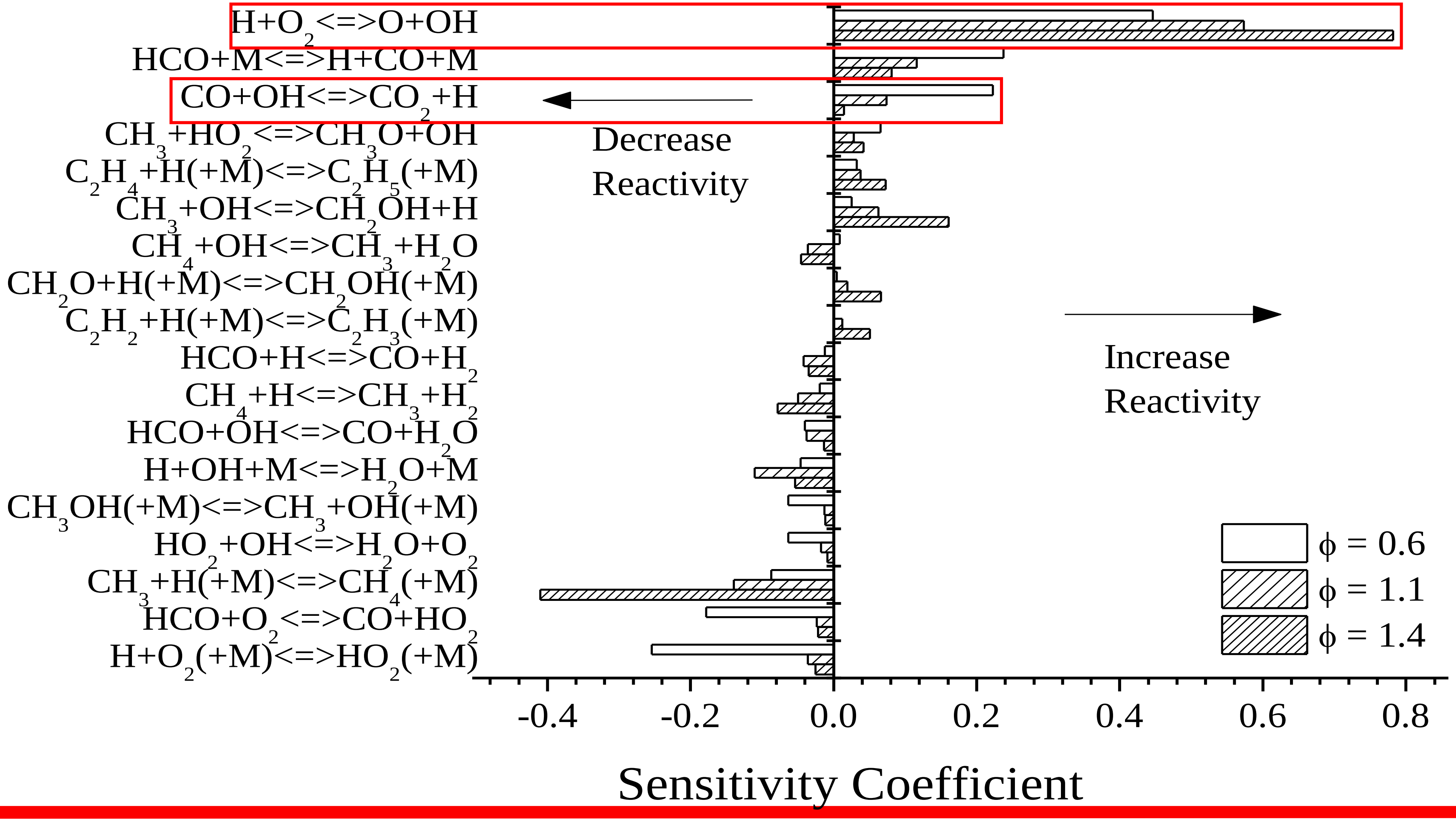
$$\underline{\cancel{\dot{O}H} + H_2 \rightarrow H_2O + \dot{H}}$$

$$\text{Net: } 2H_2 + O_2 \rightarrow \dot{O}H + \dot{H} + H_2O$$

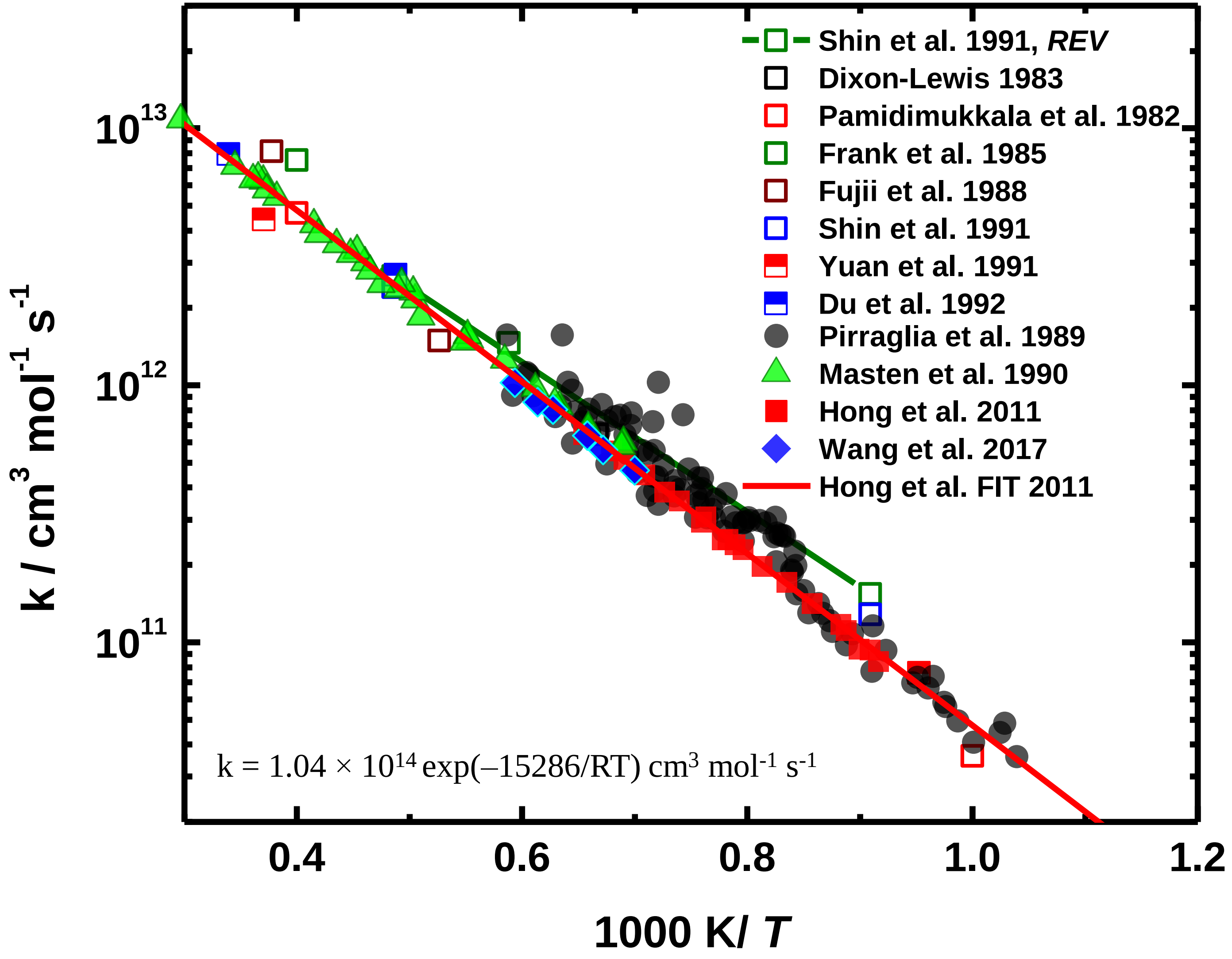
- Chain branching for oxidation, not for pyrolysis
- Lean mixtures ignite faster than rich mixtures
- Different fuels produce $\dot{H}$ atoms at different rates, their ignition rates vary correspondingly
- Additives that produce $\dot{H}$ atoms will accelerate ignition, those that remove $\dot{H}$ atoms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

Sensitivity Analysis—CH_4 Flame Speed

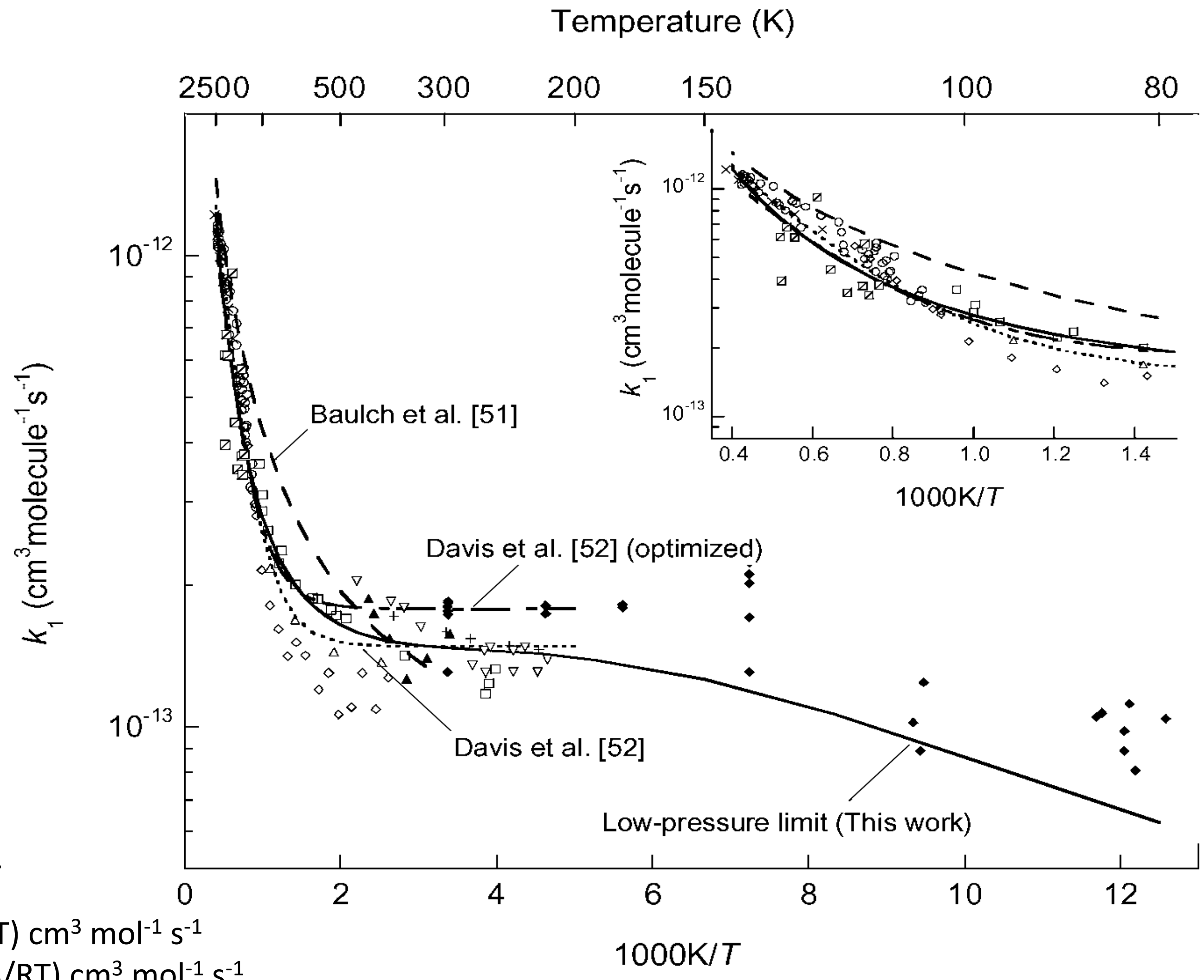
p = 1.0 atm, T_i = 298 K



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



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



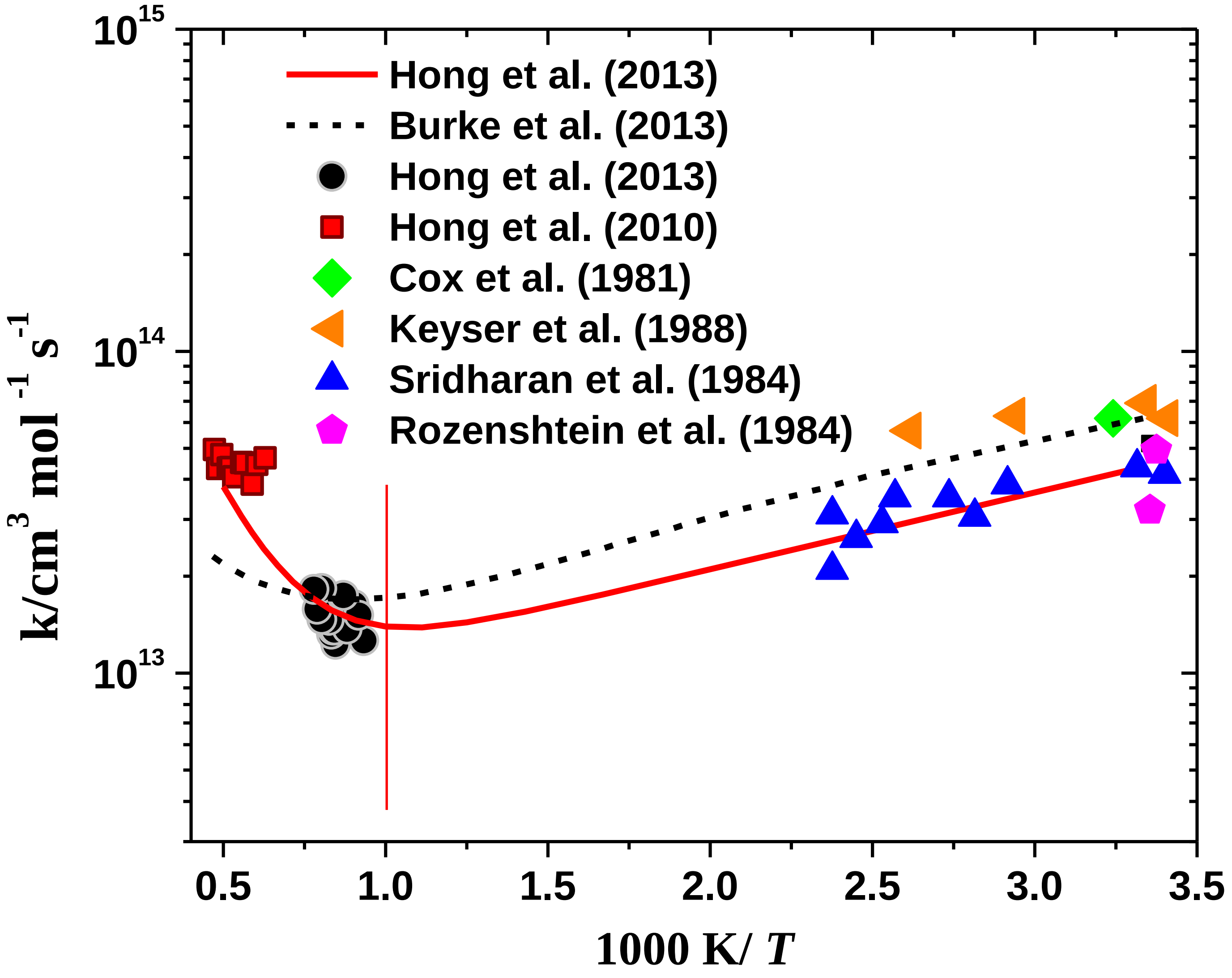
A.V. Joshi, H. Wang

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

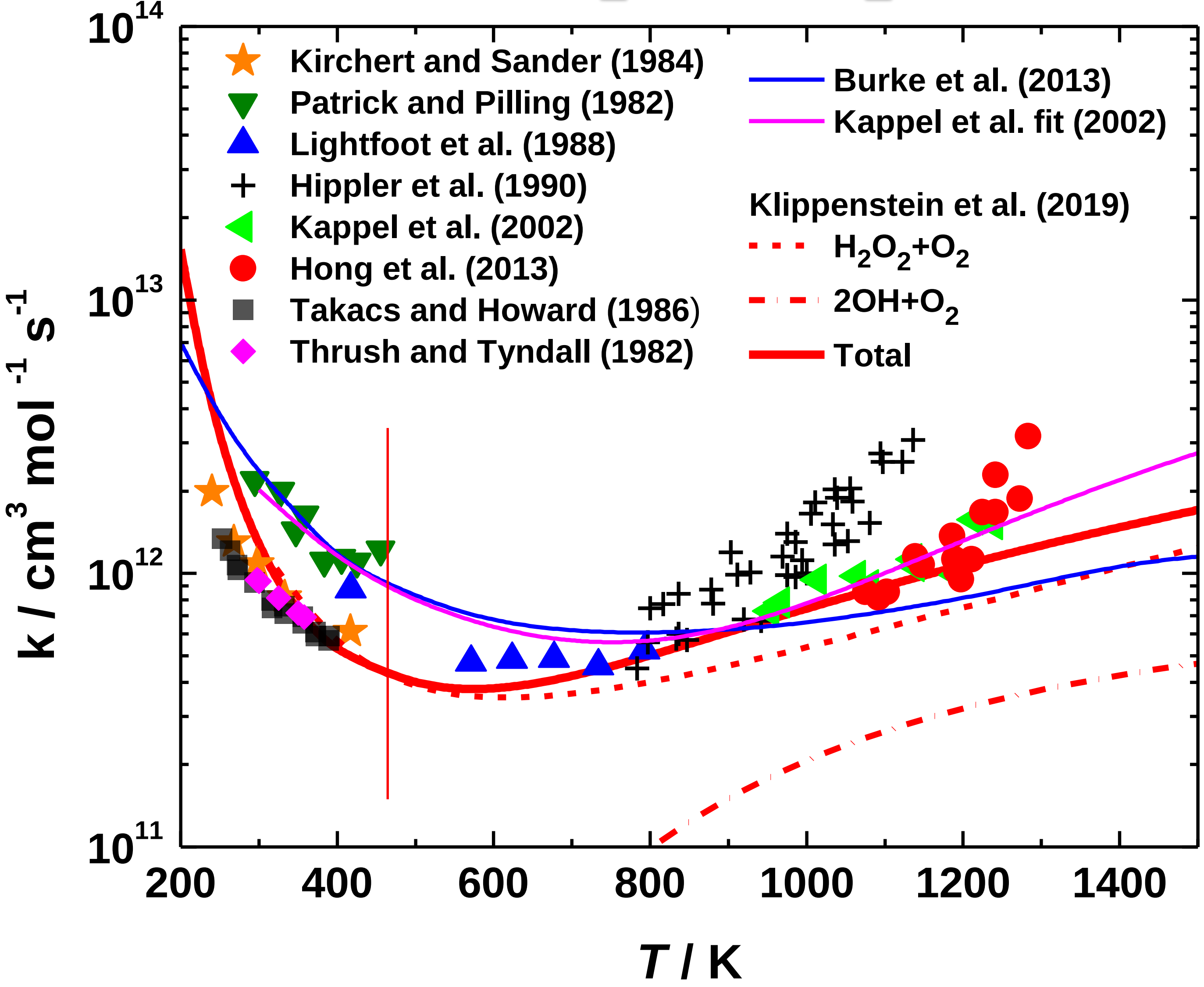
$k = 7.015\times 10^{14}\, T^{2.053} \exp(355.7/RT)$ cm^3 mol^{-1} s^{-1}

$+\, 5.757\times 10^{12}\, T^{-0.664} \exp(-331.8/RT)$ cm^3 mol^{-1} s^{-1}

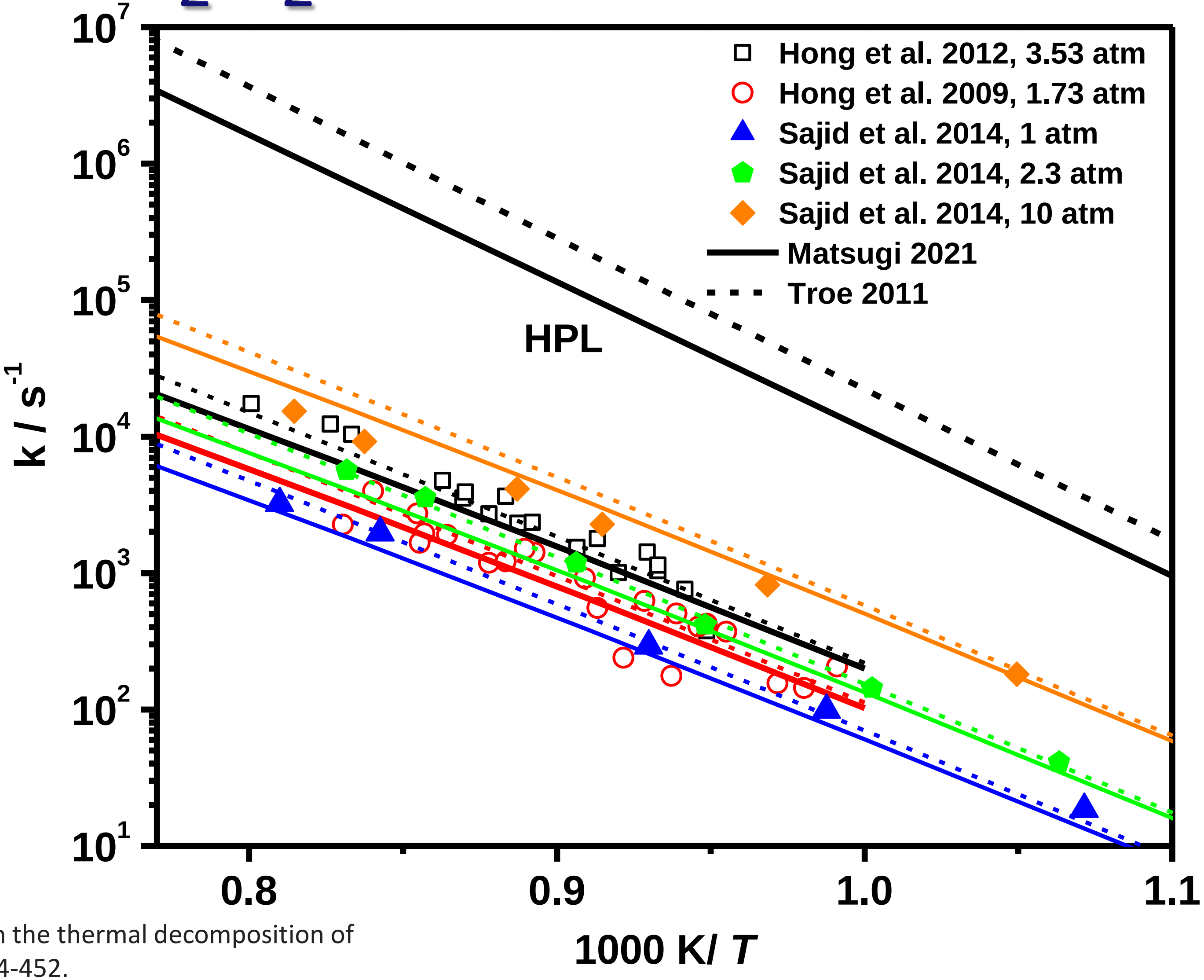
$\dot{O}H + H\dot{O}_2 = H_2O + O_2$



$H\dot{O}_2 + H\dot{O}_2$

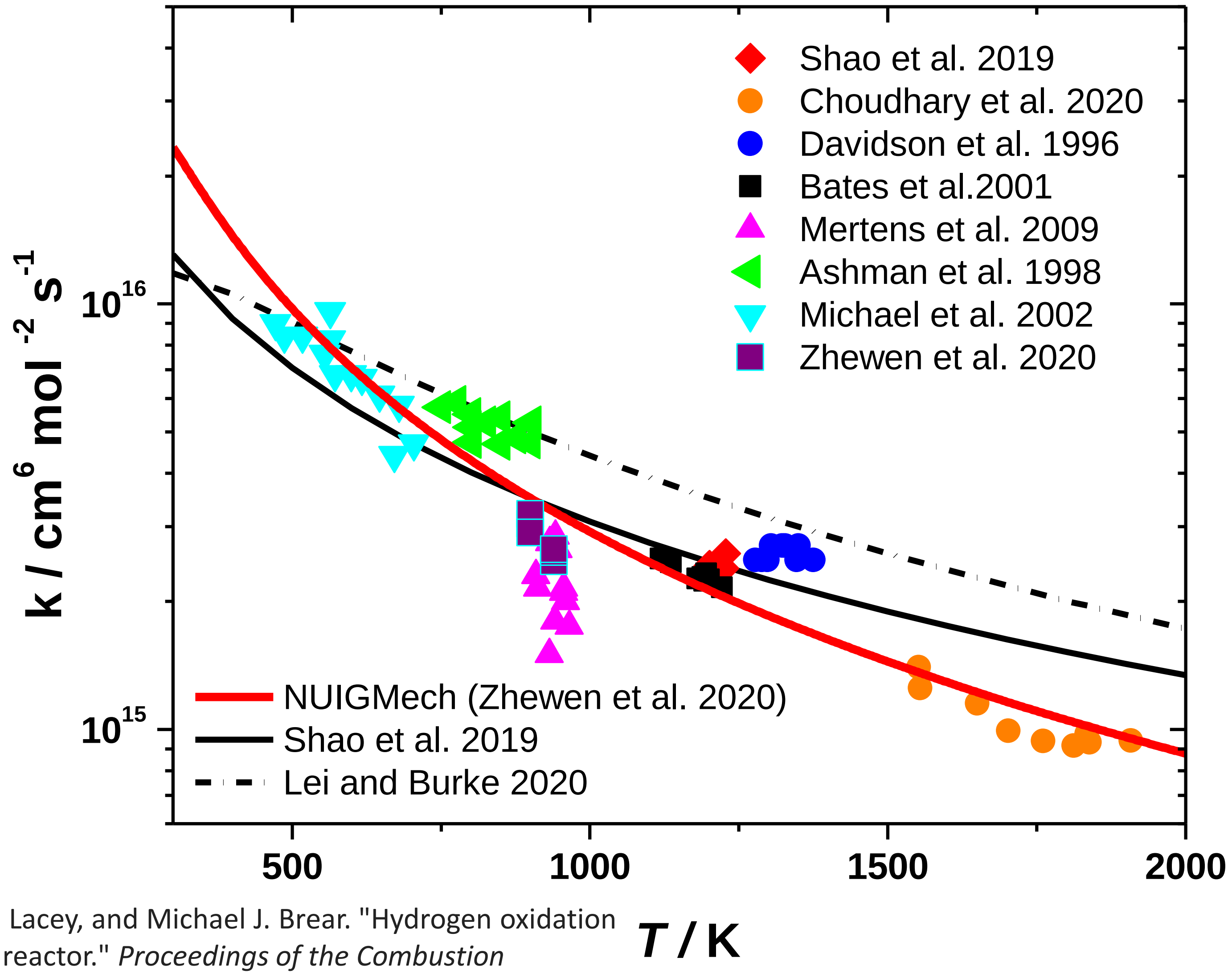


$H_2O_2 + Ar = \dot{O}H + \dot{O}H + Ar$



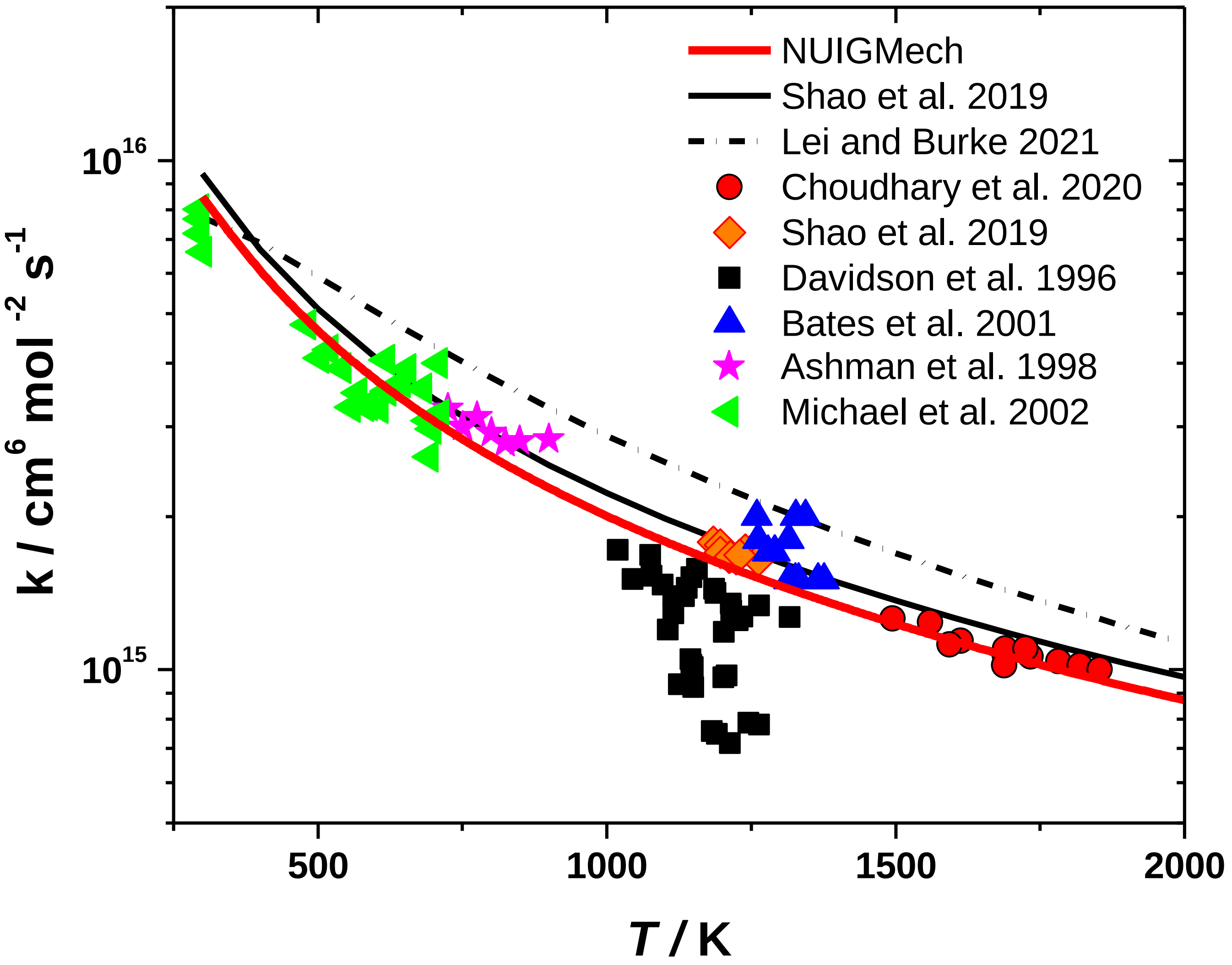
Matsugi, Akira. "Modeling third-body effects in the thermal decomposition of H2O2." *Combustion and Flame* 225 (2021): 444-452.

$\dot{H} + O_2 + N_2 = H\dot{O}_2 + N_2$

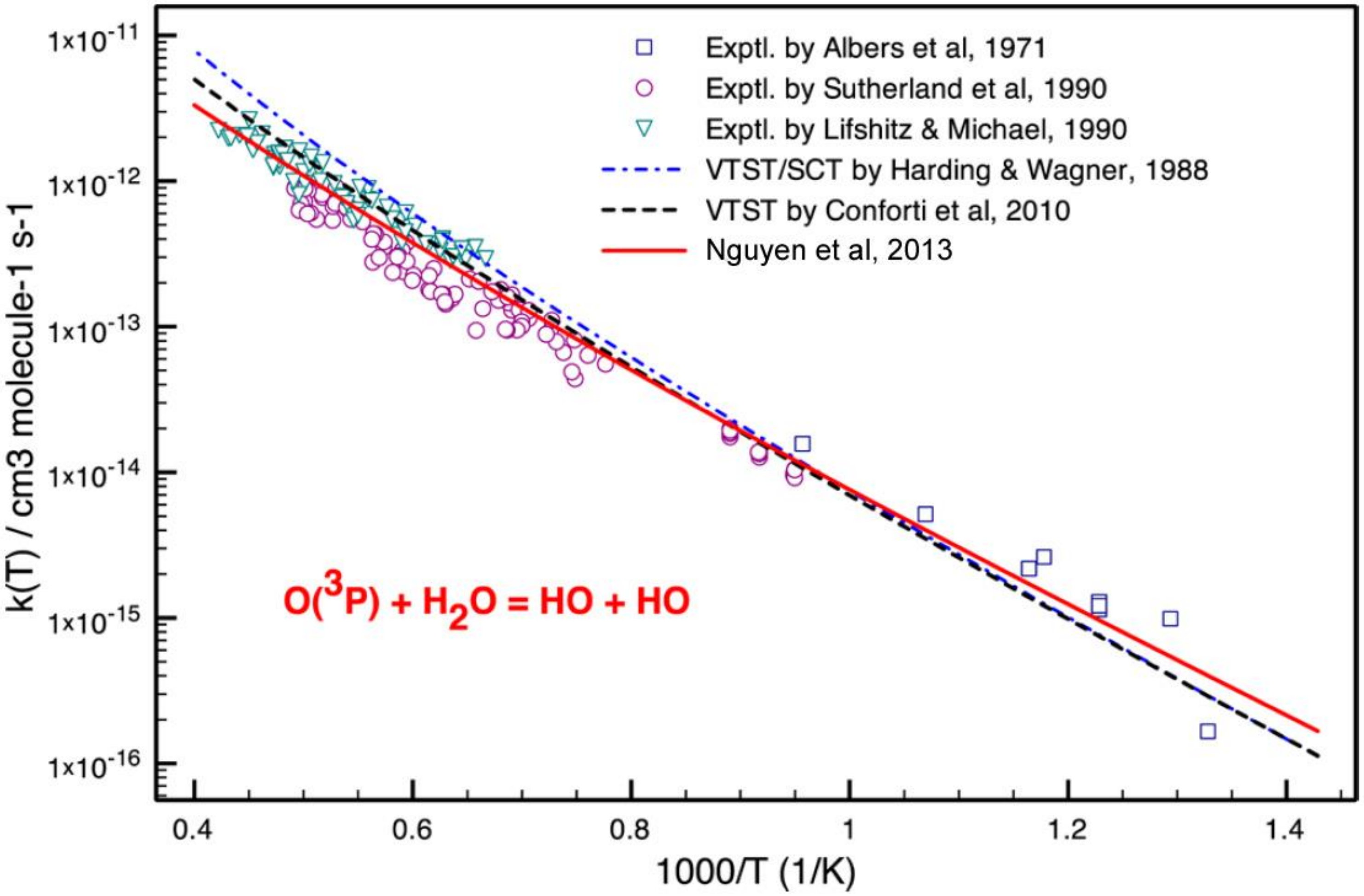


Lu, Zhewen, Junqiu Jiang, Yi Yang, Joshua Lacey, and Michael J. Brear. "Hydrogen oxidation near the second explosion limit in a flow reactor." *Proceedings of the Combustion Institute* (2020).

$\dot{H} + O_2 + Ar = H\dot{O}_2 + Ar$



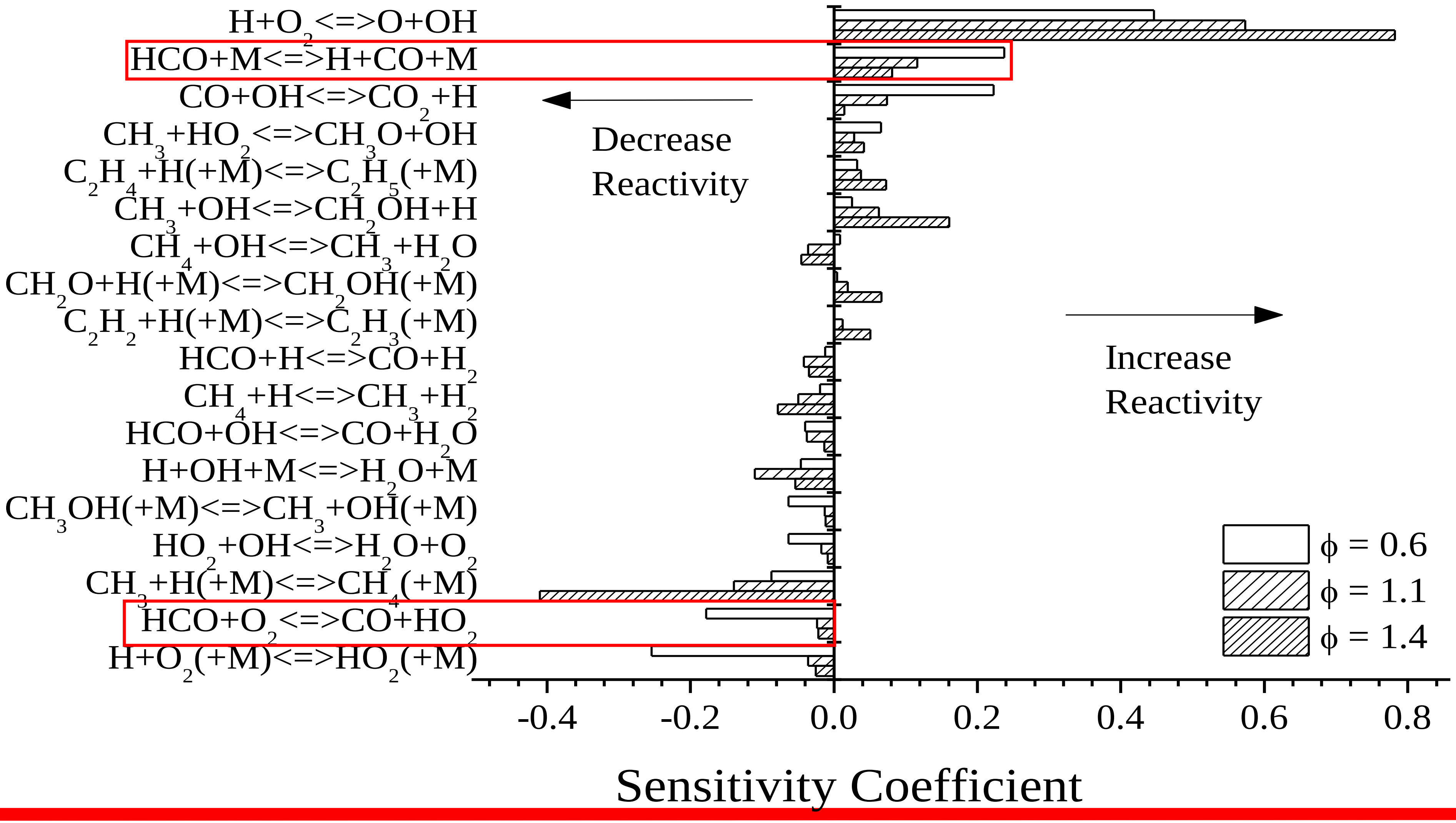
$\ddot{O} + H_2O = \dot{O}H + \dot{O}H$



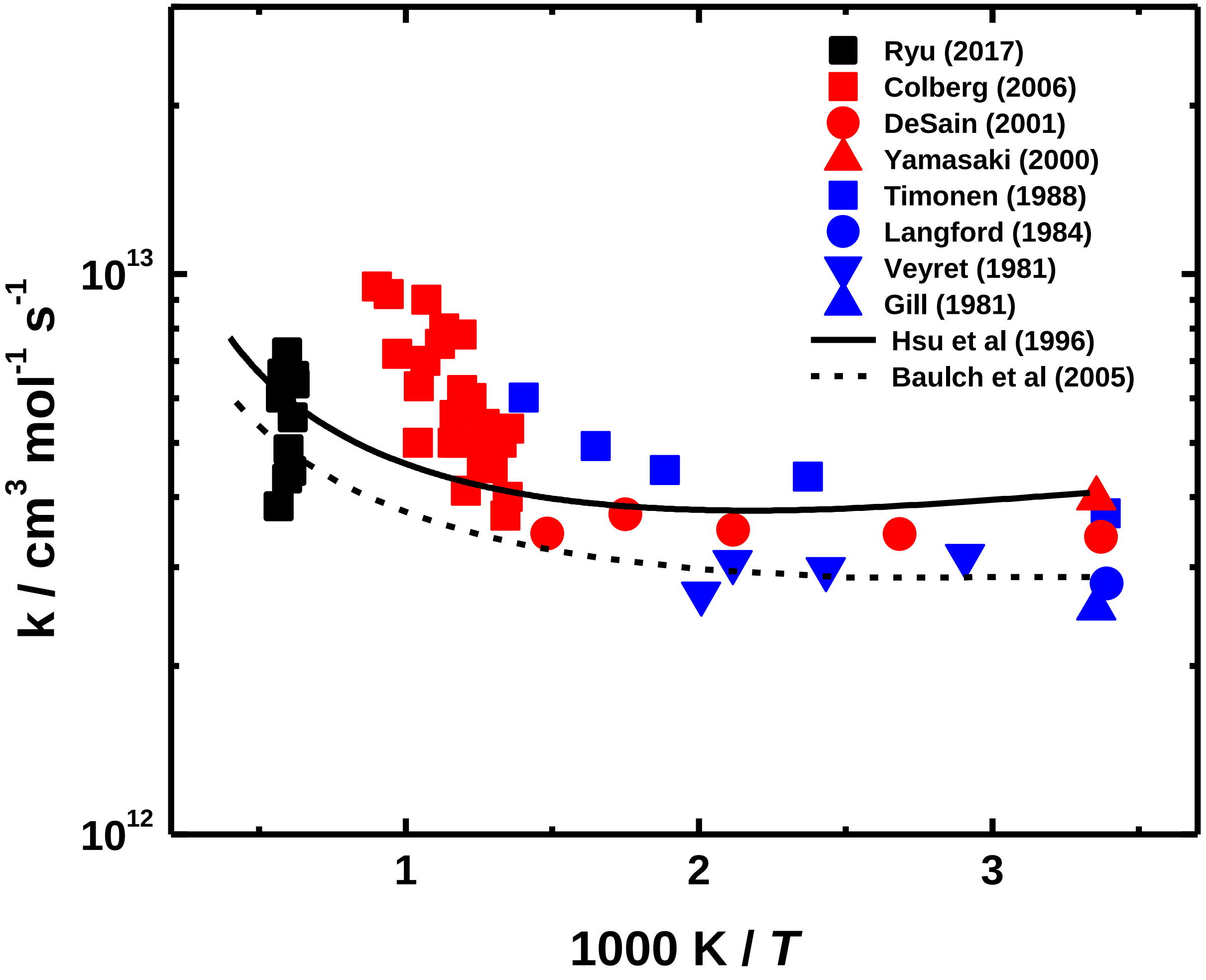
Thanh Lam Nguyen and John F. Stanton

J. Phys. Chem. A 2013, 117, 2678–2686

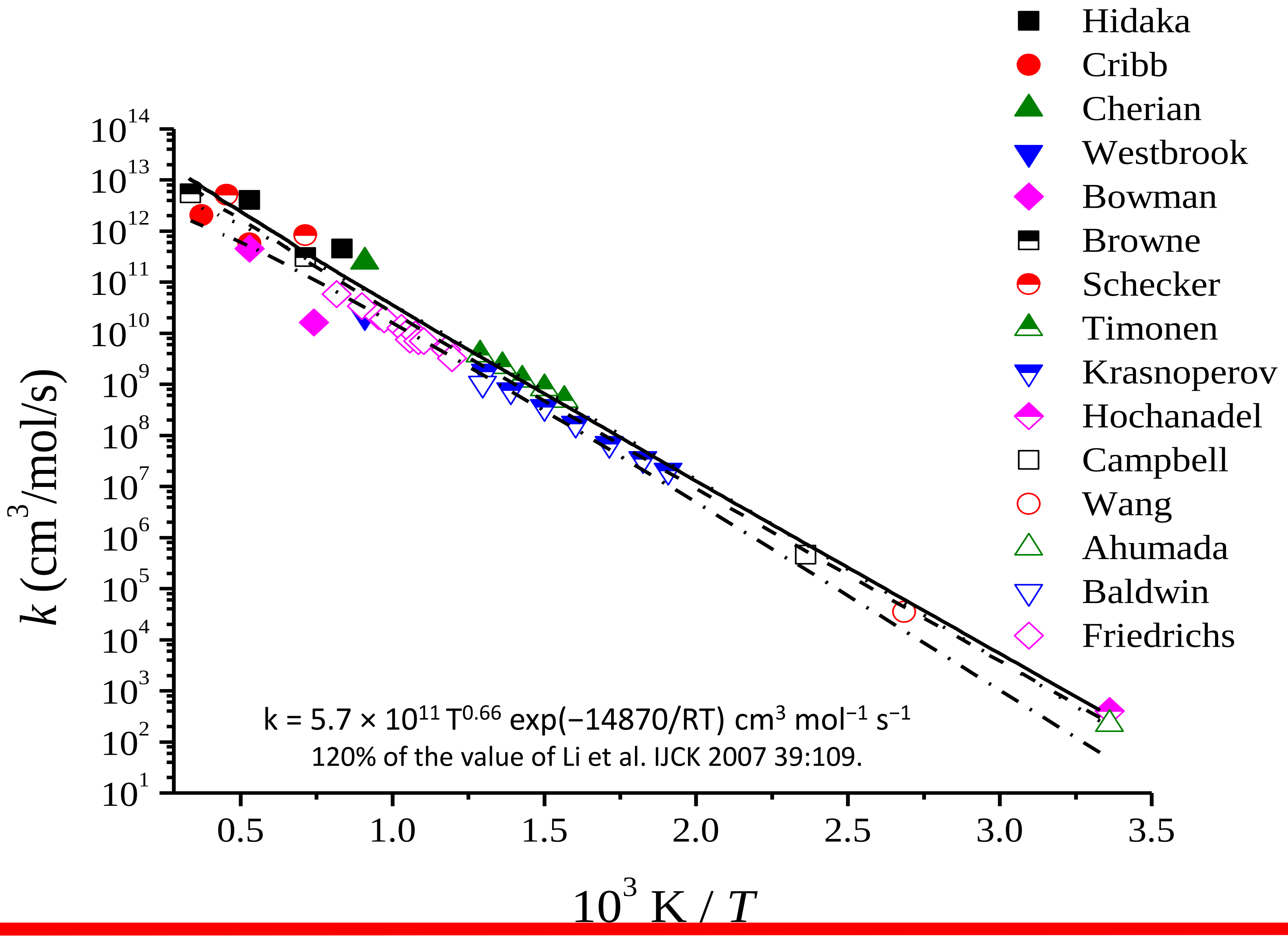
Sensitivity Analysis—CH_4 Flame Speed



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



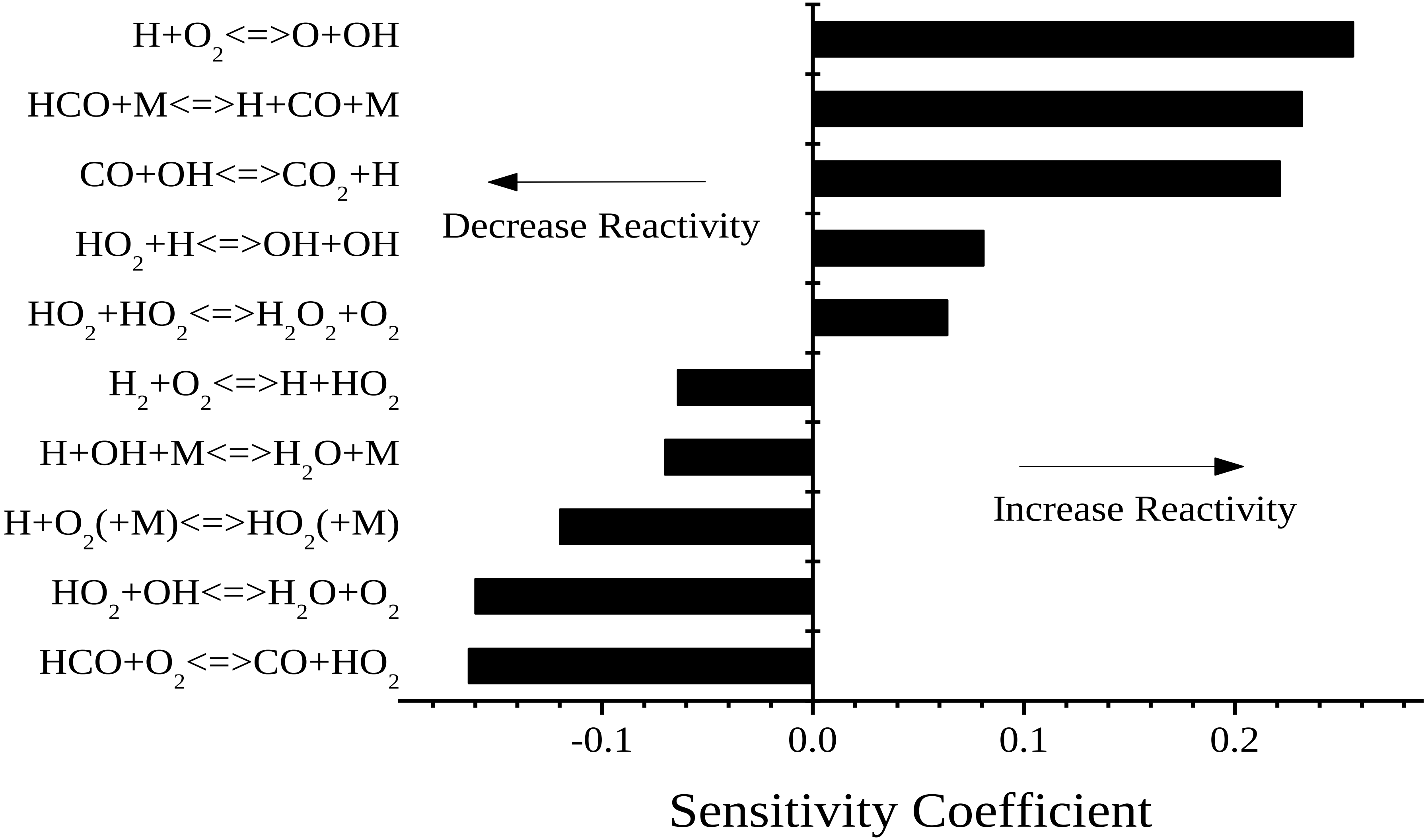
$\dot{HCO}+M = \dot{H} + CO + M$



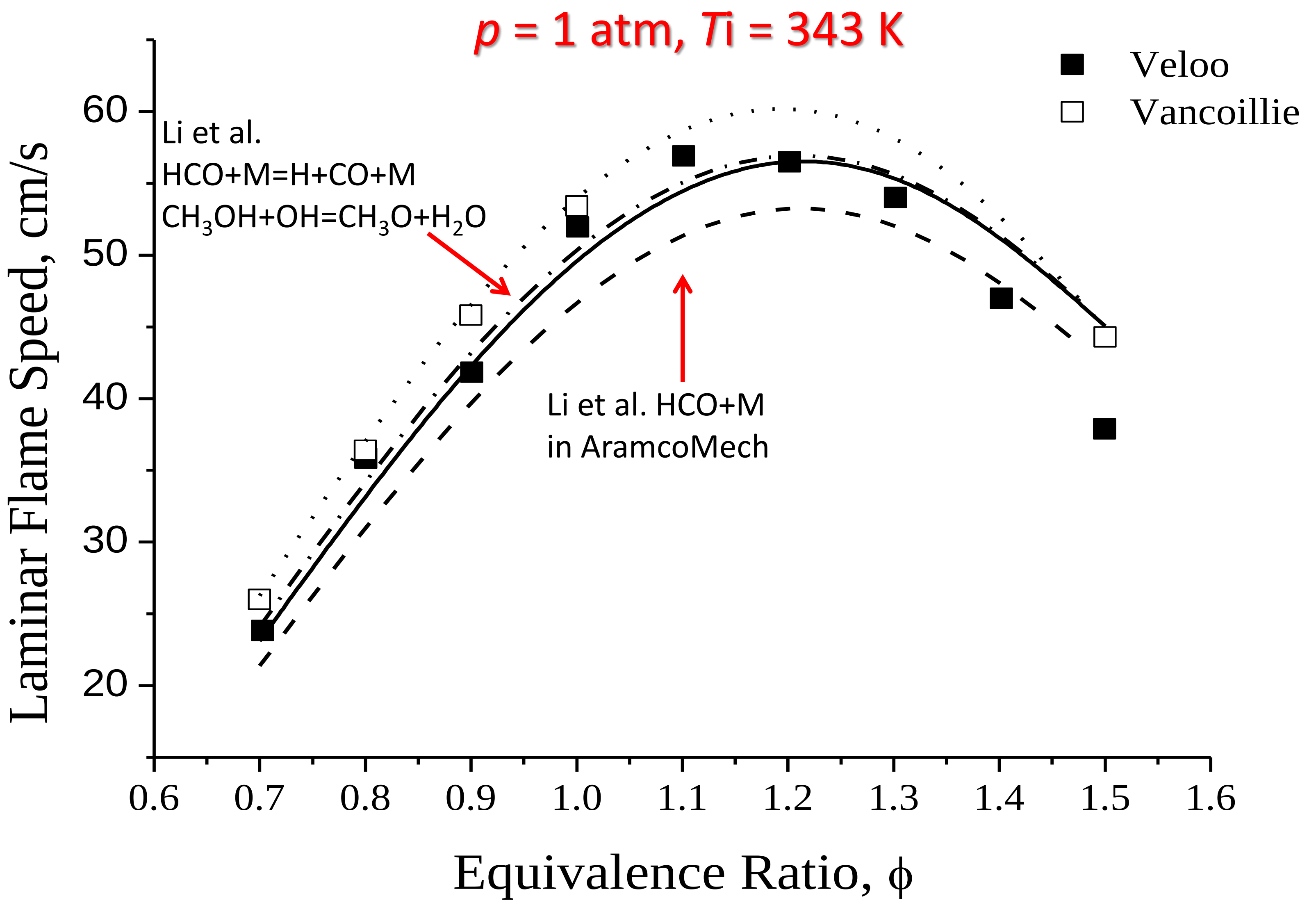
$k = 5.7 \times 10^{11}\ T^{0.66} \exp(-14870/RT)\ cm^3\ mol^{-1}\ s^{-1}$

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

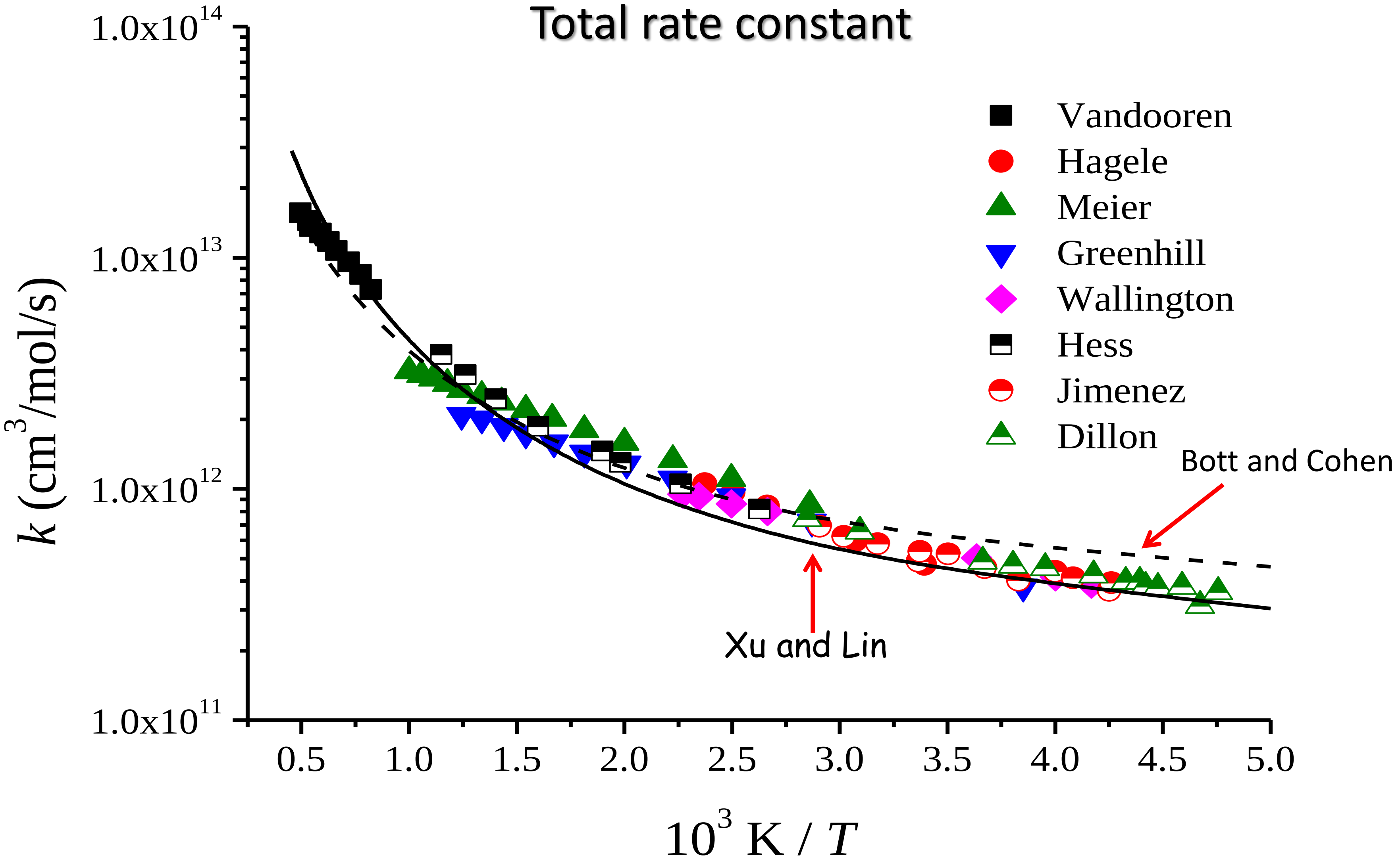
$HC\dot{O}$ + M: large influence on CH_3OH S_L



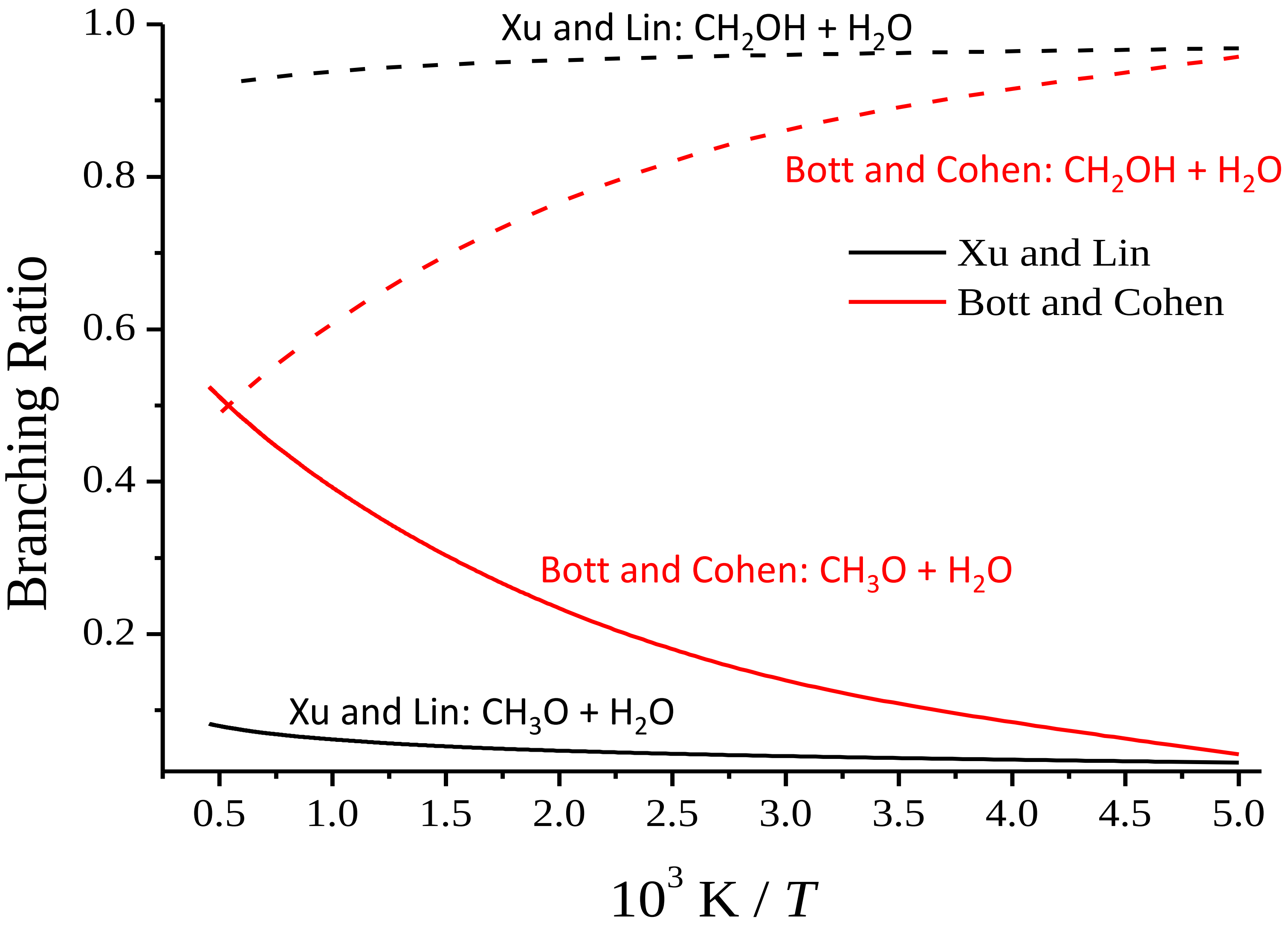
HCȮ + M: large influence on CH_3OH S_L



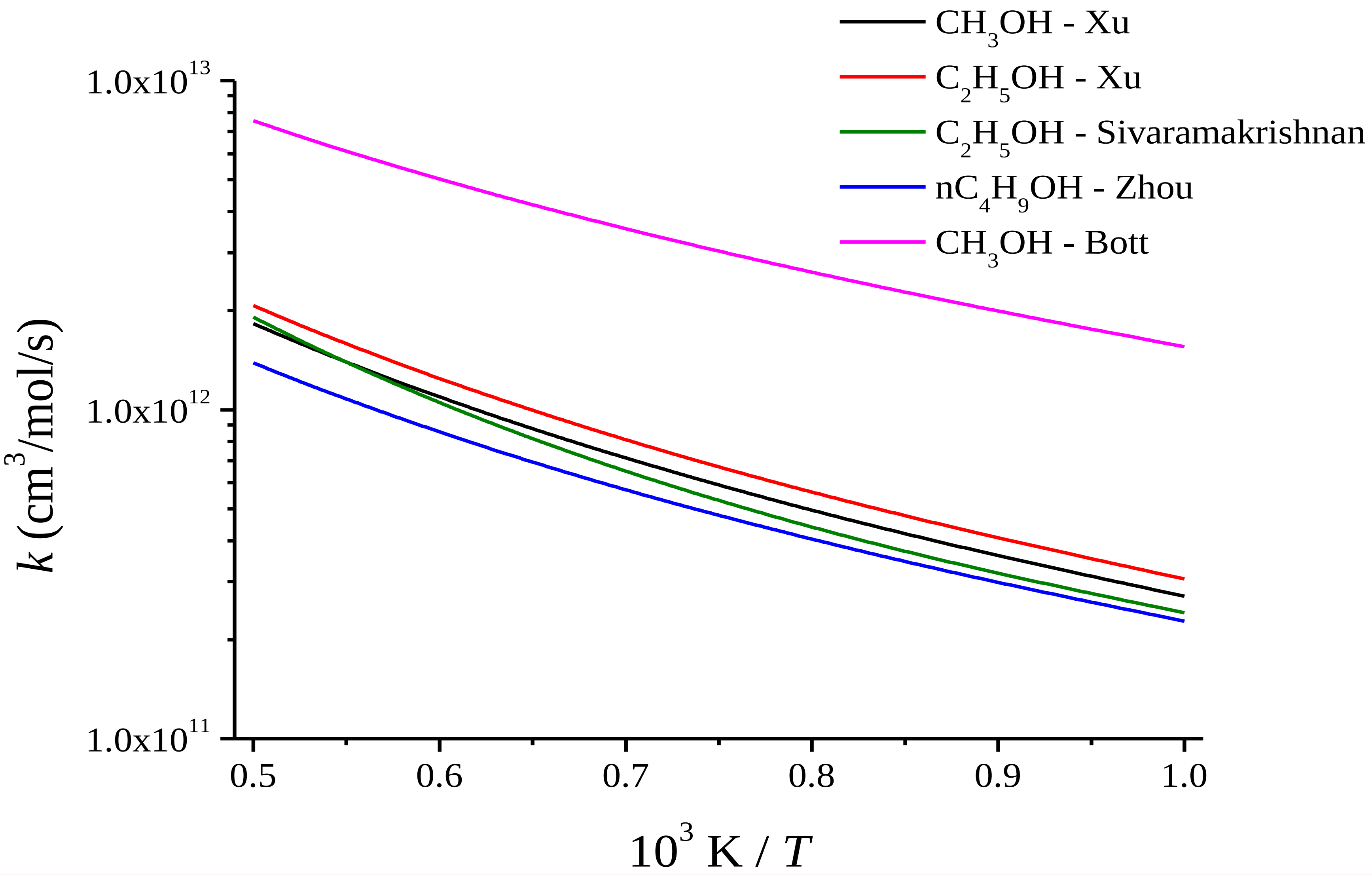
$CH_3OH + \dot{O}H = CH_3\dot{O}/\dot{C}H_2OH + H_2O$



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

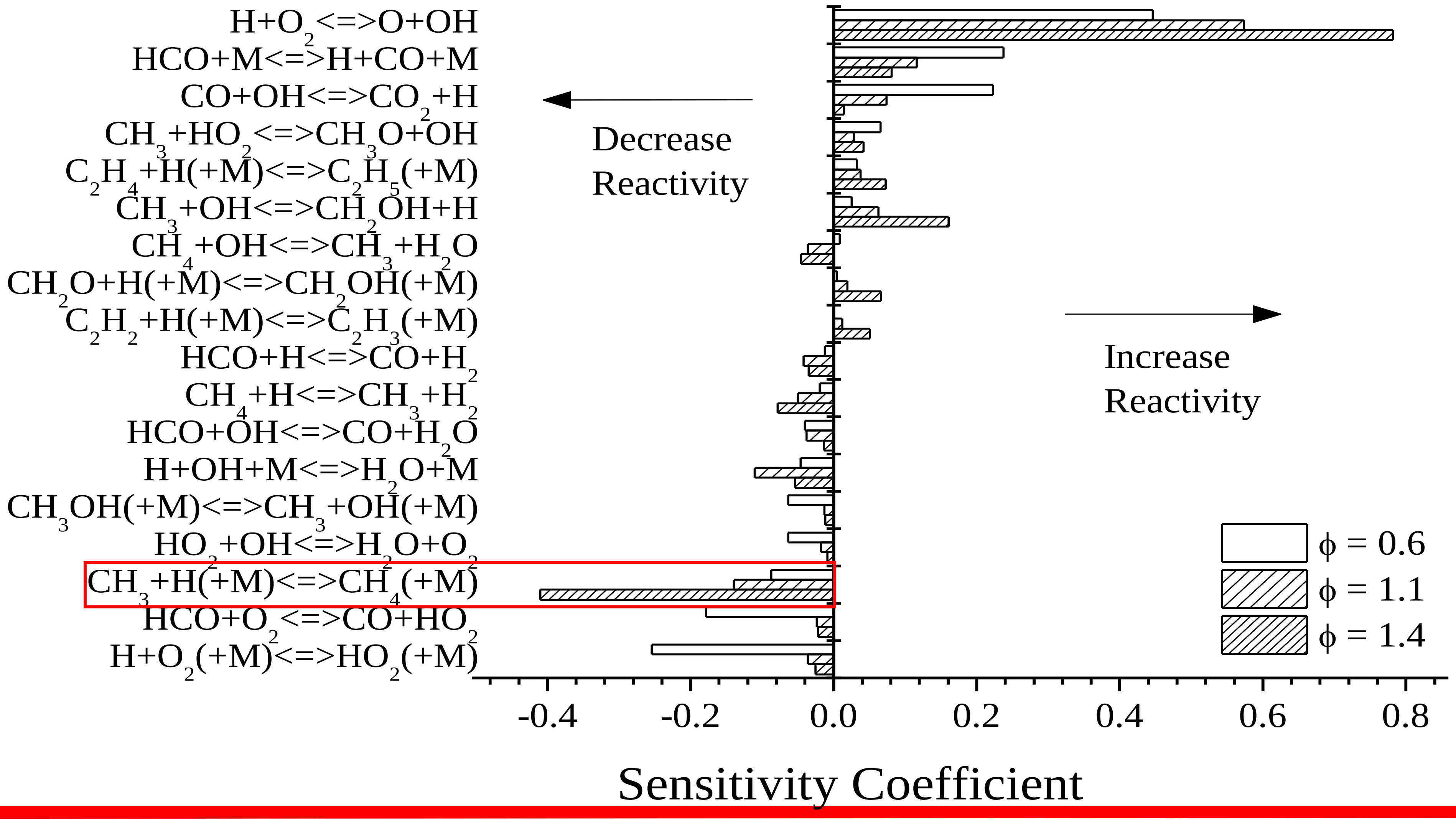


Alcohol + $\dot{O}H = R\dot{O} + H_2O$



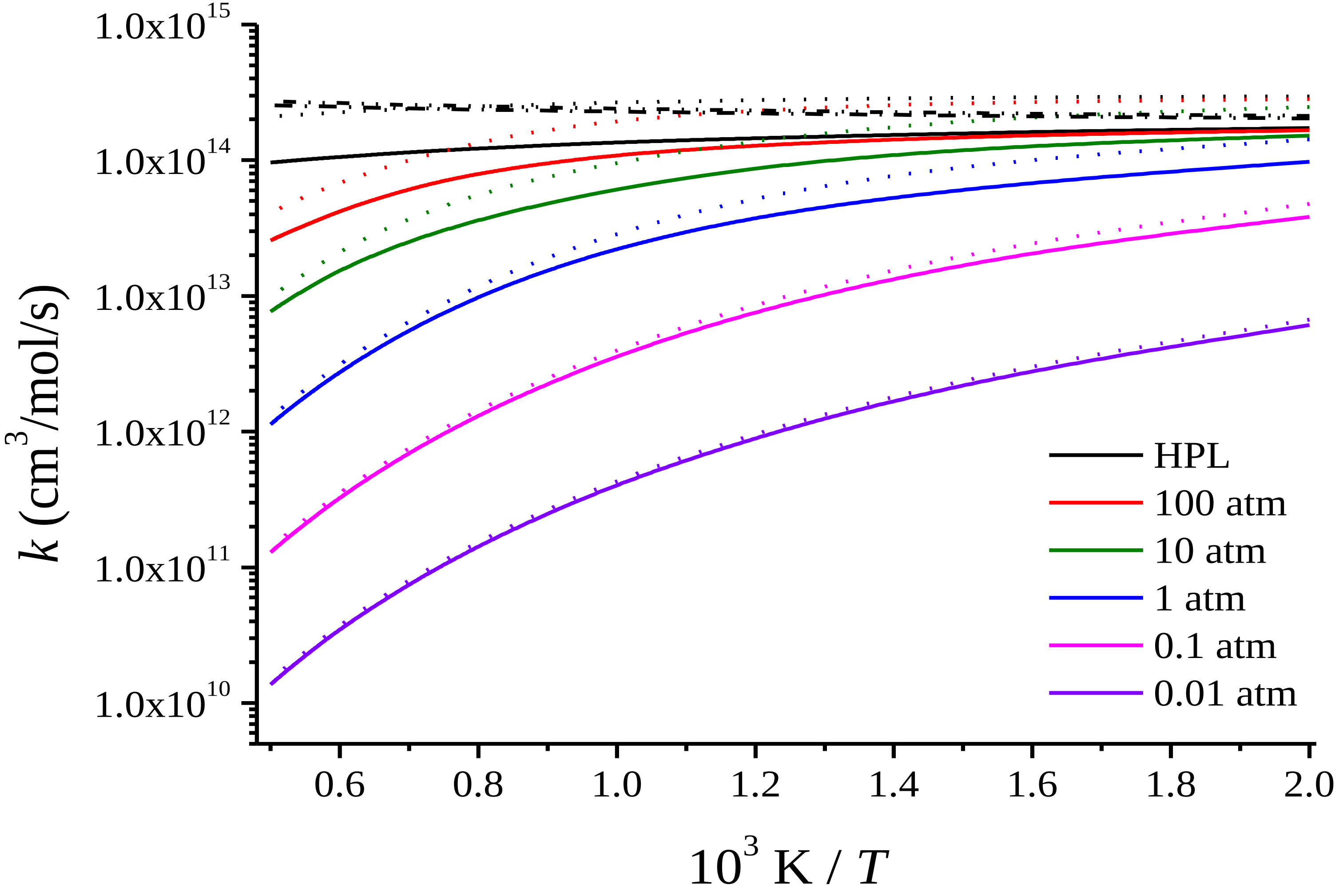
Sensitivity Analysis—CH_4 Flame Speed

p = 1.0 atm, T_i = 298 K

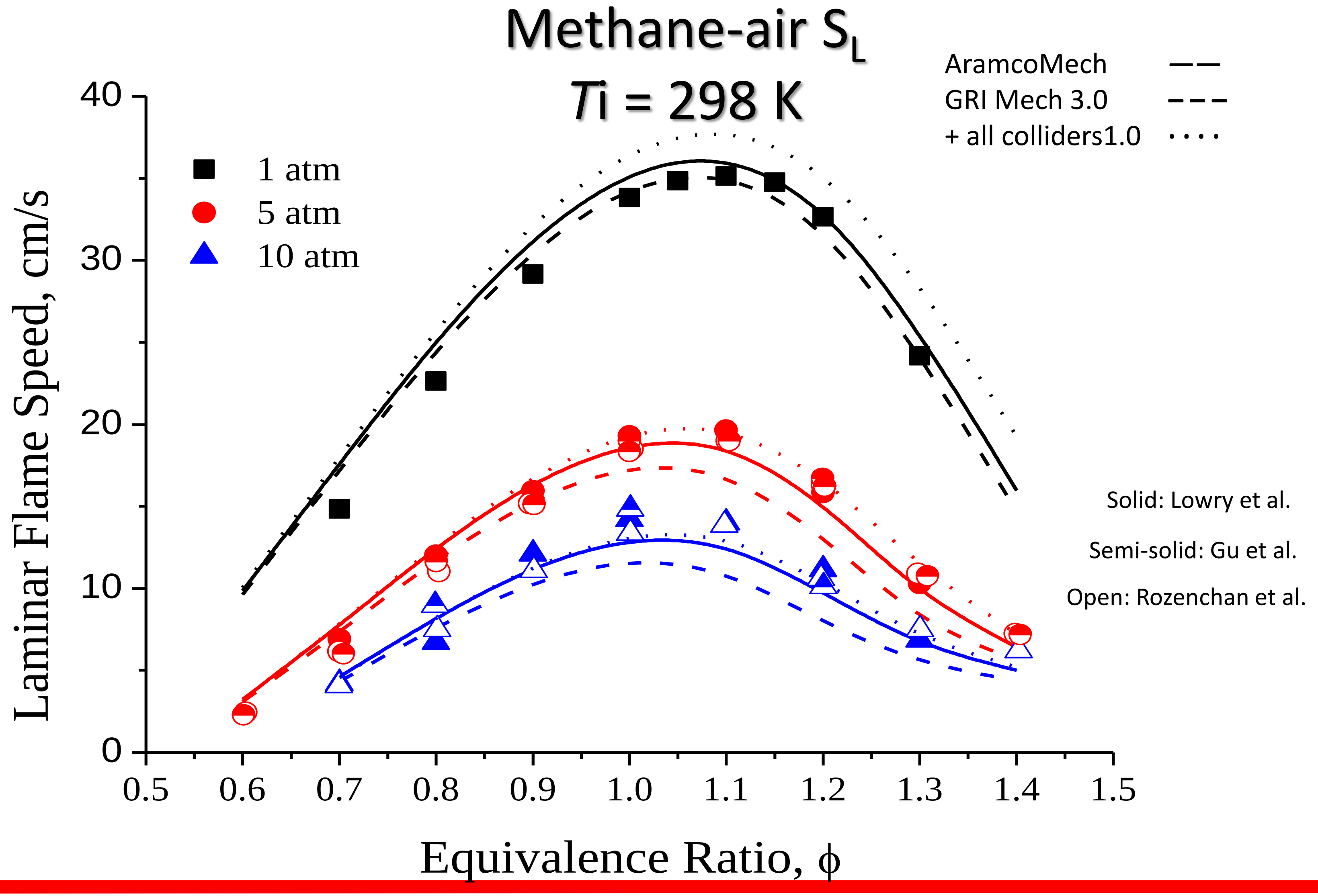


$\dot{C}H_3 + \dot{H}$ (+ M) = CH_4 (+ M)

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



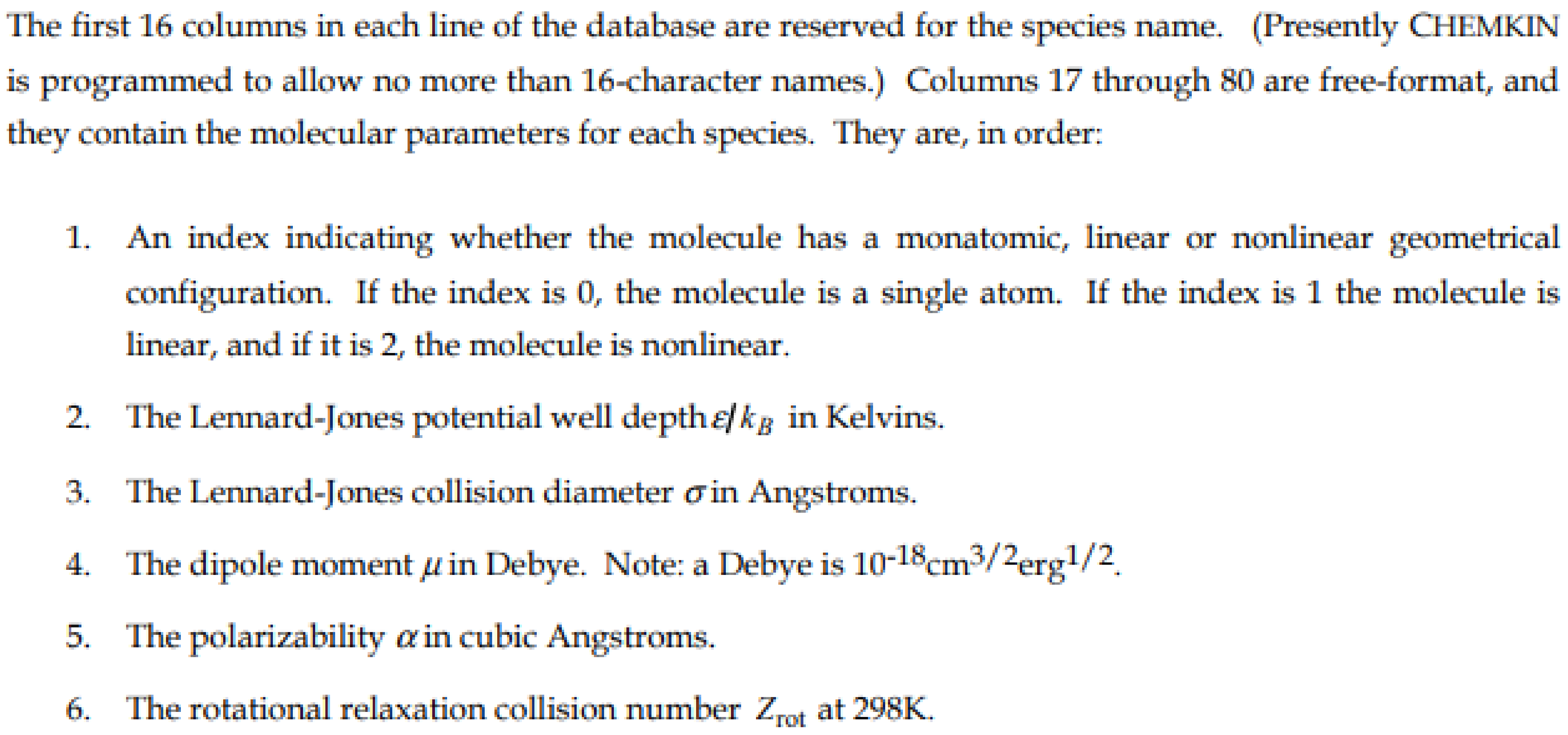
Effect of $\dot{C}H_3 + \dot{H} (+ M) = CH_4 (+ M)$



Effect of third body collider

- Has an important effect on oxy-fuel combustion
  - Fuel/pure O_2 produce high $[CO_2]$ and $[H_2O]$
  - Rate enhanced by collisions efficiencies of H_2O, CO and CO_2
  - $\dot{H} + O_2\ (+M) = H\dot{O}_2\ (+M)$ competes with $\dot{H} + O_2 = \ddot{O} + \dot{O}H$
  - Also important for gases with high concentrations of CO_2

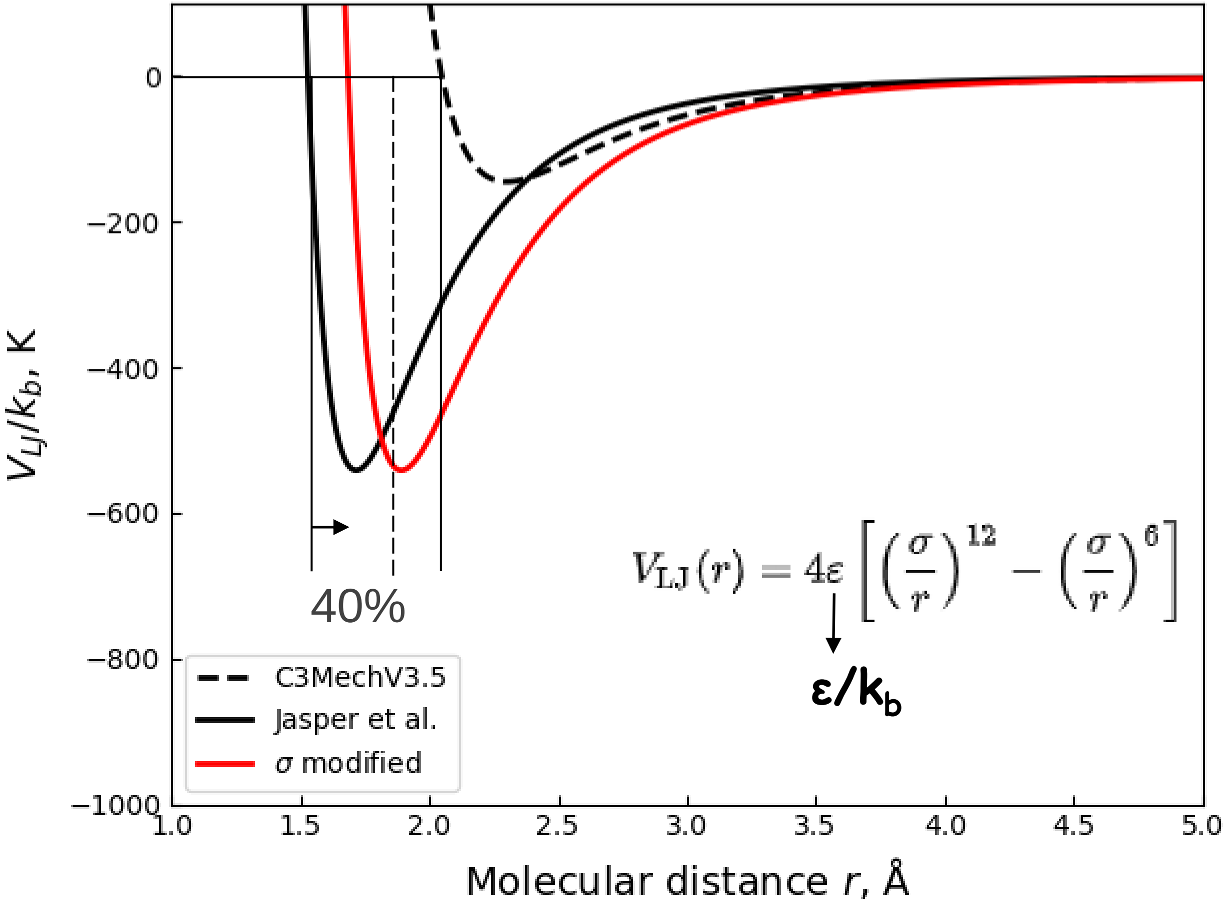
Chemkin Transport parameters



The first 16 columns in each line of the database are reserved for the species name. (Presently CHEMKIN is programmed to allow no more than 16-character names.) Columns 17 through 80 are free-format, and they contain the molecular parameters for each species. They are, in order:

1. An index indicating whether the molecule has a monatomic, linear or nonlinear geometrical configuration. If the index is 0, the molecule is a single atom. If the index is 1 the molecule is linear, and if it is 2, the molecule is nonlinear.
2. The Lennard-Jones potential well depth ε / k_B in Kelvins.
3. The Lennard-Jones collision diameter σ in Angstroms.
4. The dipole moment μ in Debye. Note: a Debye is 10^{-18}cm$^{3/2}$erg$^{1/2}$.
5. The polarizability α in cubic Angstroms.
6. The rotational relaxation collision number Z_{rot} at 298K.

LJ potential of H atm & H_2 LBV (1 atm & 298 K)



C3MechV3.5:

ε/k_b = 145.0, σ = 2.05

A. Jasper et al.[1, 2]:

ε/k_b = 541.672, σ = 1.53

Modification:

ε/k_b = 541.672

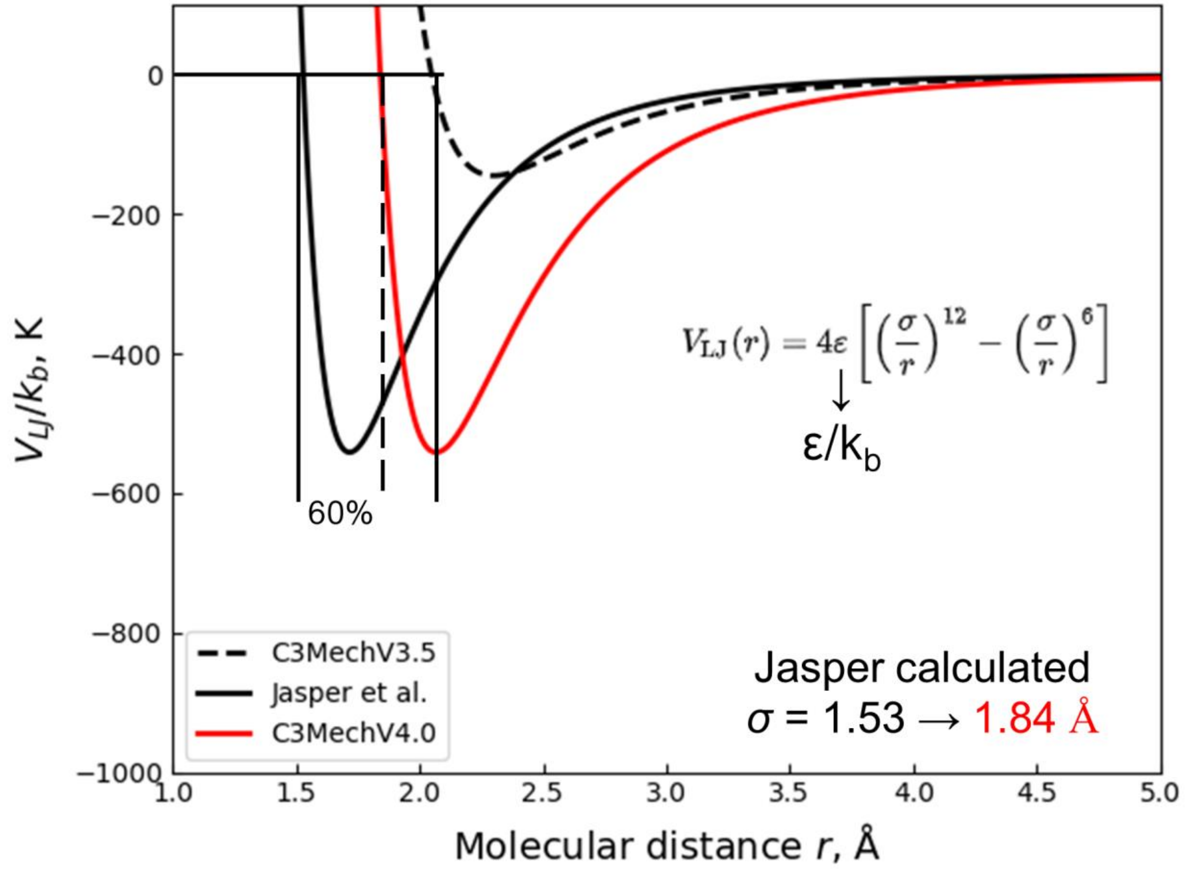
σ = (2.05 - 1.53) * 0.4 + 1.53 = 1.842

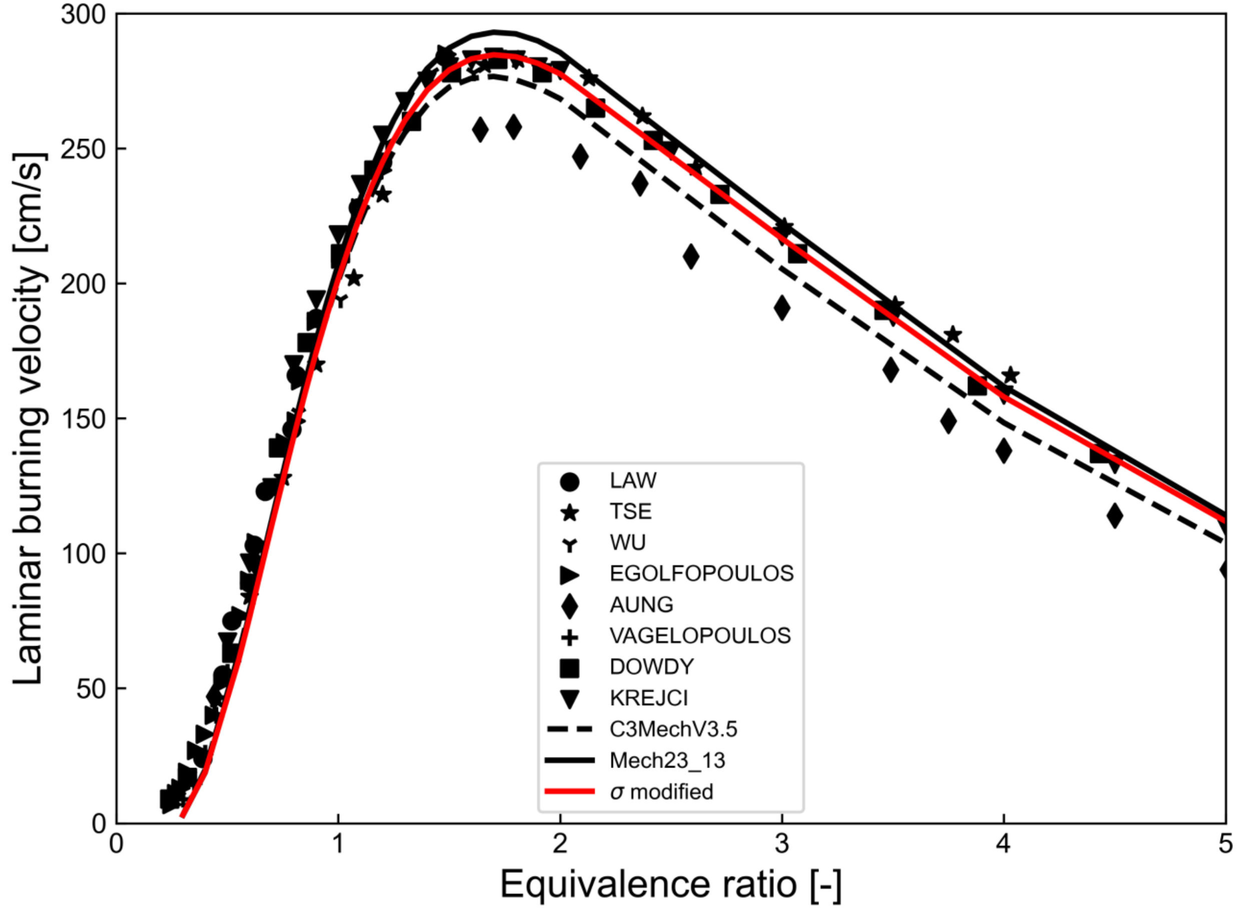
[1] A.W. Jasper, E. Kamarchik, J.A. Miller, S.J. Klippenstein, *J. Chem. Phys.* 141 (12) (2014) 124313.

[2] A.W. Jasper, J.A. Miller, Combust Flame 161 (2014) 101-110.

Mechanism	Index	ε/k_b (K)	σ (Å)	μ (10^{-18}cm$^{3/2}$erg$^{1/2}$)	α (Å^3)	Z_{rot}
C3MechV3.5	0	145.000	2.05	0	0	0
Mech23_13	0	541.672	1.53	0	0.666	0
σ modified	0	541.672	1.842	0	0.666	0

LJ potential of H atm & H_2 LBV (1 atm & 298 K)

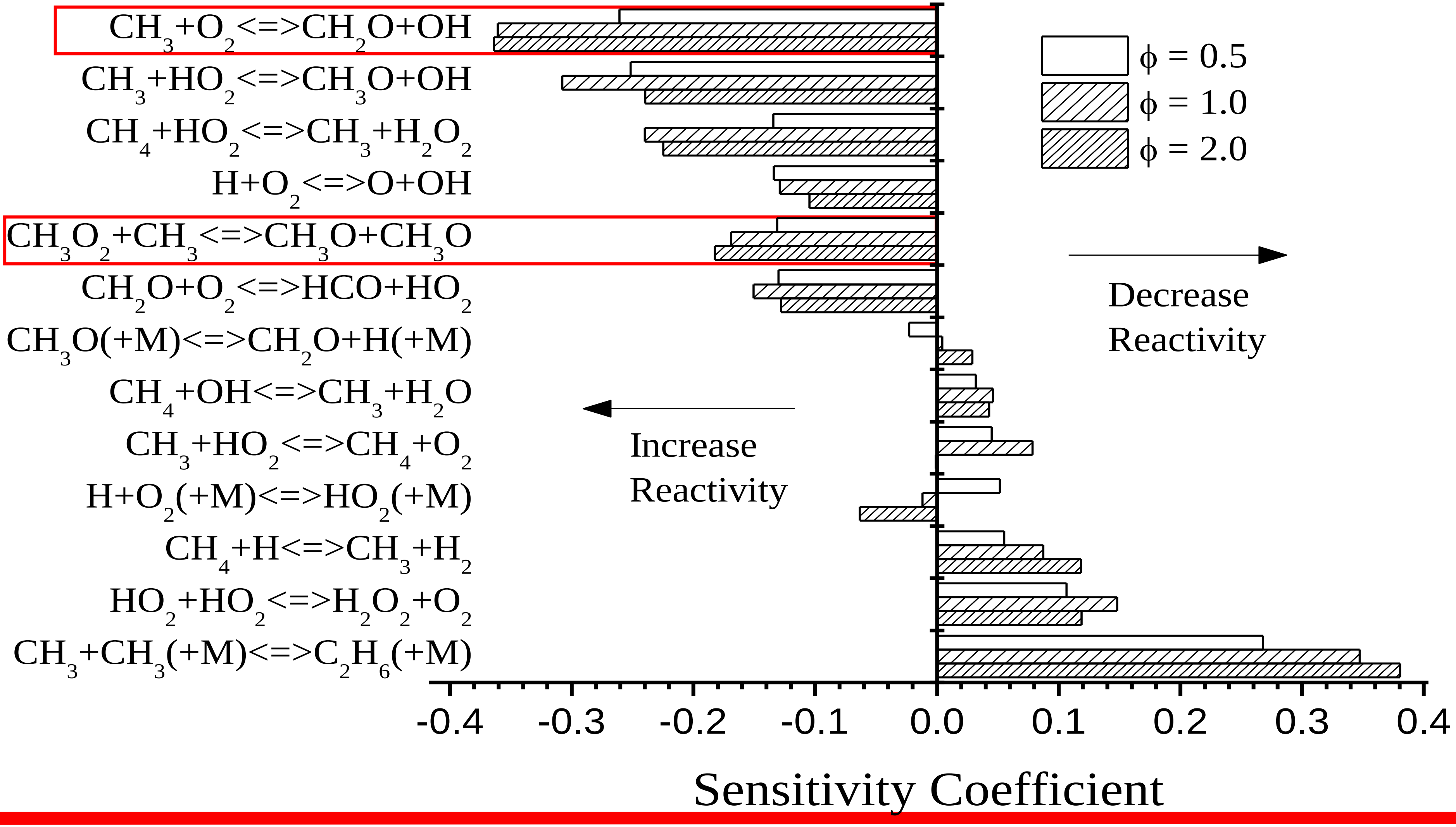




Mechanism	Index	ε/k_b (K)	σ (Å)	μ (10^{-18}cm$^{3/2}$erg$^{1/2}$)	α (Å^3)	Z_{rot}
C3MechV3.5	0	145.000	2.05	0	0	0
Mech23_13	0	541.672	1.53	0	0.666	0
σ modified	0	541.672	1.84	0	0.666	0

Sensitivity Analysis—CH_4 ST τ

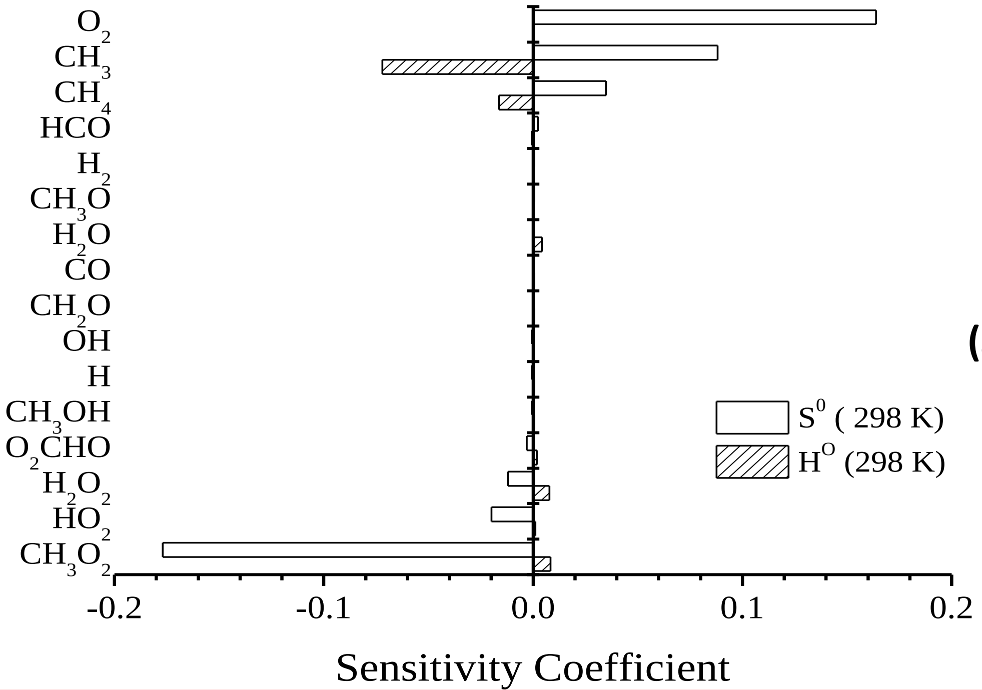
1250 K, 30 atm



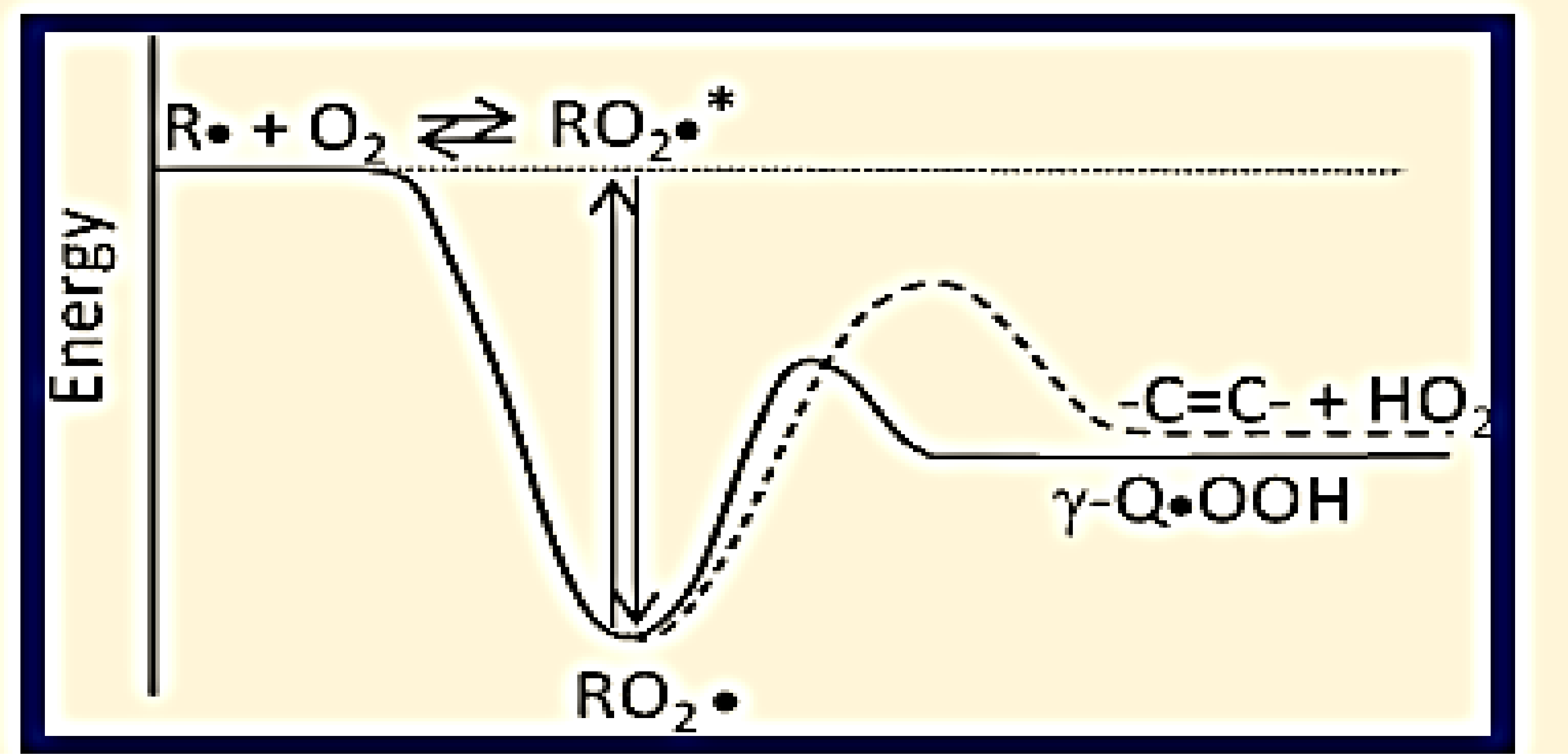
$\dot{C}H_3 + O_2 \rightarrow$ products

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

Sensitivity of τ to thermochemistry
900 K, 20 atm

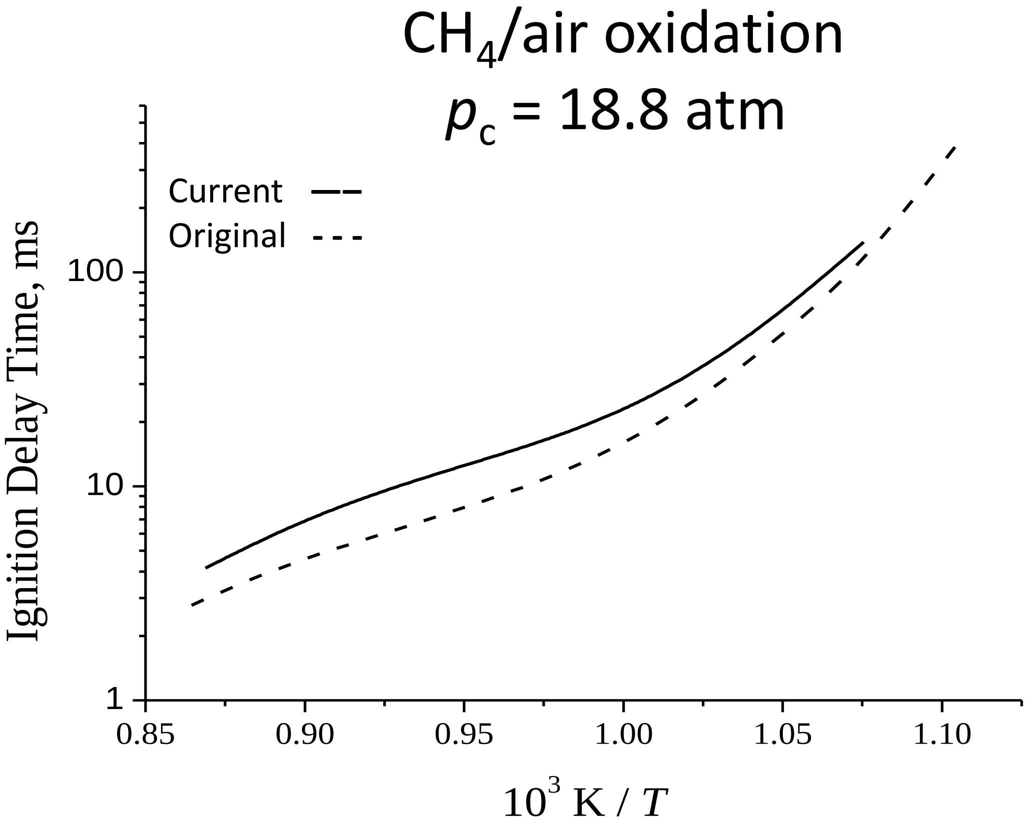


	H_f^0 @ 298 K (kcal mol⁻¹)	S_f^0 @ 298 K (cal K⁻¹ mol⁻¹)
Original	2.20	64.36
(Simmie et al.)	2.92	64.50


R• + O$_2$ ⇄ RO$_2$•*
Energy
-C=C- + HO$_2$
γ-Q•OOH
RO$_2$•

Effect of thermochemistry

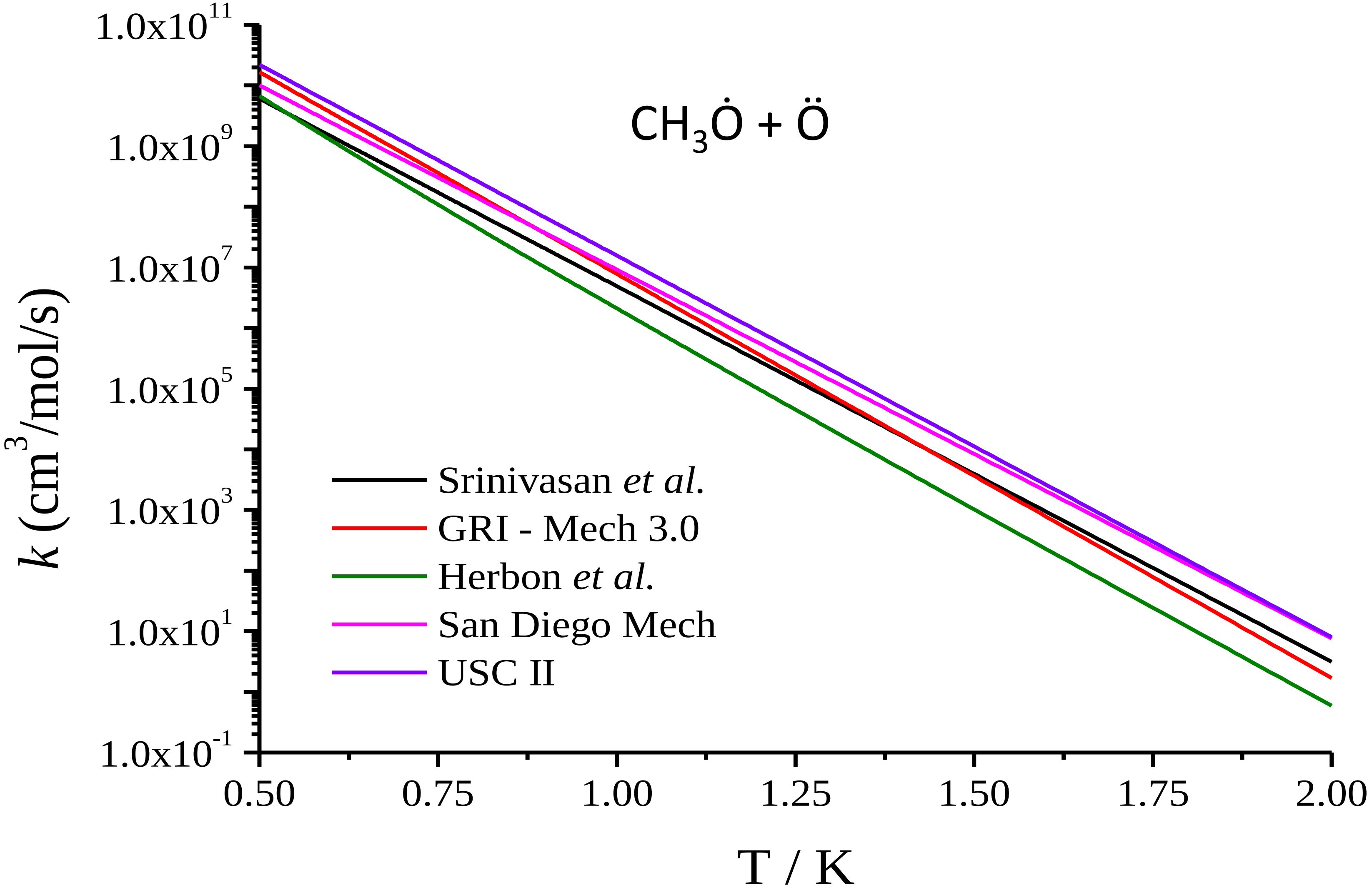
- $\dot{\mathrm{C}}\mathrm{H}_3 + \mathrm{O}_2 \overset{\longleftarrow}{\rightleftharpoons} \mathrm{CH}_3\dot{\mathrm{O}}_2$
- $\mathrm{CH}_3\dot{\mathrm{O}}_2 + \dot{\mathrm{C}}\mathrm{H}_3 = \mathrm{CH}_3\dot{\mathrm{O}} + \mathrm{CH}_3\dot{\mathrm{O}} \downarrow$



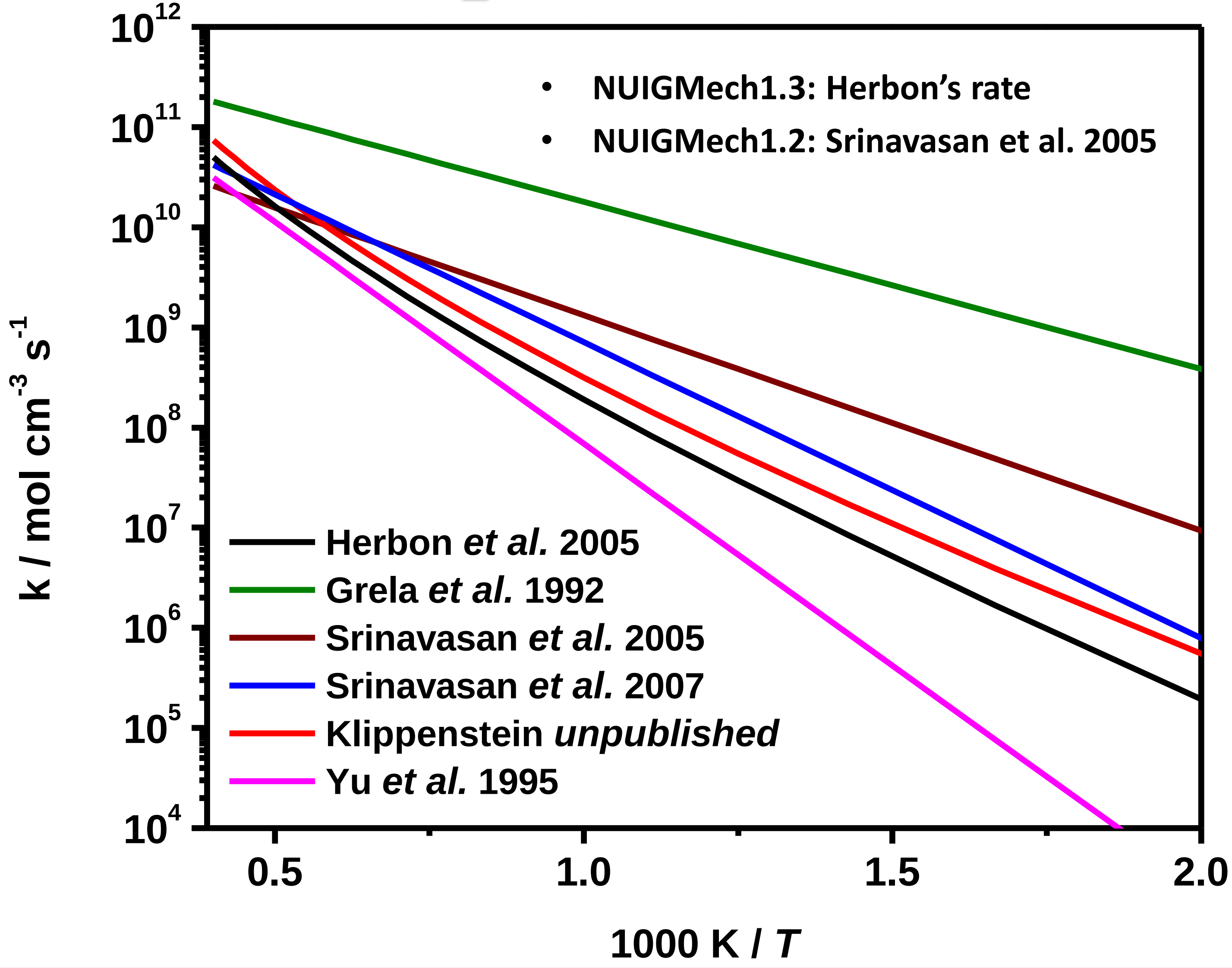
CH_4/air oxidation

$p_c = 18.8$ atm

$\dot{C}H_3 + O_2$ reactions

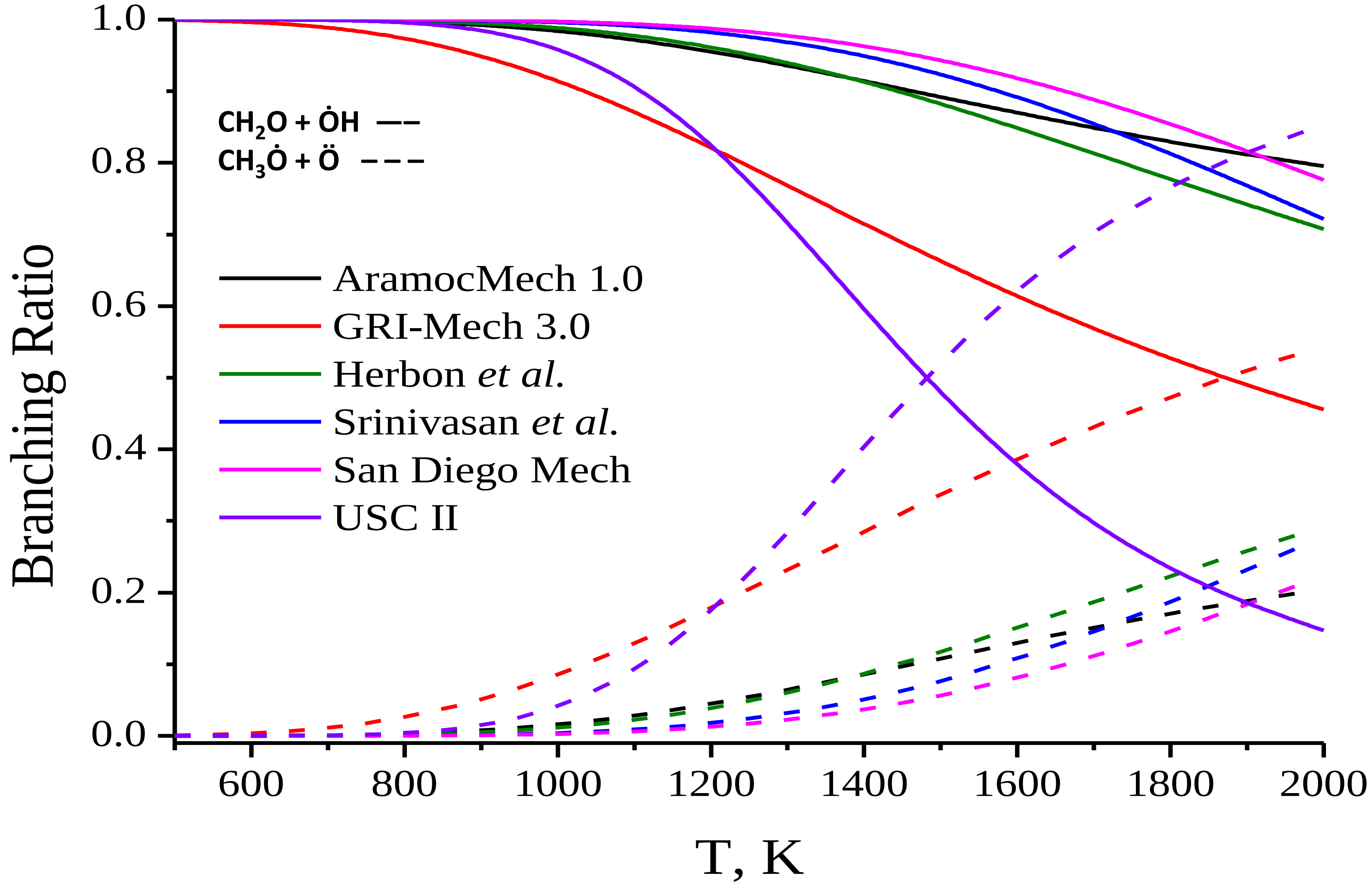


$CH_2O + \dot{O}H$ reactions

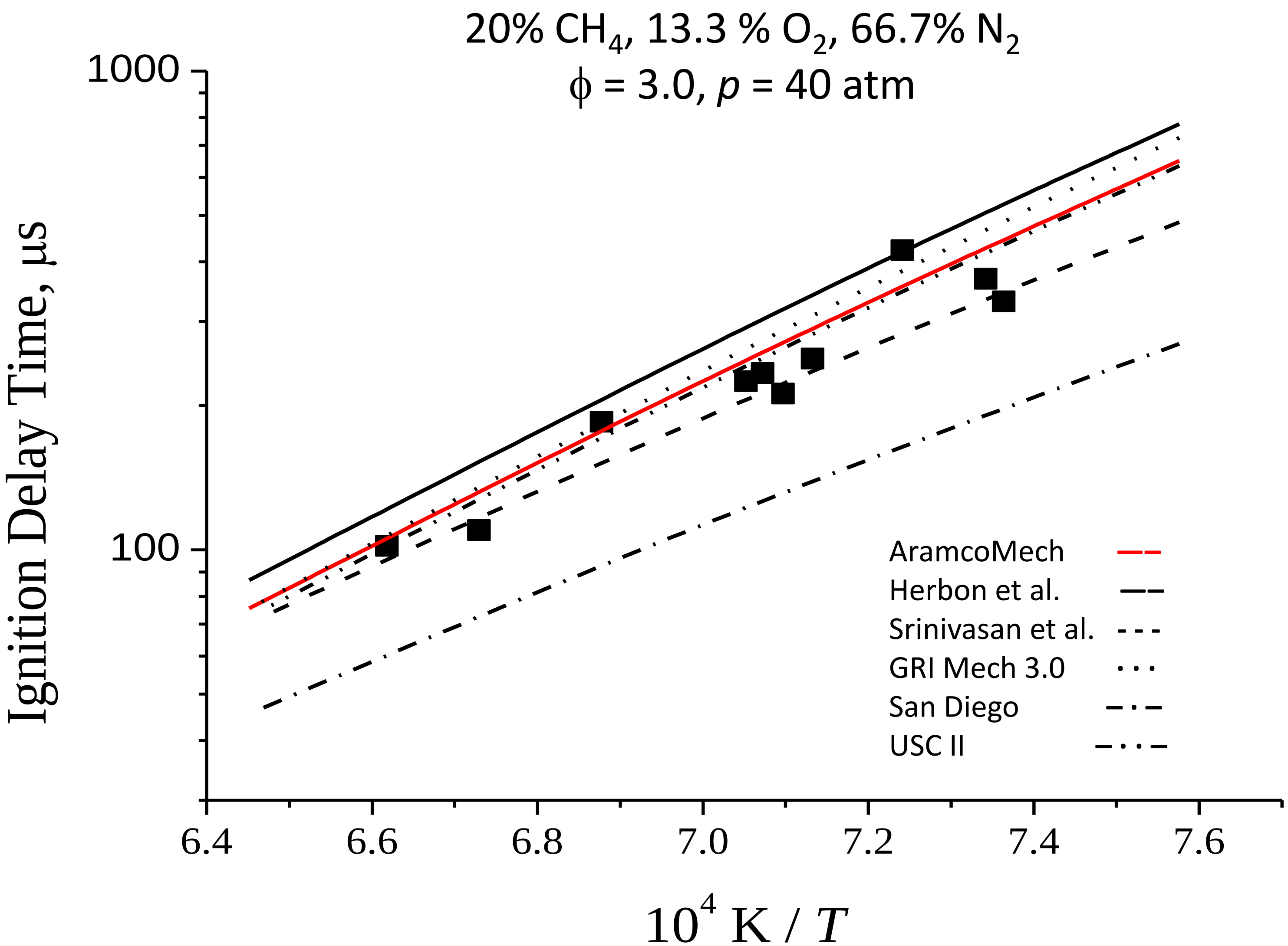


- **NUIGMech1.3: Herbon's rate**
- **NUIGMech1.2: Srinavasan et al. 2005**

$\dot{C}H_3 + O_2$ reactions

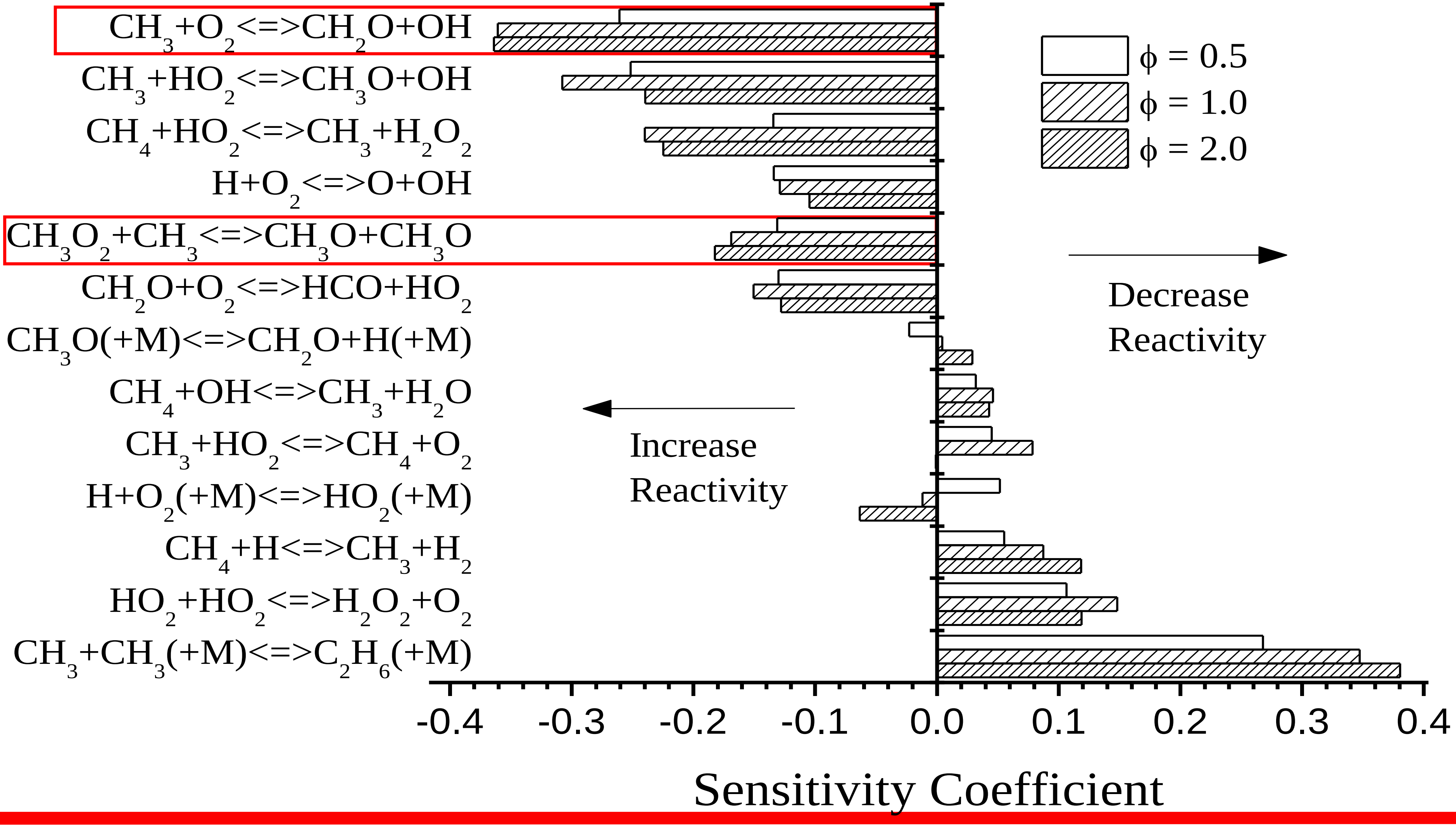


Influence of choice of $\dot{C}H_3 + O_2$ on τ

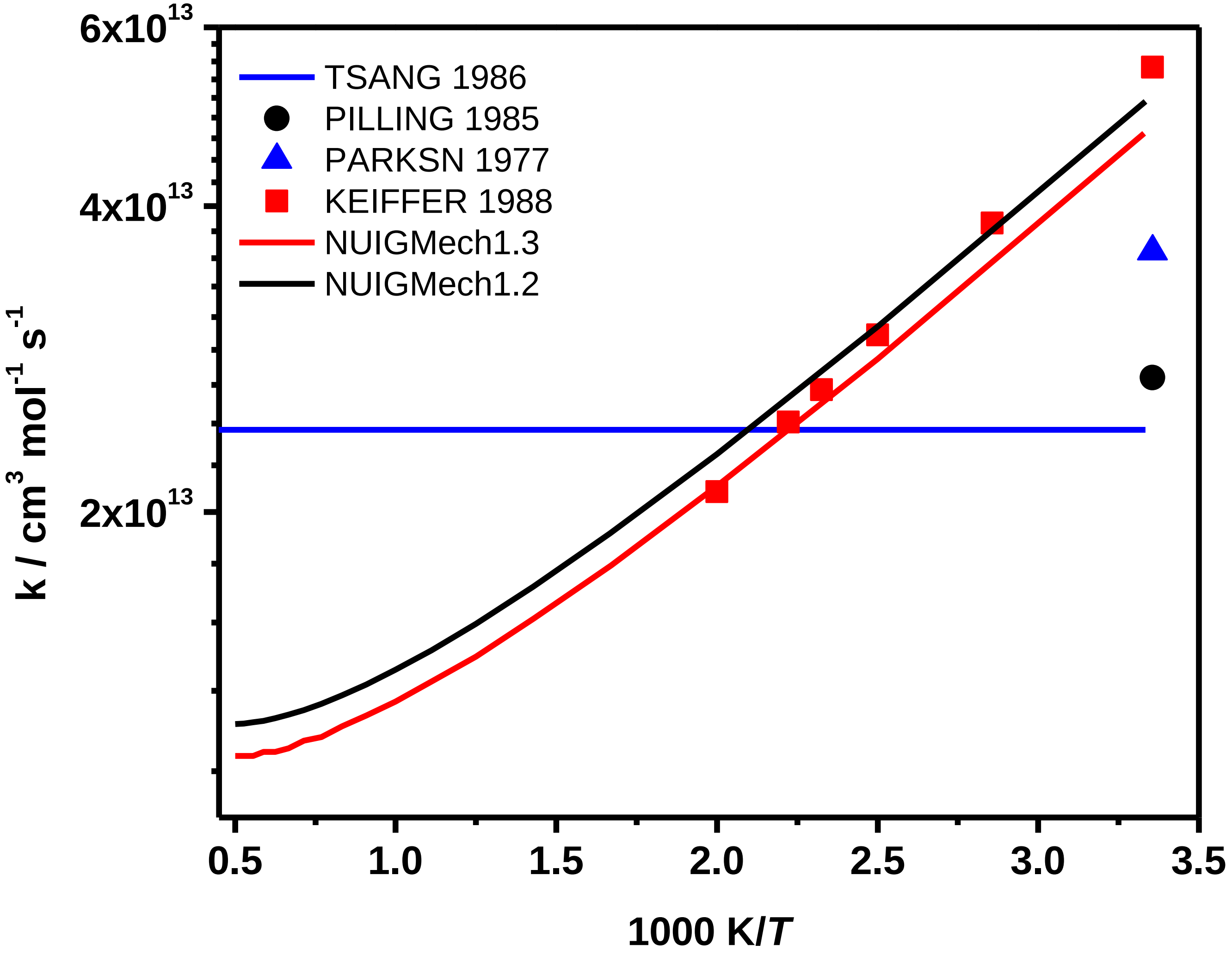


Sensitivity Analysis—CH_4 ST τ

1250 K, 30 atm

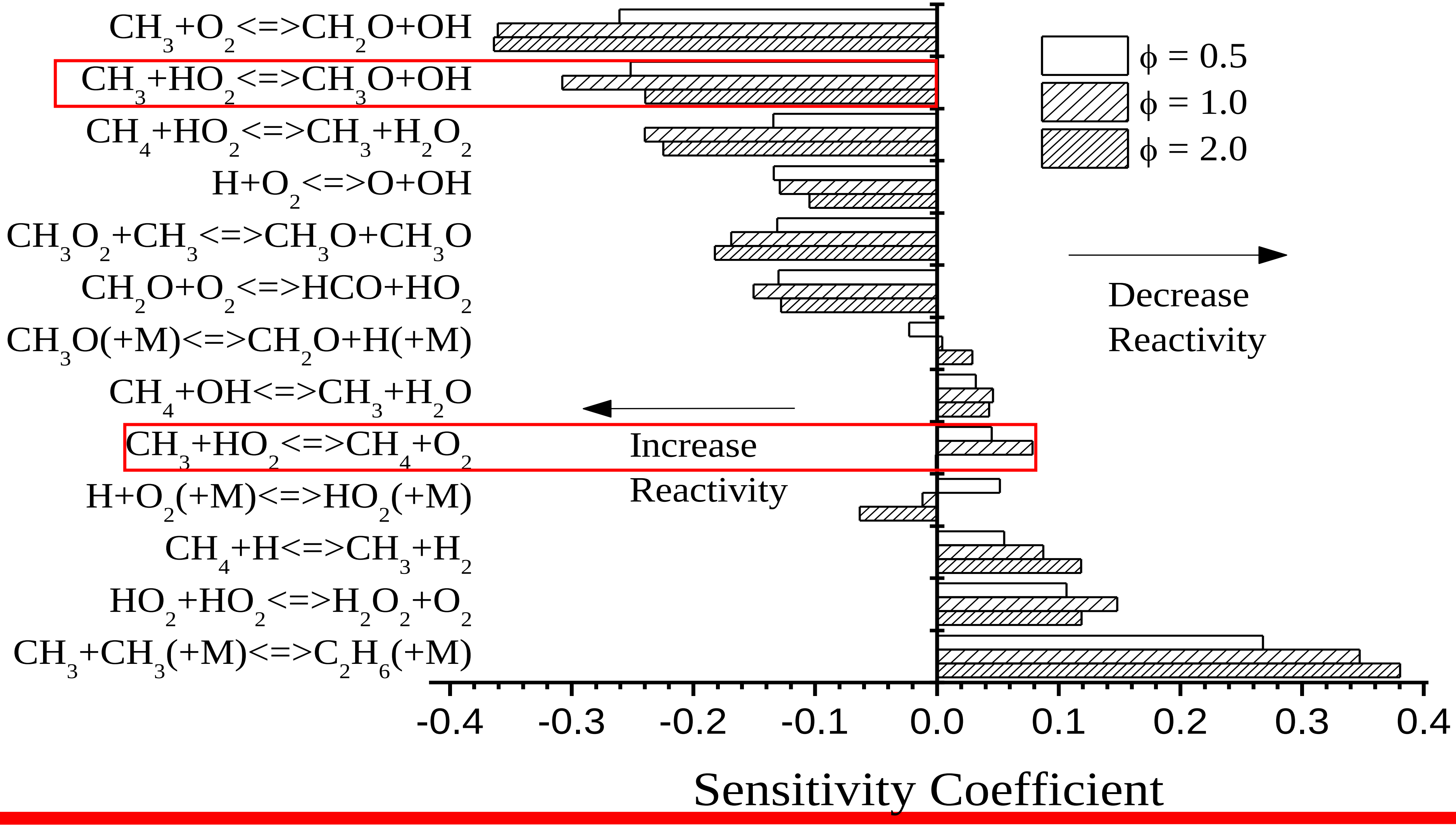


$CH_3\dot{O}_2 + \dot{C}H_3 = CH_3\dot{O} + CH_3\dot{O}$



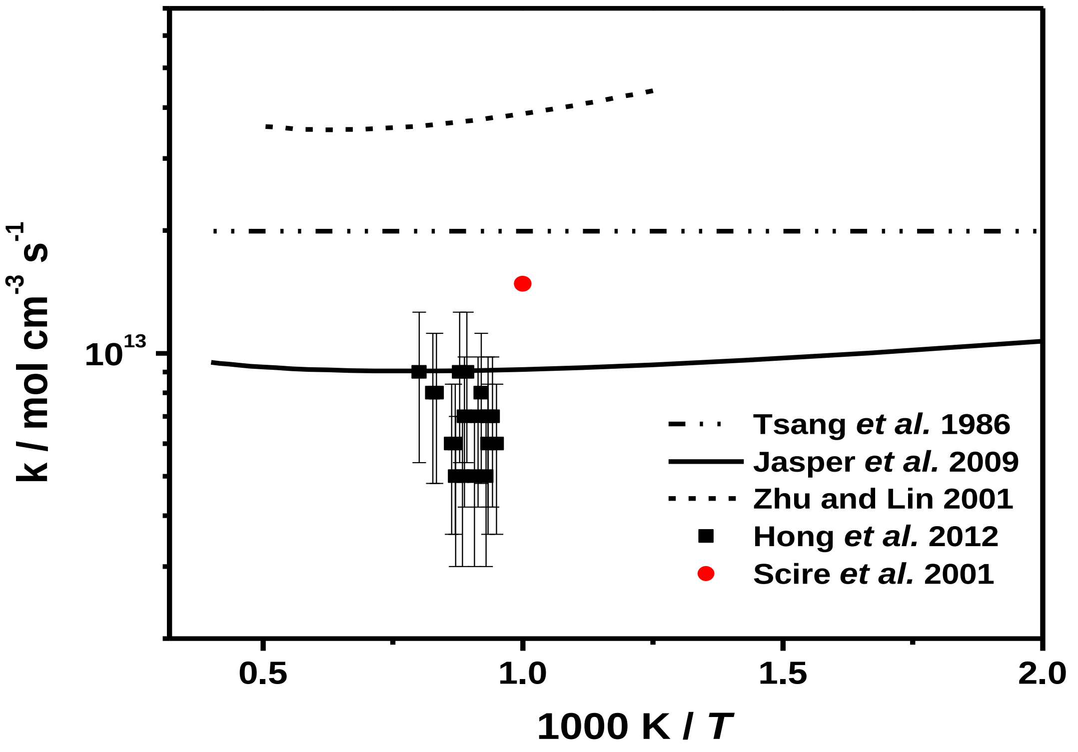
Sensitivity Analysis—CH_4 ST τ

1250 K, 30 atm

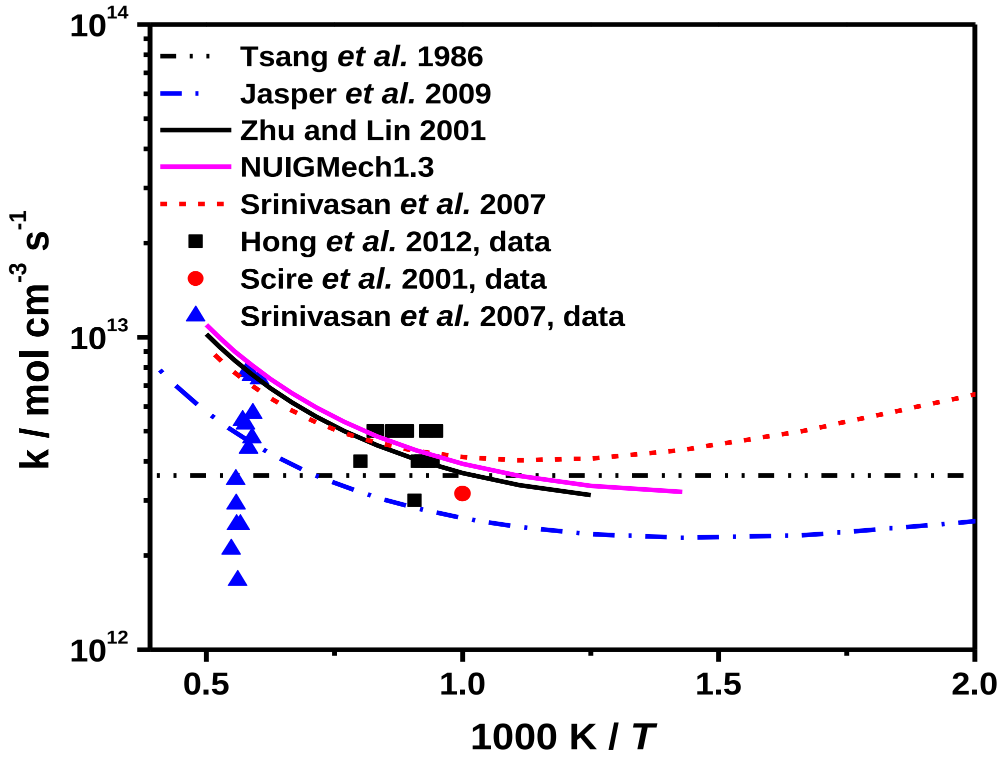


$\dot{C}H_3 + H\dot{O}_2$ branching ratio

$CH_3\dot{O} + \dot{O}H$



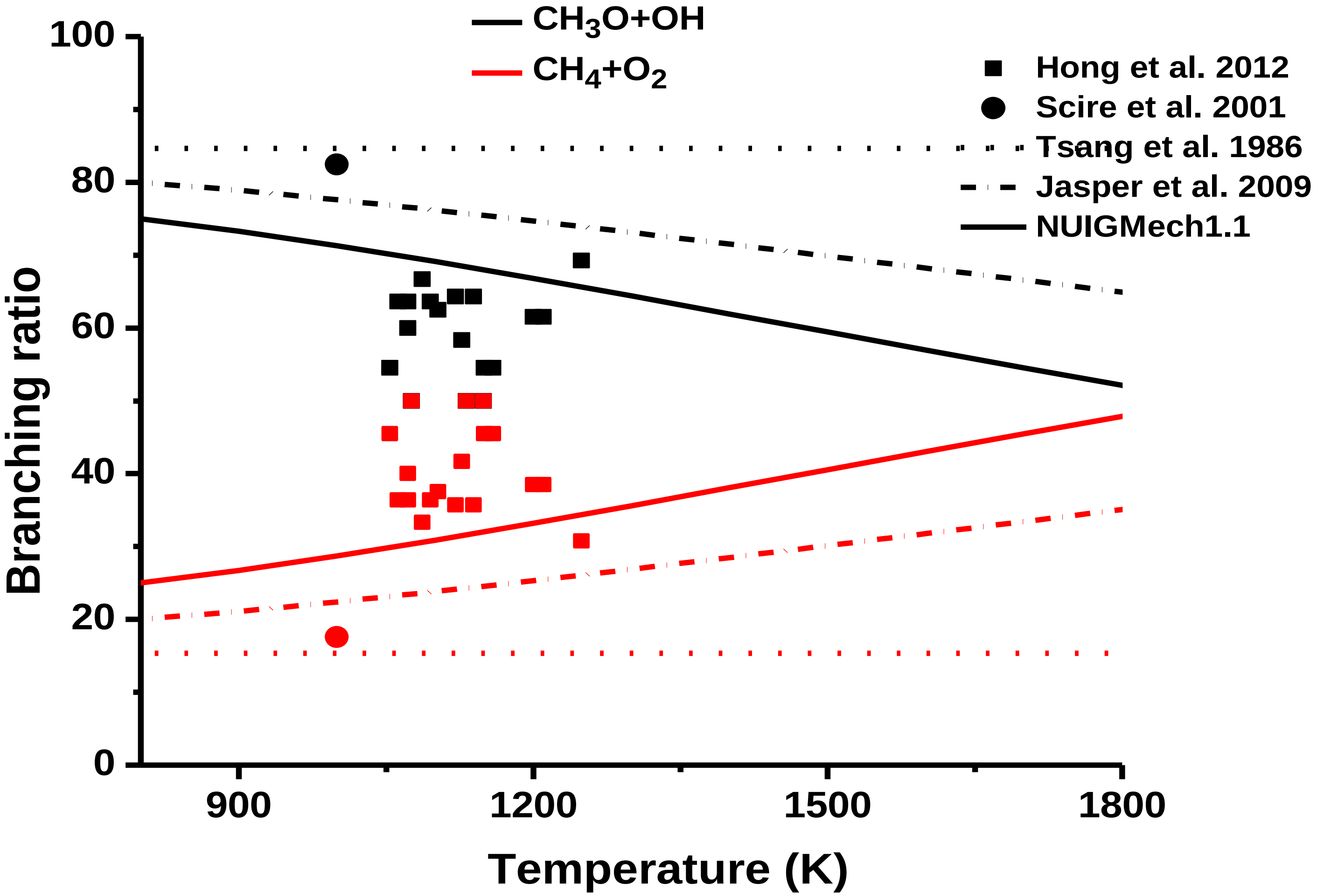
$CH_4 + O_2$



	Reaction enthalpies at 298 K $\dot{C}H_3 + H\dot{O}_2 = CH_4 + O_2$
ATCT	55.73 kcal mol^{-1}
Srinivasan et al., 2007	54.80 kcal mol^{-1}
NUIGMech1.1	55.83 kcal mol^{-1}

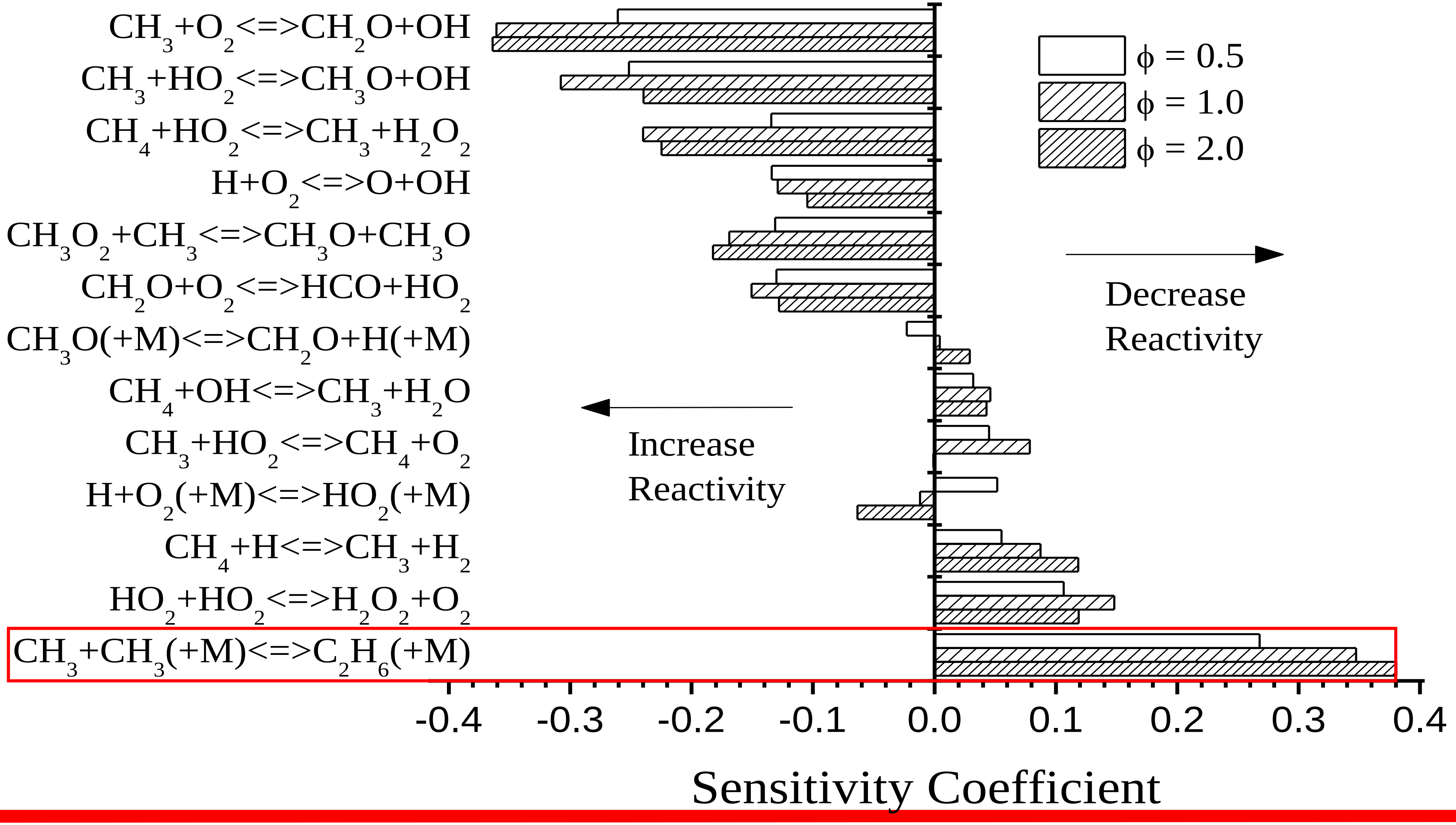
* The reverse rate constant of $CH_4 + O_2 = \dot{C}H_3 + H\dot{O}_2$ from Srinivasan et al. 2007 is obtained using the equilibrium constant based on NUIGMech1.1.

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

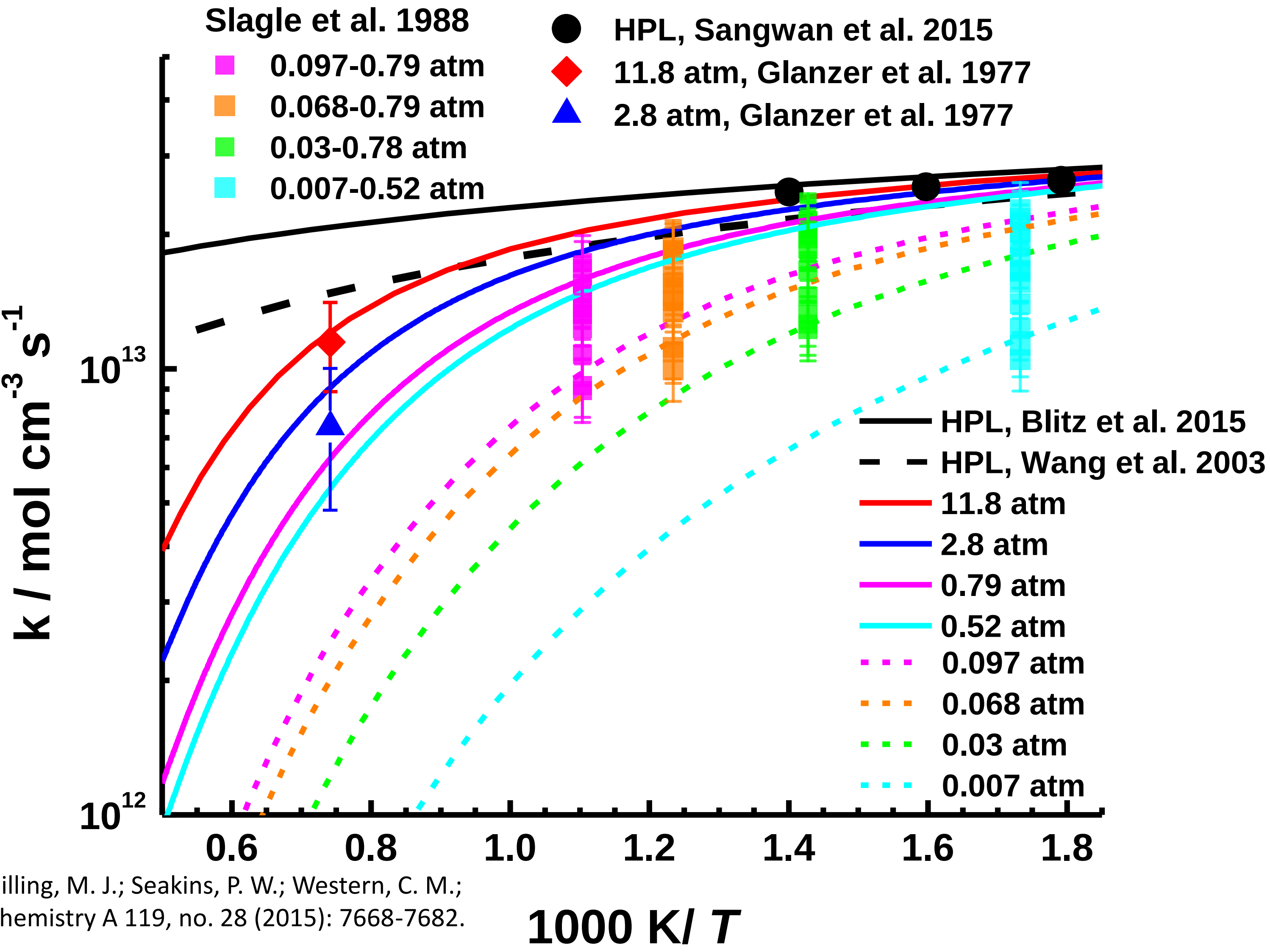


Sensitivity Analysis—ST ignition delay

1250 K, 30 atm



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

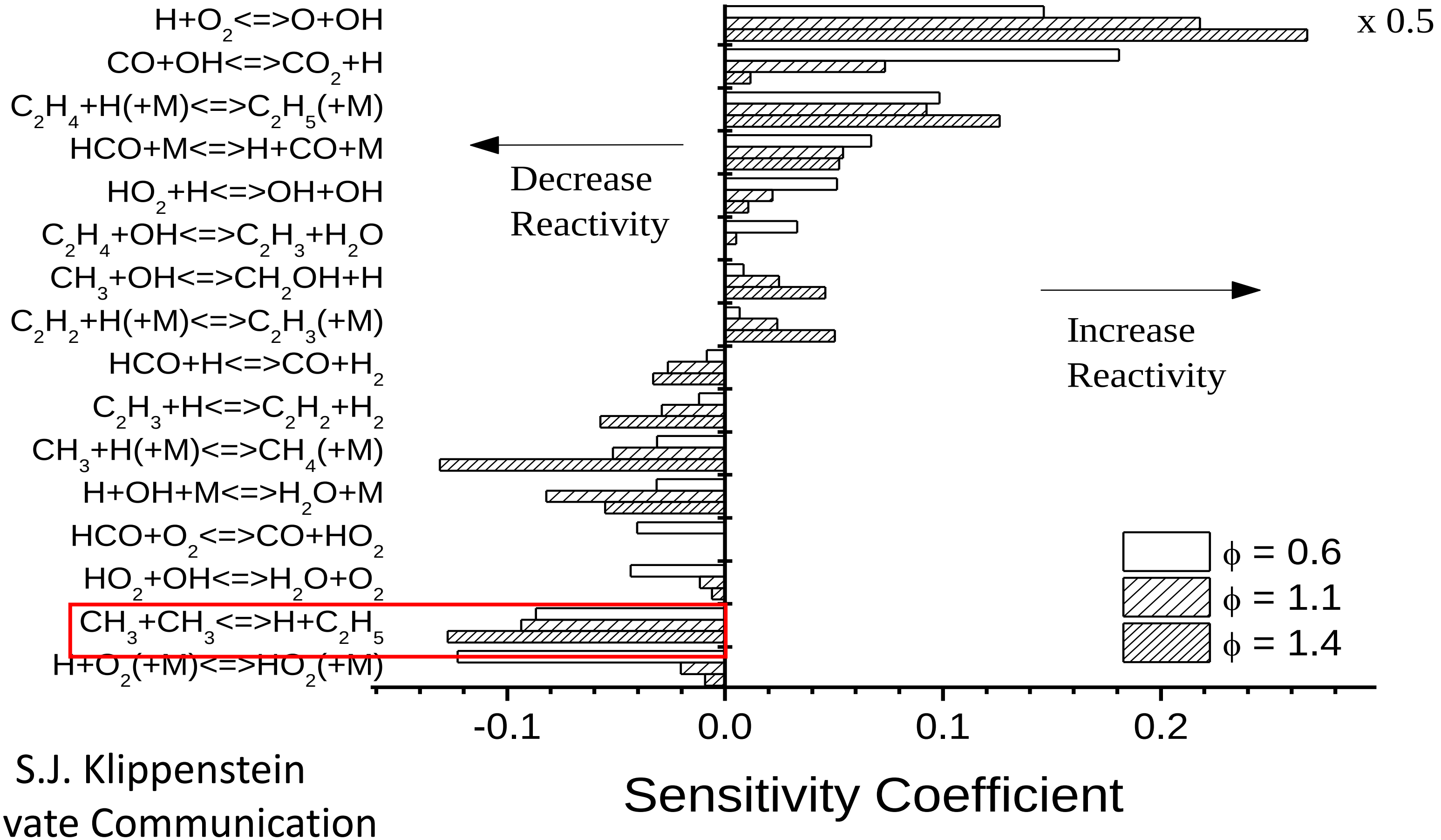


Blitz, M. A.; N.J.B, Green; Shannon, R. J.; Pilling, M. J.; Seakins, P. W.; Western, C. M.; Robertson, S. H.. The Journal of Physical Chemistry A 119, no. 28 (2015): 7668-7682.

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

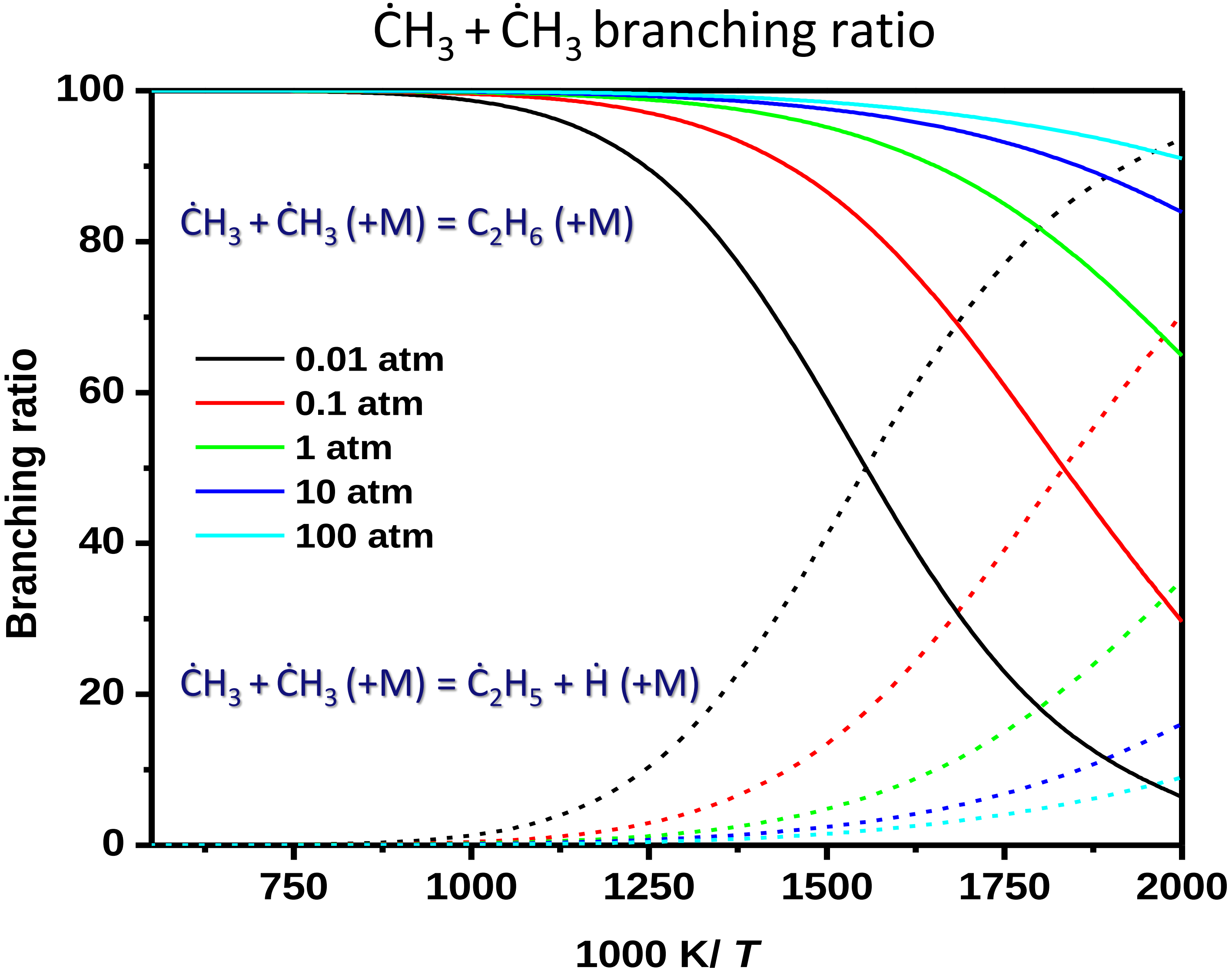
C_2H_6 S_L

***p* = 1 atm *T* = 298 K**



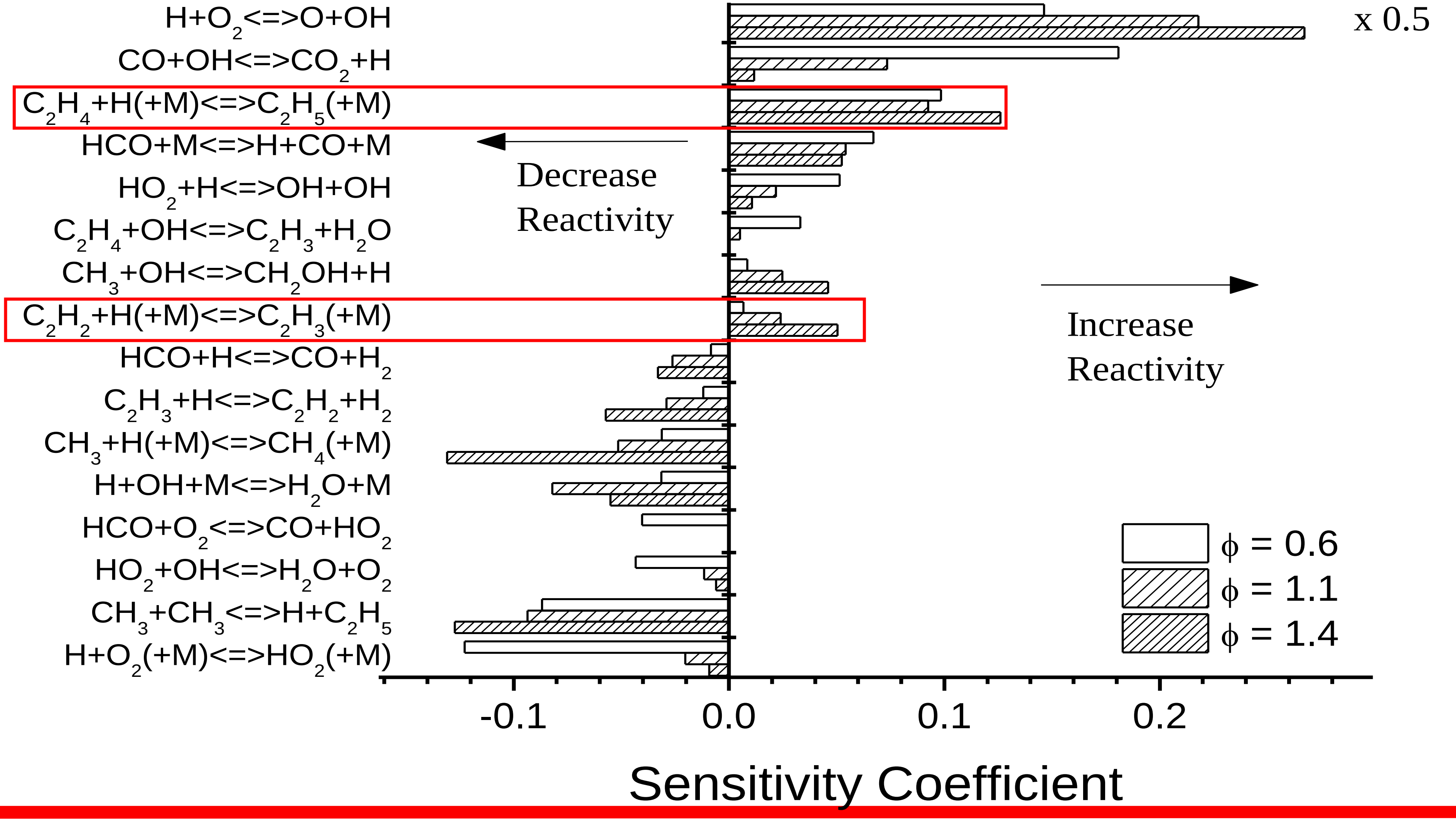
S.J. Klippenstein
Private Communication

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



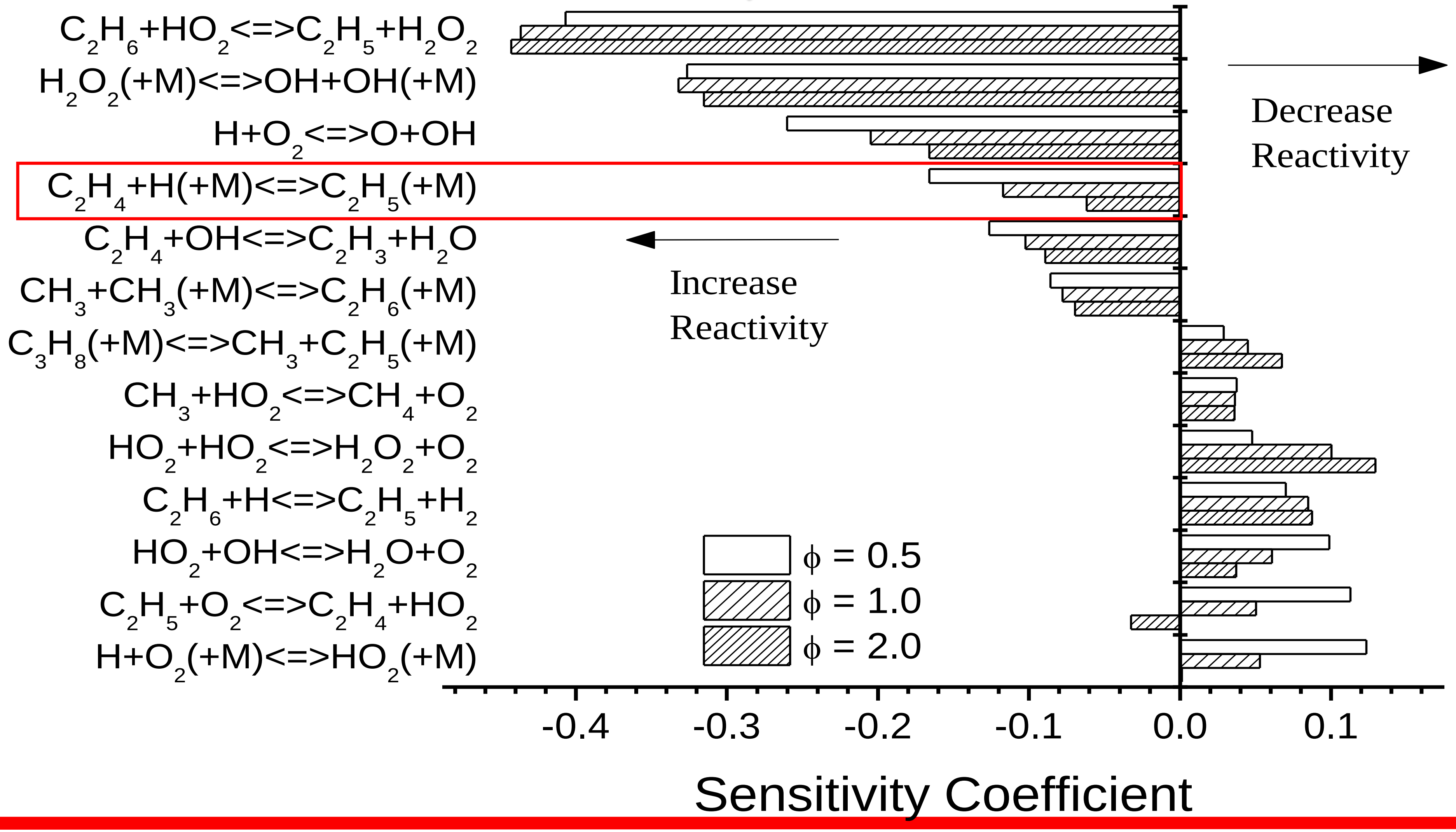
Sensitivity Analysis—C_2H_6 Flame Speed

p = 1.0 atm, T_i = 298 K

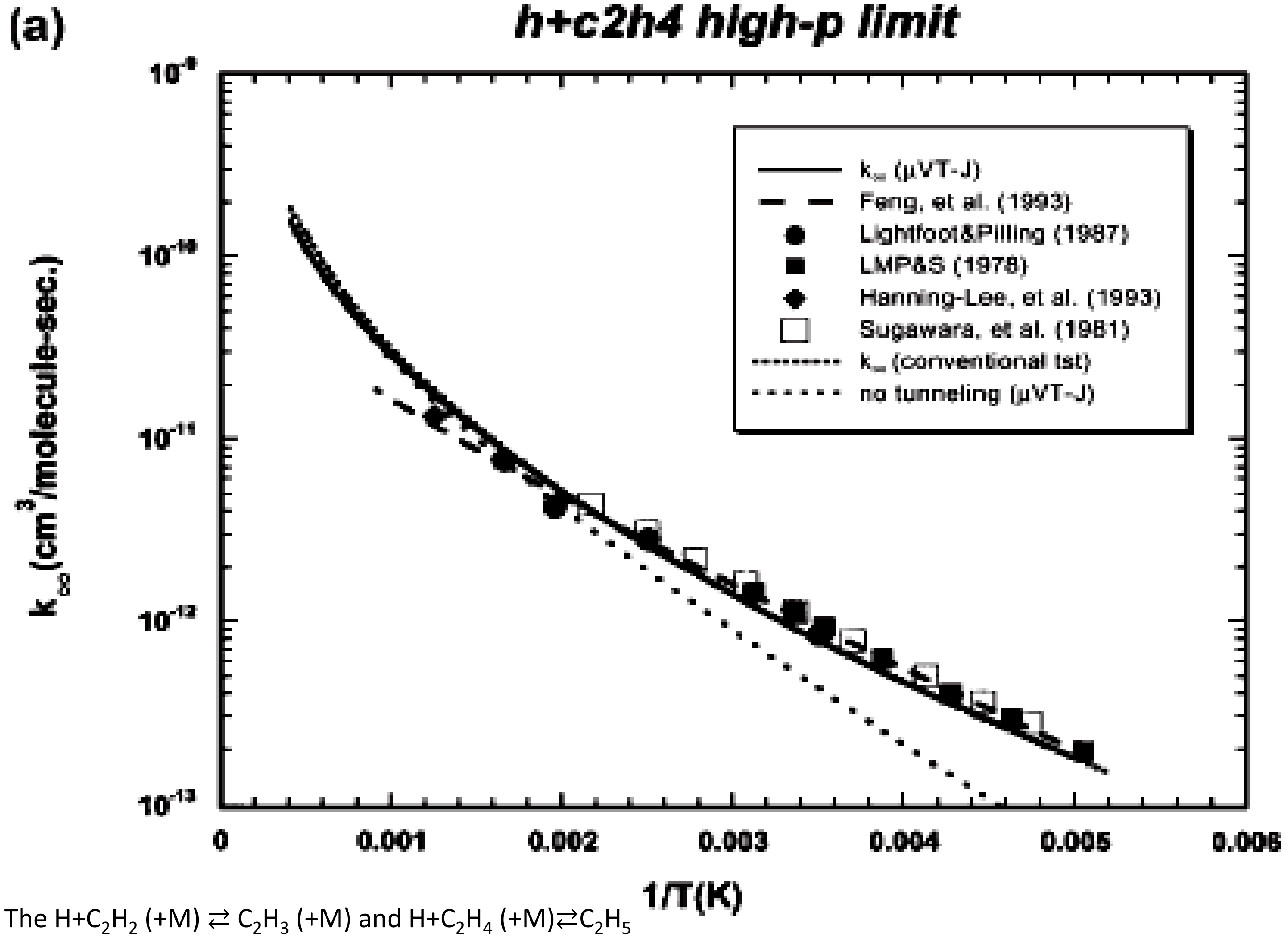


Sensitivity Analysis—C_2H_6 Ignition delay

1250 K, 30 atm

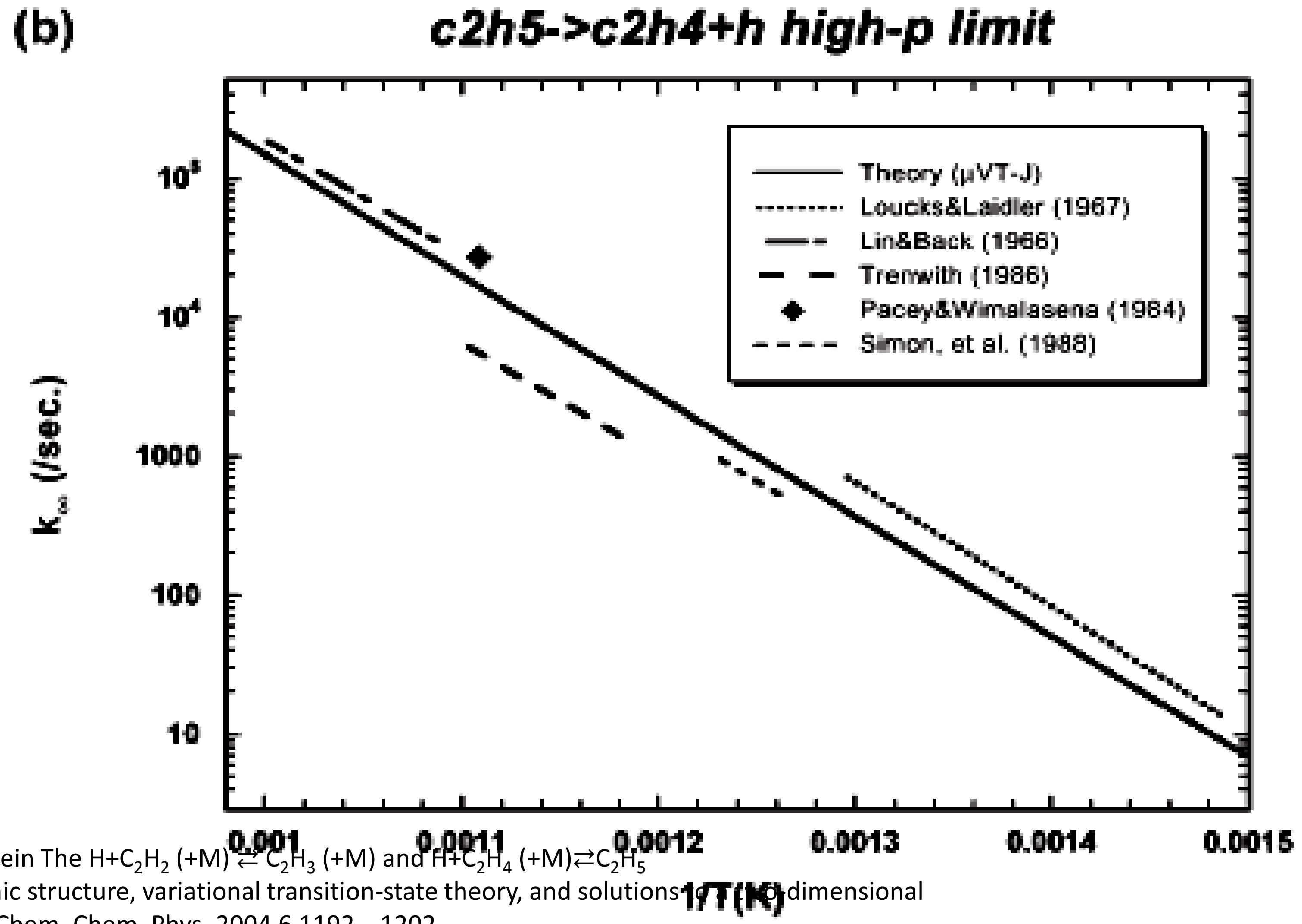


$\dot{H} + C_2H_4$ high-pressure limit



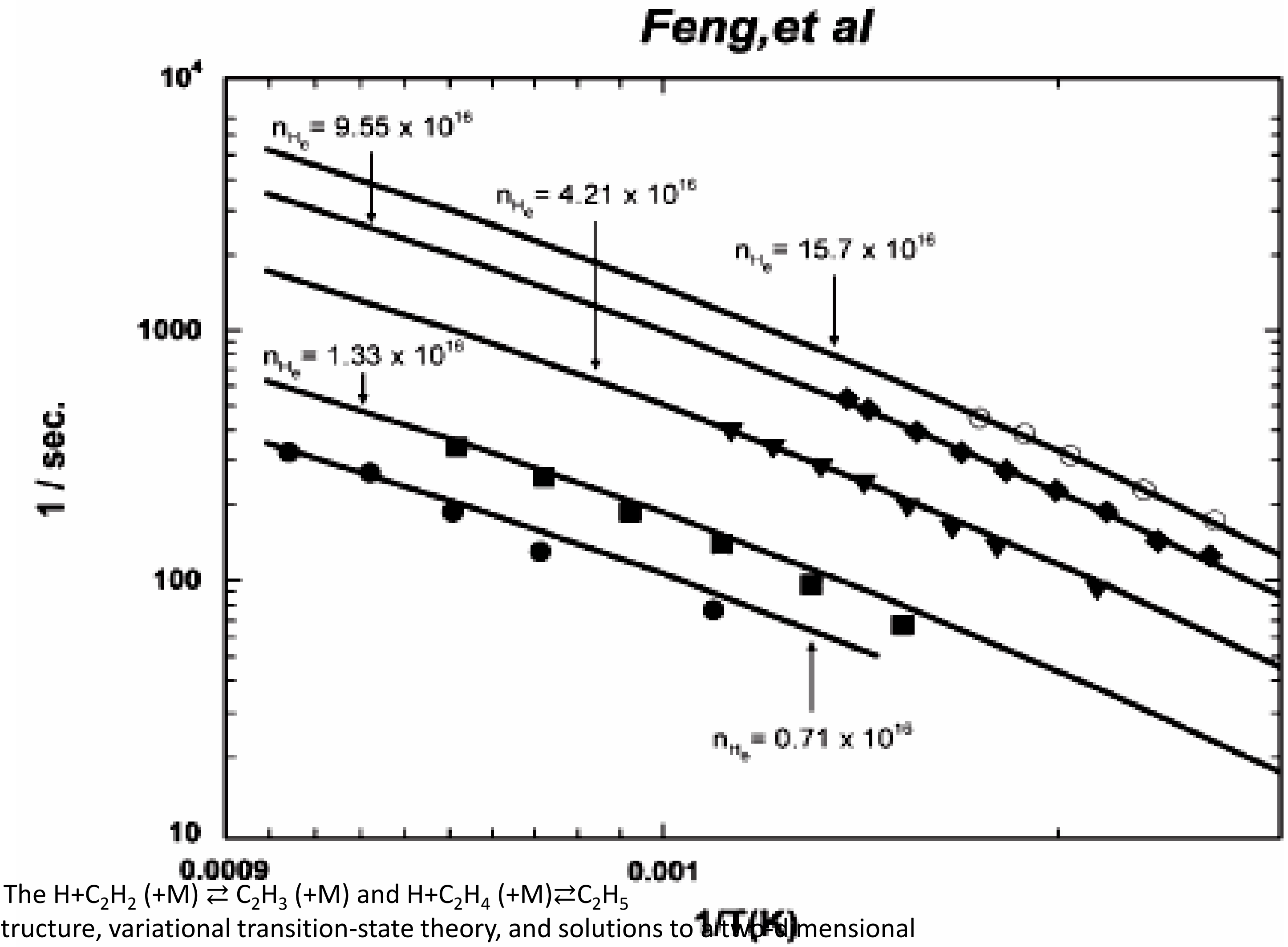
J.A. Miller, S.J. Klippenstein The $H+C_2H_2$ (+M) ⇄ C_2H_3 (+M) and $H+C_2H_4$ (+M)⇄C_2H_5 (+M) reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. Phys. Chem. Chem. Phys. 2004 6 1192—1202.

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



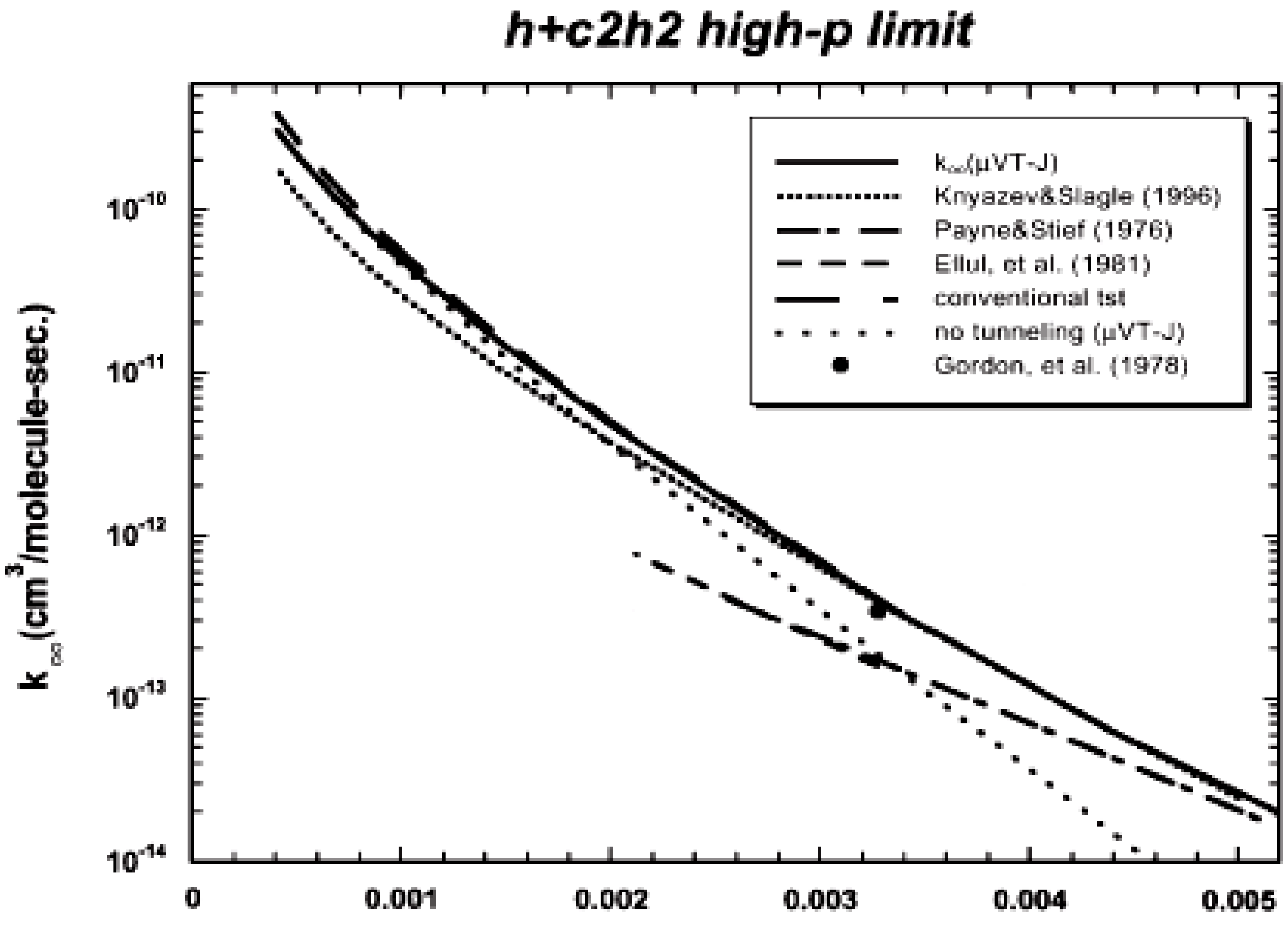
J.A. Miller, S.J. Klippenstein The H+C_2H_2 (+M) ⇄ C_2H_3 (+M) and H+C_2H_4 (+M)⇄C_2H_5 (+M) reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. Phys. Chem. Chem. Phys. 2004 6 1192—1202.

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



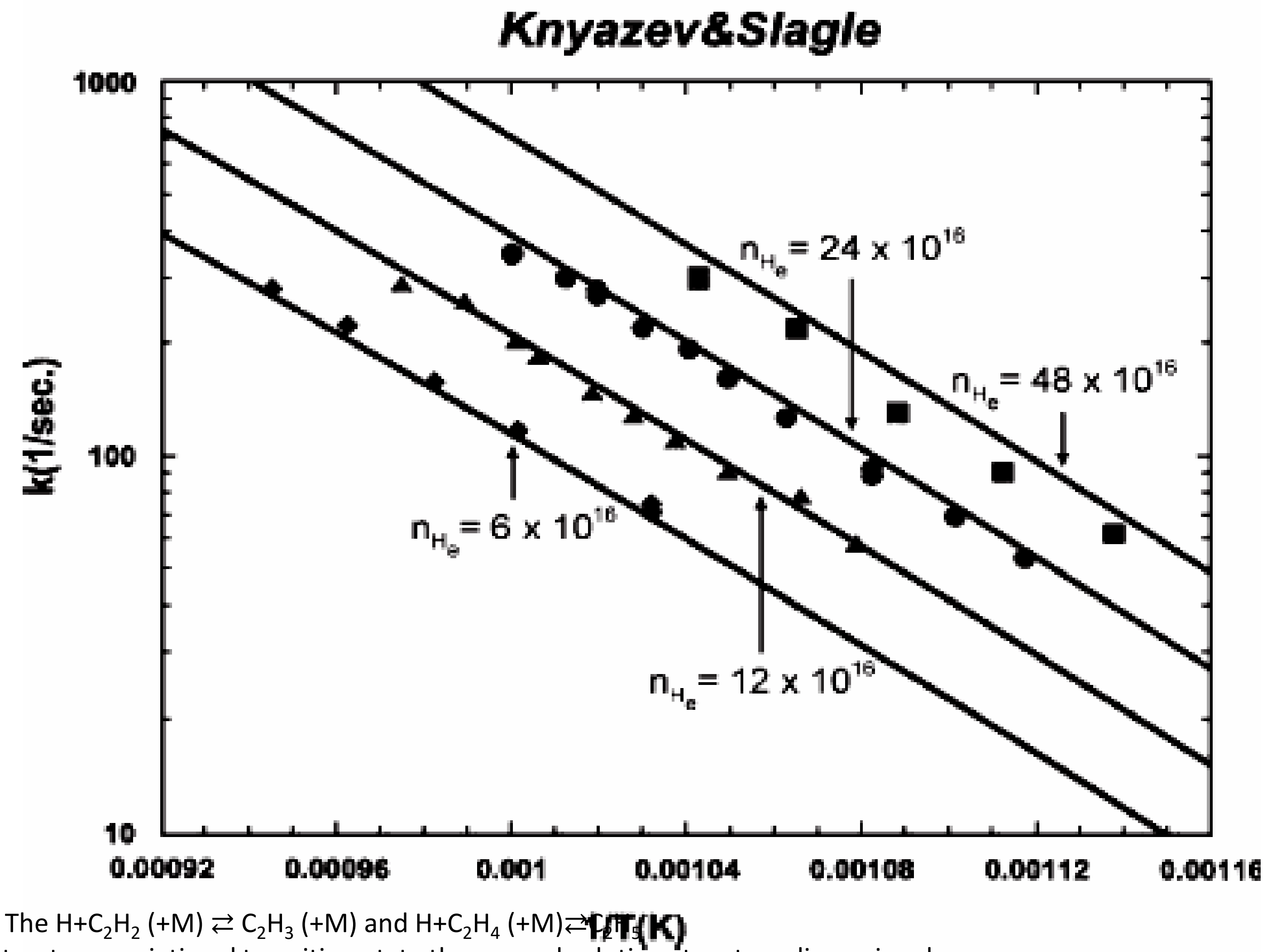
J.A. Miller, S.J. Klippenstein The H+C_2H_2 (+M) ⇄ C_2H_3 (+M) and H+C_2H_4 (+M)⇄C_2H_5 (+M) reactions: Electronic structure, variational transition-state theory, and solutions to a two-dimensional master equation. Phys. Chem. Chem. Phys. 2004 6 1192—1202.

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



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

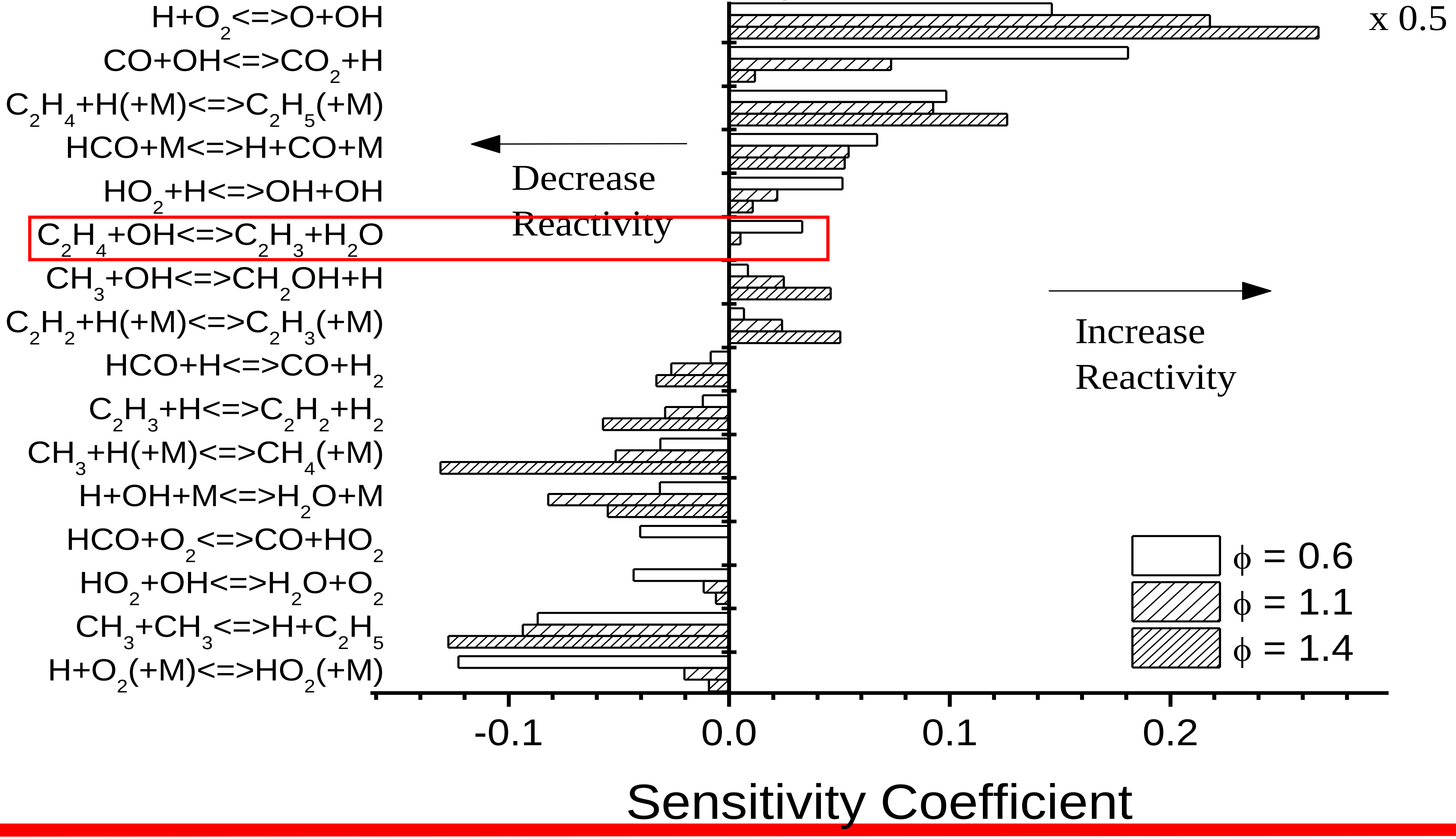
$\dot{H} + C_2H_2 = \dot{C}_2H_3$



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

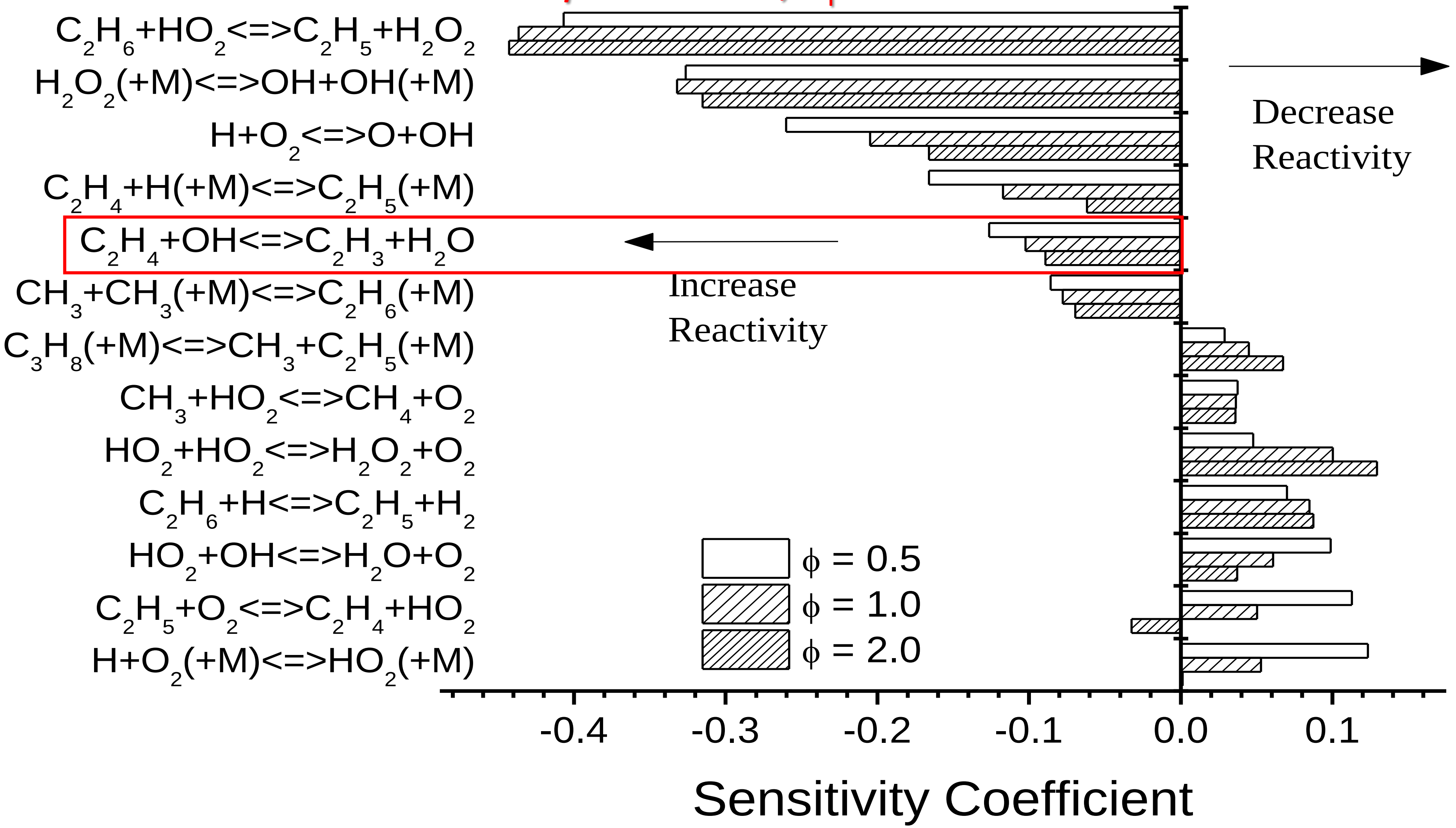
Sensitivity Analysis—C_2H_6 Flame Speed

p = 1.0 atm, T_i = 298 K

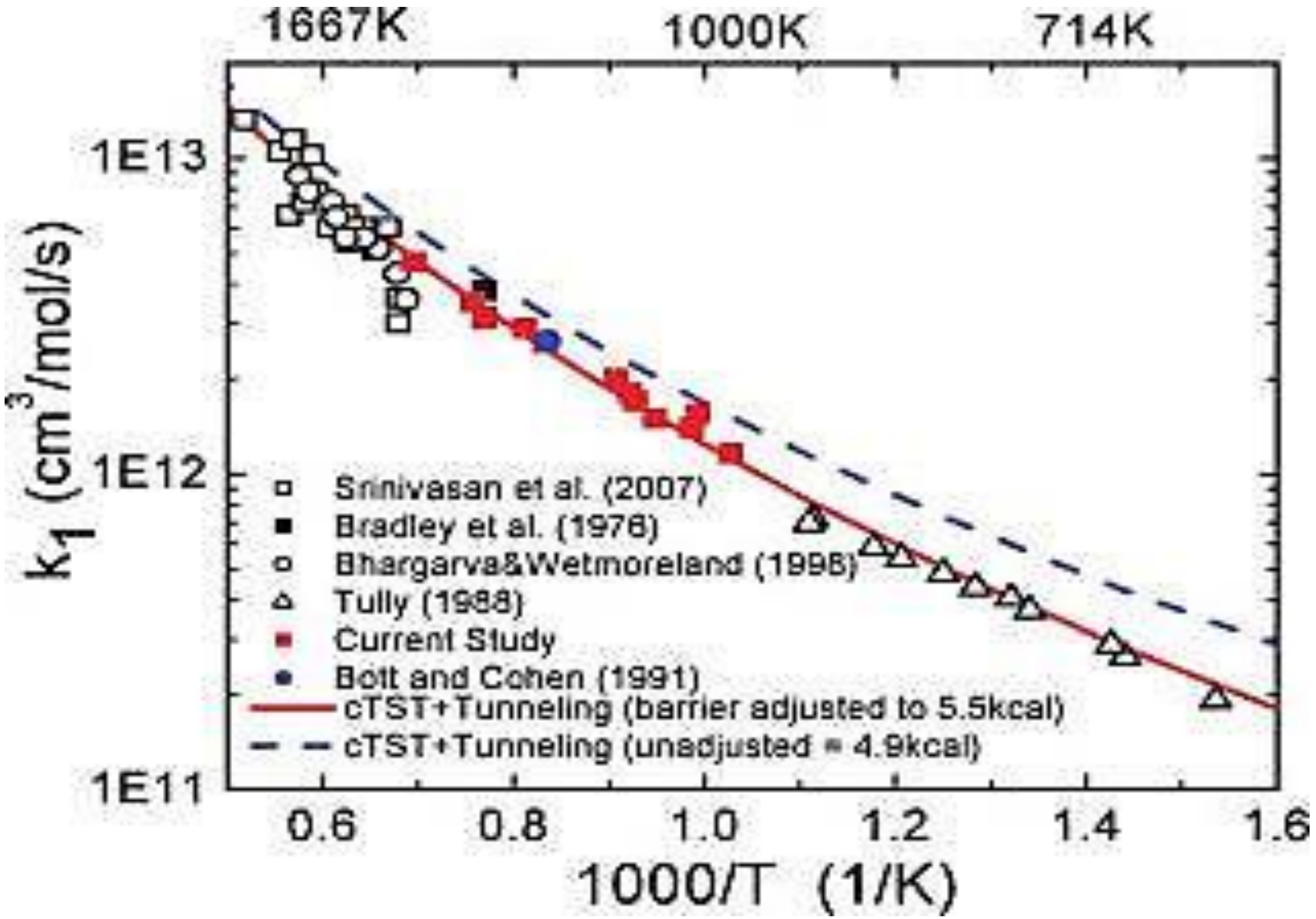


Sensitivity Analysis—C_2H_6 Ignition delay

p = 30 atm, T_i = 1250 K



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



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

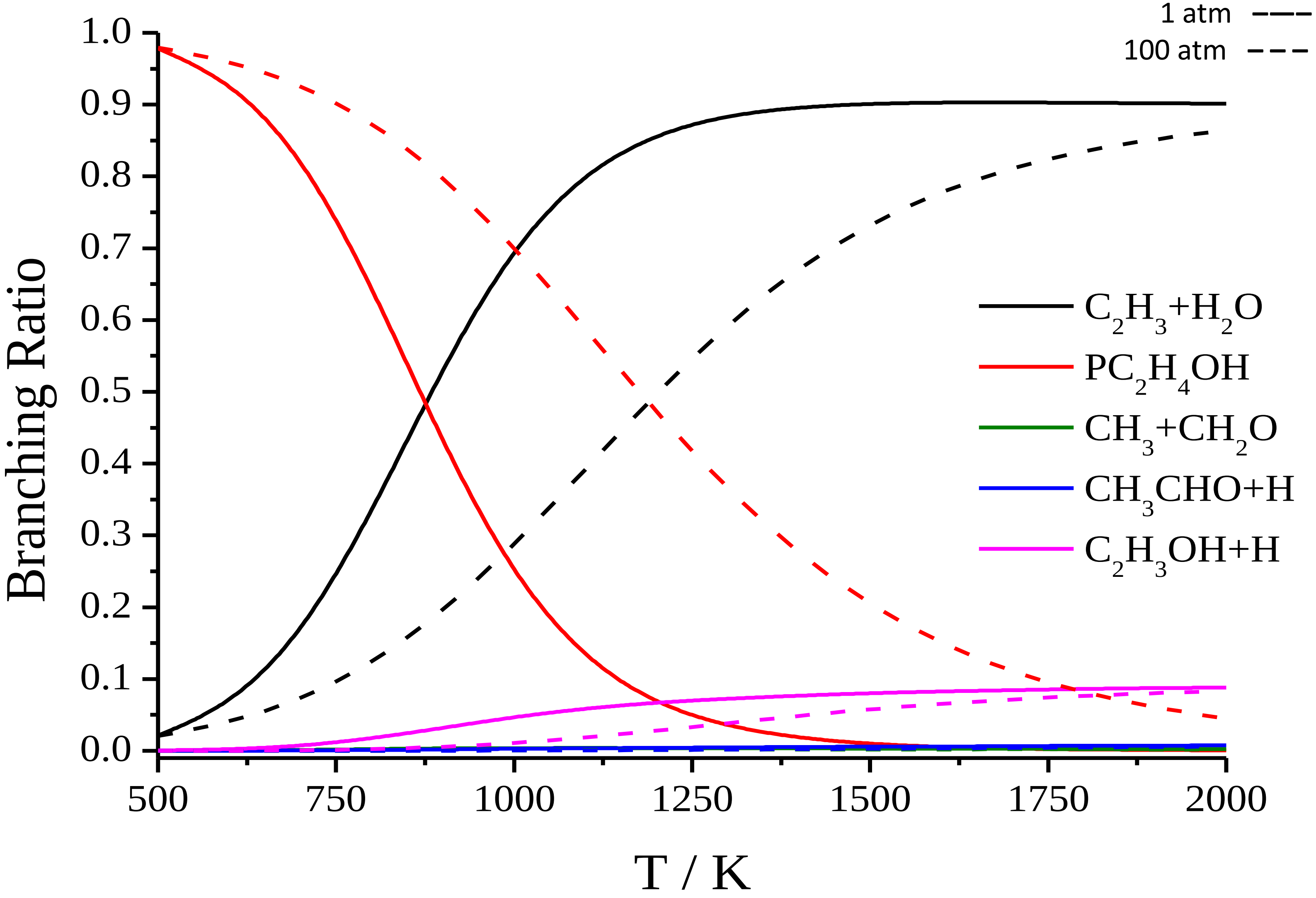
$C_2H_4 + \dot{O}H$

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

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

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

$C_2H_4 + \dot{O}H$


1 atm
100 atm
Branching Ratio
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
500
750
1000
1250
1500
1750
2000
T / K
C_2H_3+H_2O
PC_2H_4OH
CH_3+CH_2O
CH_3CHO+H
C_2H_3OH+H

Importance of continuous mechanism development

- ❑ Ethylene oxidation: $\dot{C}_2H_3 + O_2$ = products is very important
  - — Prior to 1984 written as: $\dot{C}_2H_3 + O_2 = C_2H_2 + H\dot{O}_2$
  - — Slagle et al.[1] (T < 900 K) $\dot{C}_2H_3 + O_2 = CH_2O + H\dot{C}O$
  - — Theory[2–5] confirmed low-T pathway and indicated another important path at high T

$$\dot{C}_2H_3 + O_2 = \dot{C}H_2CHO + \ddot{O}$$

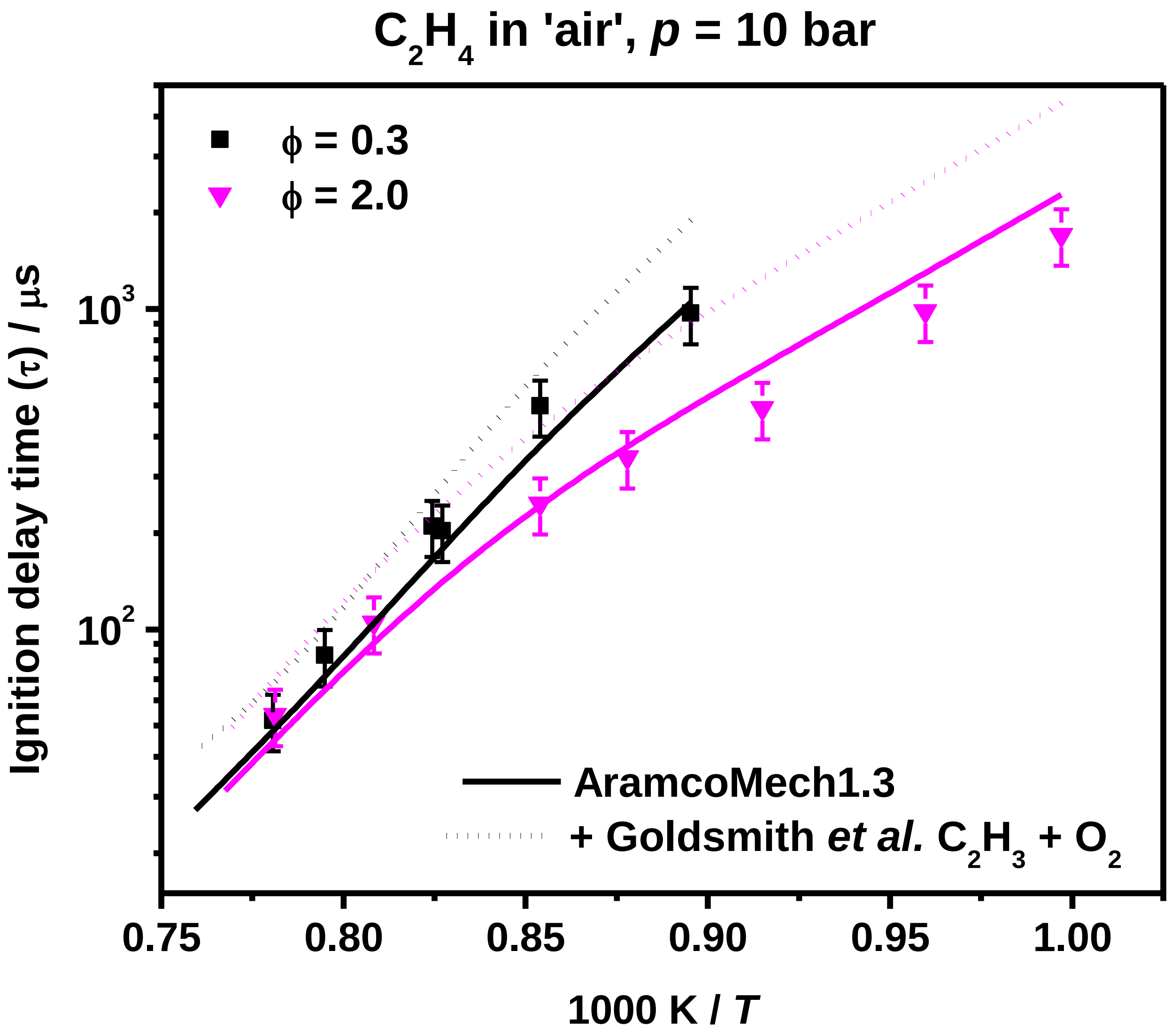
Dangerous to optimize mechanisms when critical features of PES are not fully understood

- ❑ Goldsmith et al. (2015)[6] state-of-the-art quantum chemistry on $C_2H_3\dot{O}_2$ PES
  - — Used variable reaction coordinate-, variational- and conventional TSTs
  - — $k(T, p)$ calculated confirming $CH_2O + H\dot{C}O$ as main product channel at lower Ts
  - — $\dot{C}H_2CHO + \ddot{O}$ produced at higher Ts (crossover $T \approx 1000$ K at 1 atm)
  - — Stabilization to $C_2H_3\dot{O}_2$ competing with the two channels at $p > 10$ atm

Advances are invaluable in developing high-fidelity chemical kinetic model[7]

[1] I.R. Slagle, J.-Y. Park, M.C. Heaven, D. Gutman, J. Am. Chem. Soc. 106 (1984) 4356–4361.
[2] P.R. Westmoreland, Combust. Sci. Tech. 82 (1992) 151–168.
[3] J.W. Bozzelli, A.M. Dean, J. Phys. Chem. 97 (1993) 4427–4441.
[4] B.K. Carpenter, J. Phys. Chem. 99 (1995) 9801–9810.
[5] A.M. Mebel, E.W.G. Diau, M.C. Lin, K. Morkuma, J. Am. Chem. Soc. 118 (1996) 9759–9771.
[6] C.F. Goldsmith, L.B. Harding, Y. Georgievskii, J.A. Miller, S.J. Klippenstein, J. Phys. Chem. A 119 (2015) 7766–7779.
[7] S.J. Klippenstein, Proc. Combust. Inst. 36 (2017) 77–111.

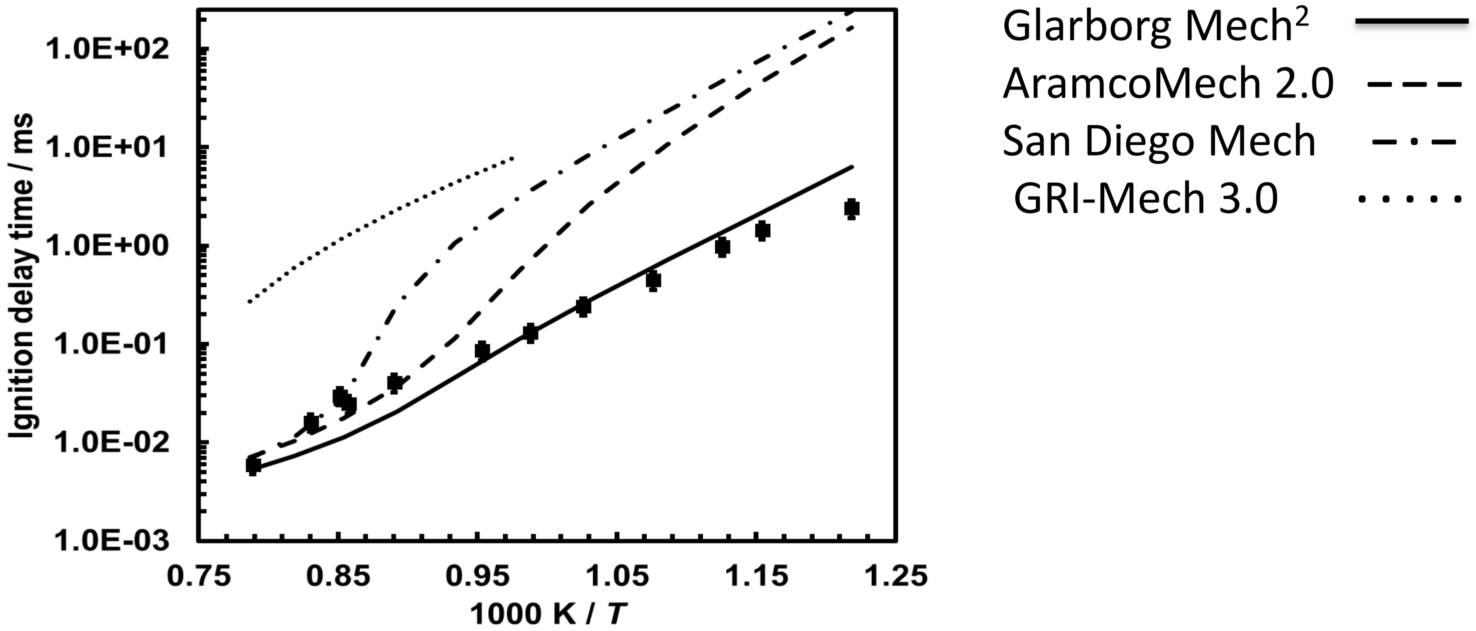
$\dot{C}_2H_3 + O_2$ = products



Importance of continuous mechanism development

- ☐ A lot of progress—but more work is needed…
- ☐ [1]Common core mechanisms predictions of C_2H_2/air τ

$\varphi = 1.0$ in air, $p = 10$ bar



- ☐ $C_2H_2 + H\dot{O}_2 = \ddot{C}HCHO + \dot{O}H$[2]
  - — $\ddot{C}HCHO + O_2 = CO_2 + \dot{H} + H\dot{C}O$[2]
    $= CHOCHO + \ddot{O}$

[1] N. Lokachari et al., Proc. Combust. Inst. 37 (2019) 583–591.
[2] J. Gimenez-Lopez Int. J. Chem. Kinet. 48 (2016) 724–738.

To develop accurate models a systematic approach to determine PES is needed

=> Use automated codes

Automated electronic structure calculations of PESs

- ☐ Growing string method[1]
- ☐ Metadynamics[2]
- ☐ AFIR[3]
- ☐ Kinbot[4] (Zádor/Najm)
  - (Used by Zádor and Miller to explore the $C_3H_5\dot{O}$ PES[5])
- ☐ EStokTP[6] – Electronic Structure to *T*, *p* dependent rate constants (Keceli et al.)
- ☐ AUTOTST[7] – West et al.

[1] P.M. Zimmerman, J. Chem. Phys. 138 (2013) 184102.

[2] Parrinello et al. Proc. Natl. Acad. Sci. 99 (2002) 12562.

[3] Morokuma et al. Chem. Rec. 16 (2016) 2232.

[4] J. Zádor, H.N. Najm "Automated exploration of the mechanism of elementary reactions (SAND2012-8095)," Sandia Nat. Lab., 2012.

[5] J. Zádor, J.A. Miller, Proc. Combust. Inst. 35 (2015) 181–188.

[6] M. Keceli, S. Elliott, Y-P. Li, M.S. Johnson, C. Cavallotti, Y. Georgievskii, W.H. Green, M. Pelucchi, J.M. Wozniak, A.W. Jasper, S.J. Klippenstein, Proc. Combust. Inst. 37 (2019) 363–371.

[7] R.H. West, N.D. Harms, C. Underkoffer, A.M. Payne, 37th Intl. Symp. Combustion. 2018 WIPP 1P003.

Developing/optimizing reaction mechanisms

- ☐ Automated computer-optimization methods exist
  - GRI-Mech approach employed by Frenklach et al. and Sheen and Wang, Turányi et al.
  - Scire et al. Monte Carlo (2001)
- ☐ More direct and indirect measurements available the more successful the optimization
  - *k*: measured directly by following decomposition/formation of reactant(s)/product(s)
  - *k*: calculated using high-level quantum chemistry
  - Optimized against extensive range of experimental validation targets
  - ST, RCM, flow- and JSR, burner stabilized flames, flame speed, etc.

Mechanism Optimization

Available online at www.sciencedirect.com

ScienceDirect

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

Proceedings of the Combustion Institute

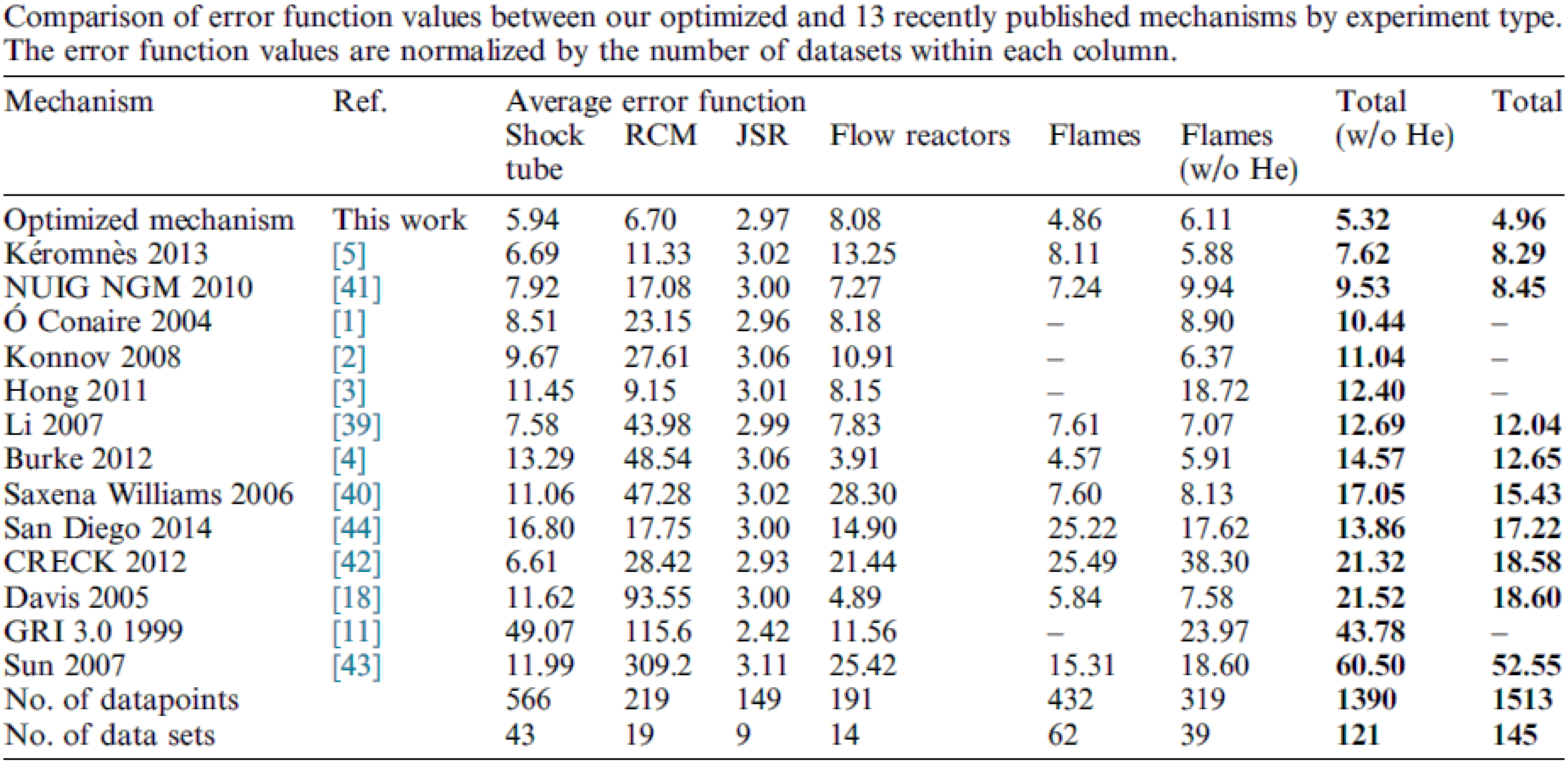
www.elsevier.com/locate/proci

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. Cserháti[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 Shock tube	 RCM	 JSR	 Flow reactors	 Flames	 Flames (w/o He)	Total (w/o He)	Total
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**

Developing reaction mechanisms: databases

- ☐ PrIME website – Frenklach et al. (http://www.primekinetics.org/)
- ☐ Cloudflame website – Sarathy et al. (https://cloudflame.kaust.edu.sa/)
- ☐ ReSpecTh – Turányi et al. (http://respecth.hu)
  - Slightly modified form of PrIME
  - Contain files of the direct and indirect data to be processed
- ☐ ChemKED – Weber and Niemeyer (Int. J. Chem. Kinet. 50(3) (2018) 135–148.)
  - Human and machine- readable data standard for storing fundamental exptl. Data
- ☐ ChemConnect – Edward Blurock (http://www.chemicalkinetics.info)

Mechanisms for small molecules

- ☐ Methane/NG mechanisms (Dagaut and co-workers 1991—1994)
- ☐ Methane/ethane (Barbé et al. 1995)
- ☐ Leeds methane mechanism (Hughes et al. 2001)
- ☐ Miller-Bowman NO mechanism (1989)
- ☐ Small oxygenated species (Dryer et al. 1991—2007)
- ☐ GRI-Mech (Frenklach et al. 1995, 1998)
  - Optimized by fitting to wide range of targets for CH_4/C_2H_6
  - Acetaldehyde/vinoxy chemistry included to better describe ethylene oxidation
  - Included prompt NO formation and reburn

Recent mechanisms for small HC molecules

- ☐ USC Mech (Wang et al. 2007)
  - H_2/CO, CH_4, C_2H_6, C_2H_4, C_2H_2, C_3, 1,3-C_4H_6
- ☐ FFCM-I (G.P. Smith, Y. Tao, H. Wang http://nanoenergy.stanford.edu/ffcm1, 2016)
  - H_2/CO/C1 reaction model
- ☐ CRECK (Politecnico di Milano)
  - H_2/CO, $C_1 – C_3$, biomass, PRF, PAH, PRF + PAH, PRF + PAH + Alcohol + Ether
- ☐ San Diego Mech (Williams et al. 2012, 2016)
  - H_2/CO, CH_4, C_2H_6, C_2H_4, C_2H_2, CH_2O, CH_3CHO, C_2H_5OH, C_3, NO, JP10, heptane, DME
- ☐ AramcoMech 1.3, 2.0, 3.0 (Metcalfe et al. 2013, Burke et al. 2014-15, Zhou et al. 2016, Li et al. 2017)
  - $C_0 – C_2$ HC + HCO, C_3H_6, i-, 1-, 2-C_4H_8
- ☐ Glarborg C_2H_2 Mech (Gimenez-Lopez et al. 2016)

All freely available on the internet

Other “core” small mechanisms

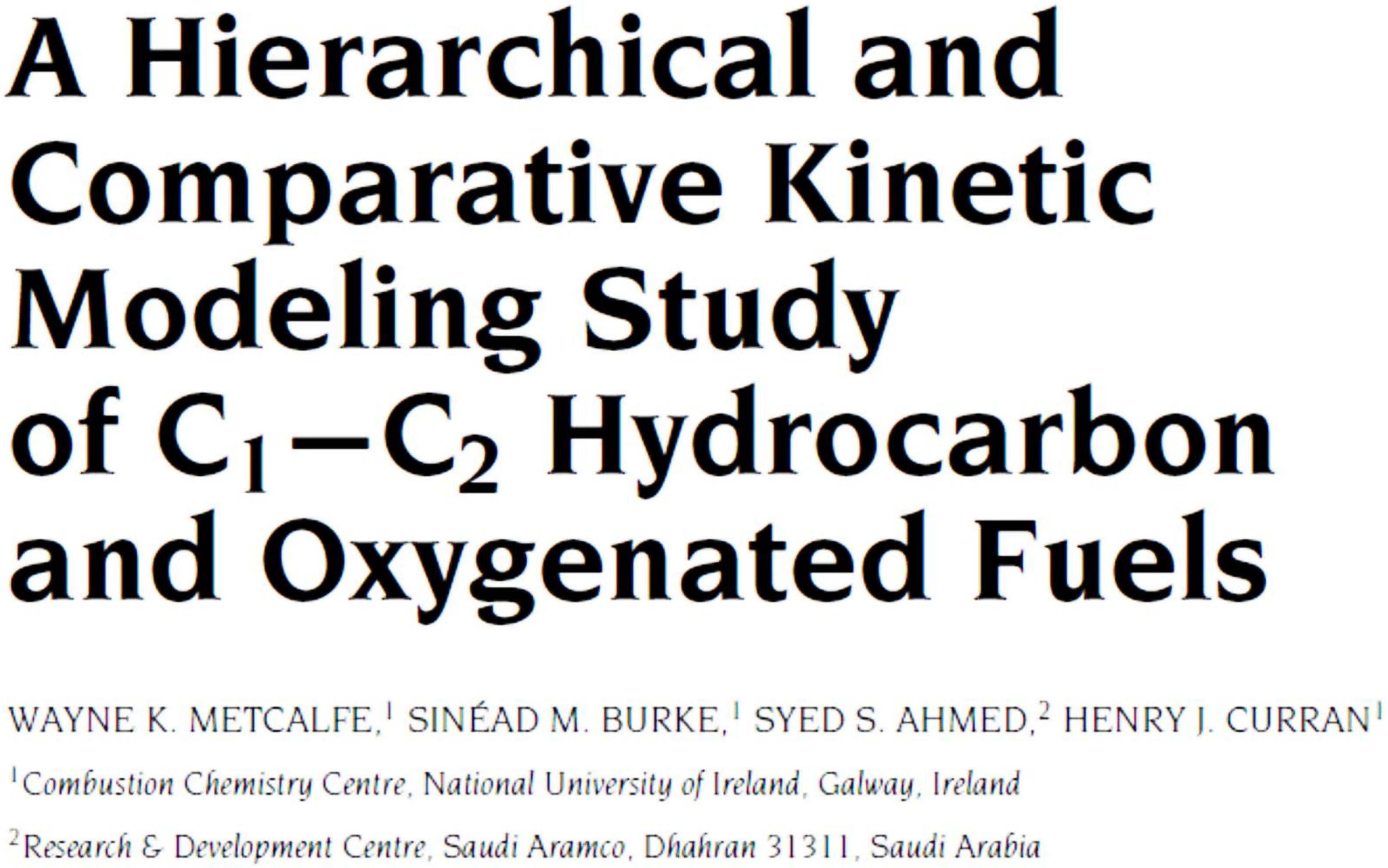
- Shanghai Jiaotong University (F. Qi)
- Université de Nancy (F. Battin-LeClerc)
- CNRS (P. Dagaut)
- Chemkin (Reaction Design: E. Meeks, C. Naik)
- MIT (W. Green)
- Lund University (A. Konnov)
- Tokyo University (A. Miyoshi)
- Technical University of Denmark (P. Glarborg)
- CRECK (Politecnico di Milano: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

Rate constants used in kinetic mechanism

- Previously rate constants reviewed/evaluated:
  - Cohen and Westberg, Tsang and Hampson, Baulch et al.
  - NIST Chemical Kinetics Database
- Rate constants reviewed reaction by reaction
- Combined effects not evaluated
- Probably incapable of reproducing experimental targets
- In practice comparisons are made and some optimization performed

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. CURRAN[1]

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

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

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

Developing/optimizing the H_2/O_2 mechanism

- ☐ Li et al. (Int. J. Chem. Kinet. 36 (2004) 566–575)
- ☐ M.P. Burke et al. (Int. J. Chem. Kinet. 44 (2012) 444–474 (Update of Li))
  - — Ab initio calculations for important reactions
  - — $\dot{H} + H\dot{O}_2 = H_2O + \ddot{O}$ should be included
  - — ST ignition times sensitive to impurity ($\dot{H}$ atom) effects
  - — Species predictions in burner-stabilized flames more sensitive to exptl. boundary conditions than to kinetics and transport
- ☐ Hashemi et al. (Proc. Combust. Inst. 35 (2015) 553–560 (Update of Burke))
  - — Flow reactor species profiles vs *T* at high *p*
  - — $H\dot{O}_2 + \dot{O}H$, $\dot{O}H + \dot{O}H$ and $H\dot{O}_2 + H\dot{O}_2$ adjusted
- ☐ Kéromnès et al. (Combust. Flame 160 (2013) 995–1011)
  - — Used an RCM to expand range of available data to lower *T*s and higher *p*s
- ☐ Varga et al. (Proc. Combust. Inst. 35 (2015) 589–596)
  - — Mathematical technique to optimize using direct/indirect measurements
  - — First proposed by Frenklach and Miller (Int. J Chem. Kinet. 15 (1983) 677–696)

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."

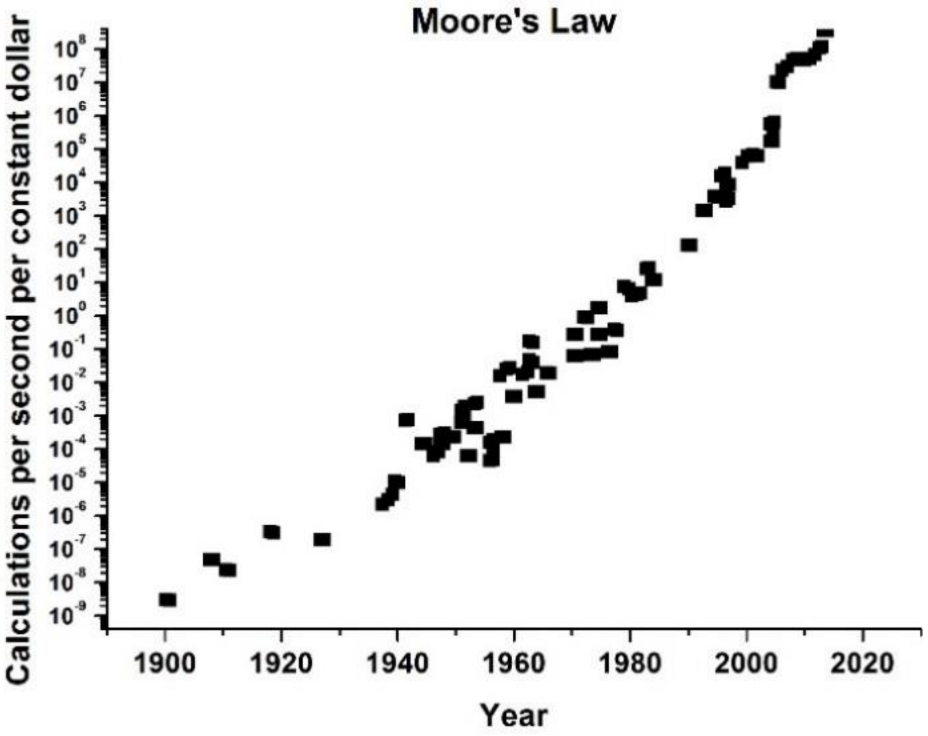
Charlie Westbrook

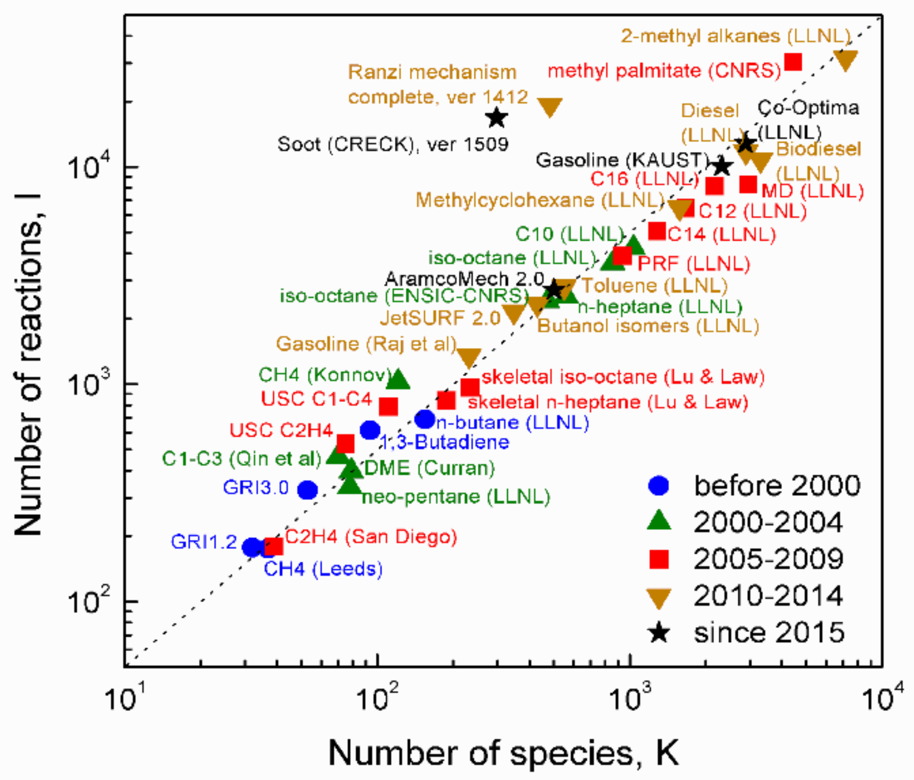
Developing kinetic mechanisms for larger hydrocarbon fuels

Larger Fuel Chemistry

- Boundary between “small” and “large” fuel molecules is somewhat arbitrary, however ...
- C_5 fuels have much more low *T* kinetics than C_4
- C_6 fuels have much more low *T* kinetics than C_5
- C_6 and larger molecules have lots of low *T* reaction pathways, “cool flames”, and lower ON values than smaller fuels

Advances in computing versus size of kinetic mechanisms





C.K. Westbrook, Y. Mizobunchi, T.J. Poinsot, P.J. Smith, J. Warnatz, Proc. Combust. Inst. 30 (2005) 125-157.

G.E. Moore, Electronics 38(8) (1965) 114.

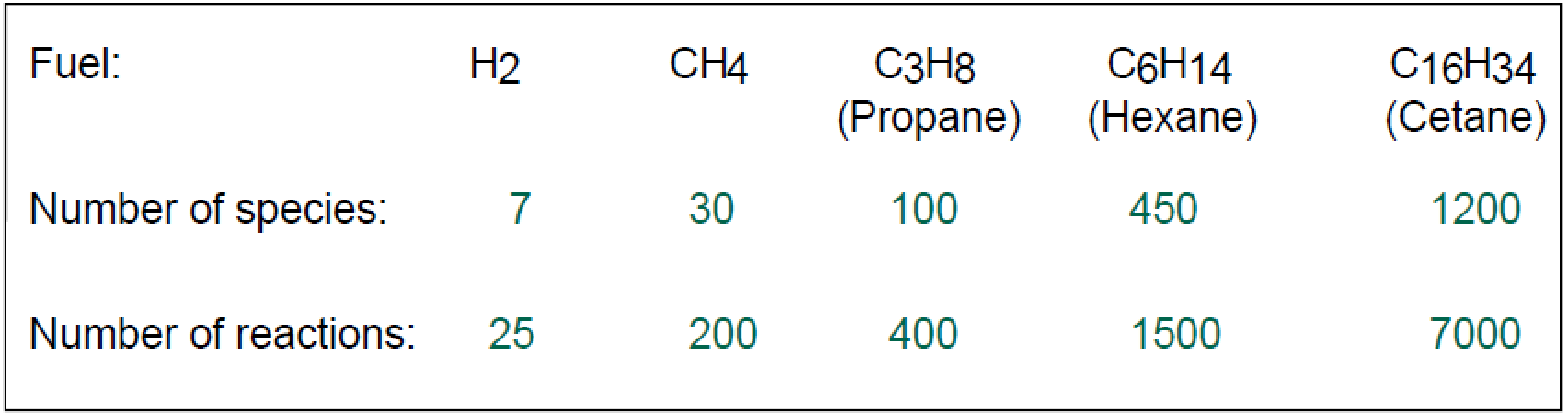
T.F. Lu and C.K. Law, Prog. Energy Combust. Sci. 35 (2009) 192–215.

F.N. Egolfopoulos, N. Hansen, Y. Ju, K. Kohse-Höinghaus, C.K. Law, F. Qi, Prog. Energy Combust. Sci. 43 (2014) 36–67.

Figure courtesy of Prof Tianfeng Lu

Mechanism Size

Mechanism size grows with molecule size



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

Dominance of 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

+ O_2 **Oxidation**

Pyrolysis

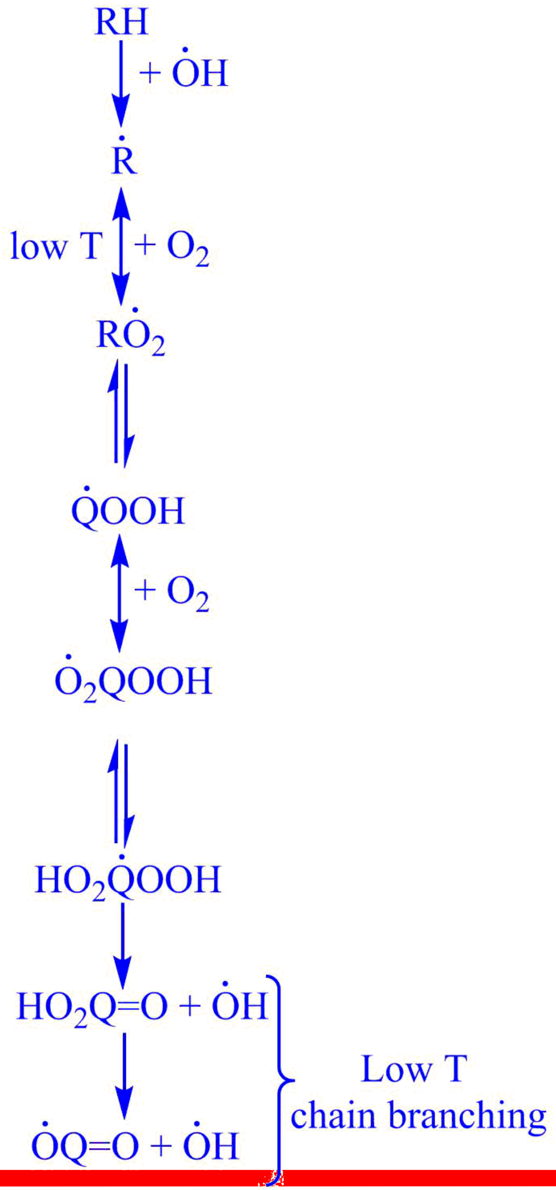
High temperature

Pyrolysis

+ O_2 **Oxidation**

Courtesy of Prof. Tiziano Faravelli, Politecnico di Milano

Three distinct temperature regimes



RH

$+ \dot{O}H$

$\dot{R}$

low T $+ O_2$

$R\dot{O}_2$

$\dot{Q}OOH$

$+ O_2$

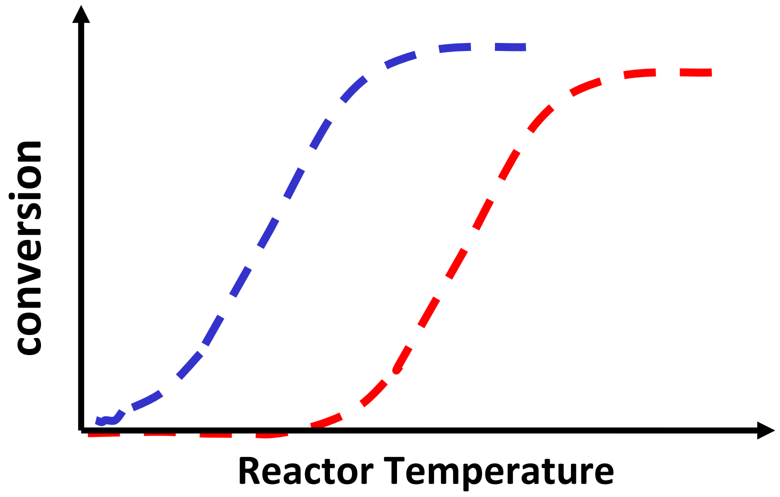
$\dot{O}_2QOOH$

$HO_2\dot{Q}OOH$

$HO_2Q{=}O + \dot{O}H$

$\dot{O}Q{=}O + \dot{O}H$

Low T
chain branching



$$\dot{R} + O_2 \leftrightarrow R\dot{O}_2$$

$$R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$$

$$\dot{Q}OOH + O_2 \leftrightarrow \dot{O}_2QOOH$$

$$\dot{O}_2QOOH \rightleftharpoons R\dot{O} + \dot{O}H + \dot{O}H$$

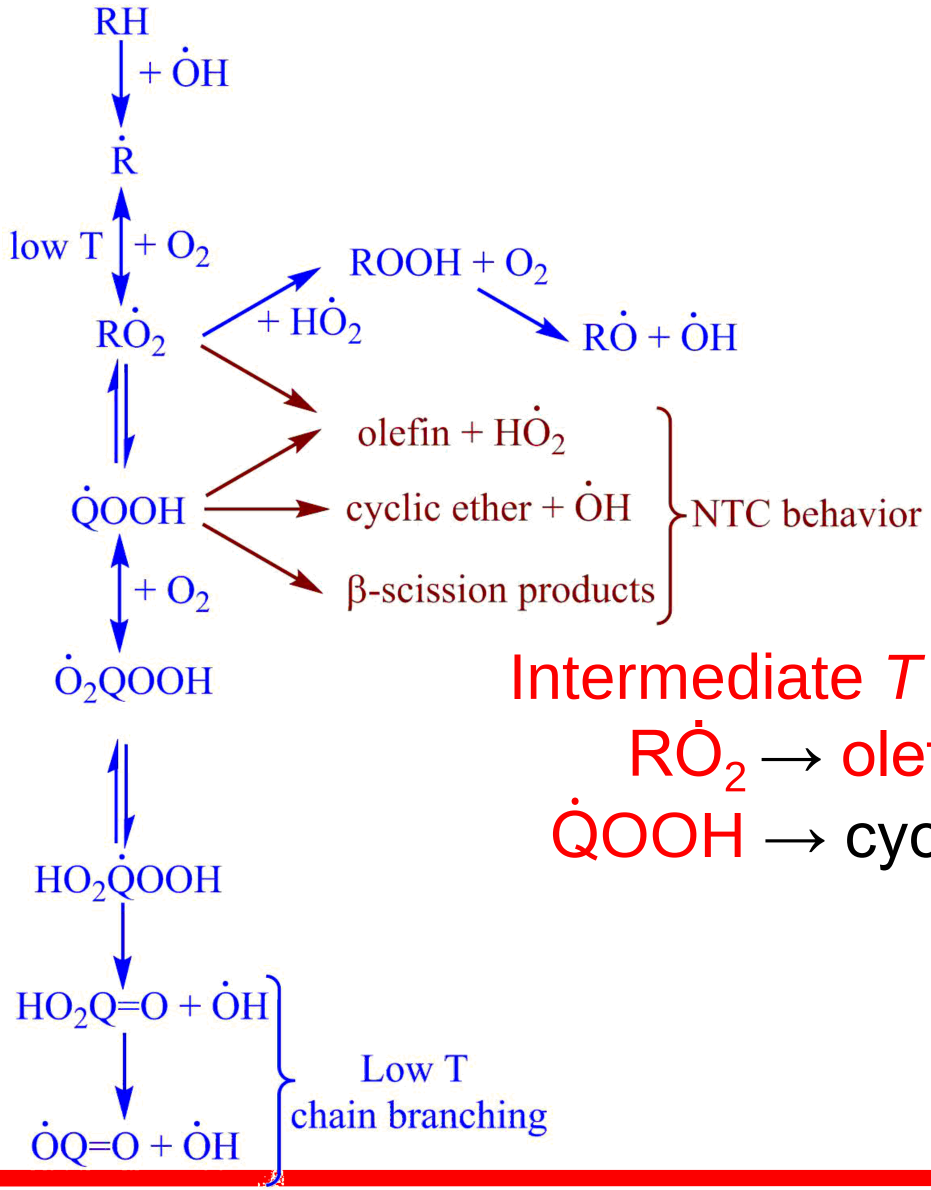
Low *T*

(~500 ≃ 850 K)

Evidence of further additions
to O_2 have been reported.

Zhandong Wang et al, Proc. Natl. Acad. Sci. 114(50) (2017) 13102–13107.
Zhandong Wang et al. Combust. Flame 187 (2018) 199–216.

Three distinct temperature regimes



RH

$+ \dot{O}H$

$\dot{R}$

low T $+ O_2$

$R\dot{O}_2$

$ROOH + O_2$

$+ H\dot{O}_2$

$R\dot{O} + \dot{O}H$

olefin $+ H\dot{O}_2$

$\dot{Q}OOH$

cyclic ether $+ \dot{O}H$

β-scission products

NTC behavior

$+ O_2$

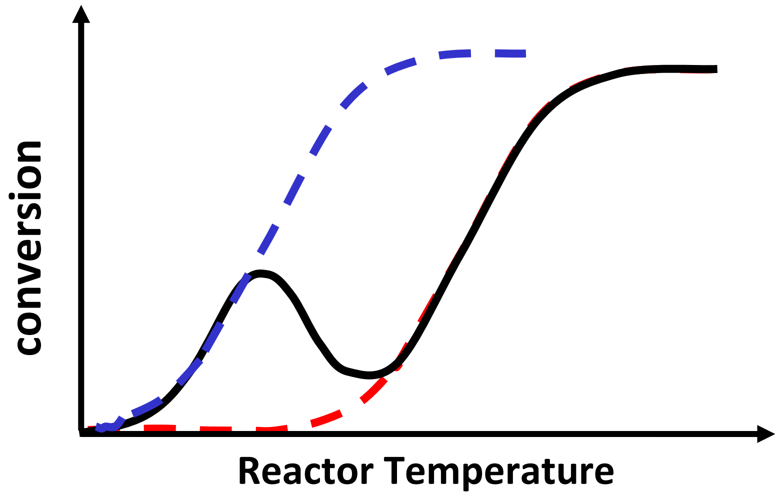
$\dot{O}_2QOOH$

$HO_2\dot{Q}OOH$

$HO_2Q{=}O + \dot{O}H$

$\dot{O}Q{=}O + \dot{O}H$

Low T
chain branching



Negative Temperature
Coefficient Regime

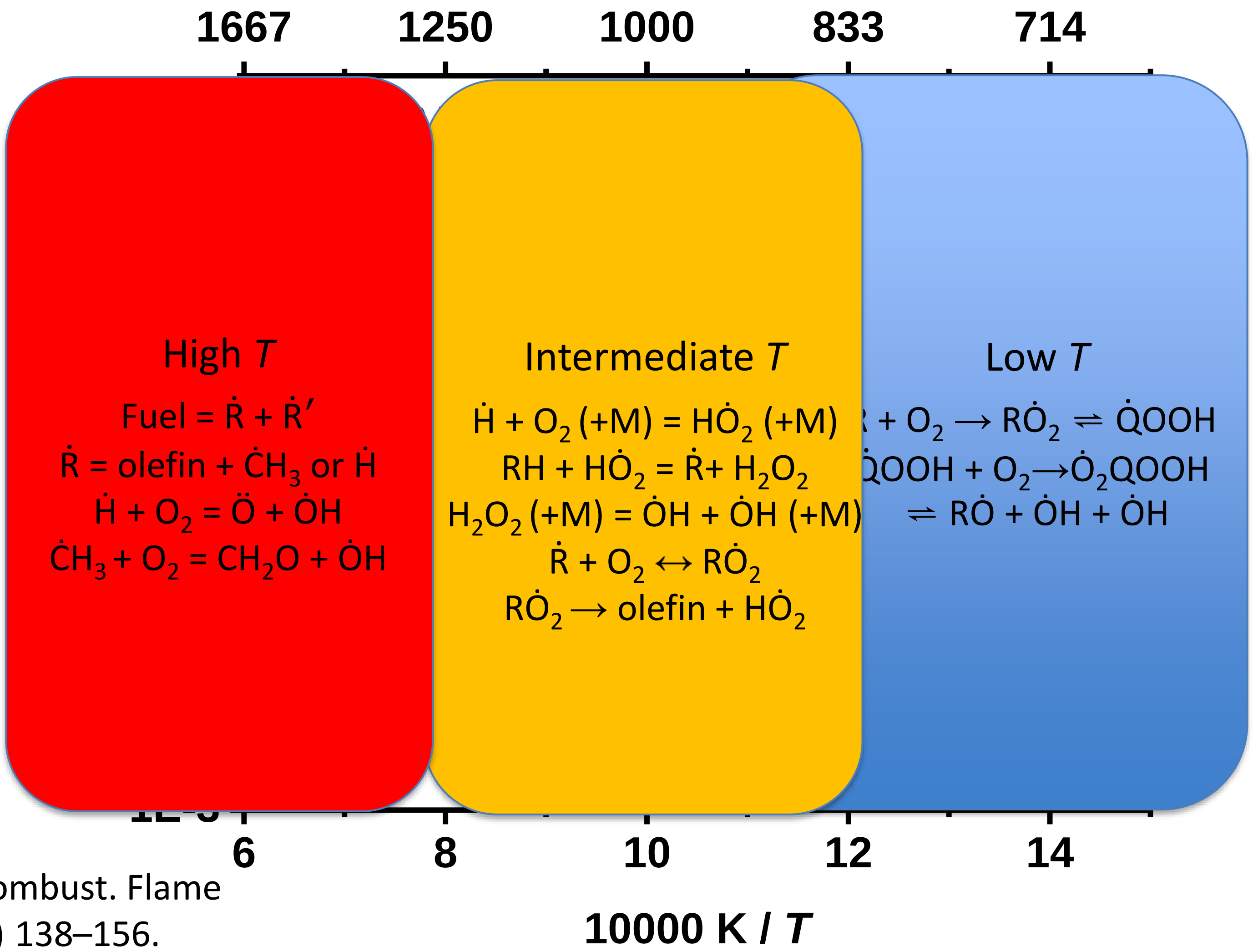
Intermediate T (850 ≃ 1100 K)

$R\dot{O}_2 \rightarrow$ olefin $+ H\dot{O}_2$ (NTC)

$\dot{Q}OOH \rightarrow$ cyclic ether $+ \dot{O}H$ (NTC)

Three distinct temperature regimes

nC_5H_{12} in air, p = 20 atm



High T

$\text{Fuel} = \dot{R} + \dot{R}'$

$\dot{R} = \text{olefin} + \dot{C}H_3 \text{ or } \dot{H}$

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

$\dot{C}H_3 + O_2 = CH_2O + \dot{O}H$

Intermediate T

$\dot{H} + O_2\,(+M) = H\dot{O}_2\,(+M)$

$RH + H\dot{O}_2 = \dot{R} + H_2O_2$

$H_2O_2\,(+M) = \dot{O}H + \dot{O}H\,(+M)$

$\dot{R} + O_2 \leftrightarrow R\dot{O}_2$

$R\dot{O}_2 \longrightarrow \text{olefin} + H\dot{O}_2$

Low T

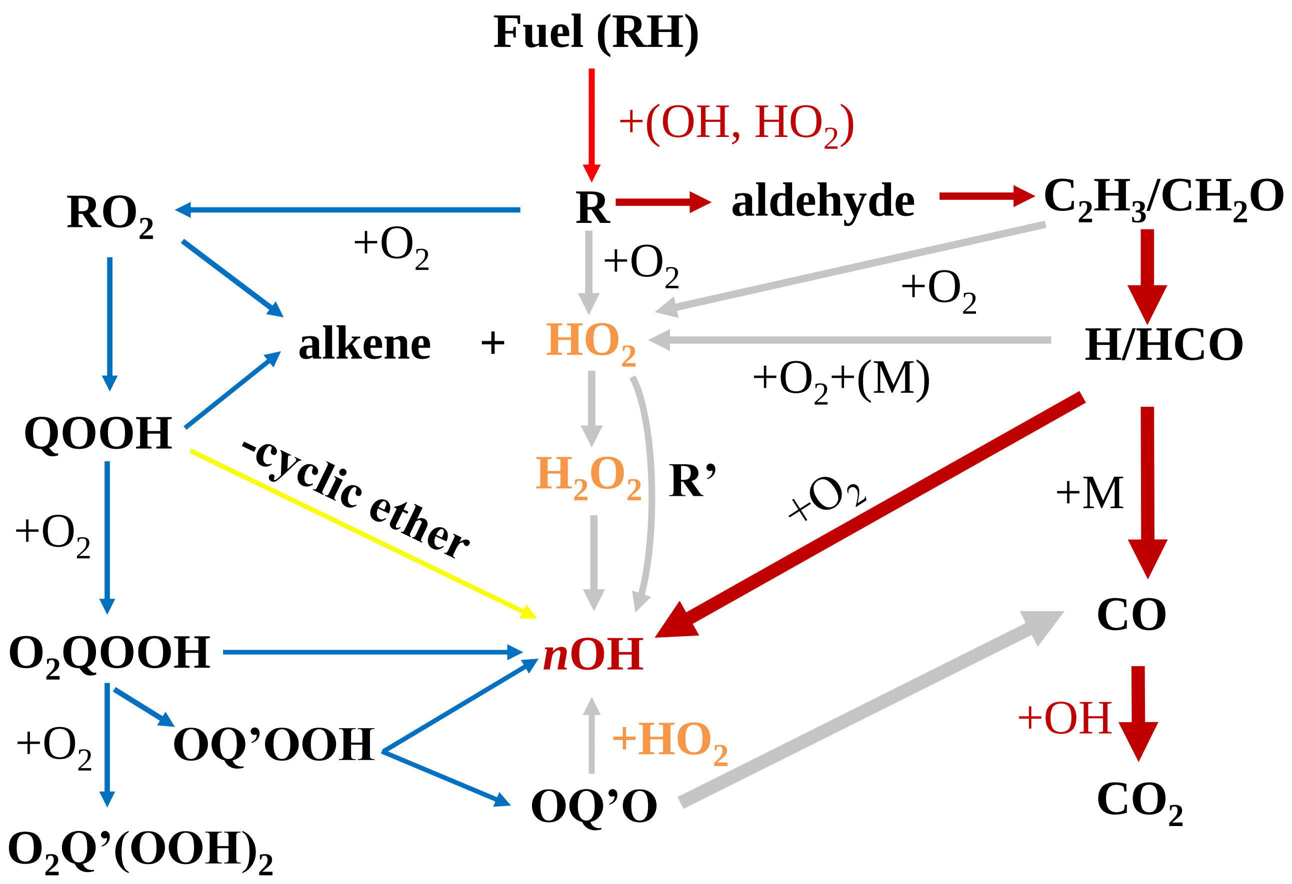
$+ O_2 \longrightarrow R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$

$\dot{Q}OOH + O_2 \longrightarrow \dot{O}_2QOOH$

$\rightleftharpoons R\dot{O} + \dot{O}H + \dot{O}H$

J. Bugler et al., Combust. Flame 163(1) (2016) 138–156.

Three distinct temperature regimes



Fuel (RH)

+(OH, HO_2)

RO_2 +O_2 R → aldehyde → C_2H_3/CH_2O

+O_2

+O_2

alkene + HO_2 +O_2+(M) H/HCO

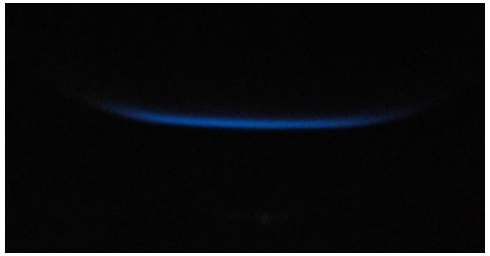
QOOH -cyclic ether H_2O_2 R' +O_2 +M

+O_2

O_2QOOH → *n*OH CO

+O_2 OQ'OOH +HO_2 +OH

$O_2Q'(OOH)_2$ OQ'O CO_2



Cool flame (500–800 K)

Warm flame (800–1100 K)

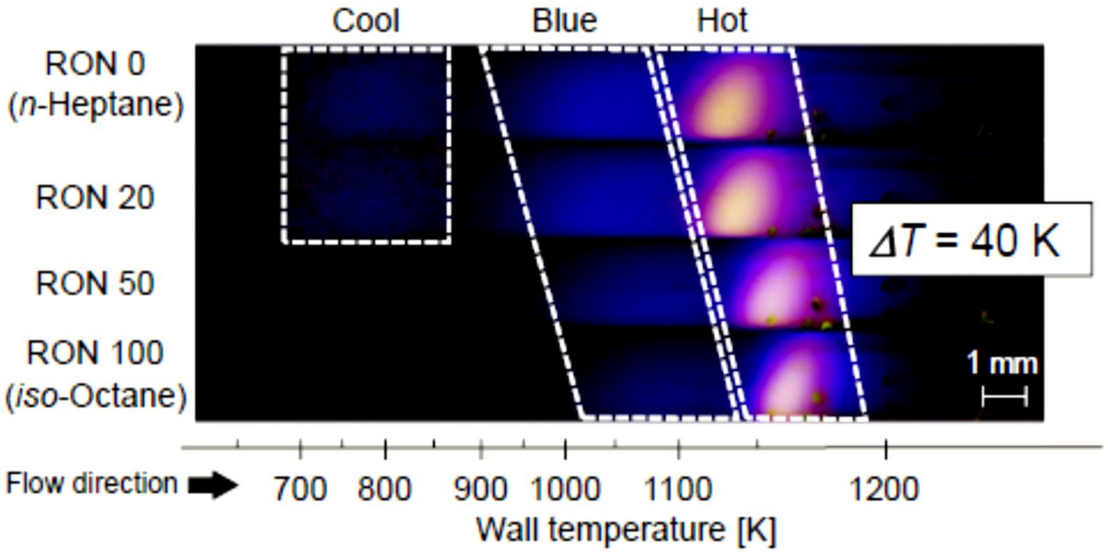
Hot flame (1100–2500 K)

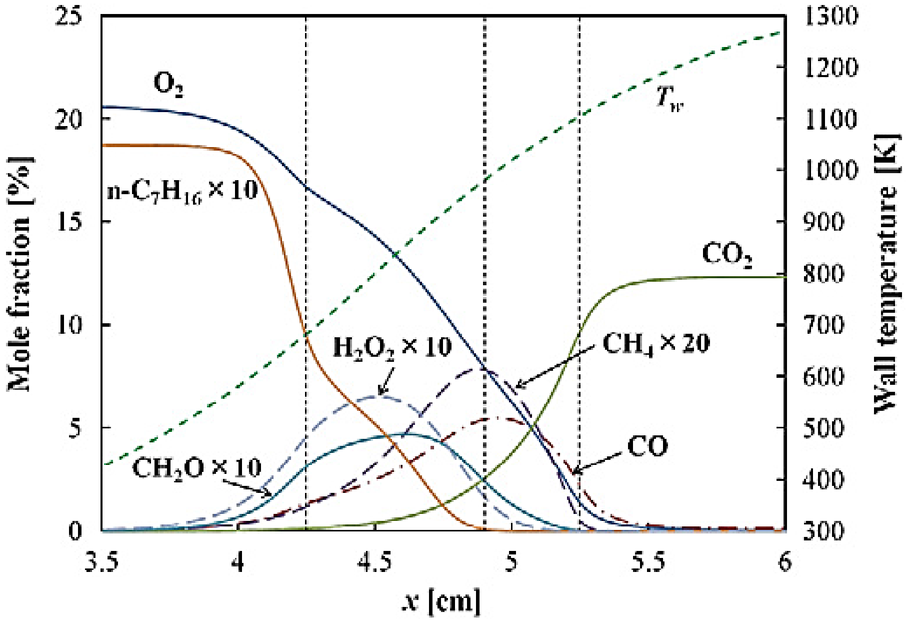
Chemistry at low, intermediate, and high temperature

Y. Ju, *Proceedings of the Combustion Institute* 38 (2021) 83–119.

Three distinct temperature regimes: nC_7H_{16}

Weak flames in a micro flow reactor[1]
Gasoline PRF (*n*-heptane and *iso*-octane)[2]

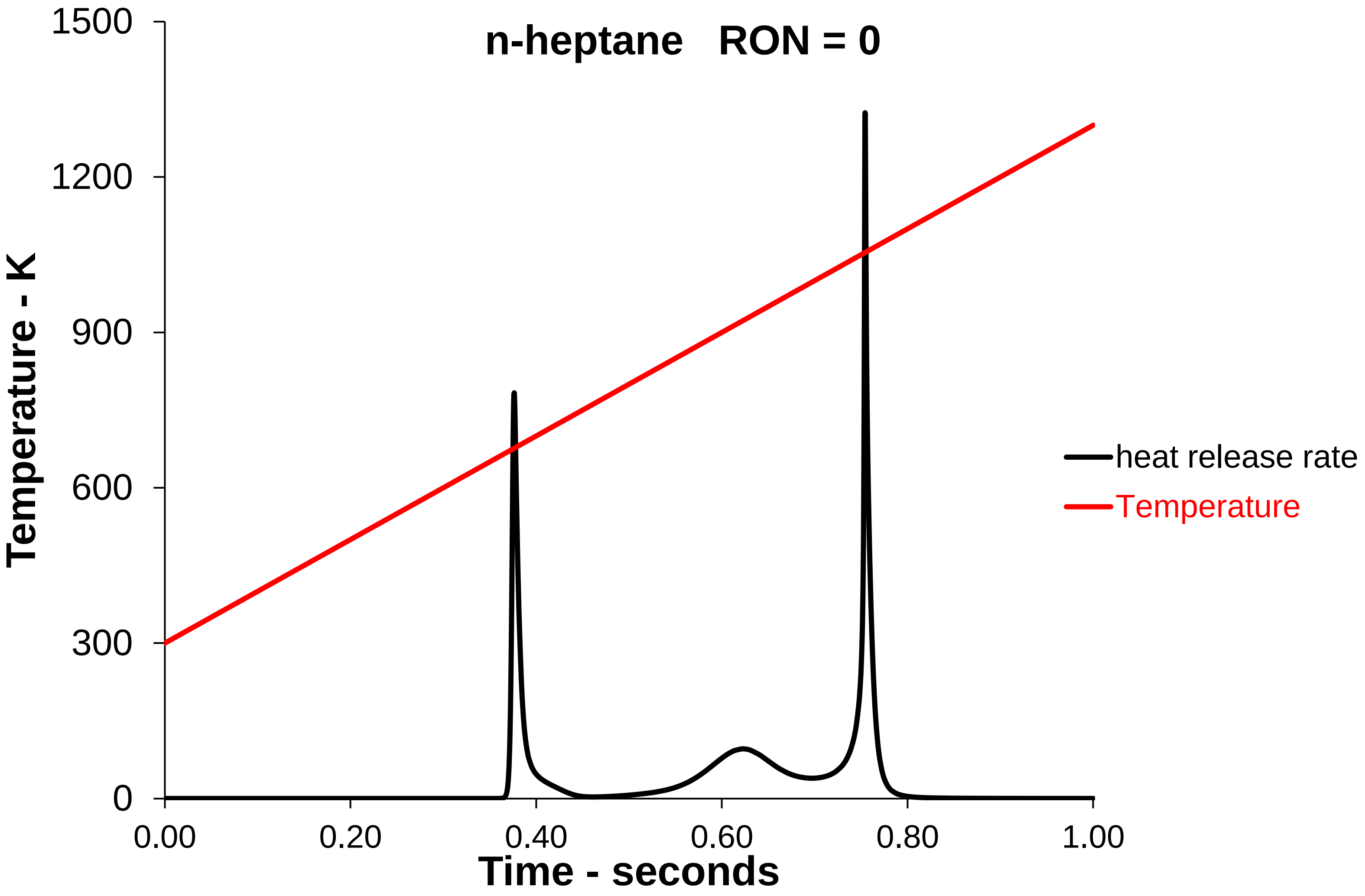




Computed profiles of major species at U = 2.0 cm/s. Vertical dotted lines indicate the locations of HRR peaks.

[1] Maruta et al., Proceedings of the Combustion Institute, 30 (2005) 2429-2436.
[2] Hori et al. Combust. Flame 159 (2012) 959-967.
A. Yamamoto et al. Proc. Combust. Inst., 33 (2011) 3259-3266.

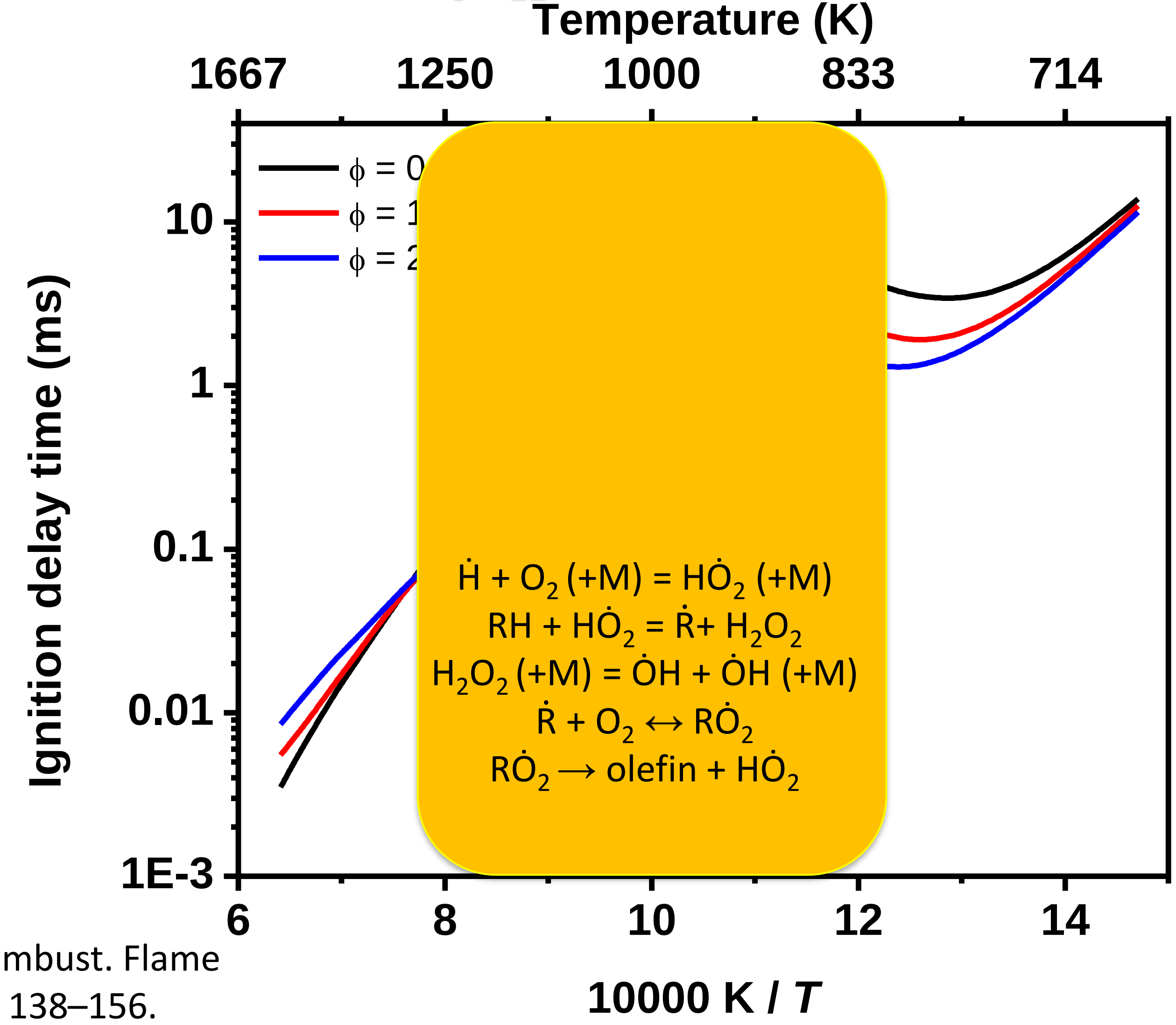
Three distinct temperature regimes: nC_7H_{16}



Slide courtesy of Dr. Charles Westbrook

Three distinct temperature regimes

nC_5H_{12} in air, p = 20 atm



$\dot{H} + O_2\ (+M) = H\dot{O}_2\ (+M)$

$RH + H\dot{O}_2 = \dot{R} + H_2O_2$

$H_2O_2\ (+M) = \dot{O}H + \dot{O}H\ (+M)$

$\dot{R} + O_2 \leftrightarrow R\dot{O}_2$

$R\dot{O}_2 \longrightarrow \text{olefin} + H\dot{O}_2$

J. Bugler et al., Combust. Flame
163(1) (2016) 138–156.

Three distinct chain branching pathways

1) $\dot{H} + O_2 \rightarrow \ddot{O} + \dot{O}H$

$\ddot{O} + H_2 \rightarrow \dot{H} + \dot{O}H$ High *T* (≳ 1100 K)

$\underline{\dot{O}H + H_2 \rightarrow H_2O + \dot{H}}$

Net: $2H_2 + O_2 \rightarrow \dot{O}H + \dot{H} + H_2O$

2) $\dot{H} + O_2\ (+M) \rightarrow H\dot{O}_2\ (+M)$ Intermediate *T*

$RH + H\dot{O}_2 \rightarrow \dot{R} + H_2O_2$ (850 ≃ 1100 K)

$H_2O_2\ (+M) \rightarrow \dot{O}H + \dot{O}H\ (+M)$ chain branching

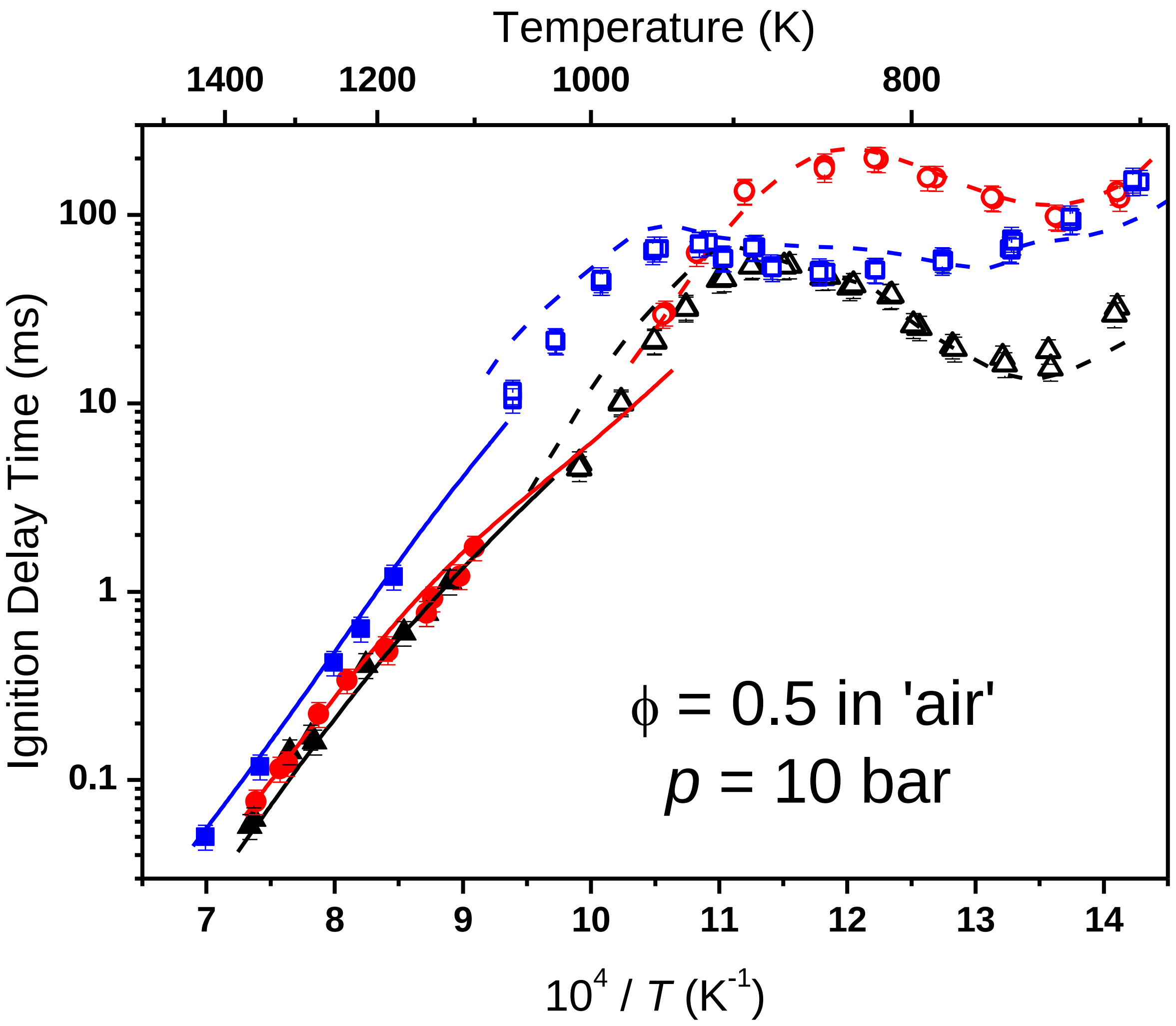
$\mathbf{R\dot{O}_2 \rightarrow olefin + H\dot{O}_2}$ (NTC)

$\dot{Q}OOH \rightarrow \text{cyclic ether} + \dot{O}H$ (NTC)

3) $\dot{R} + O_2 \leftrightarrow R\dot{O}_2$ Low *T* (~500 ≃ 850 K)

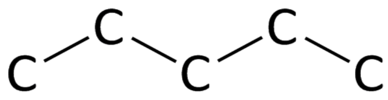
$R\dot{O}_2 \rightleftharpoons \dot{Q}OOH \leftrightarrow \dot{O}_2QOOH \rightleftharpoons R\dot{O} + \dot{O}H + \dot{O}H$

Importance of concerted $H\dot{O}_2$ elimination reaction



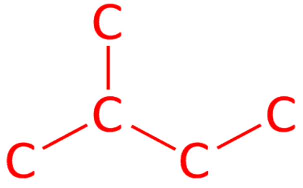
J. Bugler et al. Combust. Flame 163(1) (2016) 138–156.

***n*-Pentane**



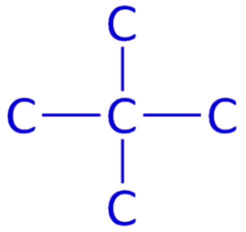
(RON = 61.7)

***iso*-Pentane**



(RON = 92.3)

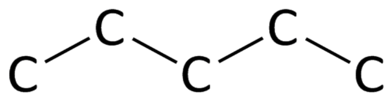
***neo*-Pentane**



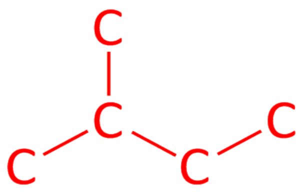
(RON = 85.5)

Pentane isomers @ 1000 K, 10 atm, $\varphi = 1.0$
20% fuel consumption

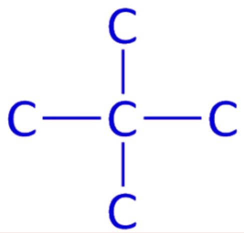
n-Pentane	**$H\dot{O}_2$ elimination from $R\dot{O}_2$**	**24.8%**
	$H\dot{C}O+O_2<=>CO+H\dot{O}_2$	7.90%
	$CH_3\dot{O}+O_2<=>CH_2O+H\dot{O}_2$	8.00%
	$\dot{C}_2H_5+\dot{O}_2<=>C_2H_4+H\dot{O}_2$	**36.1%**
	$nC_3H_7\dot{O}_2<=>C_3H_6+H\dot{O}_2$	**8.30%**



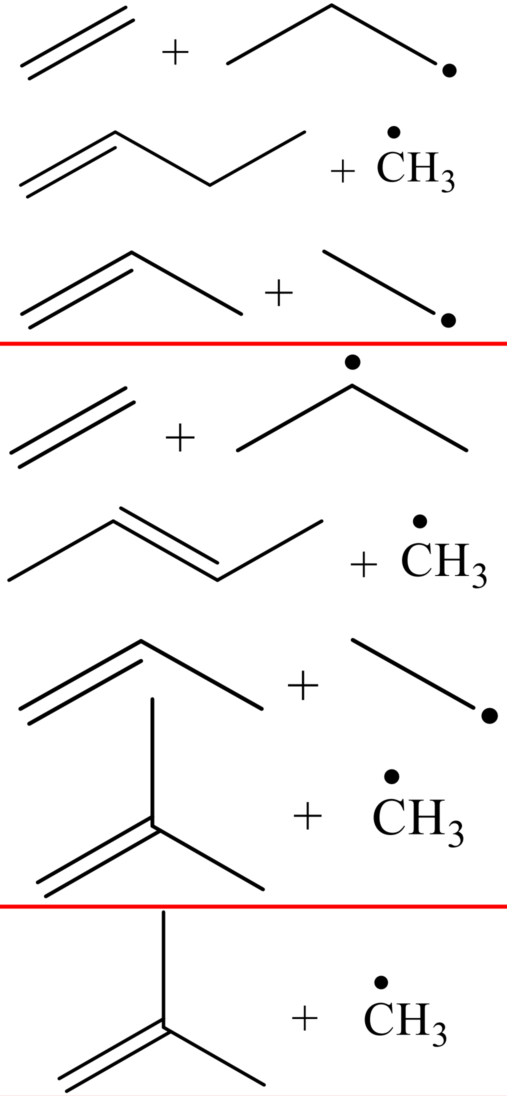
iso-Pentane	**$H\dot{O}_2$ elimination from $R\dot{O}_2$**	**19.3%**
	$H\dot{C}O+O_2<=>CO+H\dot{O}_2$	9.7%
	$CH_3\dot{O}+O_2<=>CH_2O+H\dot{O}_2$	12.7%
	$\dot{C}_2H_5+O_2<=>C_2H_4+H\dot{O}_2$	**24.0%**
	$iC_3H_7O_2<=>C_3H_6+H\dot{O}_2$	**8.20%**
	$i\dot{C}_3H_7+O_2<=>C_3H_6+H\dot{O}_2$	**10.6%**



neo-Pentane	$H\dot{C}O+O_2<=>CO+H\dot{O}_2$	36.3%
	$CH_3\dot{O}+O_2<=>CH_2O+H\dot{O}_2$	17.6%
	$tC4H9\dot{O}_2<=>iC_4H_8+H\dot{O}_2$	**23.3%**



Pentane isomers @ 1150 K, 10 atm, φ = 1.0
20% fuel consumption



n-Pentane	17.5%
	18.7%
	40.8%
iso-Pentane	12.9%
	22.5%
	22.8%
	20.1%
neo-Pentane	74.5%

Relative reaction of *neo*- vs *n*-pentane

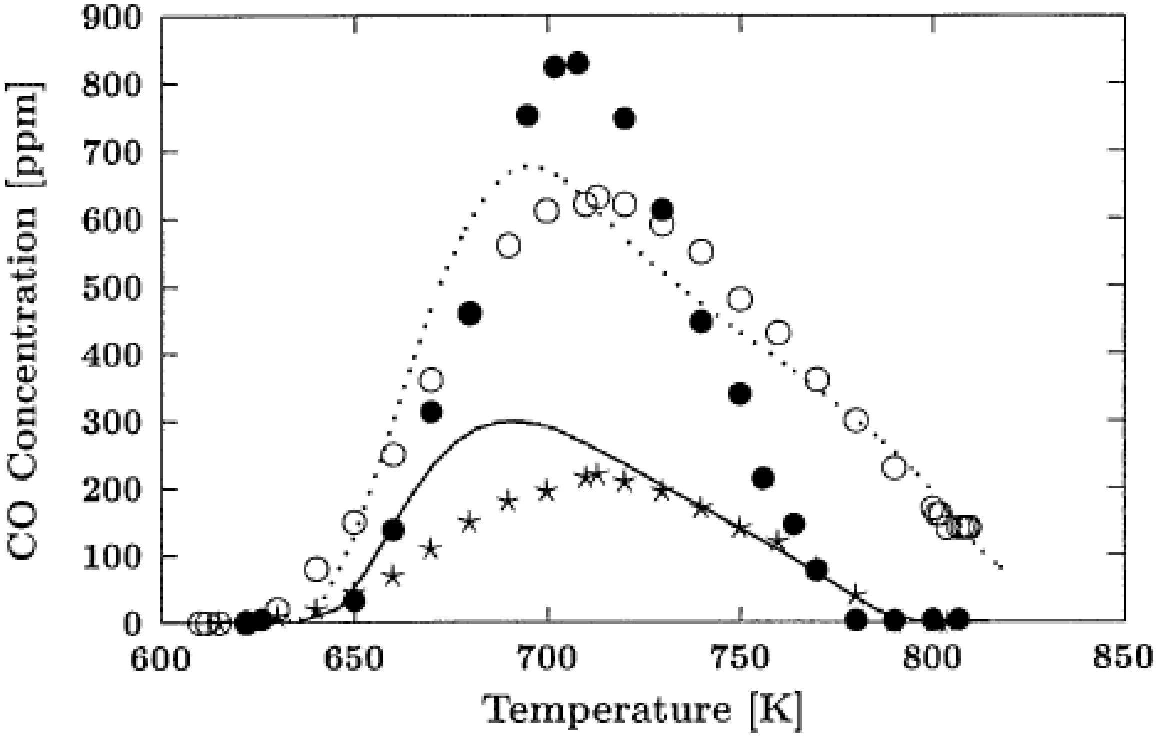
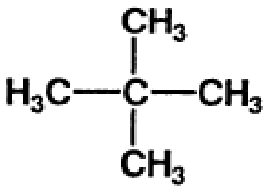


Fig. 1. Reactivity mapping for neopentane at two different nitrogen dilutions and comparison with n-pentane reactivity, P = 8 atm, ϕ = 0.3. ● n-pentane 85% N_2 dilution, ○ neopentane 75% N_2 dilution, ★ neopentane 85% N_2 dilution. Lines are model-predicted CO concentrations.

S. Wang, et al. Combust. Flame 118 (1999) 415–430.

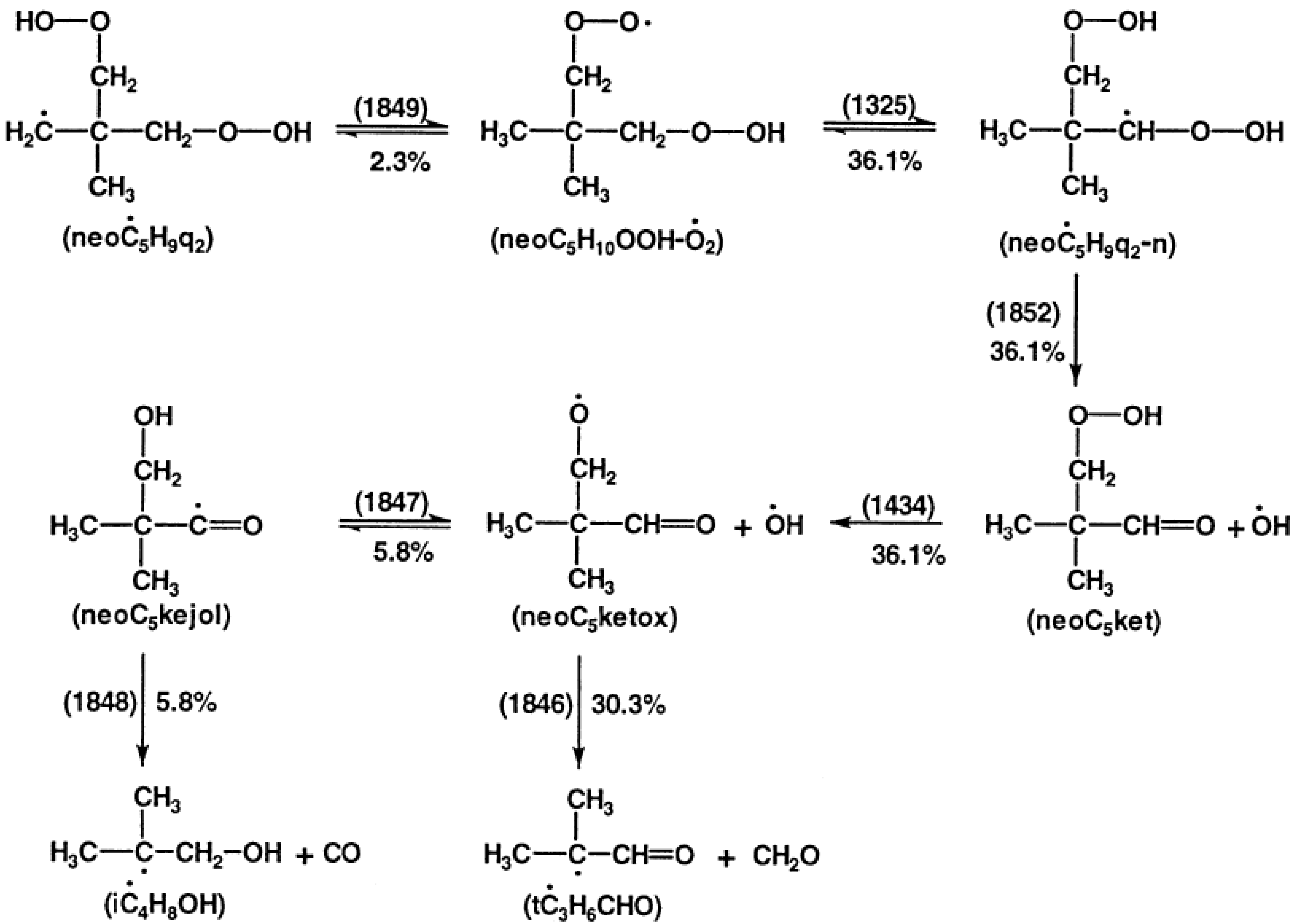
Neopentane oxidation in an engine



$$H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

($neoC_5H_{12}$)

Neopentane oxidation in an engine



Intermediate temperature chemistry

- Concerted eliminations are not well known – quantum chemistry
  - Quelch et al.[1] first proposed $\dot{C}_2H_5 + O_2 = C_2H_4 + H\dot{O}_2$ cyclic TS via concerted elimination
  - Miyoshi[2,3] variational TST and RRKM/master equation ($\dot{C}_2$/i$\dot{C}_3$/*n*-,*s*-,*t*-$\dot{C}_4 + O_2$)
  - Villano et al.[4,5] calculated 23 different straight and branched alkyl-peroxyl radicals
  - Goldsmith et al.[6] for the propyl + O_2 system

Need for further studies of these reactions due to their high importance

[1] G.E. Quelch, M.M. Gallo, M. Shen, Y. Xie, H.F. Schaefer III, D. Moncrieff, J. Am. Chem. Soc. 116 (1994) 4953–4962.
[2] A. Miyoshi, J. Phys. Chem. A 115 (2011) 3301–3325.
[3] A. Miyoshi, A. Int. J. Chem. Kinet. 44 (2012) 59–74.
[4] S.M. Villano, L.K. Huynh, H.H. Carstensen, A.M. Dean, J. Phys. Chem. A 115 (2011) 13425–13442.
[5] S.M. Villano, L.K. Huynh, H.H. Carstensen, A.M. Dean, J. Phys. Chem. A 116 (2012) 5068–5089.
[6] C.F. Goldsmith, W.H. Green, S.J. Klippenstein, J. Phys. Chem. A 2012, 116, 3325–3346.

Three distinct chain branching pathways

1) $\dot{H} + O_2 \rightarrow \ddot{O} + \dot{O}H$

$\ddot{O} + H_2 \rightarrow \dot{H} + \dot{O}H$ High T ($\gtrsim$ 1100 K)

$\underline{\dot{O}H + H_2 \rightarrow H_2O + \dot{H}}$

Net: $2H_2 + O_2 \rightarrow \dot{O}H + \dot{H} + H_2O$

2) $\dot{H} + O_2\ (+M) \rightarrow H\dot{O}_2\ (+M)$ Intermediate T

$\mathbf{RH} + \boldsymbol{H\dot{O}_2} \rightarrow \boldsymbol{\dot{R}} + \boldsymbol{H_2O_2}$ (850 ≃ 1100 K)

$H_2O_2\ (+M) \rightarrow \dot{O}H + \dot{O}H\ (+M)$ chain branching

$R\dot{O}_2 \rightarrow$ olefin + $H\dot{O}_2$ (NTC)

$\dot{Q}OOH \rightarrow$ cyclic ether + $\dot{O}H$ (NTC)

3) $\dot{R} + O_2 \leftrightarrow R\dot{O}_2$ Low T (~500 ≃ 850 K)

$R\dot{O}_2 \rightleftharpoons \dot{Q}OOH \leftrightarrow \dot{O}_2QOOH \rightleftharpoons R\dot{O} + \dot{O}H + \dot{O}H$

Intermediate temperature chemistry:
$RH + H\dot{O}_2 = \dot{R} + H_2O_2$

- Few direct measurements of H-atom abstraction by $H\dot{O}_2$ – lack of suitable precursors
  - $CH_2O + H\dot{O}_2$ Jemi-Alade et al.[1] using flash photolysis
  - Walker et al.[2,3] made indirect relative rate measurements
  - Scott and Walker[4] review of alkanes, aromatics and related compounds in 2002
- Recent developments in quantitative measurements of $H\dot{O}_2$ radicals
  - Fluorescence assay by Gas Expansion by Blocquet et al.[5] (2013)
  - Dual-modulation Faraday Spectroscopy[6,7] (2014, 2015)
  - Cavity ring-down spectroscopy[8] (2014)

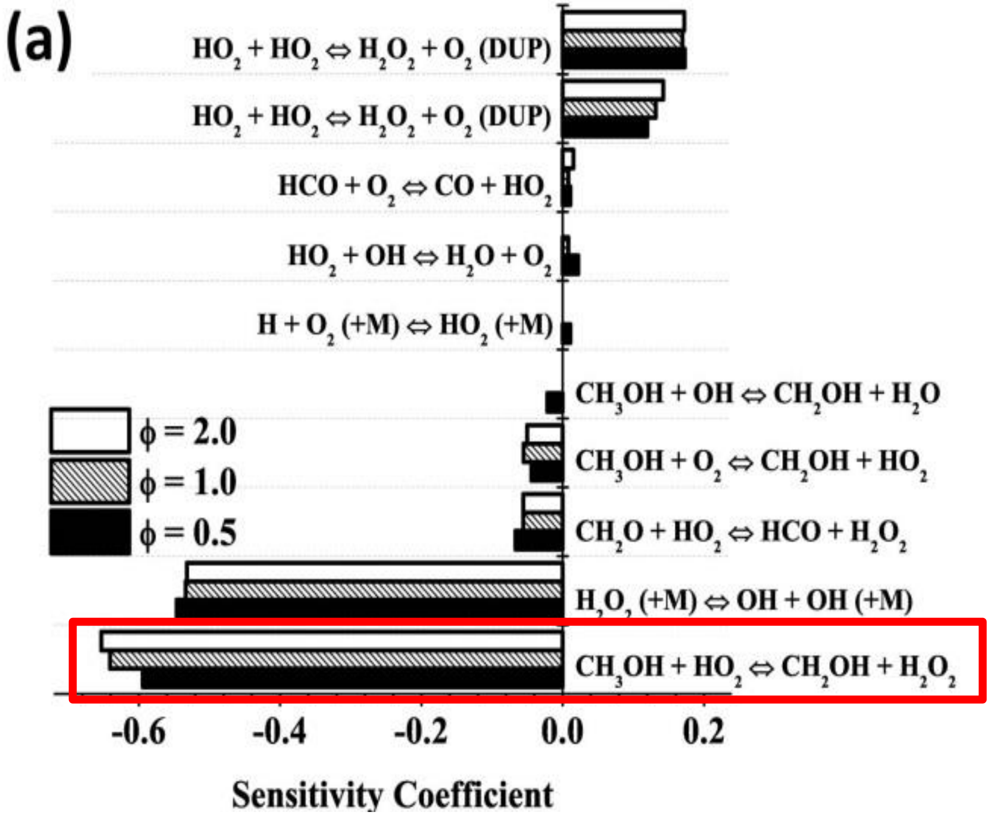
These measurements are very useful in assessing mechanism performance

[1] A.A. Jemi-Alade, P.D. Lightfoot, R. Lesclaux, Chem. Phys. Lett. 195 (1992) 25–30.
[2] R.R. Baldwin, R.W. Walker, Proc. Combust. Inst. 17 (1979) 525–533.
[3] R.W. Walker, C. Morley, in *Comprehensive Chem. Kinetics* (M. J. Pilling, Ed.), Elsevier, Amsterdam, 35:1 (1997).
[4] M. Scott, R.W. Walker, Combust. Flame 129 (2002) 365–377.
[5] M. Blocquet, C. Schoemaecker, D. Amedro, O. Herbinet, F. Battin-Leclerc, C. Fittschen, Proc. Natl. Acad. Sci. U. S. A. 110 (2013) 20014–20017.
[6] B. Brumfield, W.T. Sun, Y. Wang, Y. Ju, G. Wysocki, Opt. Lett. 39 (2014) 1783–1786.
[7] N. Kurimoto, B. Brumfield, X. Yang, T. Wada, P. Diévart, G. Wysocki, Y. Ju, Proc. Combust. Inst. 35(1) (2015) 457–464.
[8] M. Djehiche, N.L. Le Tan, C.D. Jain, G. Dayma, P. Dagaut, C. Chauveau, L. Pillier, A. Tomas, J. Am. Chem. Soc. 136 (2014) 16689–16694.

Intermediate temperature chemistry:
$RH + H\dot{O}_2 = \dot{R} + H_2O_2$

CH_3OH oxidation

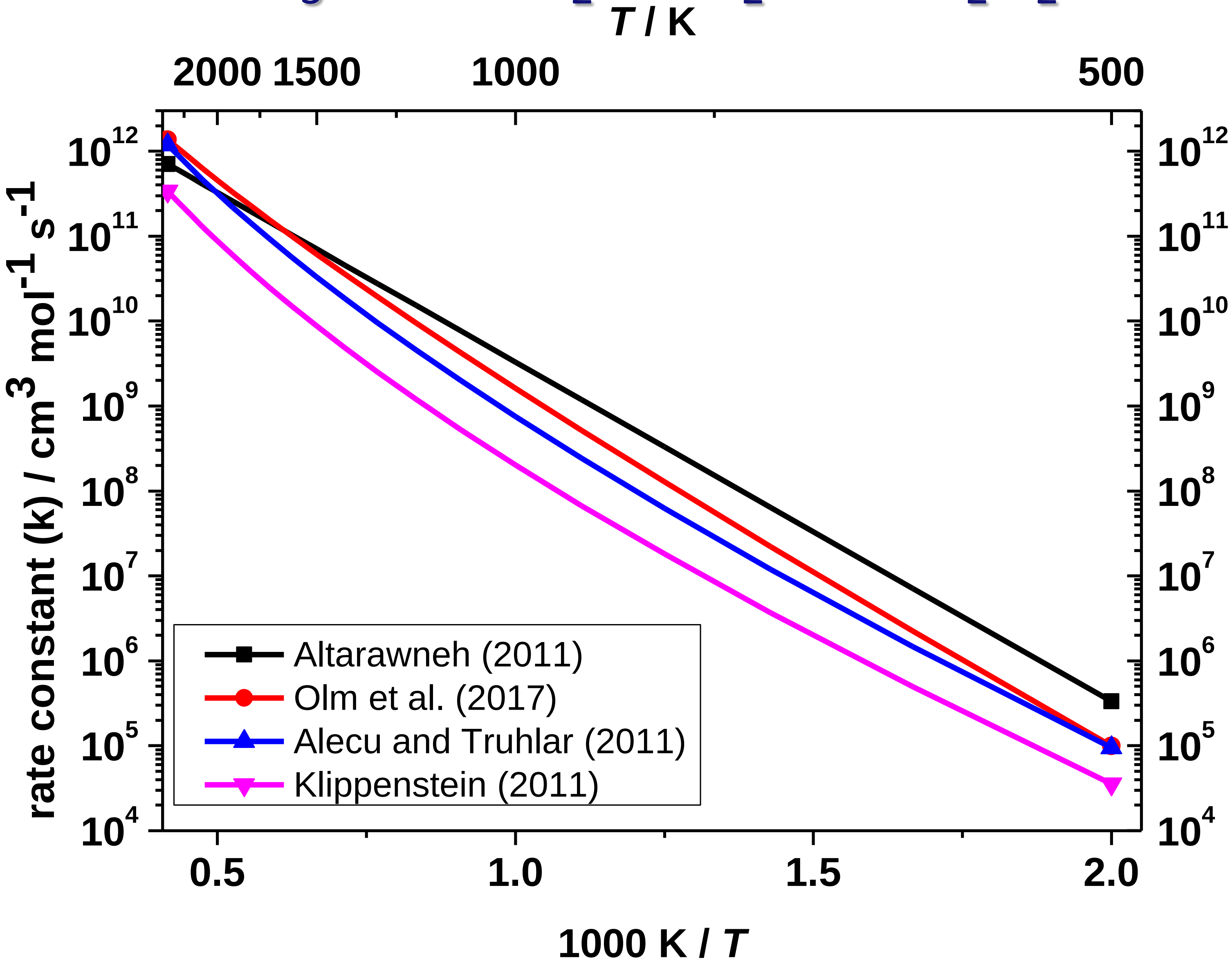
8.55% O_2, *p* = 40 atm and *T* = 885 K



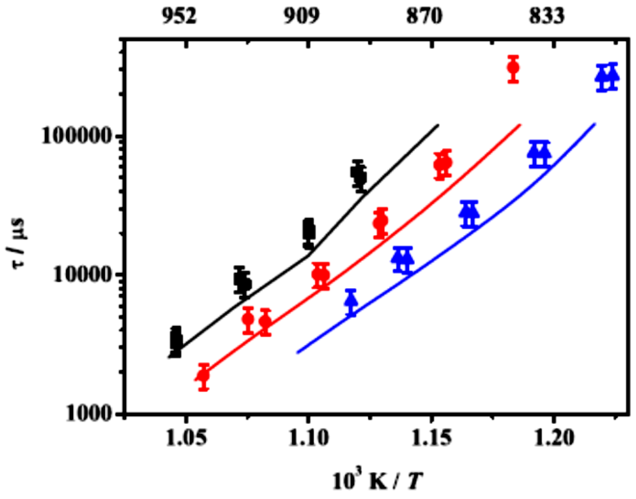
Sensitivity to ignition delay time

U. Burke, W.K. Metcalfe, S.M. Burke, K.A. Heufer, P. Dagaut, H.J. Curran, Combust. Flame 165 (2016) 125–136.

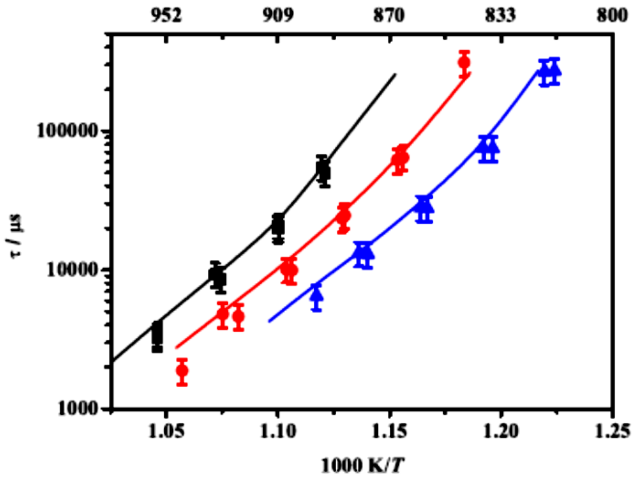
$CH_3OH + H\dot{O}_2 = \dot{C}H_2OH + H_2O_2$



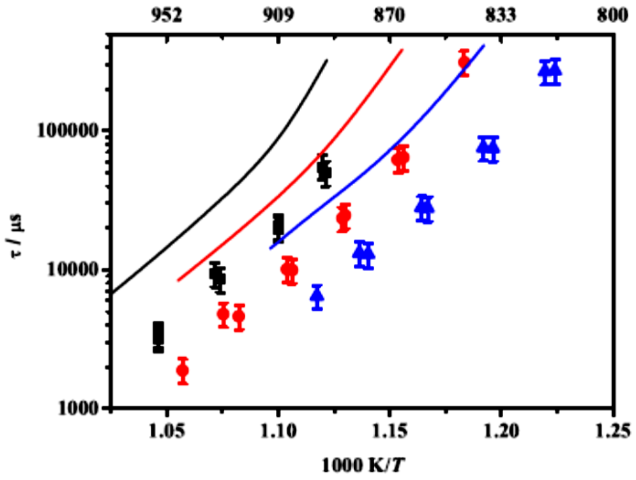
Influence of choice of k on τ



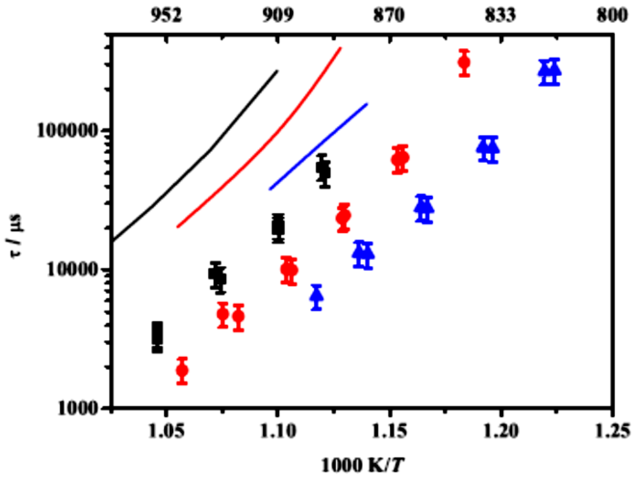
(a) Altarawneh *et al.*



(b) Olm et al.



(c) Alecu *et al.*



(d) Klippenstein *et al.*

Intermediate temperature chemistry: $RH + H\dot{O}_2 = \dot{R} + H_2O_2$

- ❑ Klippenstein et al.[1] reported high sensitivity to $CH_3OH + H\dot{O}_2$ also calculated *k*
- ❑ Altarawneh et al.[2] and Alecu and Truhlar[3]
- ❑ Olm et al.[4] via computer optimization using direct and indirect measurements
- ❑ Alecu and Truhlar attributed differences with Klippenstein et al. calculations to differences in treatment of anharmonicity

Possible chemically activated reactions involving $H\dot{O}_2$ radicals?

[1] S.J. Klippenstein, L.B. Harding, M.J. Davis, A.S. Tomlin, R.T. Skodje, Proc. Combust. Inst. 33 (2011) 351–357.
[2] M. Altarawneh, A.H. Al-Muhtaseb, B.Z. Dlugogorski, E.M. Kennedy, J.C. Mackie, J. Comp. Chem. 32 (2011) 1725–1733.
[3] I.M. Alecu, D.G. Truhlar, J. Phys. Chem. A 115 (2011) 14599–14611.
[4] C. Olm, T. Varga, É Valkó, H.J. Curran, T. Turányi, Combust. Flame 186 (2017) 45–64.

Intermediate temperature chemistry: $RH + H\dot{O}_2 = \dot{R} + H_2O_2$

- ☐ Carstensen and Dean[1,2] for CH_4, C_2H_6, C_3H_8, $C_4H_{10} + H\dot{O}_2$
- ☐ Aguilera-Iparraguirre et al.[3] CH_4, C_2H_6, C_3H_8, nC_4H_{10}, $iC_4H_{10} + H\dot{O}_2$
  - Agree well with the determinations of Walker et al.

[1] H.-H. Carstensen, A.M. Dean, Proc. Combust. Inst. 30 (2005) 995–1003.
[2] H.-H. Carstensen, A.M. Dean, O. Deutschmann, Proc. Combust. Inst. 31 (2007) 149–157.
[3] J. Aguilera-Iparraguirre, H.J. Curran, W. Klopper, J.M. Simmie, J. Phys. Chem. A 112 (2008) 7047–7054.

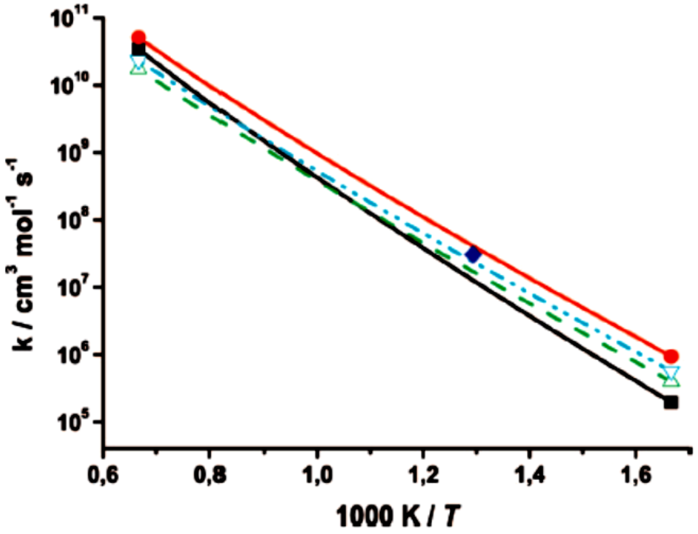


Figure 5. $k(C_3H_8 + HO_2^\bullet \rightarrow n\text{-}C_3H_7^\bullet + H_2O_2)$. This work (—■—), Carstensen[18] (—●—), Scott[8] (--Δ--), Orme[14] (-••▽-••), Baldwin[11] (◆).

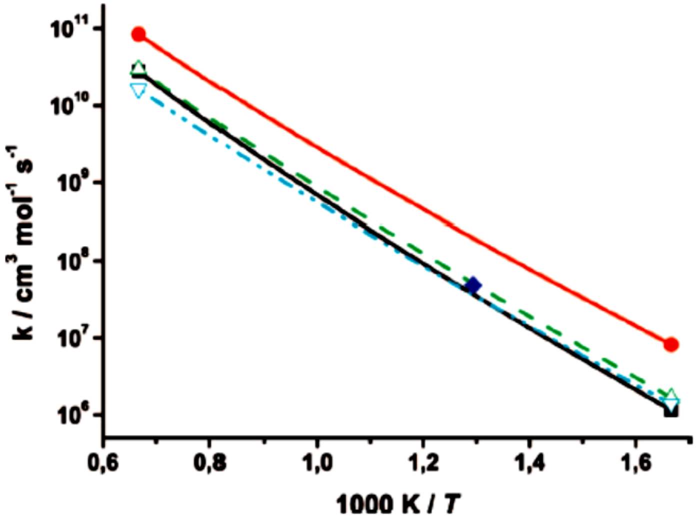


Figure 6. $k(C_3H_8 + HO_2^\bullet \rightarrow i\text{-}C_3H_7^\bullet + H_2O_2)$. This work (—■—), Carstensen[18] (—●—), Scott[8] (--Δ--), Orme[14] (-••▽-••), Baldwin[11] (◆).

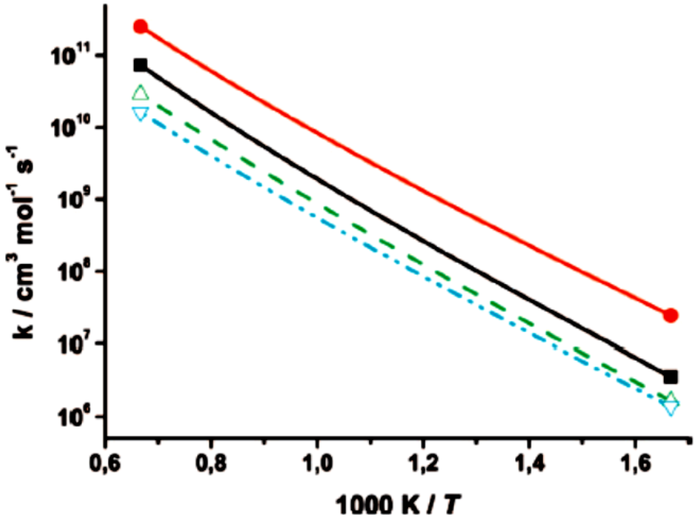


Figure 8. $k(n\text{-}C_4H_{10} + HO_2^\bullet \rightarrow s\text{-}C_4H_9^\bullet + H_2O_2)$. This work (—■—), Carstensen[18] (—●—), Scott[8] (--Δ--), Orme[14] (-••▽-••).

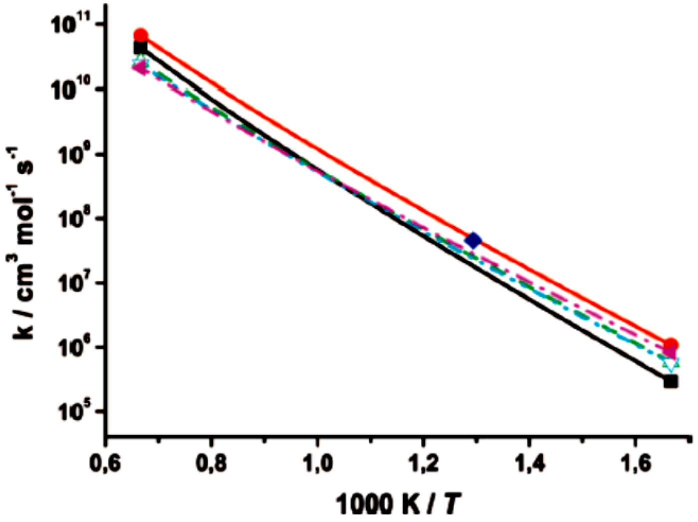
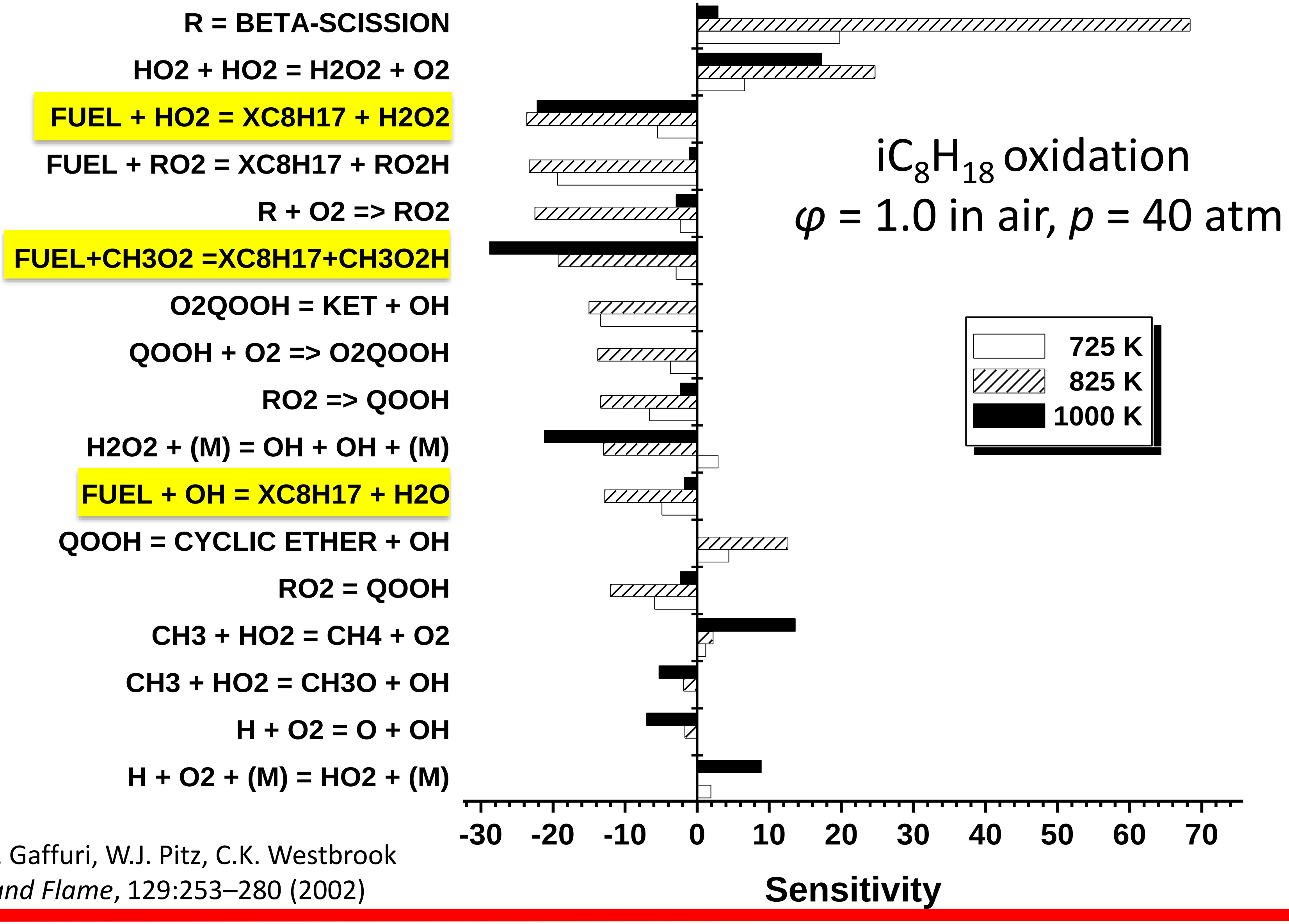


Figure 9. $k(i\text{-}C_4H_{10} + HO_2^\bullet \rightarrow i\text{-}C_4H_9^\bullet + H_2O_2)$. This work (—■—), Carstensen[18] (—●—), Scott[8] (--Δ--), Orme[14] (-••▽-••), Baldwin[11] (◆), Tsang[13] (-••-).

RH + $CH_3\dot{O}_2$ = $\dot{R}$ + CH_3O_2H can also be important



H.J. Curran, P. Gaffuri, W.J. Pitz, C.K. Westbrook
Combustion and Flame, 129:253–280 (2002)

$RH + CH_3\dot{O}_2 = \dot{R} + CH_3O_2H$

$$\dot{C}H_3 + O_2 = CH_3\dot{O}_2$$

$$RH + CH_3\dot{O}_2 = \dot{R} + CH_3O_2H$$

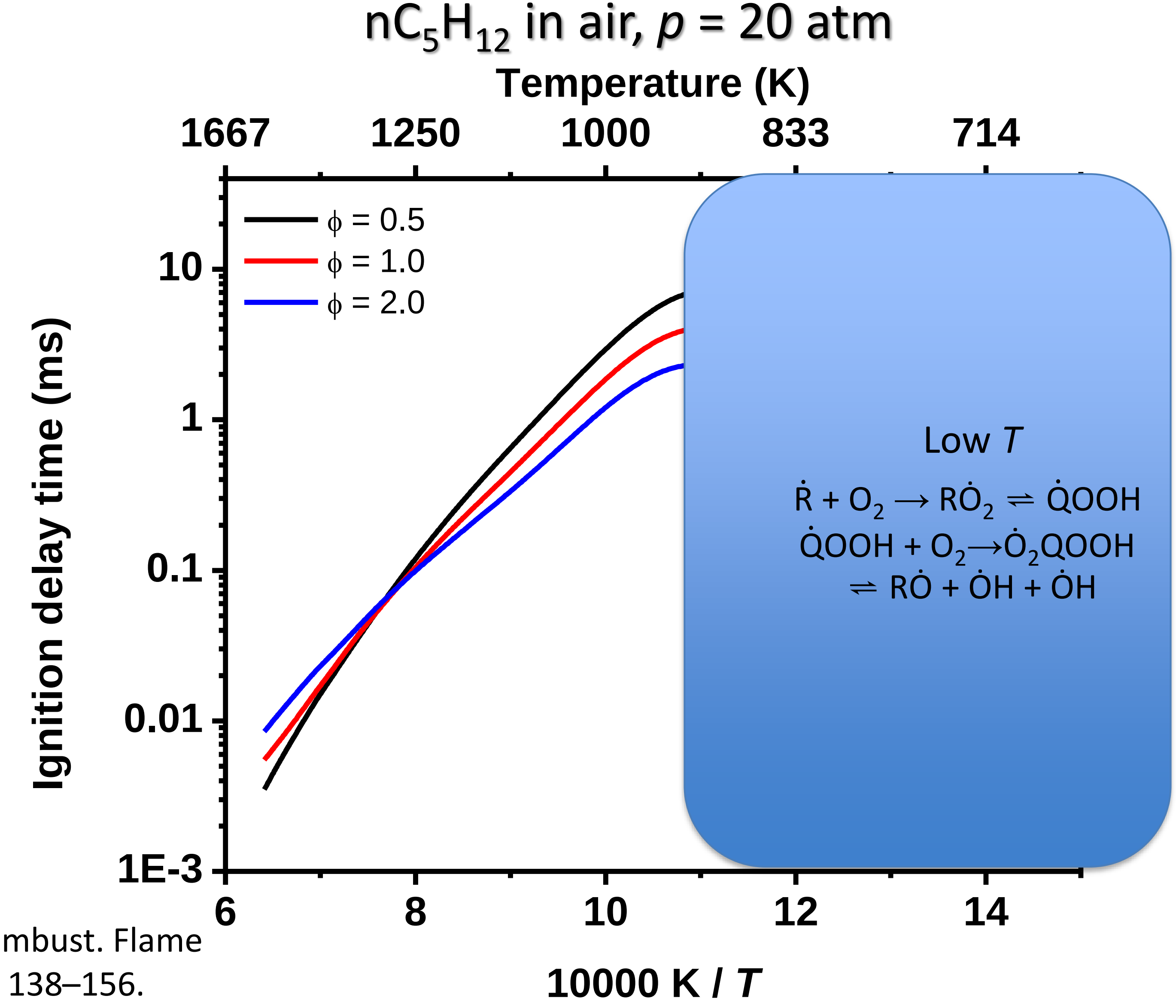
$$CH_3O_2H = CH_3\dot{O} + \dot{O}H$$

- Carstensen and Dean[1] for $CH_4/C_2H_6 + \dot{H}/CH_3\dot{O}_2/C_2H_5\dot{O}_2$
- Carstensen,Dean,Deutschmann[2] for CH_4, C_2H_6, C_3H_8, C_4H_{10} + $H\dot{O}_2$, $CH_3\dot{O}_2$, $C_2H_5\dot{O}_2$, $C_3H_7\dot{O}_2$, $C_3H_7\dot{O}_2$, $HC(O)\dot{O}_2$, $CH_3C(O)\dot{O}_2$

[1] H.-H. Carstensen, A.M. Dean, Proc. Combust. Inst. 30 (2005) 995–1003.

[2] H.-H. Carstensen, A.M. Dean, O. Deutschmann, Proc. Combust. Inst. 31 (2007) 149–157.

Three distinct temperature regimes



Low *T*

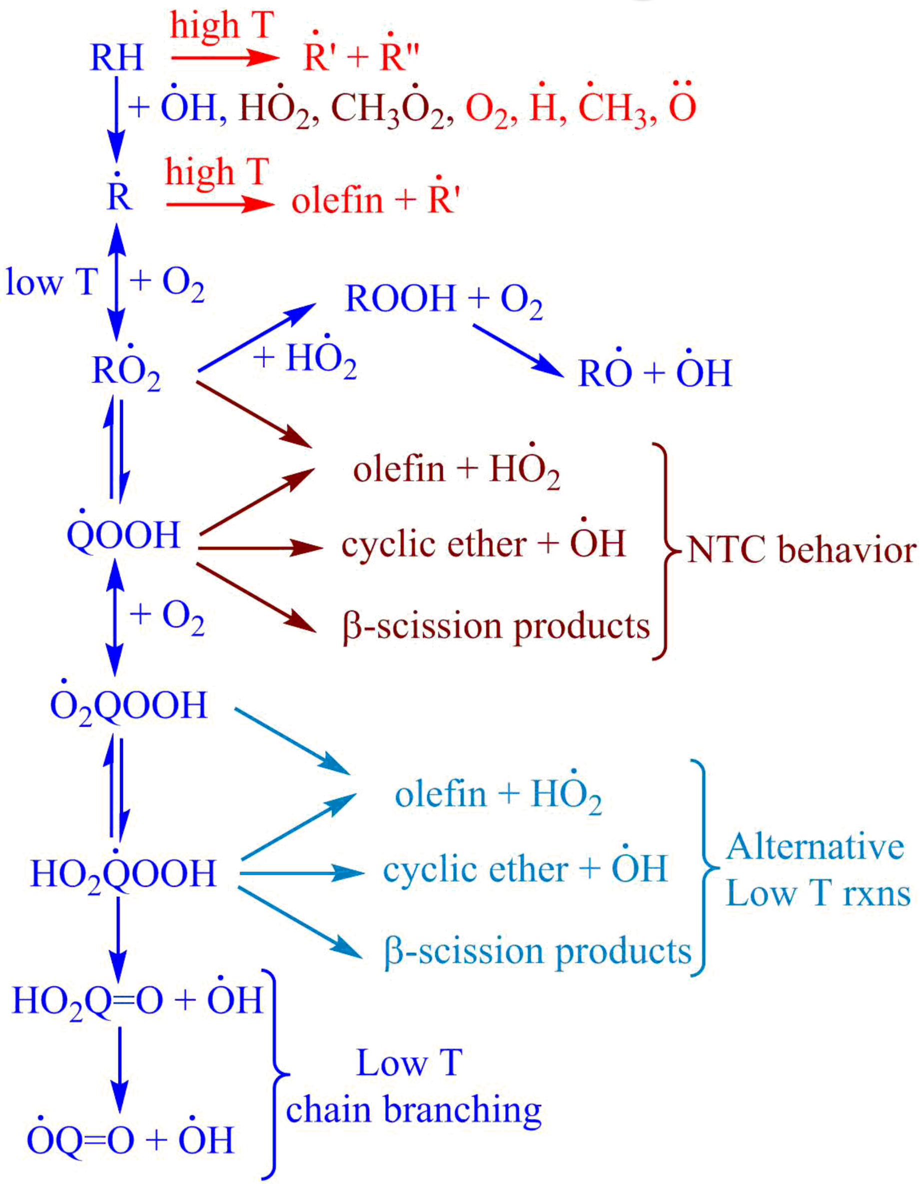
$\dot{R} + O_2 \longrightarrow R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$

$\dot{Q}OOH + O_2 \longrightarrow \dot{O}_2QOOH$

$\rightleftharpoons R\dot{O} + \dot{O}H + \dot{O}H$

J. Bugler et al., Combust. Flame 163(1) (2016) 138–156.

Rate rules for large molecular weight molecules



$RH \xrightarrow{\text{high T}} \dot{R}' + \dot{R}''$

$+\ \dot{O}H,\ H\dot{O}_2,\ CH_3\dot{O}_2,\ O_2,\ \dot{H},\ \dot{C}H_3,\ \ddot{O}$

$\dot{R} \xrightarrow{\text{high T}} \text{olefin} + \dot{R}'$

low T $+\ O_2$

$R\dot{O}_2$

$+\ H\dot{O}_2$

$ROOH + O_2$

$R\dot{O} + \dot{O}H$

olefin + $H\dot{O}_2$

cyclic ether + $\dot{O}H$

β-scission products

NTC behavior

$\dot{Q}OOH$

$+\ O_2$

$\dot{O}_2QOOH$

olefin + $H\dot{O}_2$

cyclic ether + $\dot{O}H$

β-scission products

Alternative
Low T rxns

$HO_2\dot{Q}OOH$

$HO_2Q{=}O + \dot{O}H$

$\dot{O}Q{=}O + \dot{O}H$

Low T
chain branching

Reaction rate rules for higher MW species

- *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 + O_2 = olefin + $H\dot{O}_2$

  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

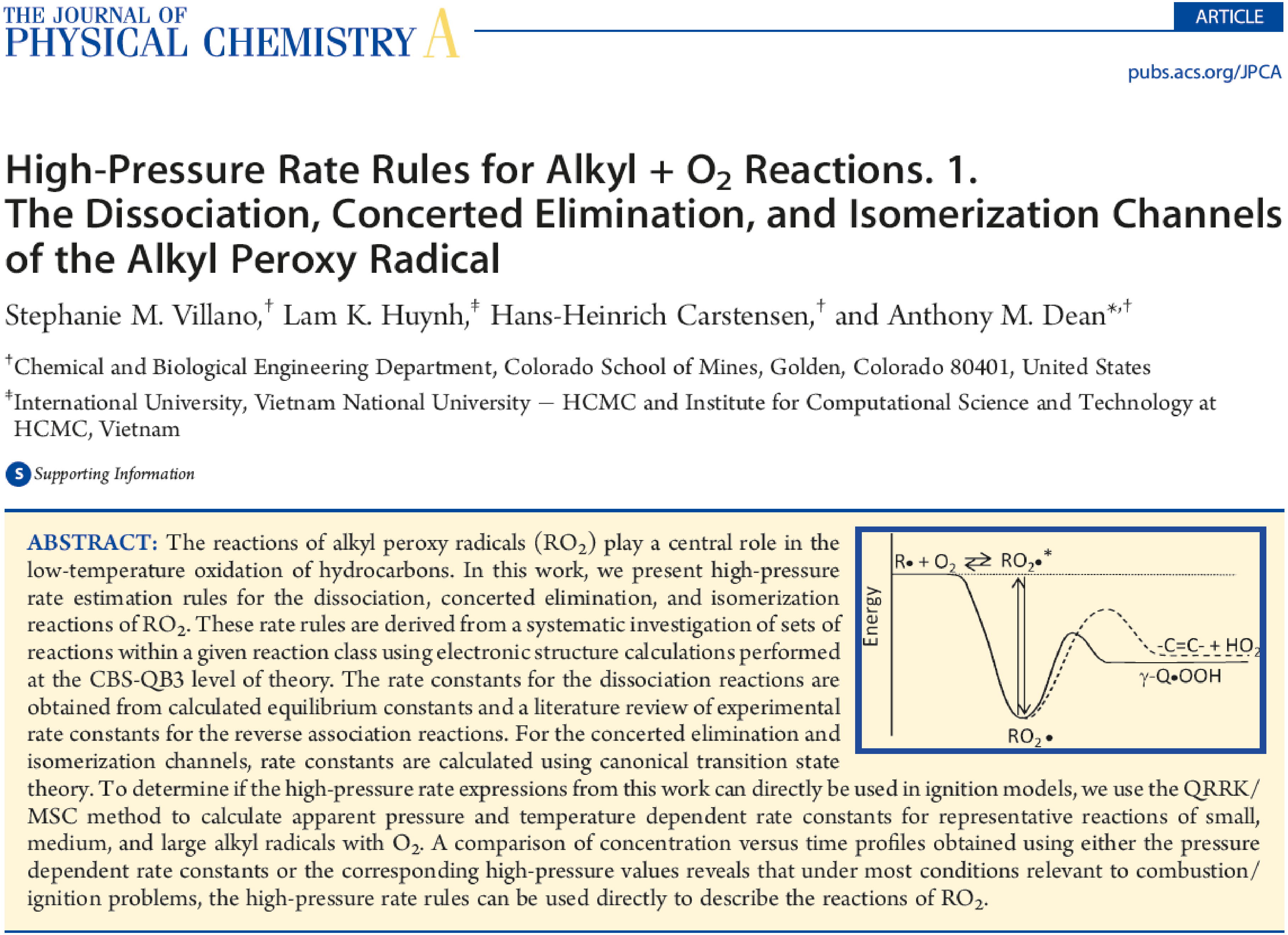
Slide Courtesy of Dr. William Pitz

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 = Cyclic Ether + $\dot{O}H$
Reaction class 20: QOOH = Olefin + $H\dot{O}_2$
Reaction class 21: QOOH = Olefin + 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 $H\dot{O}_2$

Slide Courtesy of Dr. William Pitz



THE JOURNAL OF PHYSICAL CHEMISTRY A

ARTICLE

pubs.acs.org/JPCA

High-Pressure Rate Rules for Alkyl + O_2 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

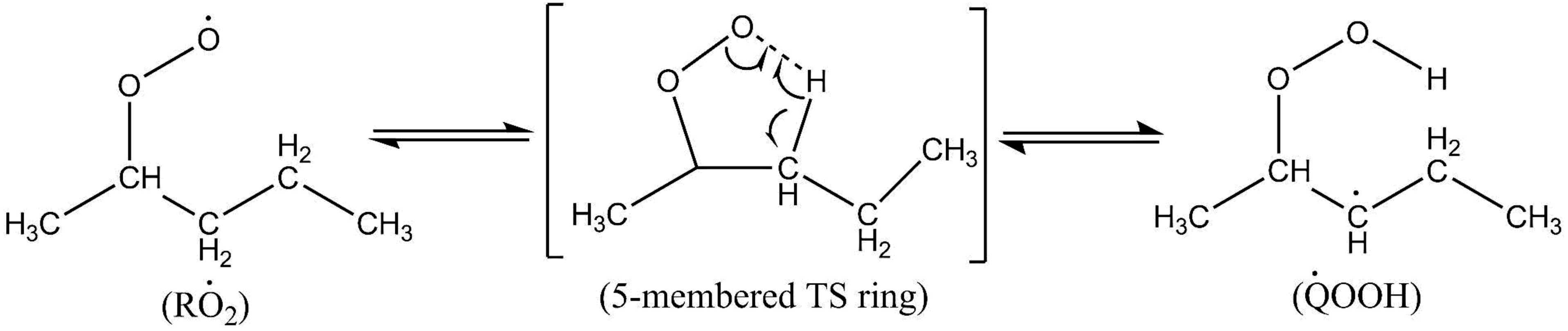
Ⓢ *Supporting Information*

ABSTRACT: The reactions of alkyl peroxy radicals (RO_2) 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 RO_2. 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 O_2. 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 RO_2.

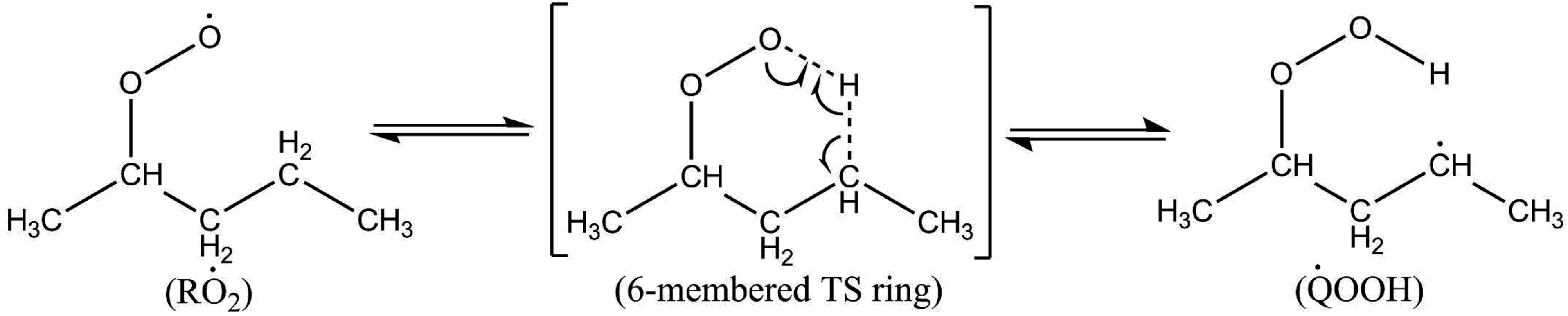
$R\dot{O}_2 \rightleftharpoons$ QOOH isomerization reactions

Class 12

5-membered ring isomerization: $k_5 = 2.0\times10^{11}\exp(-26450/RT)$

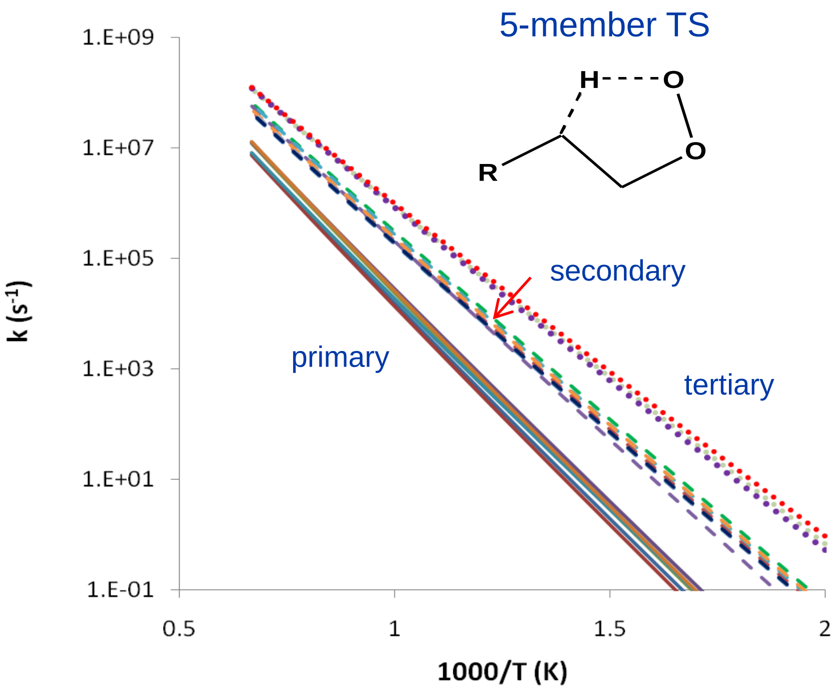


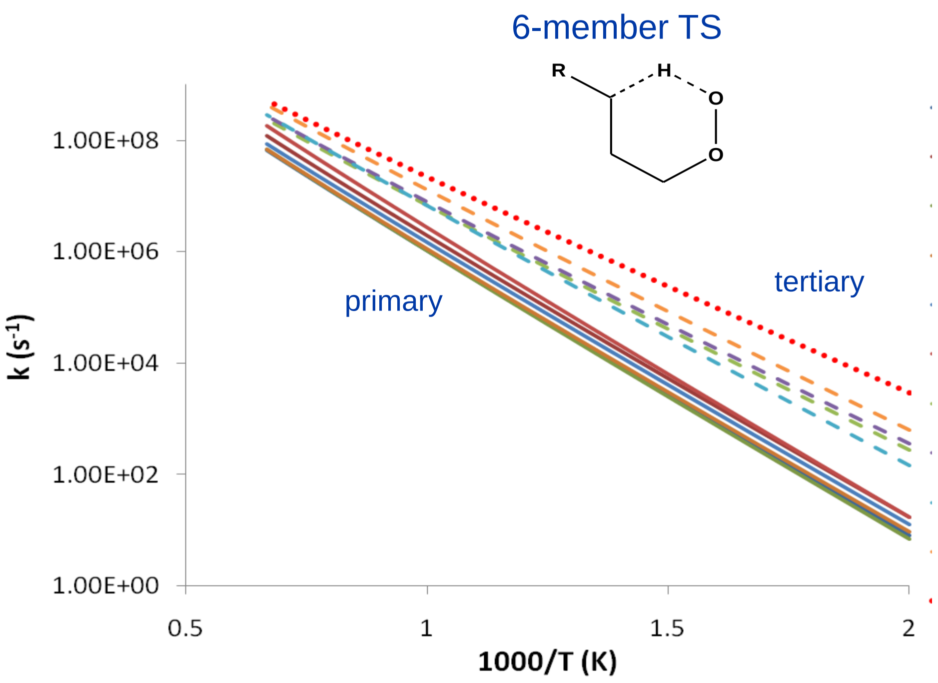
6-membered ring isomerization: $k_6 = 2.5\times10^{10}\exp(-20450/RT)$



Correlations between structure and reactivity

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

$R\dot{O}_2 \rightleftharpoons$ QOOH isomerization

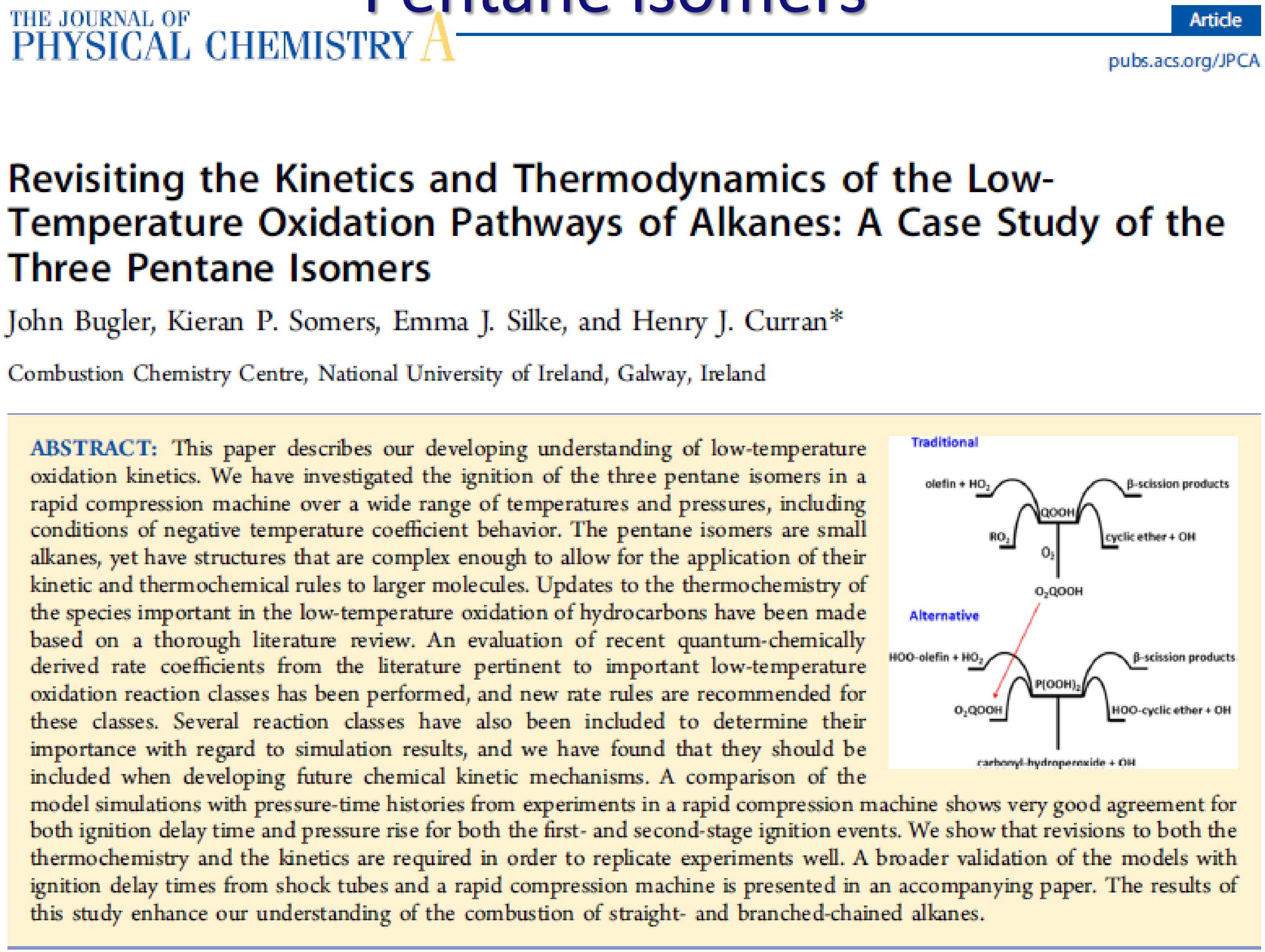
$R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$

		Curran *et al.*			Villano *et al.*		
Ring size	Site	*A*	*n*	*E*	*A*	*n*	*E*
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.

Pentane isomers



THE JOURNAL OF
PHYSICAL CHEMISTRY A

Article

pubs.acs.org/JPCA

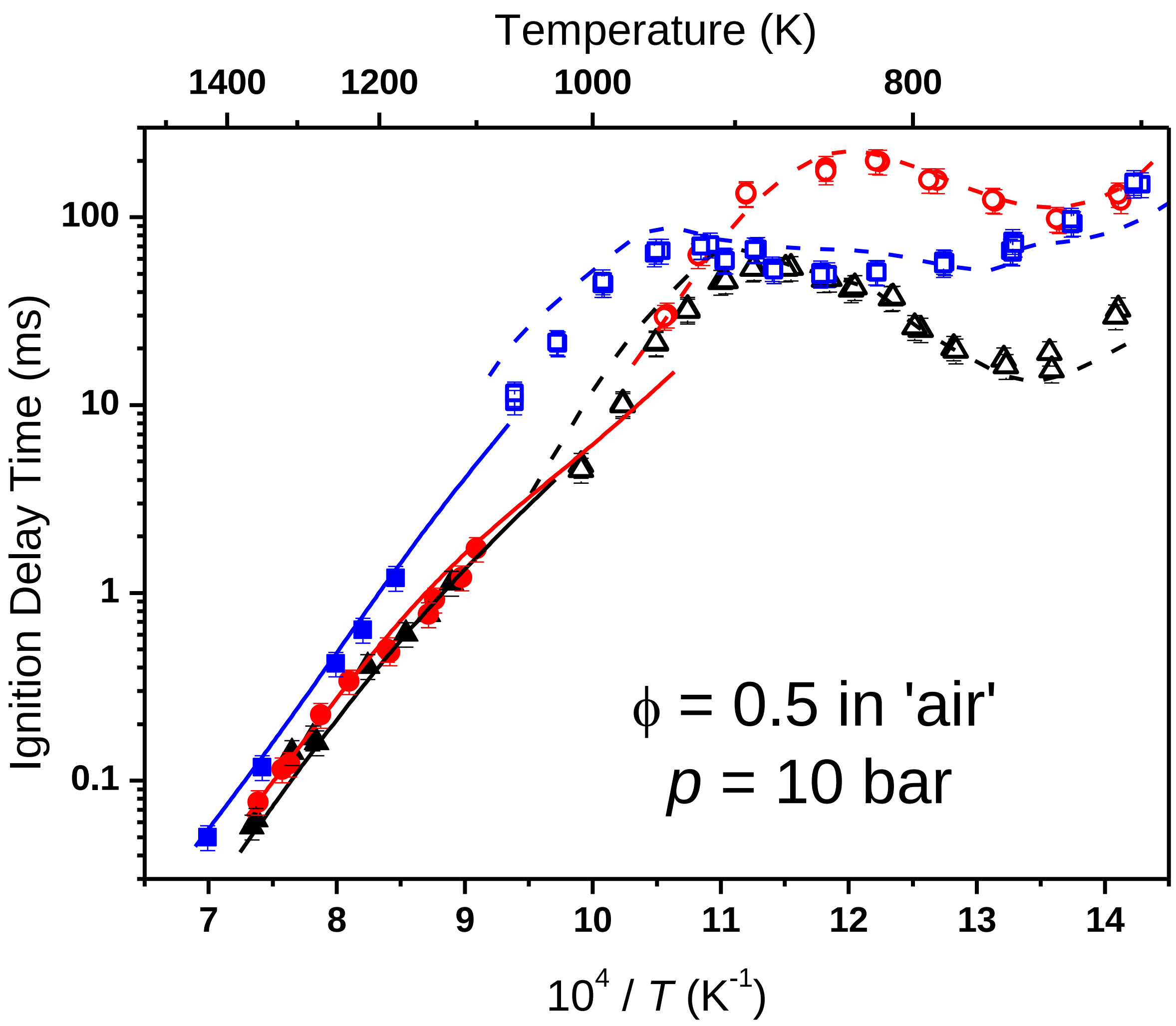
Revisiting the Kinetics and Thermodynamics of the Low-Temperature Oxidation Pathways of Alkanes: A Case Study of the Three Pentane Isomers

John Bugler, Kieran P. Somers, Emma J. Silke, and Henry J. Curran*

Combustion Chemistry Centre, National University of Ireland, Galway, Ireland

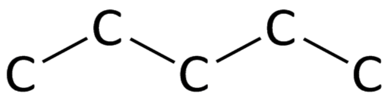
ABSTRACT: This paper describes our developing understanding of low-temperature oxidation kinetics. We have investigated the ignition of the three pentane isomers in a rapid compression machine over a wide range of temperatures and pressures, including conditions of negative temperature coefficient behavior. The pentane isomers are small alkanes, yet have structures that are complex enough to allow for the application of their kinetic and thermochemical rules to larger molecules. Updates to the thermochemistry of the species important in the low-temperature oxidation of hydrocarbons have been made based on a thorough literature review. An evaluation of recent quantum-chemically derived rate coefficients from the literature pertinent to important low-temperature oxidation reaction classes has been performed, and new rate rules are recommended for these classes. Several reaction classes have also been included to determine their importance with regard to simulation results, and we have found that they should be included when developing future chemical kinetic mechanisms. A comparison of the model simulations with pressure-time histories from experiments in a rapid compression machine shows very good agreement for both ignition delay time and pressure rise for both the first- and second-stage ignition events. We show that revisions to both the thermochemistry and the kinetics are required in order to replicate experiments well. A broader validation of the models with ignition delay times from shock tubes and a rapid compression machine is presented in an accompanying paper. The results of this study enhance our understanding of the combustion of straight- and branched-chained alkanes.

Success of reaction rate rules: e.g. pentane isomers



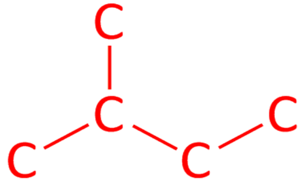
J. Bugler et al. Combust. Flame 163(1) (2016) 138–156.

***n*-Pentane**



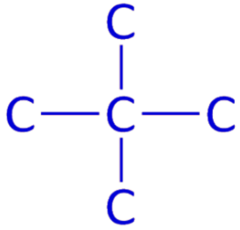
(RON = 61.7)

***iso*-Pentane**



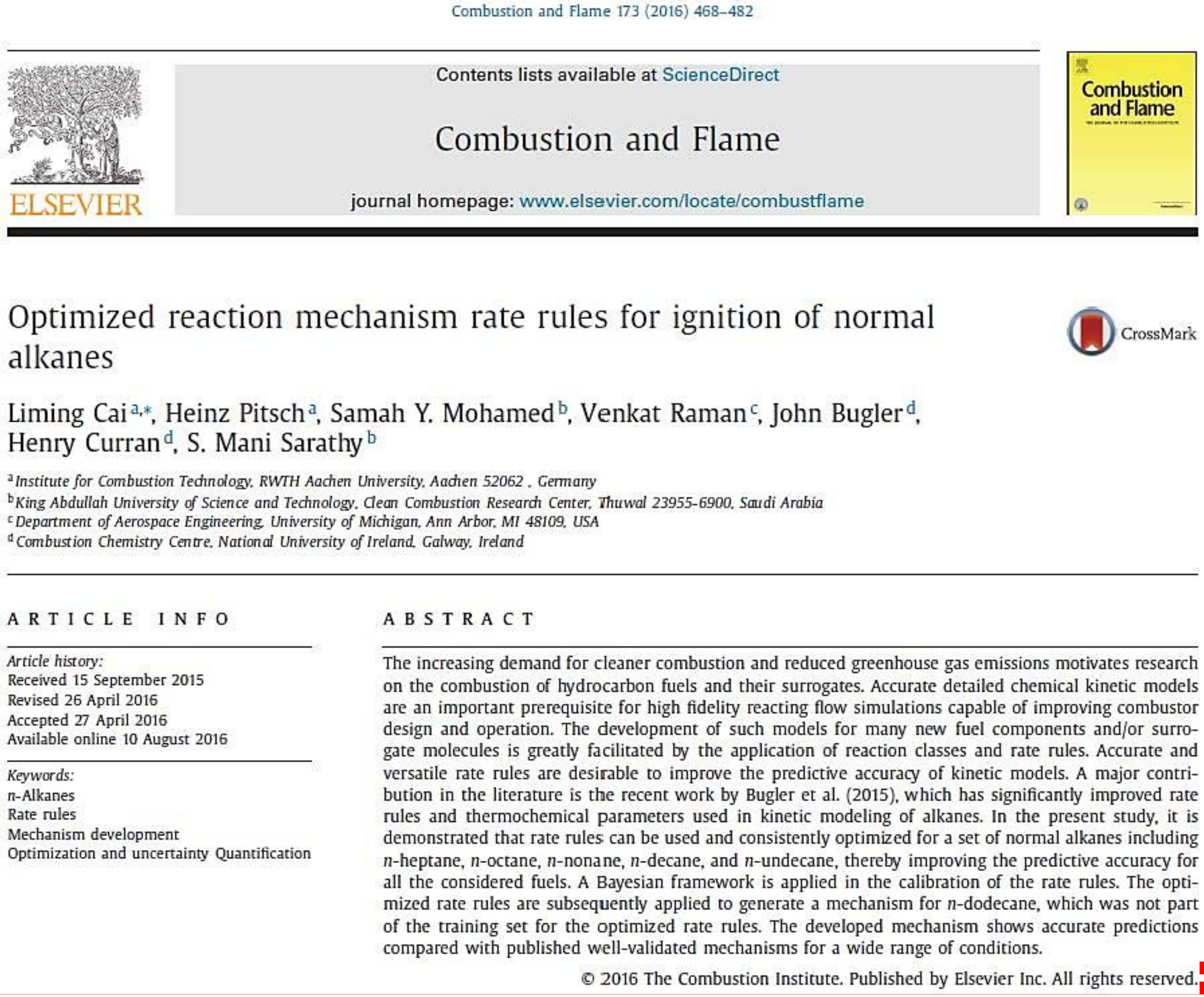
(RON = 92.3)

***neo*-Pentane**



(RON = 85.5)

Rate rules applied to larger alkanes



Combustion and Flame 173 (2016) 468–482

Contents lists available at ScienceDirect

Combustion and Flame

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

Optimized reaction mechanism rate rules for ignition of normal alkanes

Liming Cai[a,*], Heinz Pitsch[a], Samah Y. Mohamed[b], Venkat Raman[c], John Bugler[d], Henry Curran[d], S. Mani Sarathy[b]

[a] Institute for Combustion Technology, RWTH Aachen University, Aachen 52062 , Germany
[b] King Abdullah University of Science and Technology, Clean Combustion Research Center, Thuwal 23955-6900, Saudi Arabia
[c] Department of Aerospace Engineering, University of Michigan, Ann Arbor, MI 48109, USA
[d] Combustion Chemistry Centre, National University of Ireland, Galway, Ireland

ARTICLE INFO

Article history:
Received 15 September 2015
Revised 26 April 2016
Accepted 27 April 2016
Available online 10 August 2016

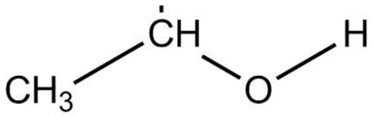
Keywords:
n-Alkanes
Rate rules
Mechanism development
Optimization and uncertainty Quantification

ABSTRACT

The increasing demand for cleaner combustion and reduced greenhouse gas emissions motivates research on the combustion of hydrocarbon fuels and their surrogates. Accurate detailed chemical kinetic models are an important prerequisite for high fidelity reacting flow simulations capable of improving combustor design and operation. The development of such models for many new fuel components and/or surrogate molecules is greatly facilitated by the application of reaction classes and rate rules. Accurate and versatile rate rules are desirable to improve the predictive accuracy of kinetic models. A major contribution in the literature is the recent work by Bugler et al. (2015), which has significantly improved rate rules and thermochemical parameters used in kinetic modeling of alkanes. In the present study, it is demonstrated that rate rules can be used and consistently optimized for a set of normal alkanes including *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, and *n*-undecane, thereby improving the predictive accuracy for all the considered fuels. A Bayesian framework is applied in the calibration of the rate rules. The optimized rate rules are subsequently applied to generate a mechanism for *n*-dodecane, which was not part of the training set for the optimized rate rules. The developed mechanism shows accurate predictions compared with published well-validated mechanisms for a wide range of conditions.

Expanded for other classes e.g. Alcohols

- Alcohols are less reactive than their corresponding alkane
  - n-pentanol (RON = 80) slower to ignite compared to pentane (RON = 61.7)
  - Hydrogen atoms on carbon alpha to –OH alcohol functional group are weakest
  - Da Silva et al.[1] showed concerted elimination reaction Ea = 11.4 kcal mol^{-1}

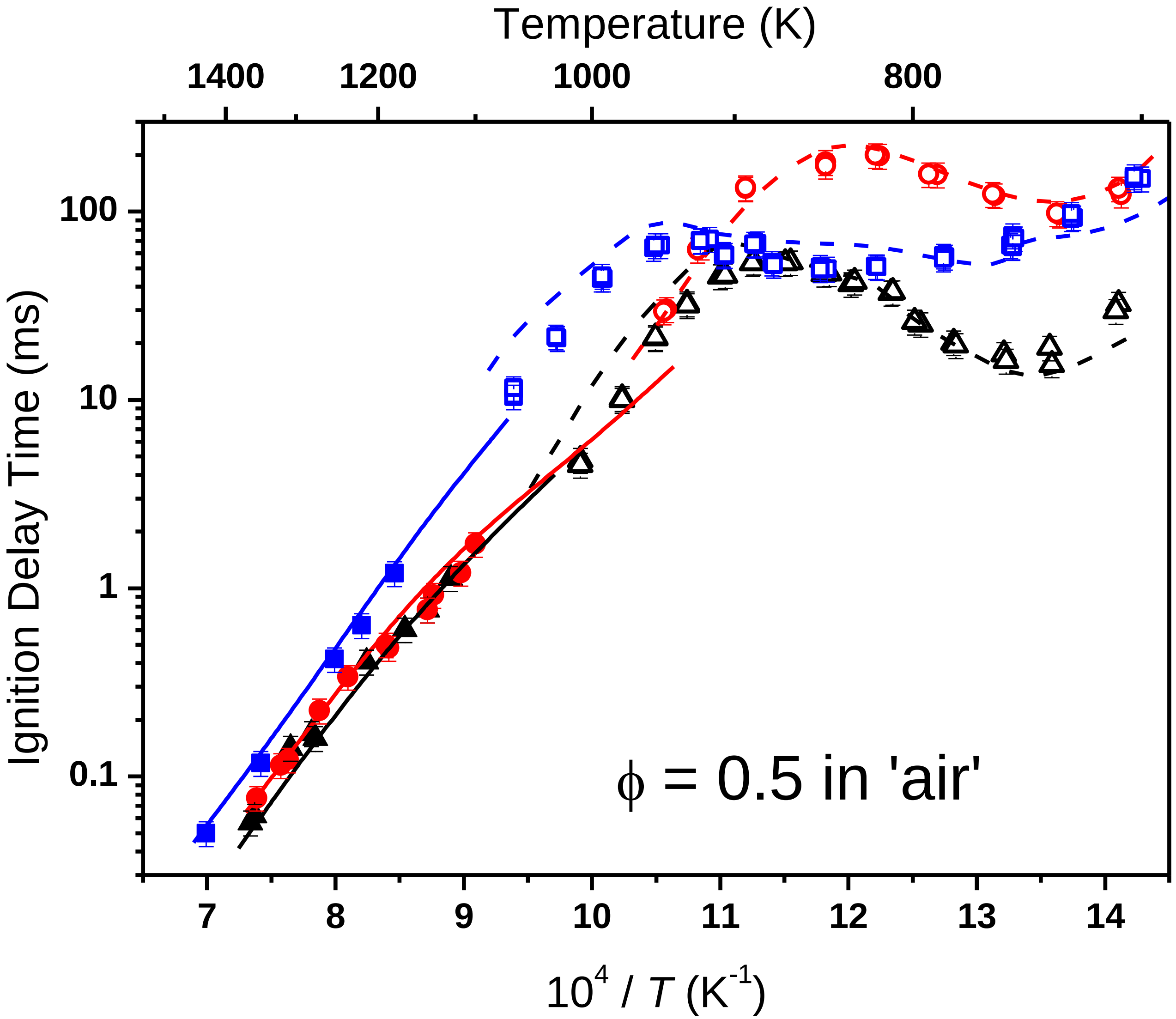


[1] G. da Silva, J.W. Bozzelli, L. Liang, J.T. Farrell, J. Phys. Chem. A 113 (2009) 8923–8933.

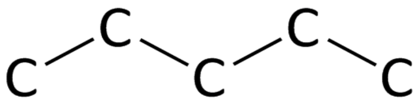
Software for automatic mechanism development

- ☐ Semi-detailed mechanisms using automatic reaction generator MAMOX code (Ranzi and Faravelli, 1995—1997)
- ☐ Computer-aided automatic generation for large aliphatic HC molecules
  - Chevalier et al. 1990 (did not include reaction rate details)
  - REACTION (Morley and Blurock, 1993—1995)
    - Enhanced by Moréac – generated nC_7H_{16}, $nC_{10}H_{22}$
  - EXGAS – Battin-Leclerc et al. (2005) (initial work by Haux et al. 1985—1988)
    - Comprehensive C_0–C_2 base with lumped secondary mechanism from KINGAS
    - Thermodynamic parameters from THERGAS
  - Genesys[1,2] – Van Geem 2012—2015 (Ghent University)
  - Reaction Mechanism Generator (RMG) – Green and West (MIT/Northwestern)
    - Mechanisms include elementary reaction steps
    - Include species identifiers

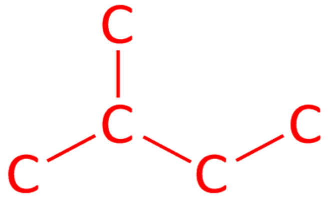
Model vs Experiments



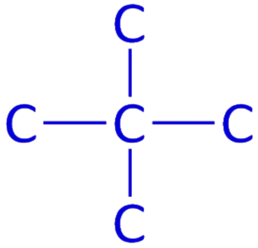
***n*-Pentane**



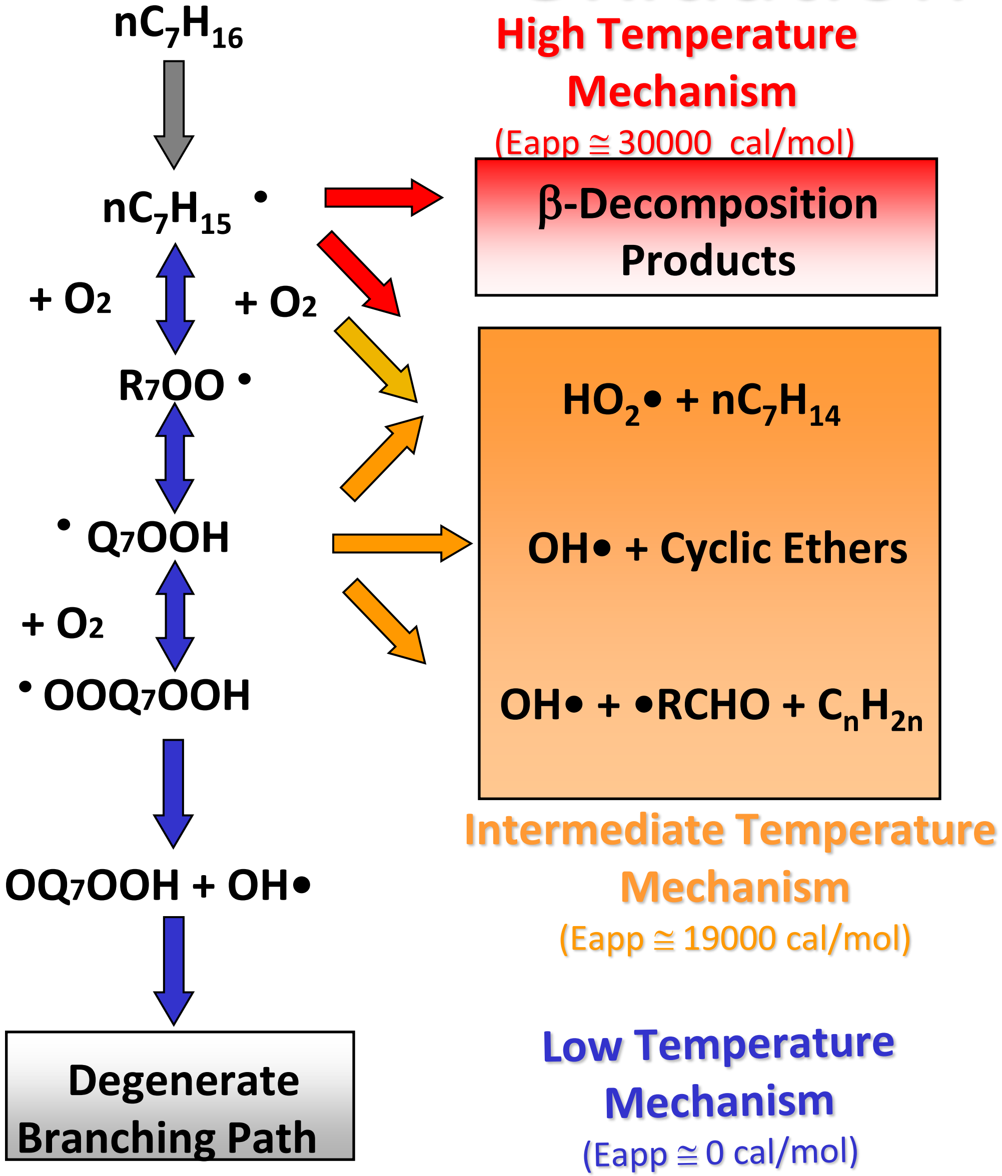
***iso*-Pentane**



***neo*-Pentane**



Oxidation of alkanes



nC_7H_{16}

$nC_7H_{15}\bullet$

$+ O_2$

$+ O_2$

$R_7OO\bullet$

$\bullet Q_7OOH$

$+ O_2$

$\bullet OOQ_7OOH$

$OQ_7OOH + OH\bullet$

Degenerate Branching Path

High Temperature Mechanism

(Eapp ≅ 30000 cal/mol)

β-Decomposition Products

$HO_2\bullet + nC_7H_{14}$

$OH\bullet$ + Cyclic Ethers

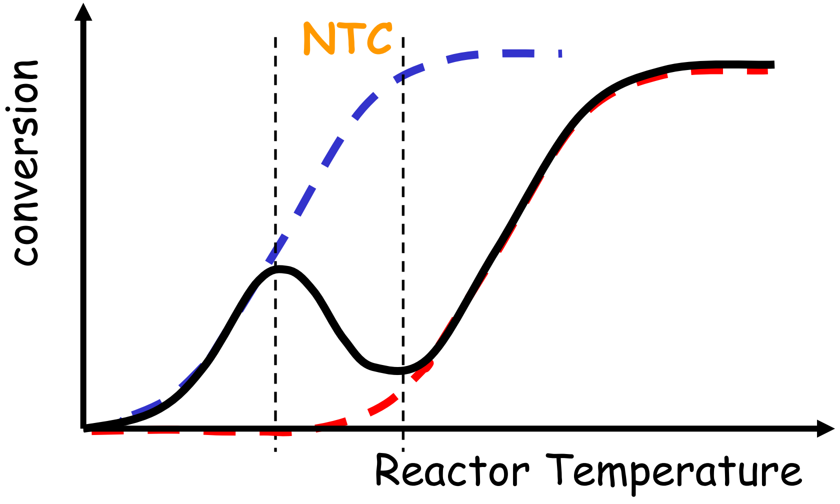
$OH\bullet + \bullet RCHO + C_nH_{2n}$

Intermediate Temperature Mechanism

(Eapp ≅ 19000 cal/mol)

Low Temperature Mechanism

(Eapp ≅ 0 cal/mol)



Courtesy of Prof. Tiziano Faravelli, Politecnico di Milano

Mechanism competition

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

$$\boxed{R\bullet + O_2 \rightleftharpoons ROO\bullet}$$

$k_{add} = 10^9$ [L/mol/s]

$k_{dec} = 10^{13} \exp(-28000/RT)$ [1/s]

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:

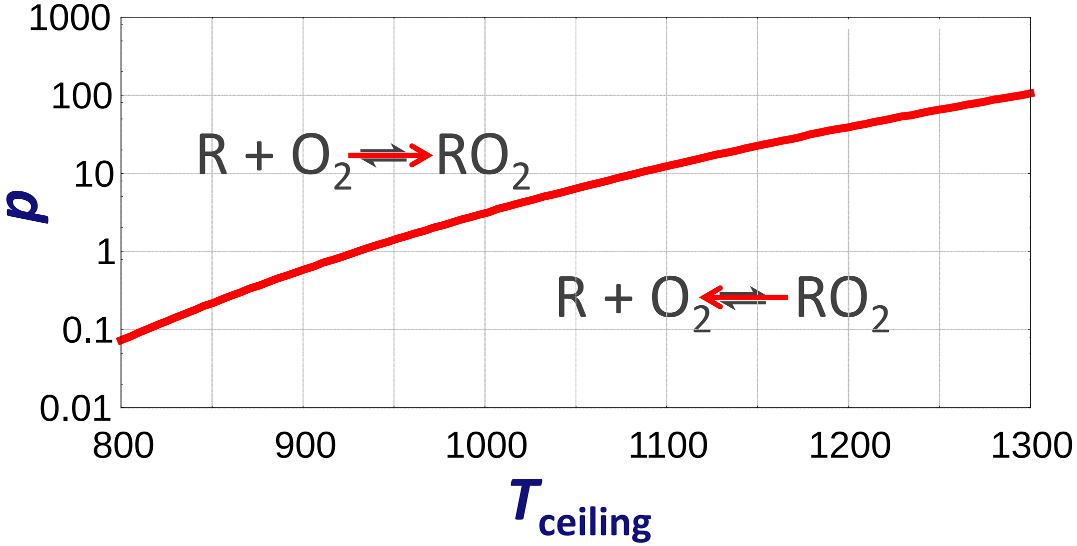
$$r_{add} = r_{dec} \Longrightarrow k_{add}[R\bullet][O_2] = k_{dec}[ROO\bullet]$$

Courtesy of Prof. Tiziano Faravelli, Politecnico di Milano

Ceiling temperature vs. pressure

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

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

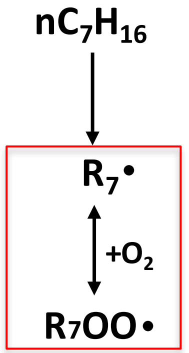


p in atm, R = 0.0821 L atm K^{-1} mol^{-1}

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

Courtesy of Prof. Tiziano Faravelli, Politecnico di Milano

Ceiling temperature vs. pressure



nC_7H_{16}

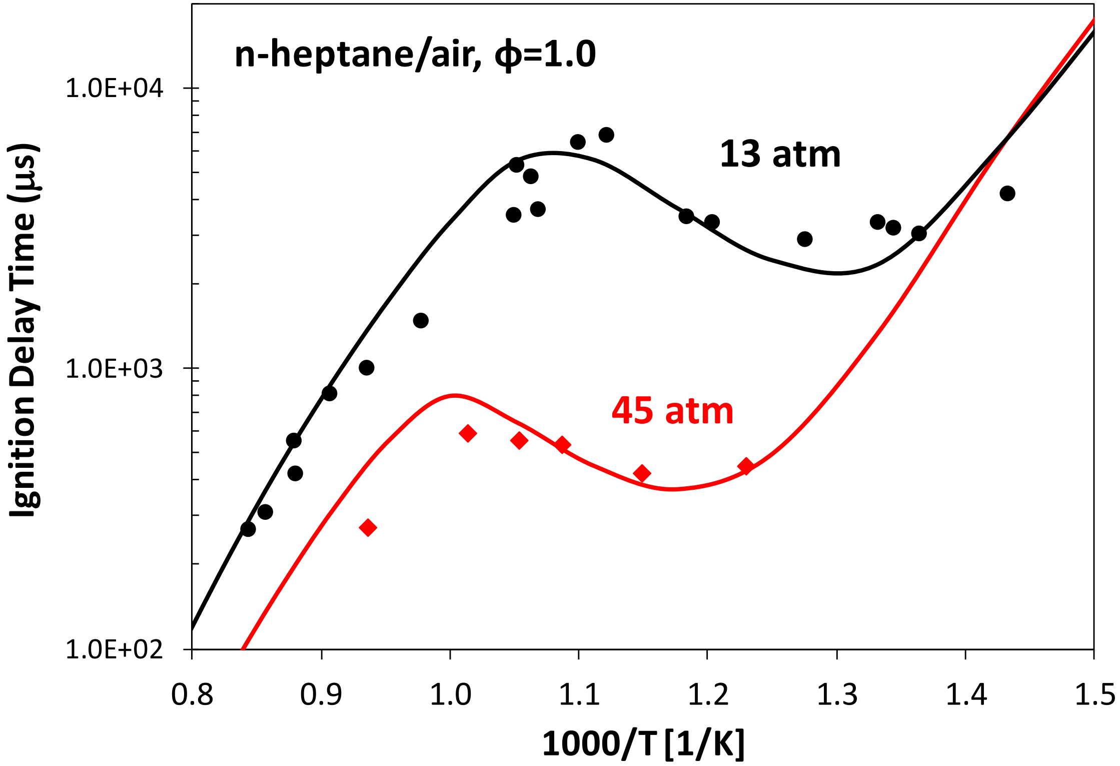
$R_7\bullet$

$+O_2$

$R_7OO\bullet$

$T_{ceiling}$

$$\frac{[R]}{[RO_2]} = \frac{k_{DEC}}{k_{ADD}[O_2]}$$



Bugler et al., *Journal of Physical Chemistry A, 2015*

Goldsmith et al., *Journal of Physical Chemistry A, 2012*

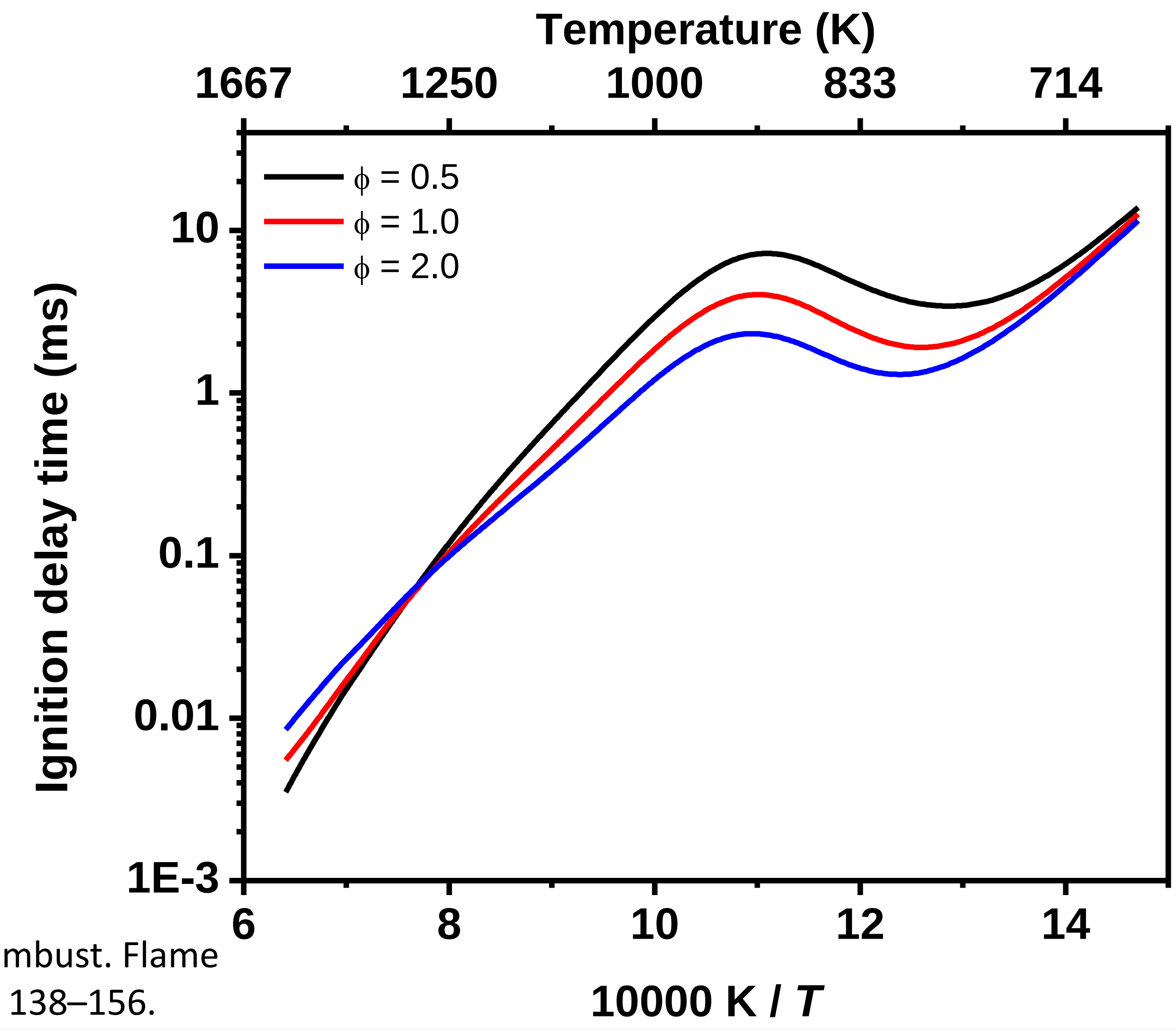
Ciezki et al., *Combustion and Flame, 1993*

Pelucchi et al., *Energy & Fuels, 2014*

Courtesy of Dr Matteo Pelucchi, Politecnico di Milano

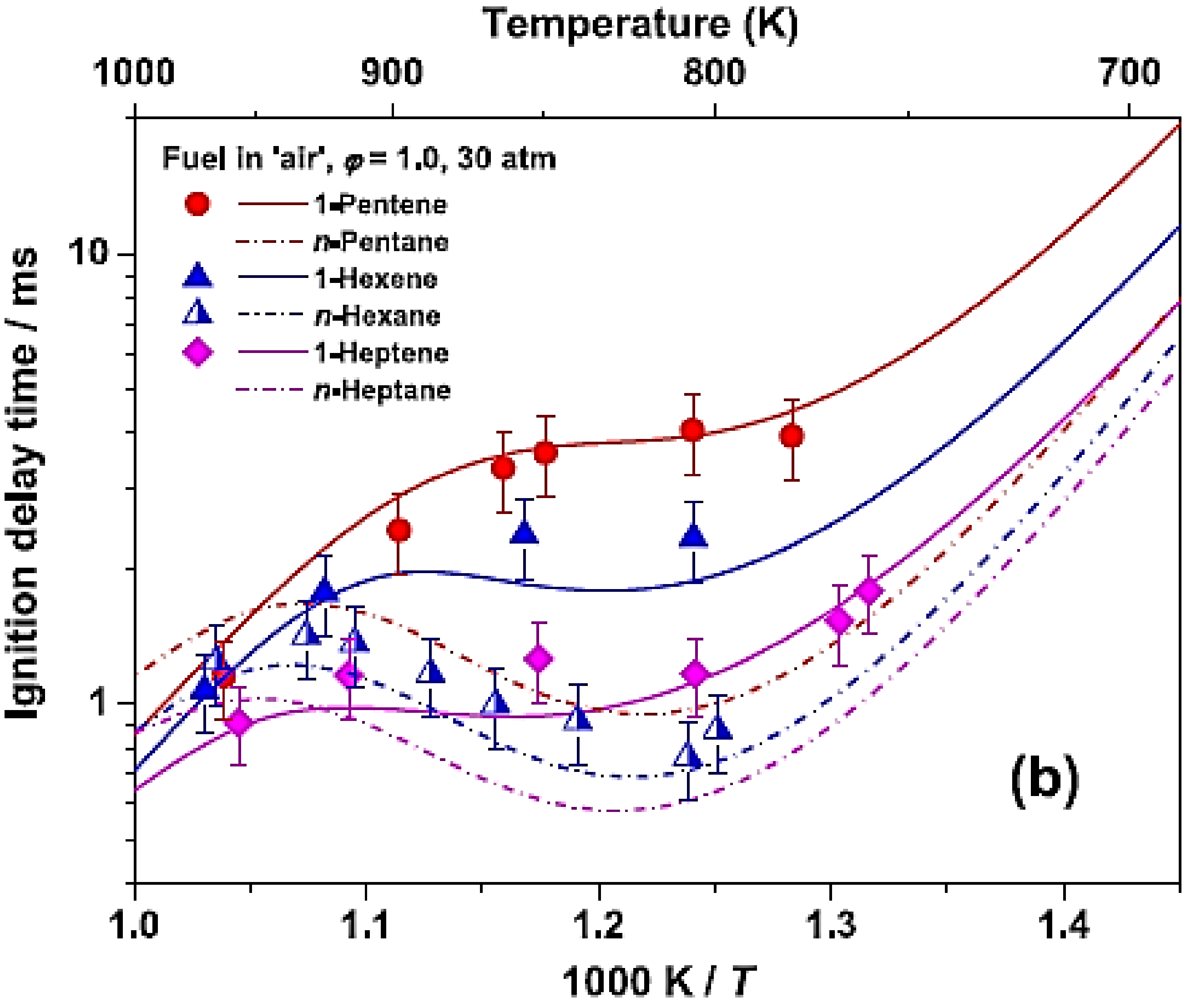
Three distinct temperature regimes

nC_5H_{12} in air, p = 20 atm



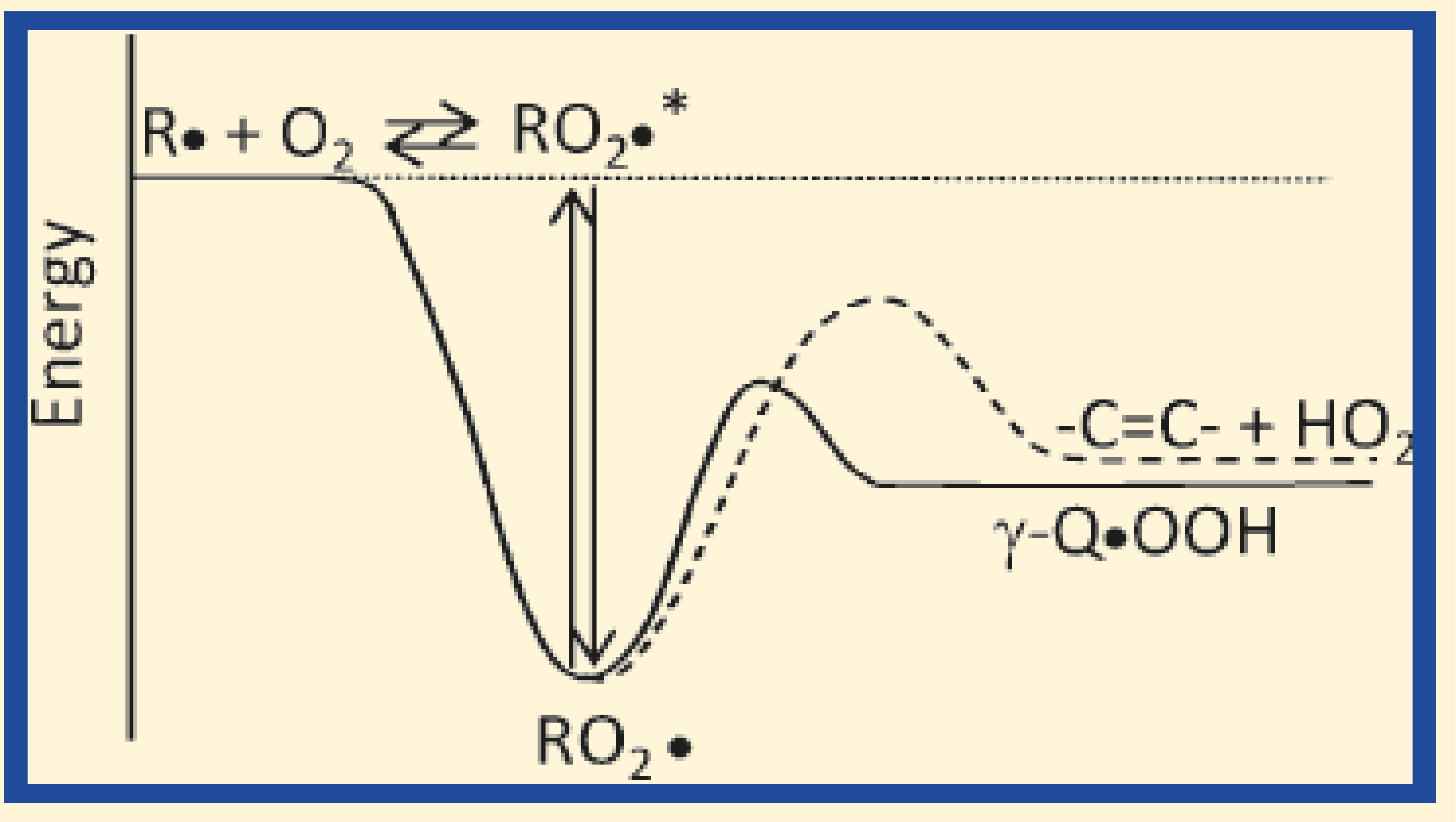
J. Bugler et al., Combust. Flame 163(1) (2016) 138–156.

Alkane/Alkene different reactivity

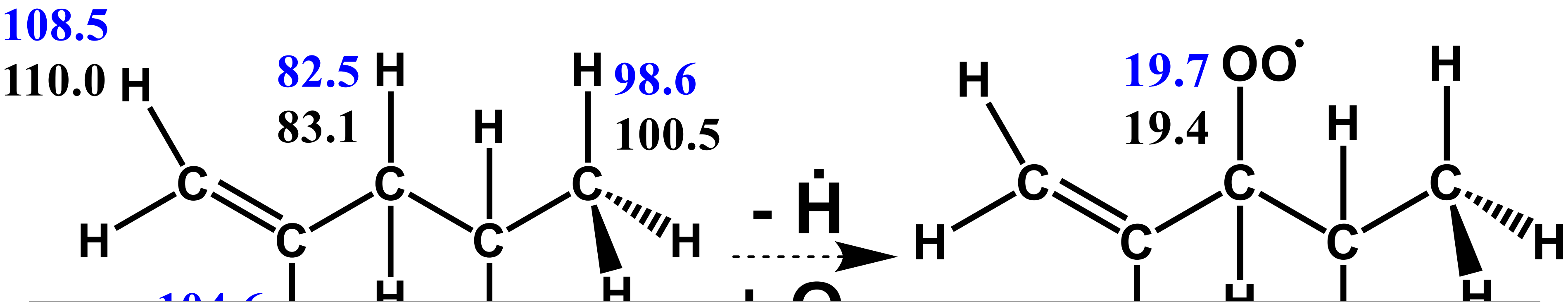


S. Dong et al. Proc. Combust. Inst. 38 (2021) 611—619.

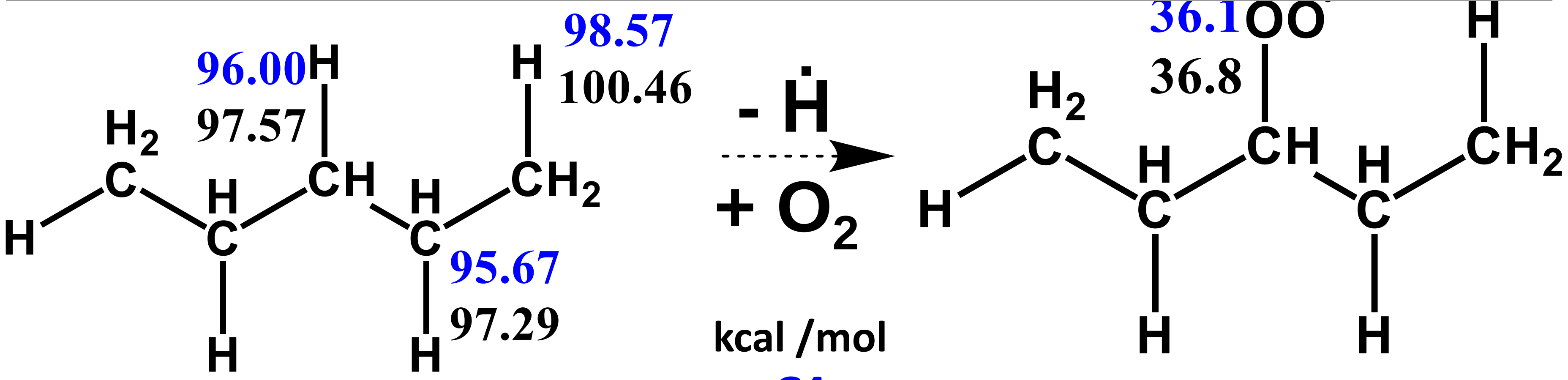
PES for $\dot{R} + O_2 \leftrightarrow R\dot{O}_2$



Structure Difference



Alkanes/Alkenes Different LTC

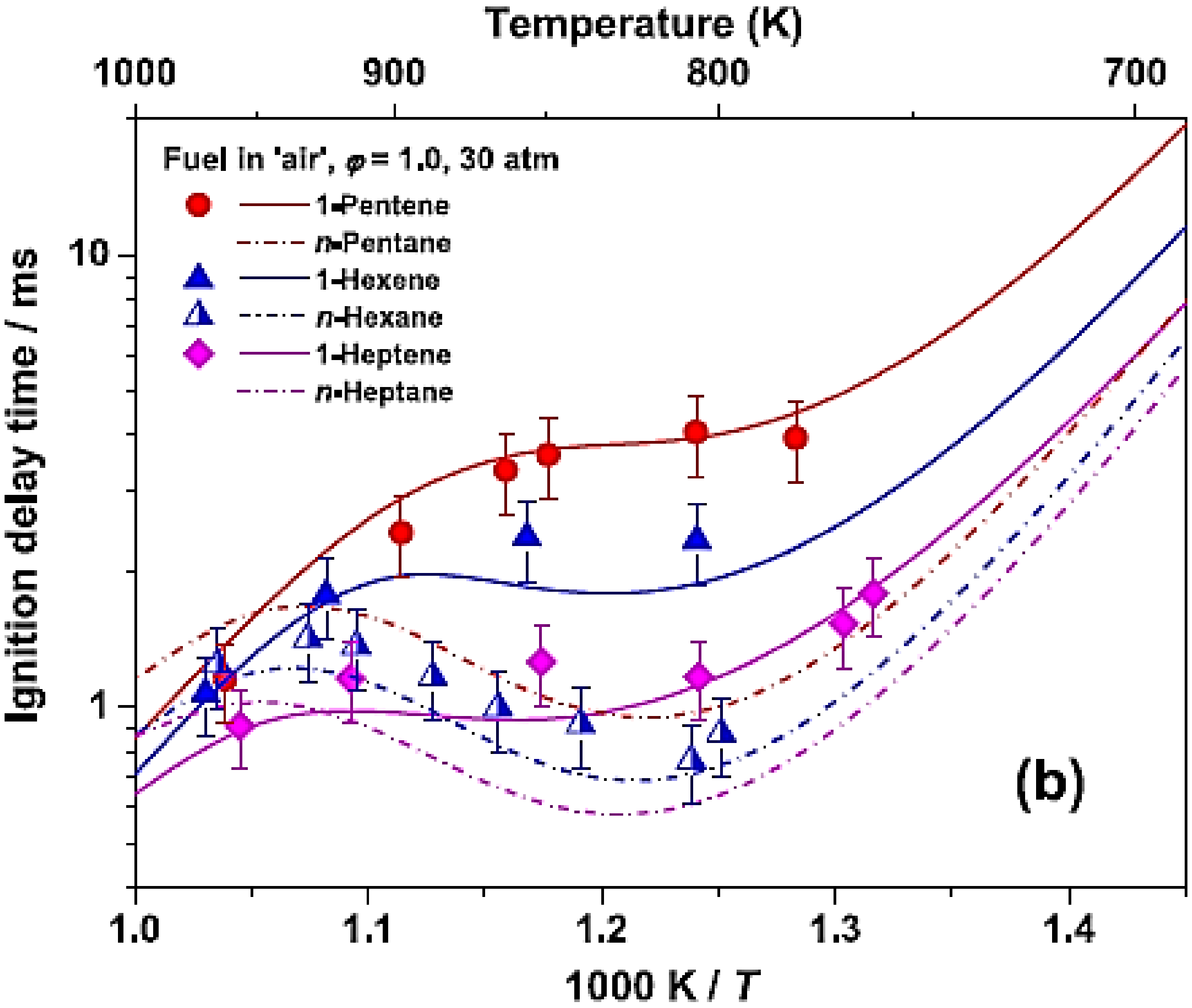


kcal /mol

G4

CBS-QB3

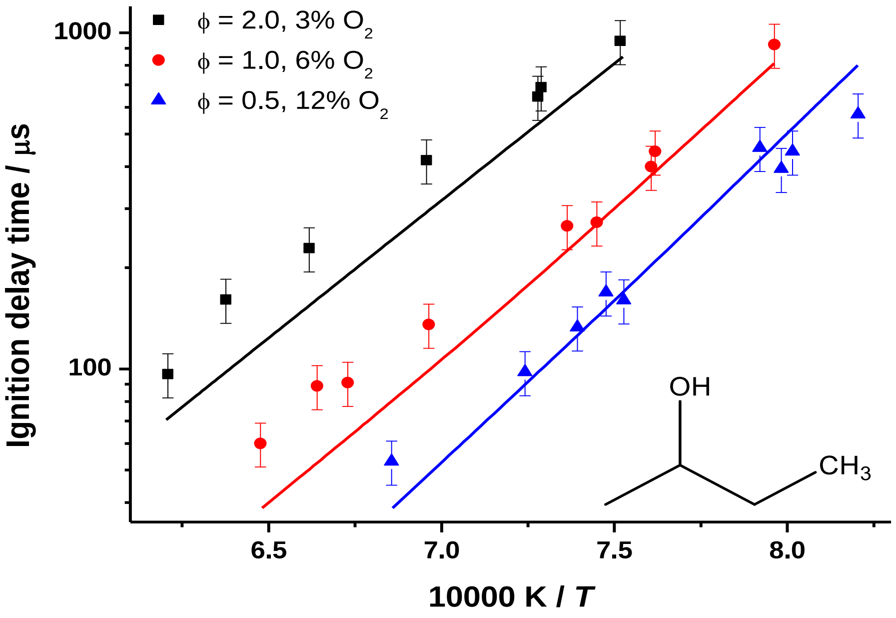
Alkane/Alkene different reactivity



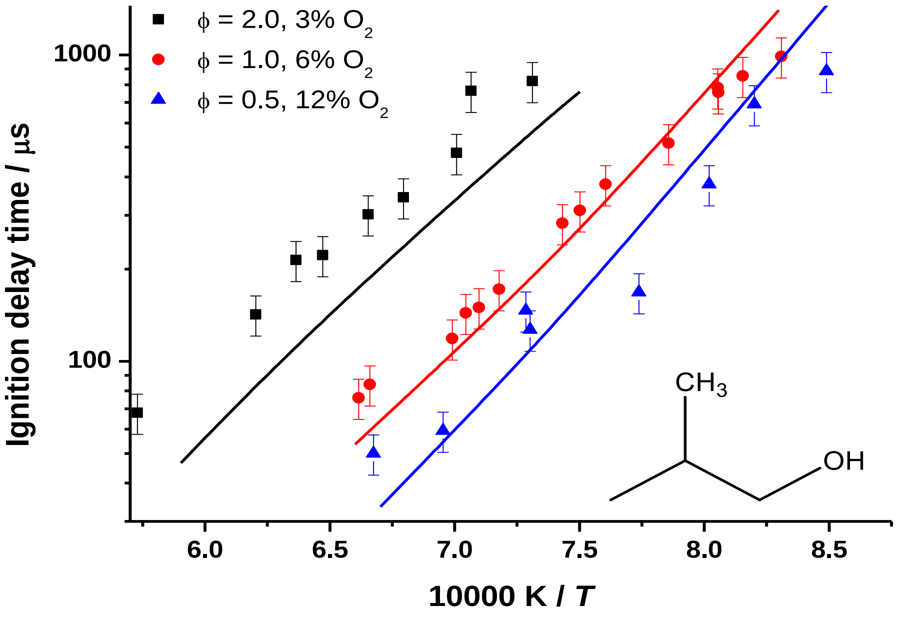
S. Dong et al. Proc. Combust. Inst. 38 (2021) 611—619.

Lean Mixtures faster at High T/Low *p*

- Butanol isomers (ST/RCM) (Dr. Kenji Yasunaga, Ministry of Defense)
  - 1% fuel, T = 1150−1750 K, p = 3.5 atm



***sec*-Butanol, *p* = 3.5 atm**



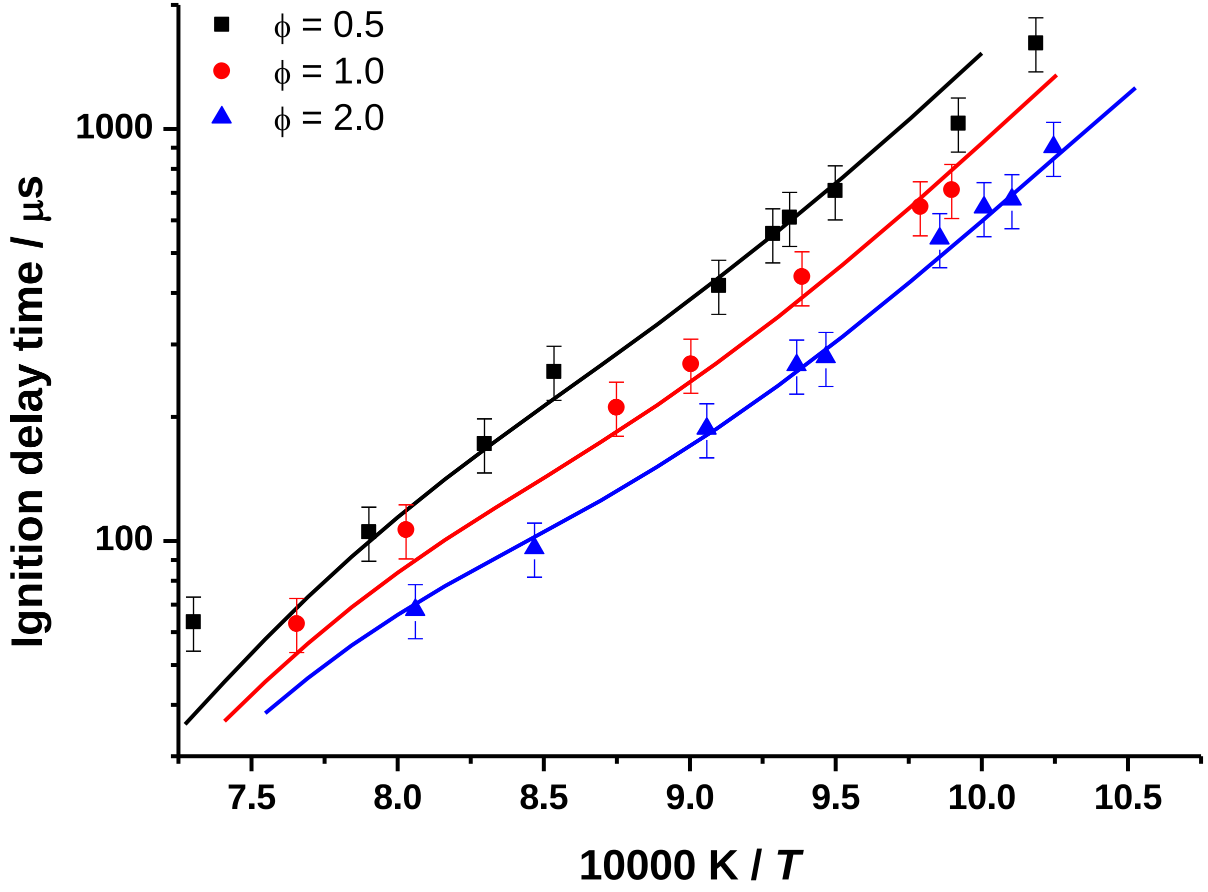
iso-Butanol, *p* = 3.5 atm

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

Rich Mixtures faster at Low T/High *p*

iso-Pentanol in air, *p* = 21 bar

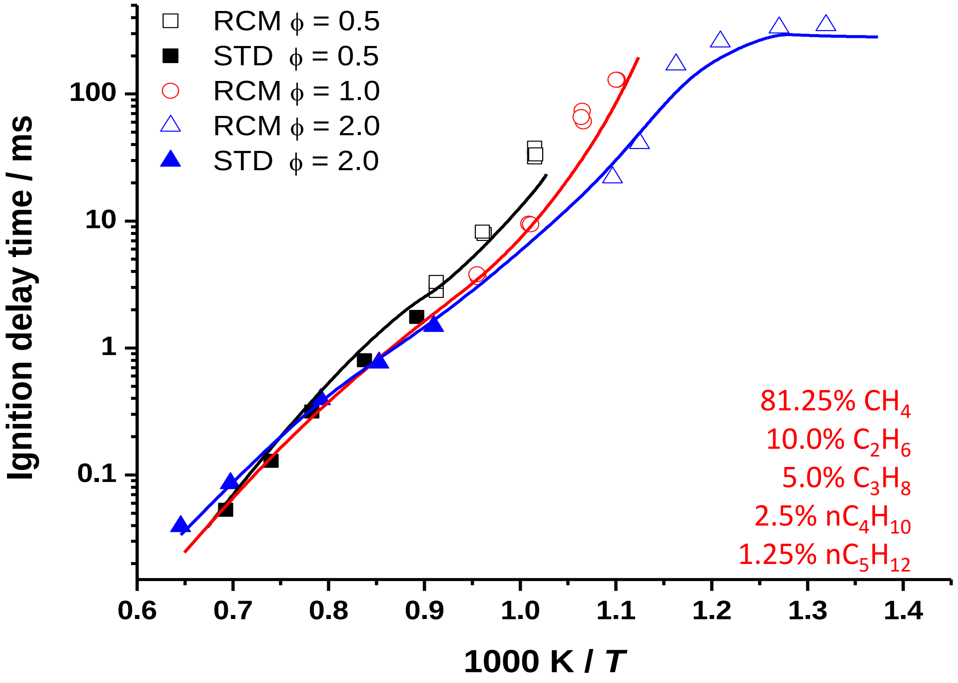
Dr. Taku Tsujimura
Advanced Industrial
Science Technology

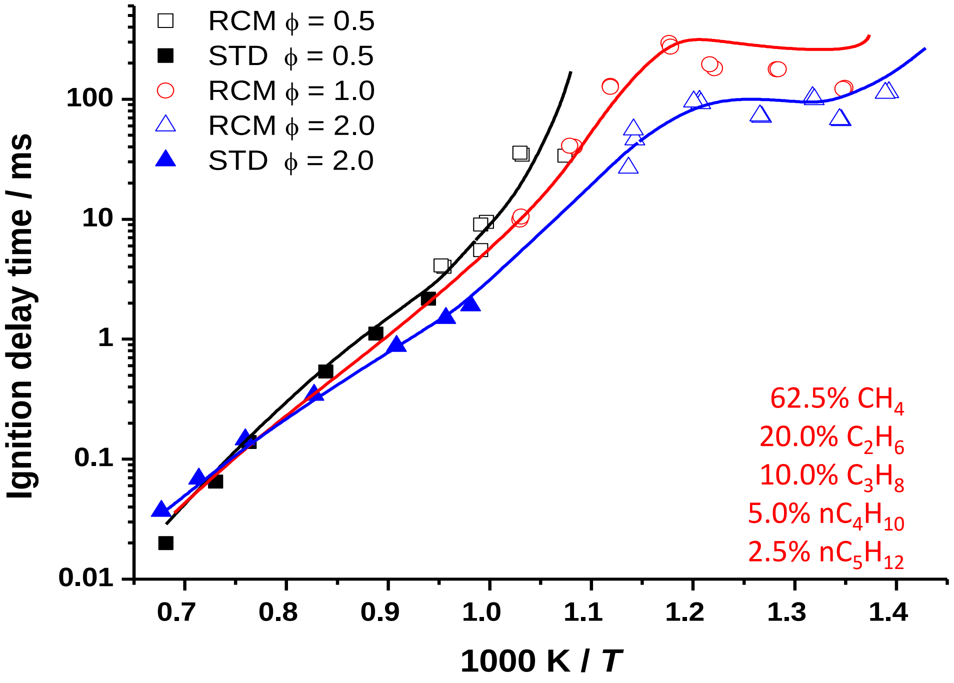


T. Tsujimura, W. J. Pitz, F. Gillespie, H. J. Curran, B. W. Weber, Y. Zhang, C.-J. Sung, Development of isopentanol reaction mechanism reproducing autoignition character at high and low temperatures. Energy Fuels 26(8) (2012) 4871–4886.

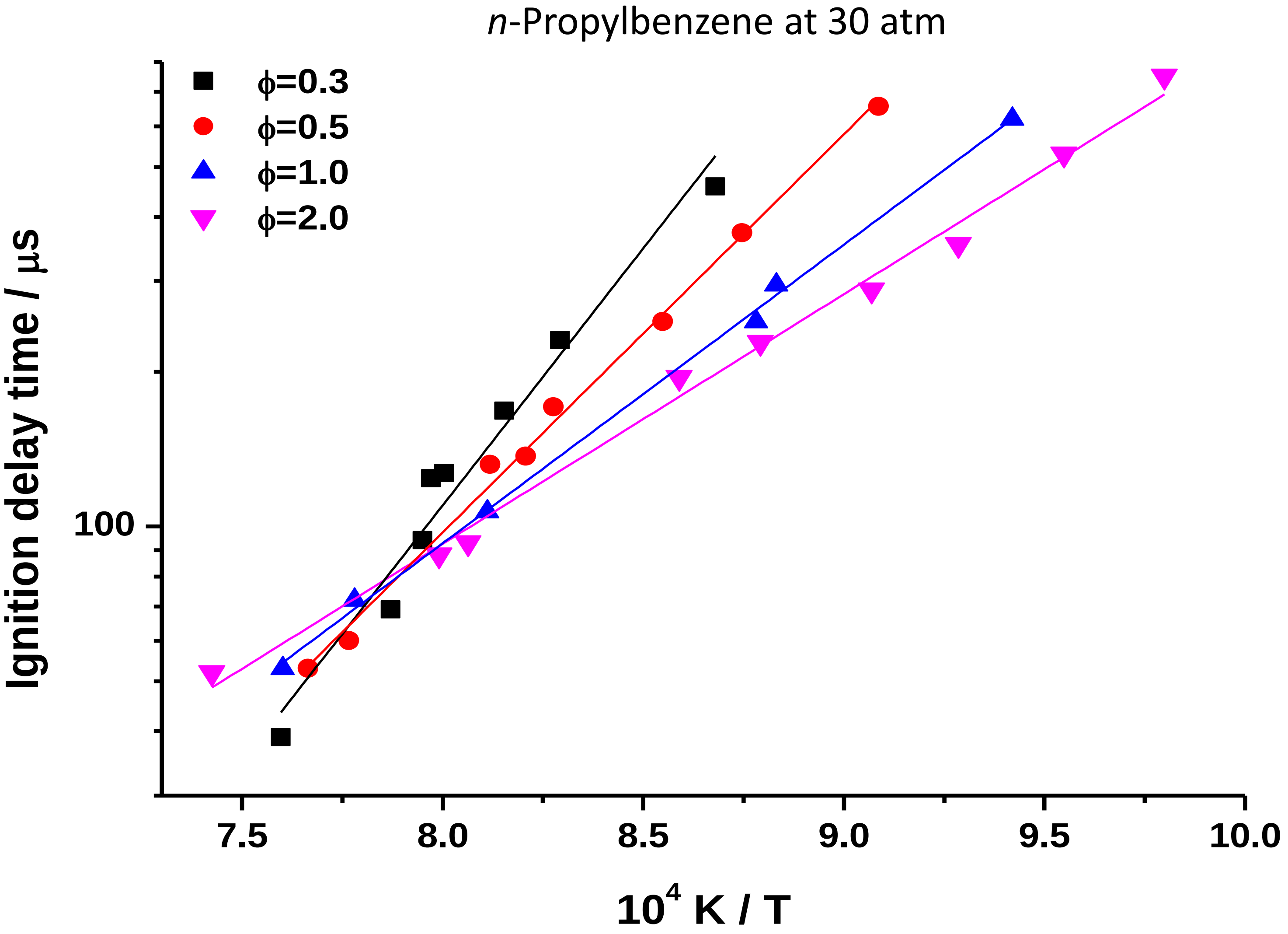
NG: Effect of Equivalence Ratio

p = 20 atm

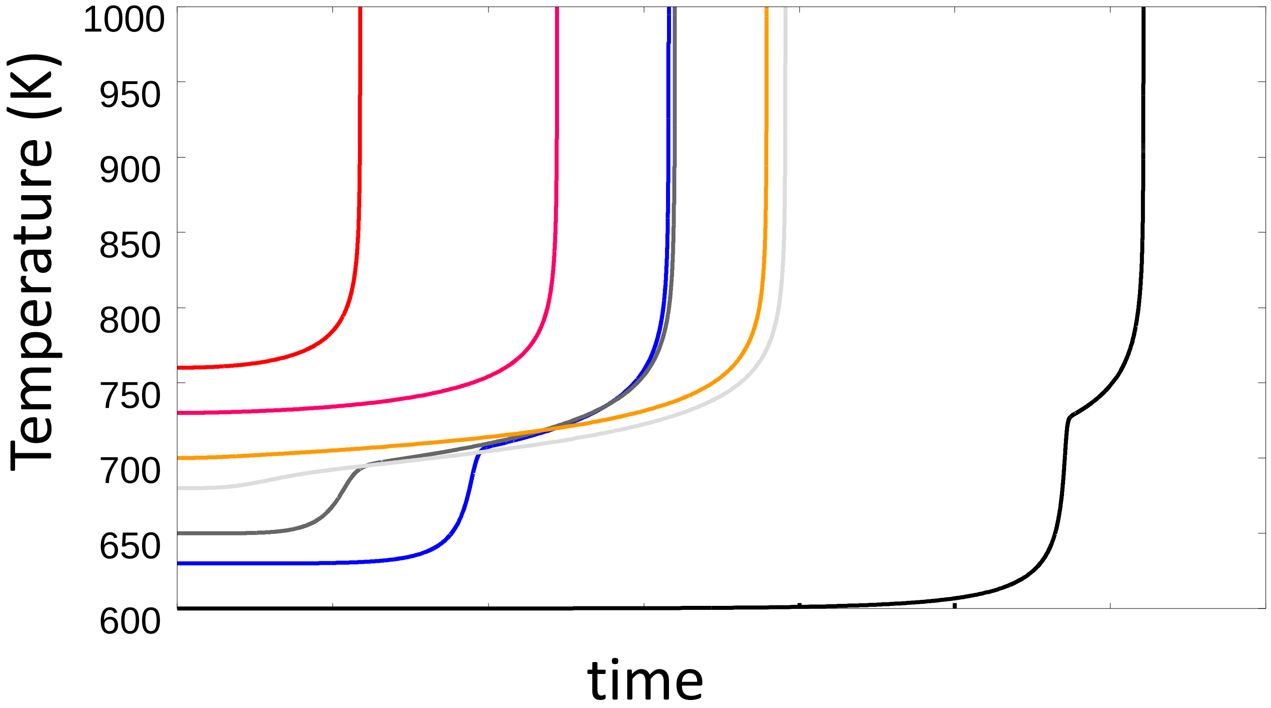


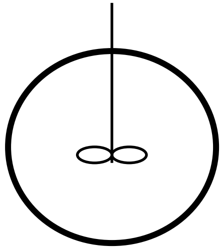


n-PB: Effect of Equivalence Ratio



Ignition of C_3H_8/O_2 in closed adiabatic system





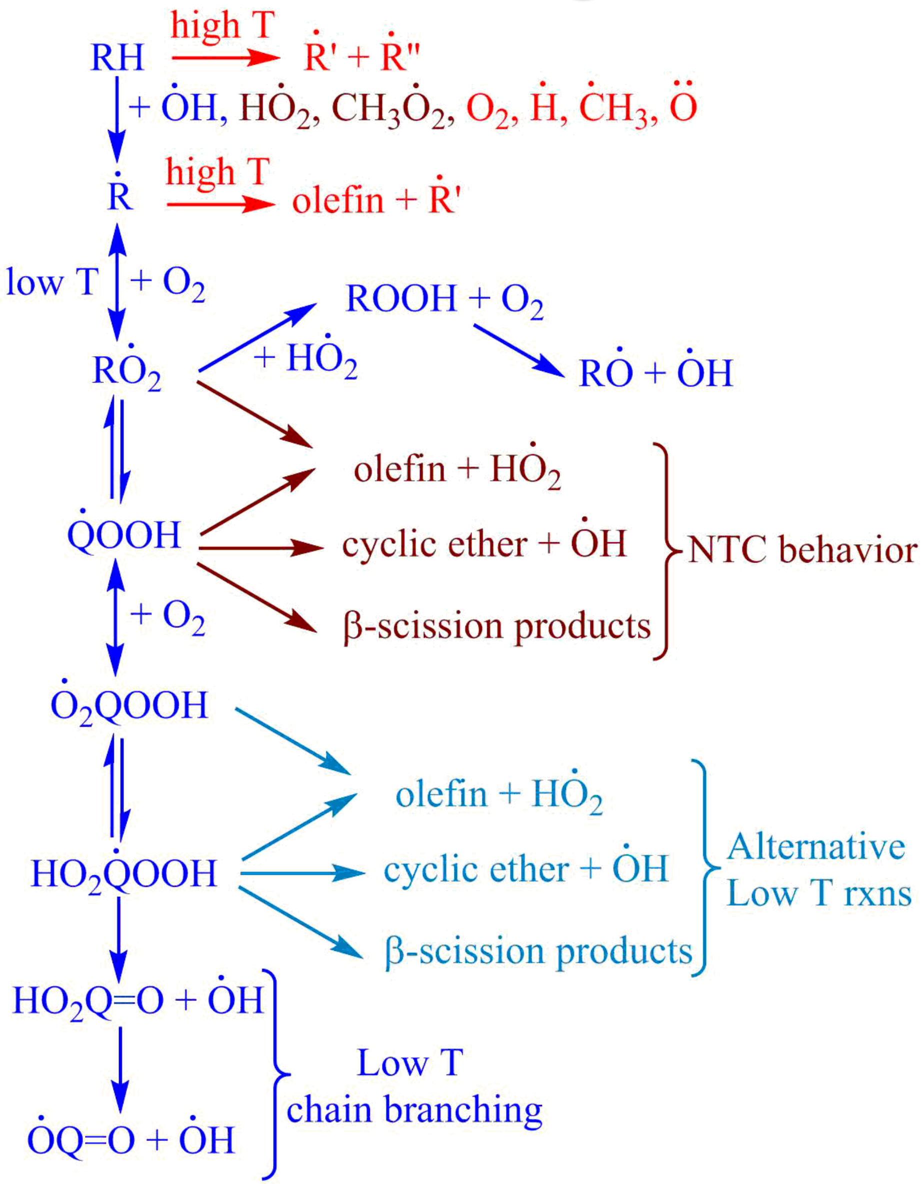
No heat exchange
No mass exchange

- One or two stage ignition.

- NTC between 650-700 K

Courtesy of Prof. Tiziano Faravelli, Politecnico di Milano

Rate rules for large molecular weight molecules



$RH \xrightarrow{\text{high T}} \dot{R}' + \dot{R}''$

$RH \xrightarrow{+\dot{O}H,\ H\dot{O}_2,\ CH_3\dot{O}_2,\ O_2,\ \dot{H},\ \dot{C}H_3,\ \ddot{O}} \dot{R}$

$\dot{R} \xrightarrow{\text{high T}} \text{olefin} + \dot{R}'$

$\dot{R} \underset{\text{low T}}{\overset{+O_2}{\rightleftharpoons}} R\dot{O}_2$

$R\dot{O}_2 \xrightarrow{+H\dot{O}_2} ROOH + O_2 \rightarrow R\dot{O} + \dot{O}H$

$R\dot{O}_2 \rightarrow \text{olefin} + H\dot{O}_2$

$R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$

$\dot{Q}OOH \rightarrow \text{olefin} + H\dot{O}_2$

$\dot{Q}OOH \rightarrow \text{cyclic ether} + \dot{O}H$

$\dot{Q}OOH \rightarrow \beta\text{-scission products}$

NTC behavior

$\dot{Q}OOH \overset{+O_2}{\rightleftharpoons} \dot{O}_2QOOH$

$\dot{O}_2QOOH \rightarrow \text{olefin} + H\dot{O}_2$

$\dot{O}_2QOOH \rightleftharpoons HO_2\dot{Q}OOH$

$HO_2\dot{Q}OOH \rightarrow \text{olefin} + H\dot{O}_2$

$HO_2\dot{Q}OOH \rightarrow \text{cyclic ether} + \dot{O}H$

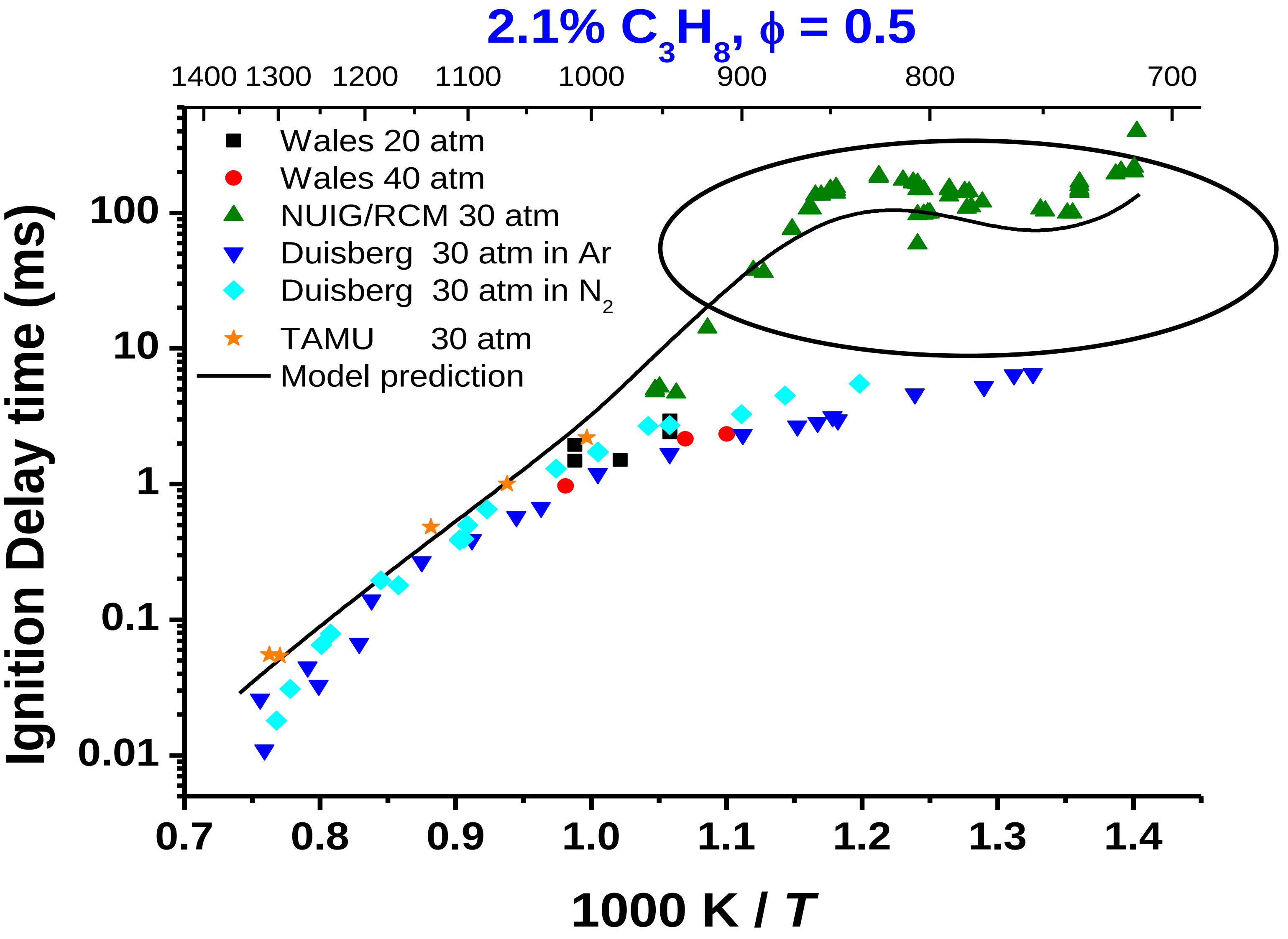
$HO_2\dot{Q}OOH \rightarrow \beta\text{-scission products}$

Alternative
Low T rxns

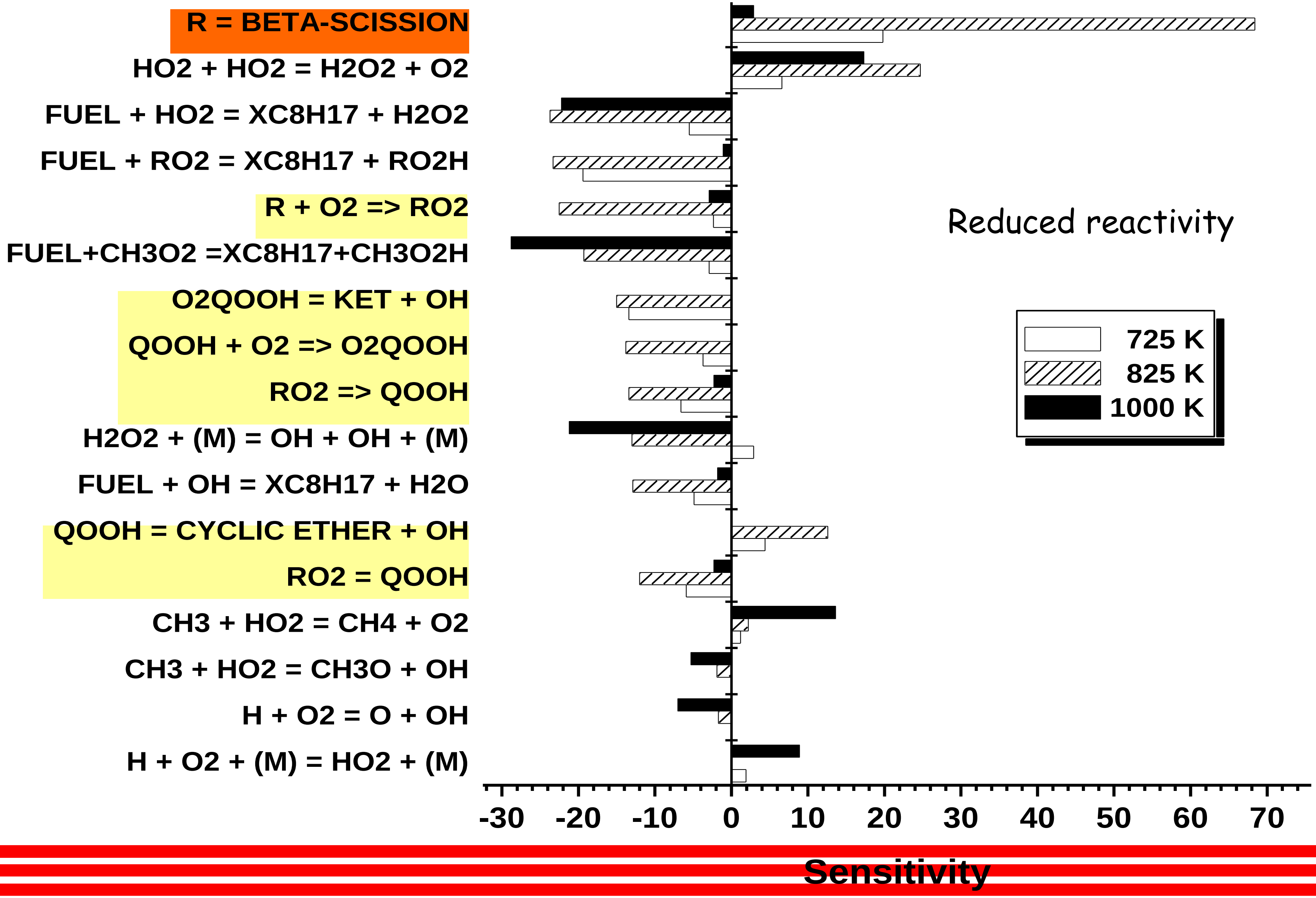
$HO_2\dot{Q}OOH \rightarrow HO_2Q{=}O + \dot{O}H \rightarrow \dot{O}Q{=}O + \dot{O}H$

Low T
chain branching

NTC Behavior



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

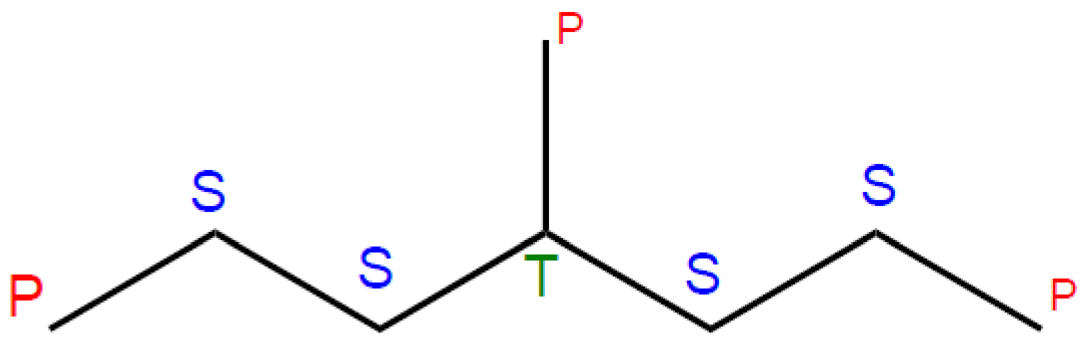


Assign reaction rate rules by reaction classes

- *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 + O_2 = olefin + $H\dot{O}_2$
  - 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

Courtesy of Dr. William Pitz, Lawrence Livermore National Laboratory

Test molecule: 4-methyl heptane

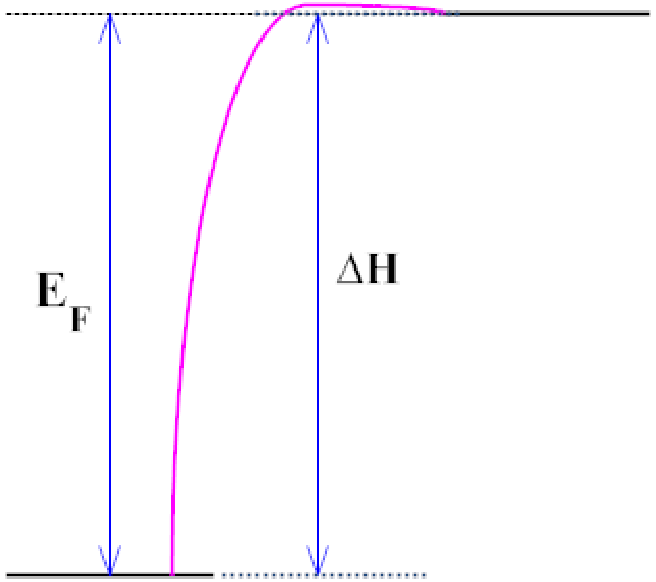


4-methylheptane

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

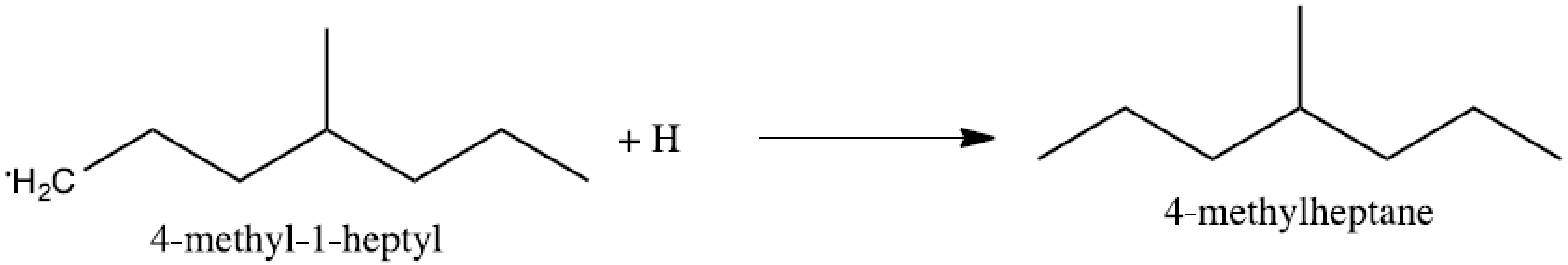
1: Unimolecular fuel decomposition

- Very important for ignition delay times in a ST
  - High *p* limit usually estimated in the reverse (exothermic) direction: radical-radical recombination with no Ea
- 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 with no Ea

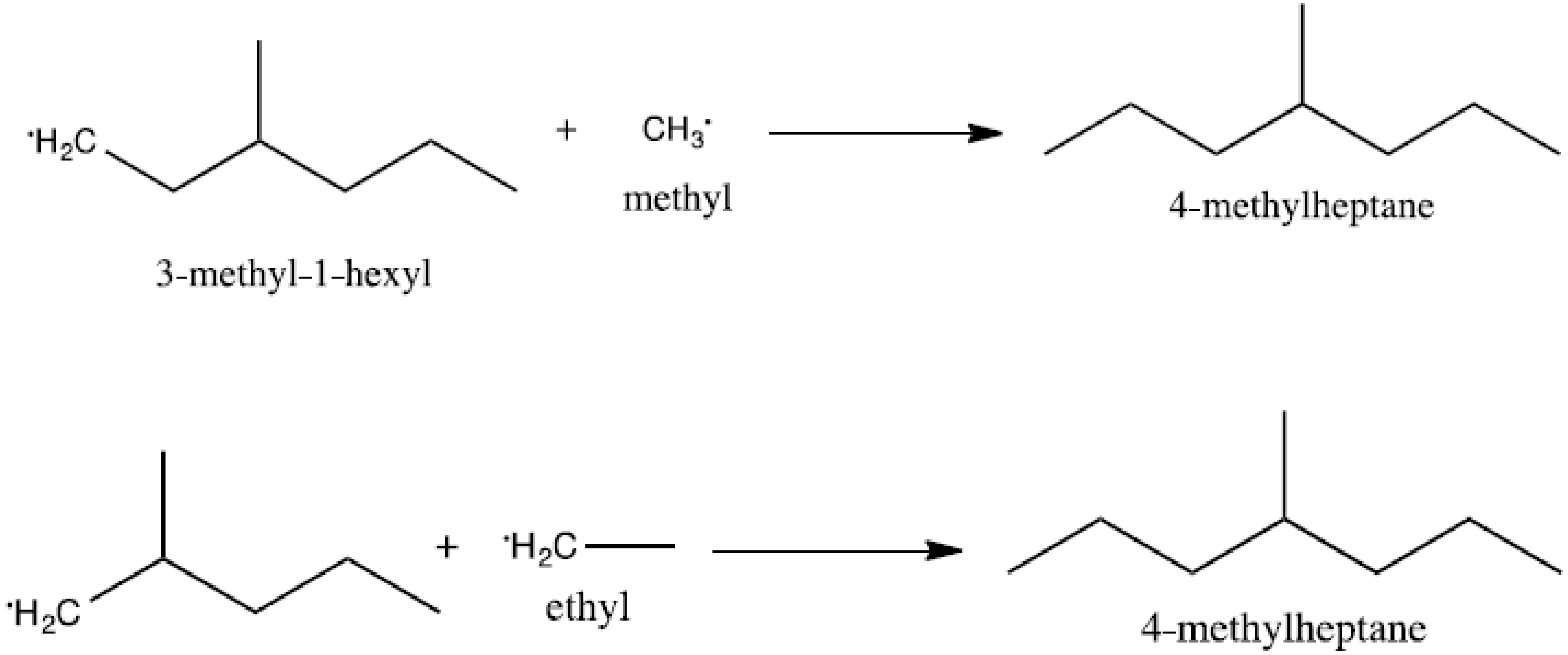


$k = 10^{14}\ \mathrm{cm^3\ mol^{-1}\ s^{-1}}$

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



$$(A_f/A_r) * \exp((E_f - E_r)/RT) = k_f/k_r = \exp(\Delta S/R)*\{ \exp(-\Delta H/RT)\} / (RT/p_o)^{\Delta n}$$

$$A\ (+M) \leftrightarrow B + C\ (+M)$$

$$\exp(\Delta S/R)$$

$$= \exp[(S_B+S_C - S_A)/R]$$

$$= \exp\ [\{(S_{B,gr} - R*\ln(\sigma_B))\ + (S_{C,gr} - R\ln(\sigma_C)) - (S_{A,gr} - R\ln(\sigma_A))\}/R]$$

$$= \exp\ [(S_{B,gr} + S_{C,gr} - S_{A,gr})/R - (\ln(\sigma_B) + \ln(\sigma_C) - \ln(\sigma_A))]$$

$$= \exp[(\Delta S_{,gr}/R) * \exp(\ln(\sigma_A / \sigma_B / \sigma_C)]$$

$$= \exp[(\Delta S_{,gr}/R)*(\sigma_A/(\sigma_B.\sigma_C)]$$

GROUP VALUE FACTOR

SYMMETRY NUMBER FACTOR

Effect of symmetry: neoC_5H_{12} vs nC_5H_{12}

- neoC_5H_{12} = tC_4H_9 + CH_3
- $\sigma_A/(\sigma_B.\sigma_C) = 972/(81\times3) = 4$

- nC_5H_{12} = nC_3H_7 + C_2H_5
- $\sigma_A/(\sigma_B.\sigma_C) = 18/(6\times6) = 0.5$

neoC_5H_{12} decomposition is 8 times faster compared to nC_5H_{12}

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.

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

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

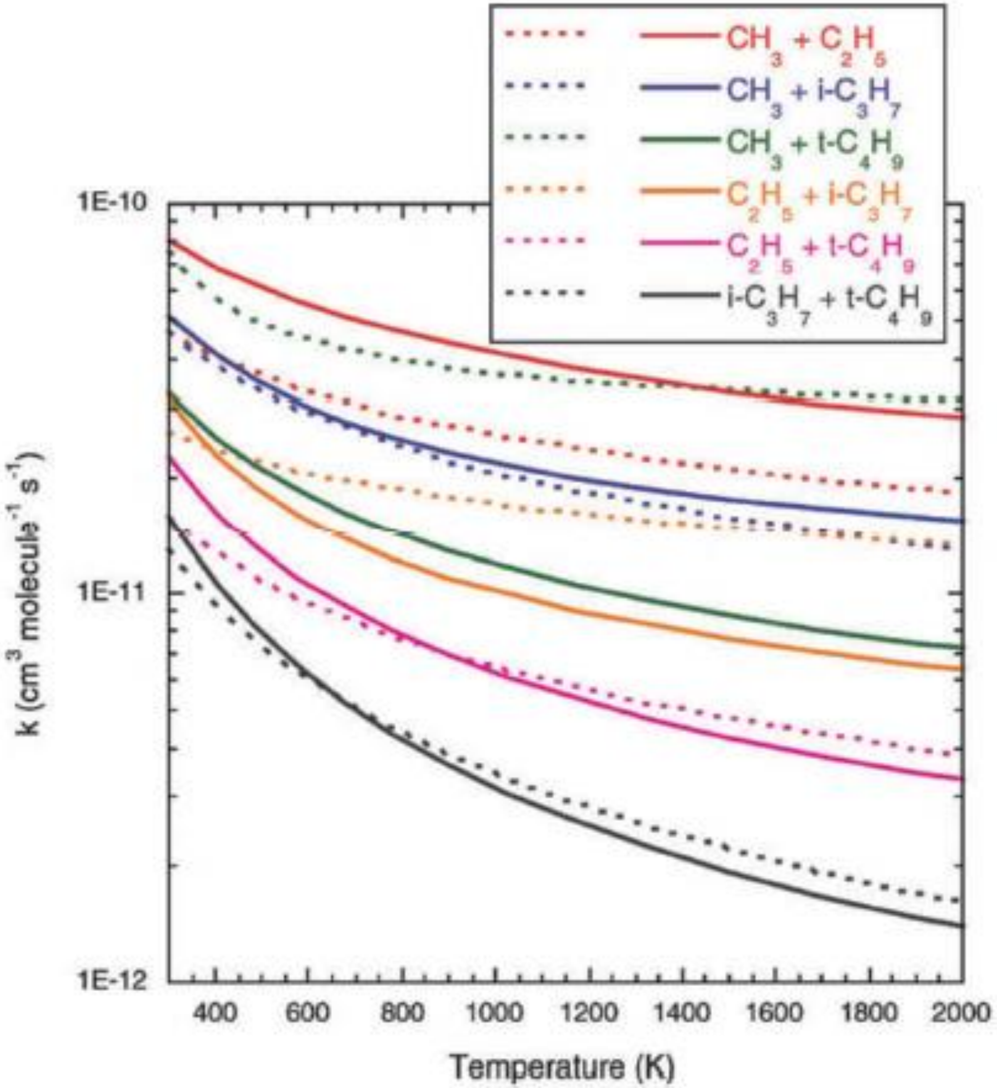
$5.33 \times 10^{-10}\ T^{-0.474} \exp(97.7/T)$ $CH_3 + \textit{i}\text{-}C_3H_7$

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

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

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

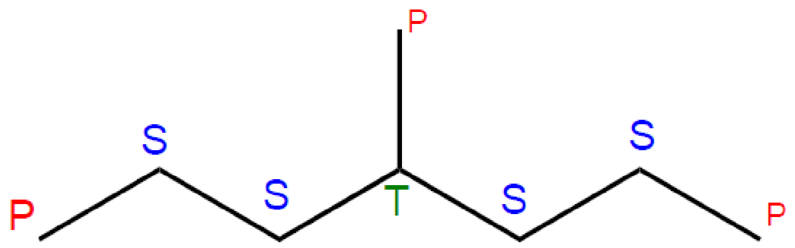
$2.79 \times 10^{-9}\ T^{-0.892} \exp(73.1/T)$ $C_2H_5 + \textit{t}\text{-}C_4H_9$



Klippenstein et al. Phys. Chem. Chem. Phys. 8 (2006) 1133—1147.

2: H-atom abstraction from fuel

- Abstraction of H atoms from the fuel by radical species (e.g., $\dot{H}$, $\dot{O}H$, $H\dot{O}_2$, $\dot{C}H_3$, 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.

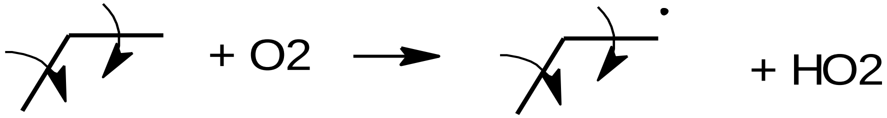


4-methylheptane

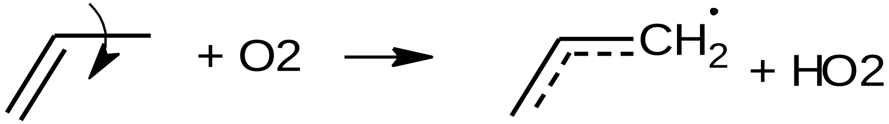
2: H-atom abstraction by O_2

Bimolecular initiations $RH + O_2 \rightarrow R^{\cdot} + H\dot{O}_2$

$R^{\cdot}$ alkyl $k = 7.0\times10^{12}\exp(-\Delta_r H^\circ/RT)$



$R^{\cdot}$ allyl $k = 7.0\times10^{11}\exp(-\Delta_r H^\circ/RT)$

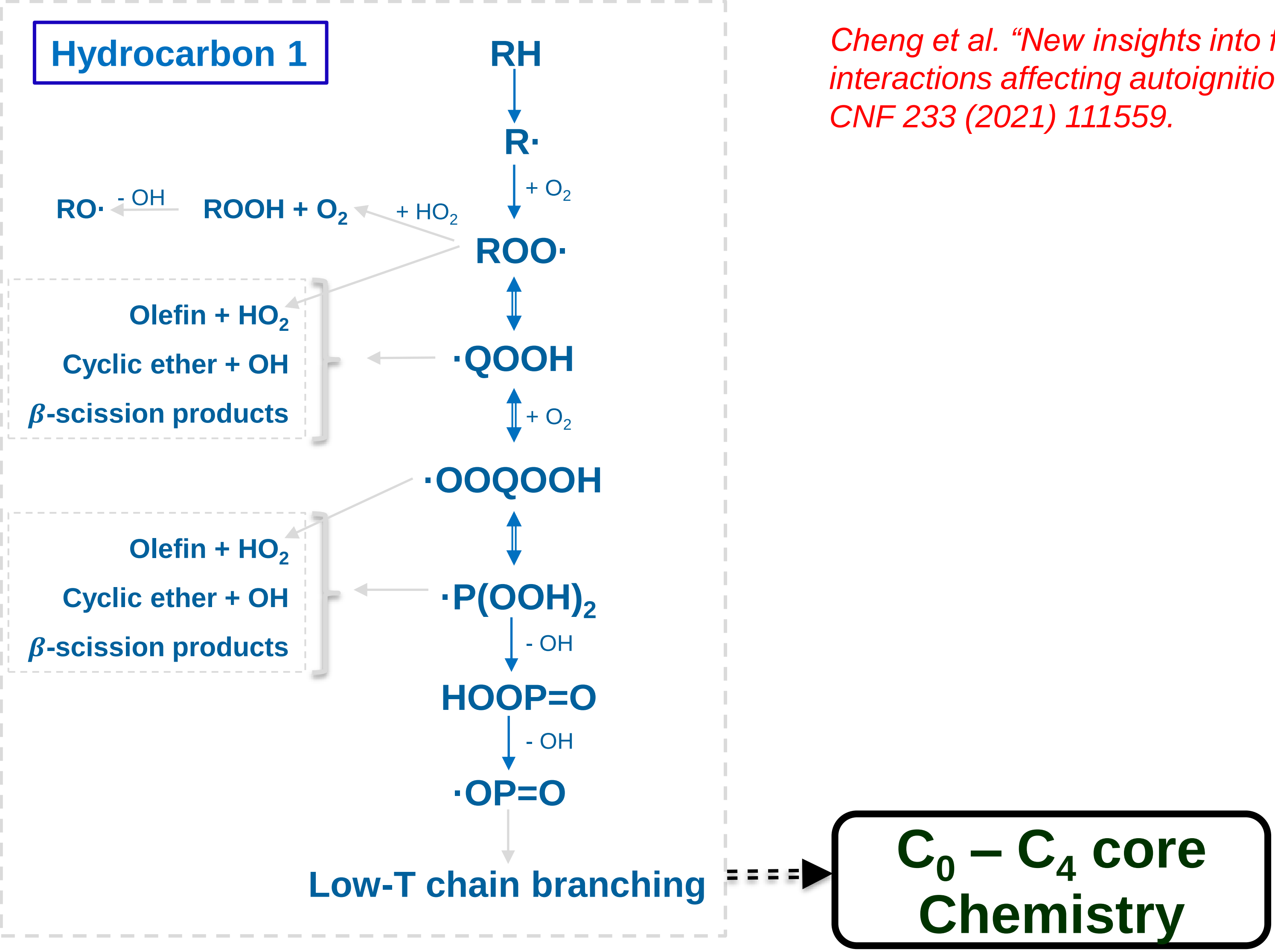


on a per C–H bond basis, taking into account the loss of a rotor in the second case

(T. Ingham, R. Walker, R. Woolford, Proc. Combust. Inst. 25 (1994) 767–774.)

Competition for radicals

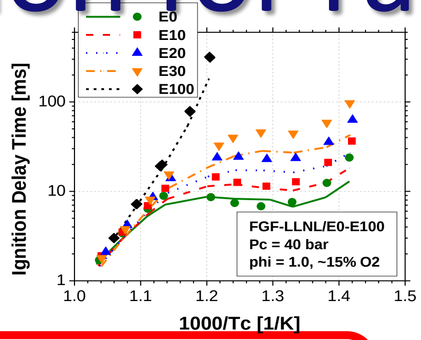
- Fuel-specific interacting reaction network

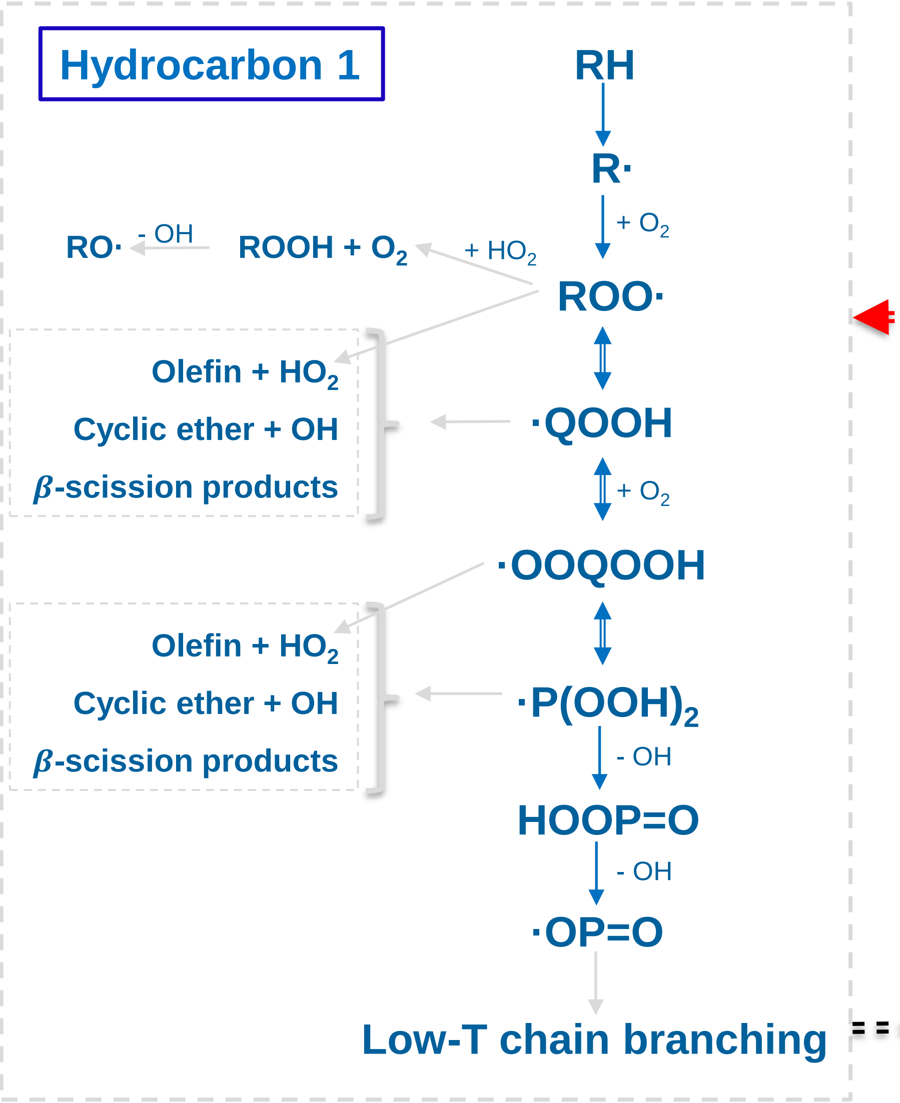


Cheng et al. "New insights into fuel blending effects: intermolecular chemical kinetic interactions affecting autoignition times and intermediate-temperature heat release", CNF 233 (2021) 111559.

Competition for radicals

- Fuel-specific interacting reaction network





Hydrocarbon 1

RH

R·

+ O_2

RO· - OH ROOH + O_2 + HO_2

ROO·

Olefin + HO_2

Cyclic ether + OH

β-scission products

·QOOH

+ O_2

·OOQOOH

Olefin + HO_2

Cyclic ether + OH

β-scission products

·$P(OOH)_2$

- OH

HOOP=O

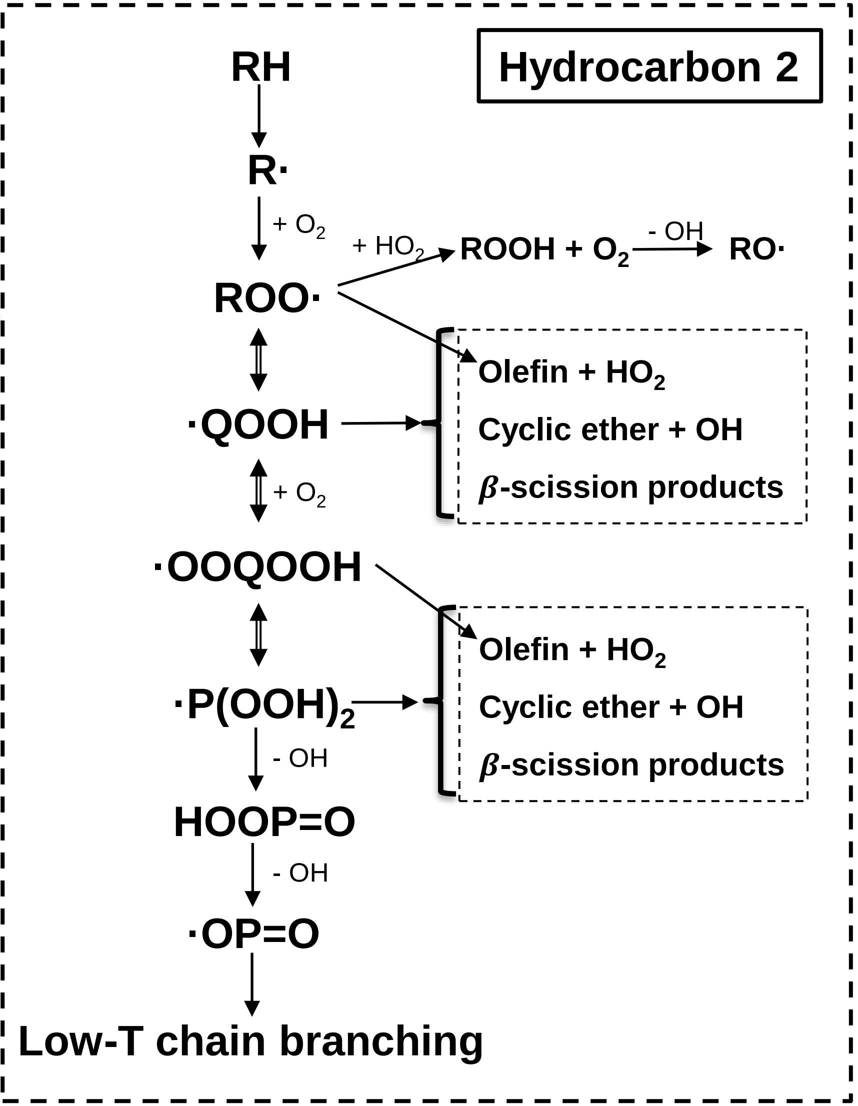
- OH

·OP=O

Low-T chain branching

$\dot{O}H$, $H\dot{O}_2$, $CH_3\dot{O}_2$

$C_0 – C_4$ core Chemistry



Hydrocarbon 2

RH

R·

+ O_2

ROO· + HO_2 ROOH + O_2 - OH RO·

Olefin + HO_2

Cyclic ether + OH

β-scission products

·QOOH

+ O_2

·OOQOOH

Olefin + HO_2

Cyclic ether + OH

β-scission products

·$P(OOH)_2$

- OH

HOOP=O

- OH

·OP=O

Low-T chain branching

Competition for radicals

- Fuel-specific interacting reaction network

Hydrocarbon 1

RH

R·

+ O_2

RO· - OH ROOH + O_2 + HO_2

ROO·

Olefin + HO_2

Cyclic ether + OH

β-scission products

·QOOH

+ O_2

·OOQOOH

Olefin + HO_2

Cyclic ether + OH

β-scission products

·P(OOH)$_2$

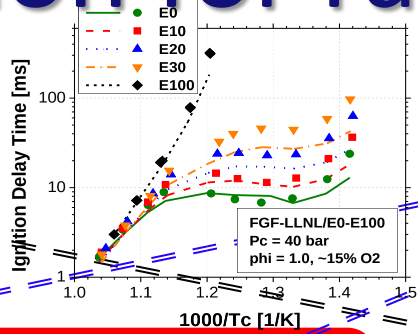
- OH

HOOP=O

- OH

·OP=O

Low-T chain branching



$\dot{O}H$, $H\dot{O}_2$, etc.

Fuel-specific interaction network

C_0 – C_4 core Chemistry

Hydrocarbon 2

RH

R·

+ O_2

ROO· + HO_2 ROOH + O_2 - OH RO·

Olefin + HO_2

Cyclic ether + OH

β-scission products

·QOOH

+ O_2

·OOQOOH

Olefin + HO_2

Cyclic ether + OH

β-scission products

·P(OOH)$_2$

- OH

HOOP=O

- OH

·OP=O

Low-T chain branching

Reaction rate rules make the assignment of reaction rate constants manageable

Fuel + ($\dot{H}$, $\dot{O}H$, $\dot{C}H_3$, $H\dot{O}_2$) => fuel radical + (H_2, H_2O, CH_4, H_2O_2)

Class 2

H- atom abstraction rate rules for alkanes

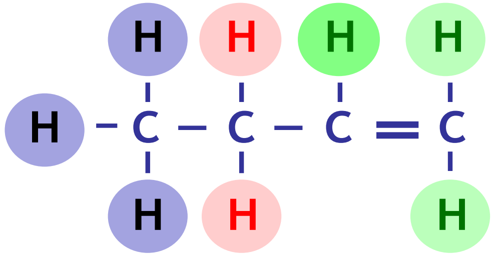
	C-H type	A (cm^3 mol^{-1} s^{-1})	n	E_A (cal)
$\dot{H}$	1°	2.22E+05	2.54	6,756
	2°	6.50e+05	2.40	4,471
	3°	6.02E+05	2.40	2,583
$\dot{O}H$	1°	1.76E+09	0.97	1,586
	2°	2.34E+07	1.61	-35
	3°	5.73E+10	0.51	63
$\dot{C}H_3$	1°	1.51E-01	3.65	7,154
	2°	7.55E-01	3.46	5,481
	3°	6.01E-10	6.36	893
$H\dot{O}_2$	1°	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

Courtesy of Dr. William Pitz, Lawrence Livermore National Laboratory

Correlations between structure and reactivity

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



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
•O•	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
•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
•OH	6.0	2	-1	6.2	2	-6	6.1	2	-11	6.0	2	12	6.0	2	6
$\bullet CH_3$	-1.3	3.5	24	11.9	0	29	11.9	0	22	-1.7	3.5	54	-1.7	3.5	50
$\bullet HO_2$	3.5	2.6	58	3.5	2.6	52	4.2	2.6	45						

E_a in kJ mol^{-1}

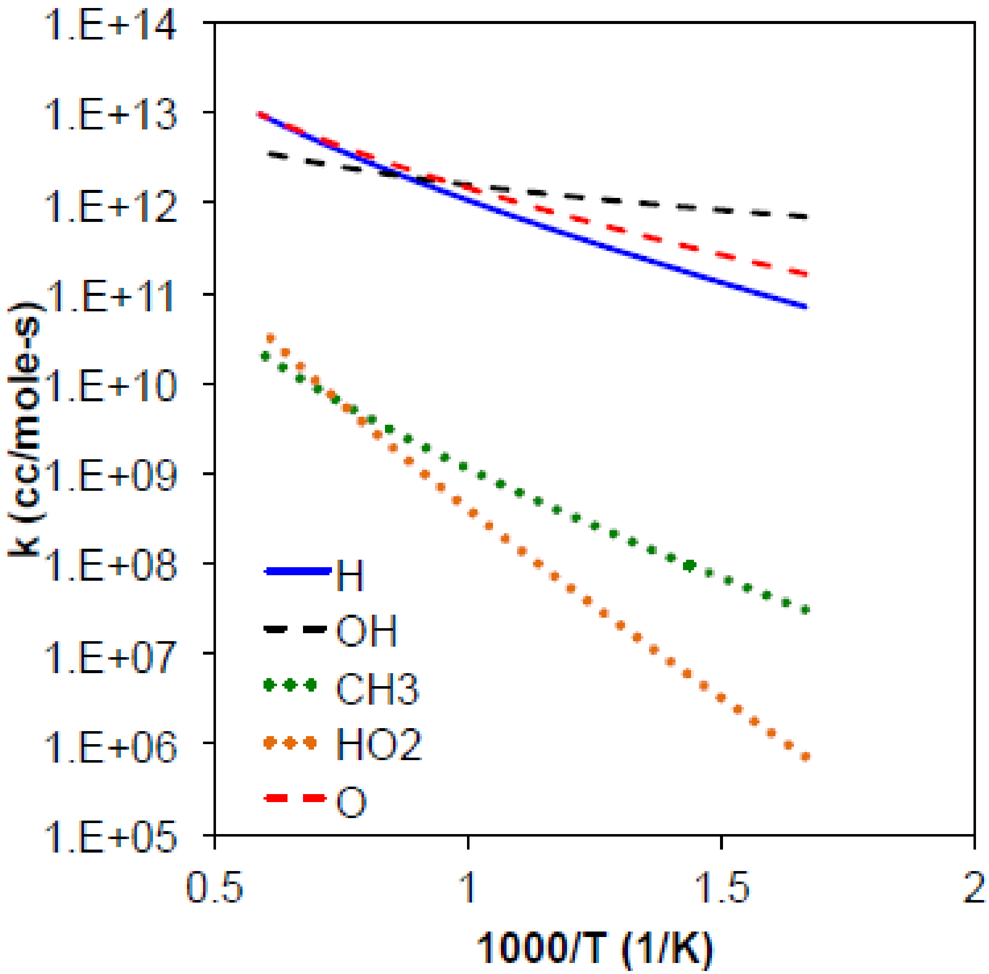
There are more complex correlations of incremental type depending on the nature of RH and X$^{\bullet}$ (Atkinson, 1986, Ranzi et al. 1994)

Courtesy of Dr. Pierre-Alexandre Glaude

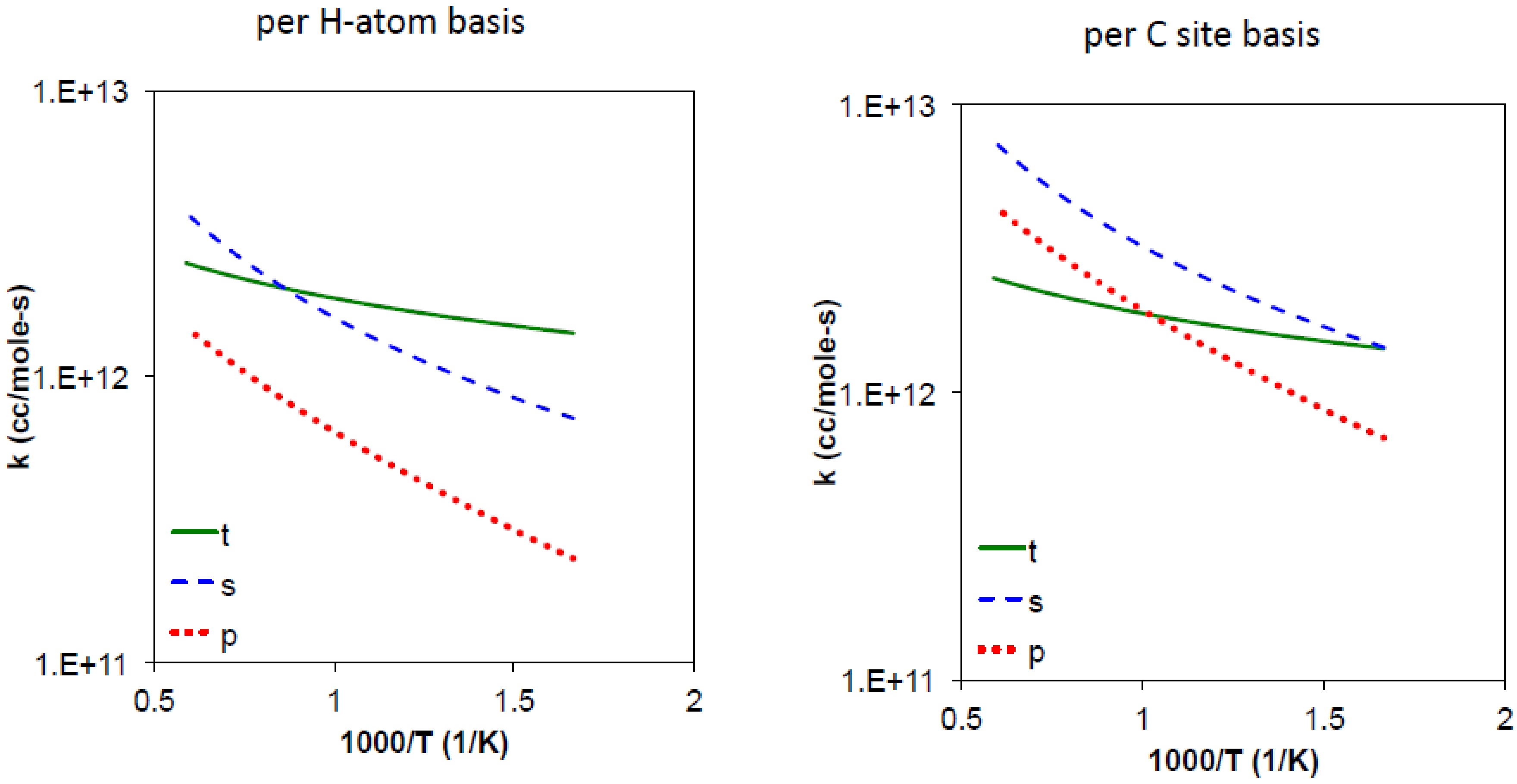
2: H-atom abstraction from fuel

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

per H-atom basis from a secondary site



2: H-atom abstraction by ȮH radials



per H-atom basis

per C site basis

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

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

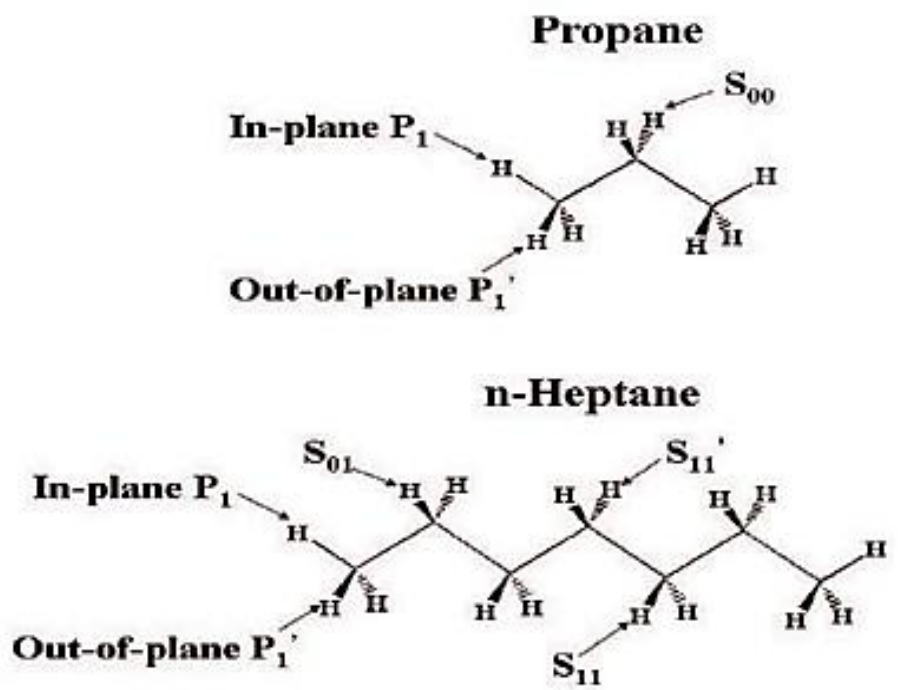


Figure 10. Types of primary and secondary C—H bonds in propane and *n*-heptane.

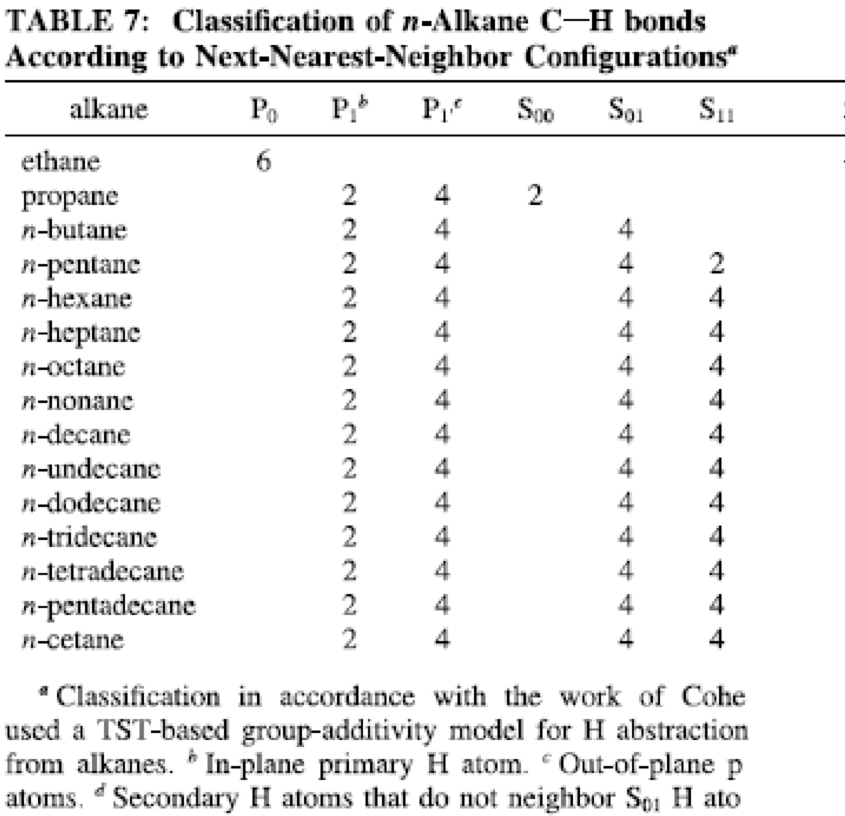


TABLE 7: Classification of *n*-Alkane C—H bonds According to Next-Nearest-Neighbor Configurations[a]

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

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

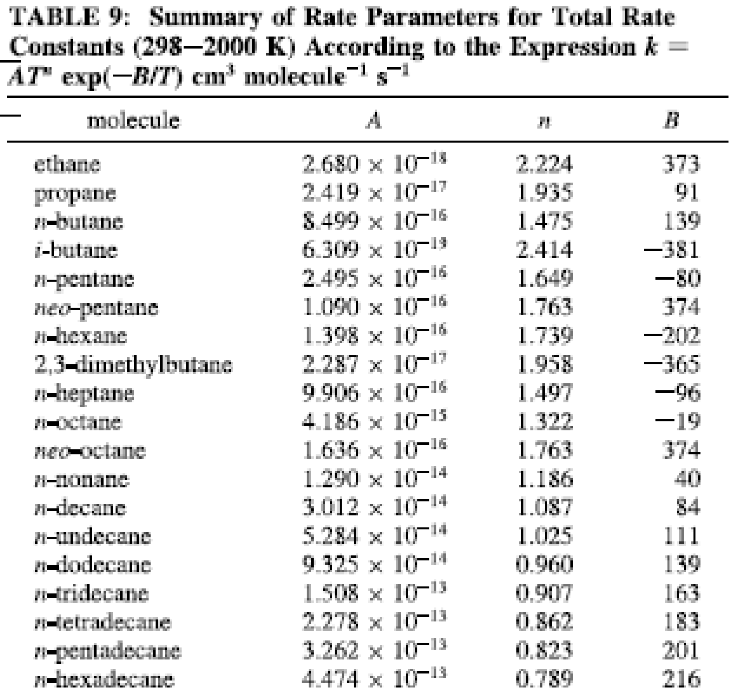
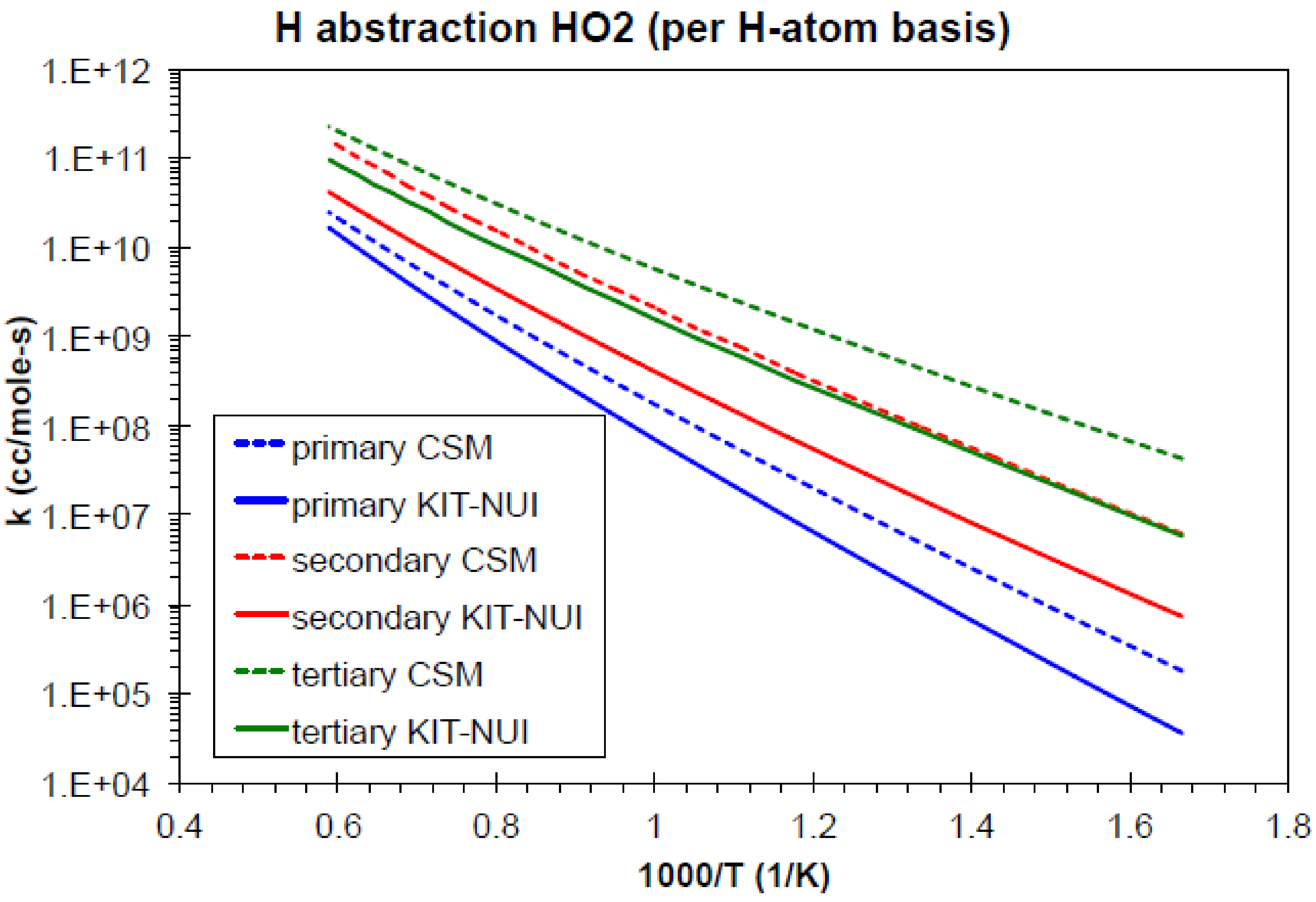


TABLE 9: Summary of Rate Parameters for Total Rate Constants (298—2000 K) According to the Expression $k = AT^n \exp(-B/T)$ cm^3 molecule^{-1} s^{-1}

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

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

Uncertainty in fuel + $H\dot{O}_2$ 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: $H\dot{O}_2$ + alkanes
Uncertainty in rate of a factor of 3 - 6

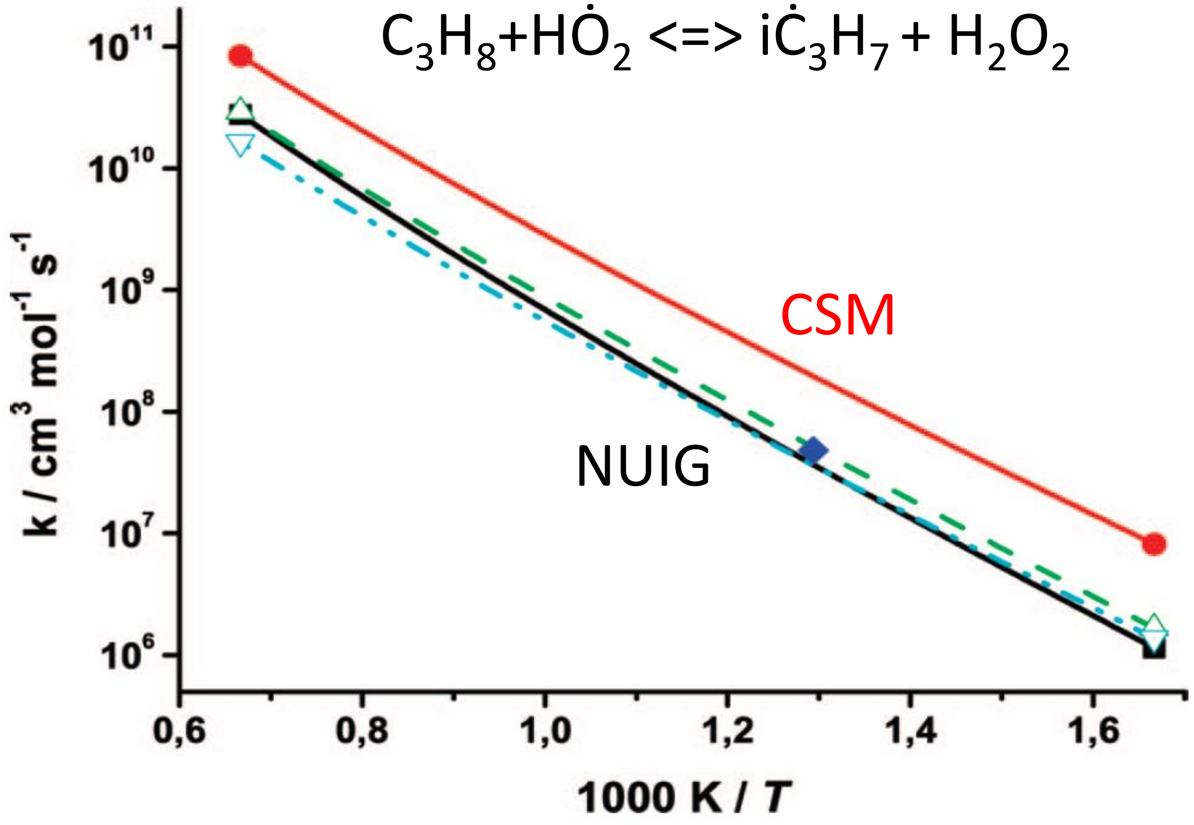
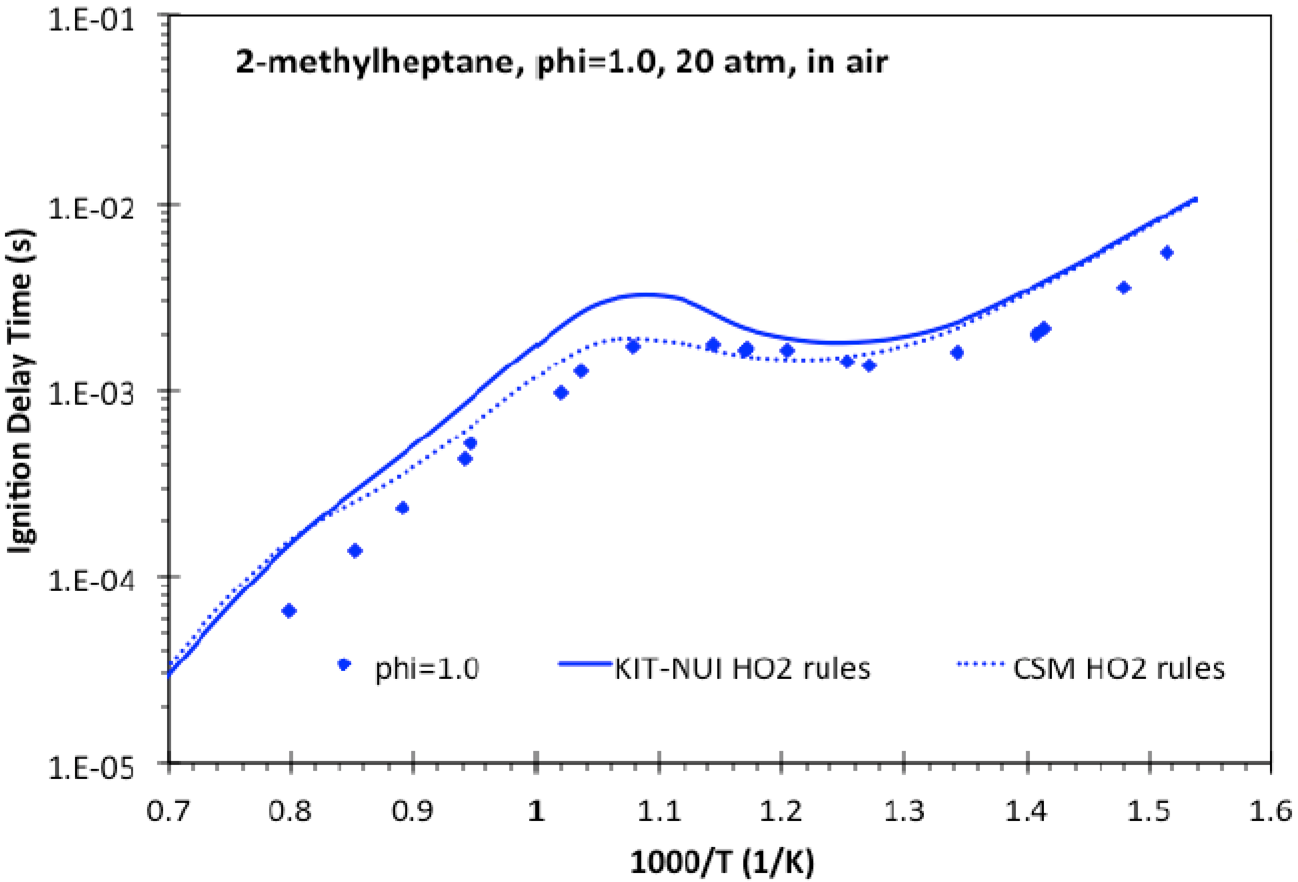

$C_3H_8 + H\dot{O}_2 \Leftrightarrow i\dot{C}_3H_7 + H_2O_2$

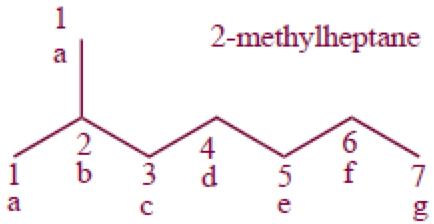
Figure 6. $k(C_3H_8 + HO_2^\bullet \rightarrow i\text{-}C_3H_7^\bullet + H_2O_2)$. This work (—■—), Carstensen[18] (—●—), Scott[8] (--Δ--), Orme[14] (-••▽-••), Baldwin[11] (◆).

Ignition very sensitive to this rate constant under RCM conditions

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

Courtesy of Dr. Pierre-Alexandre Glaude

Evans-Polanyi type correlations

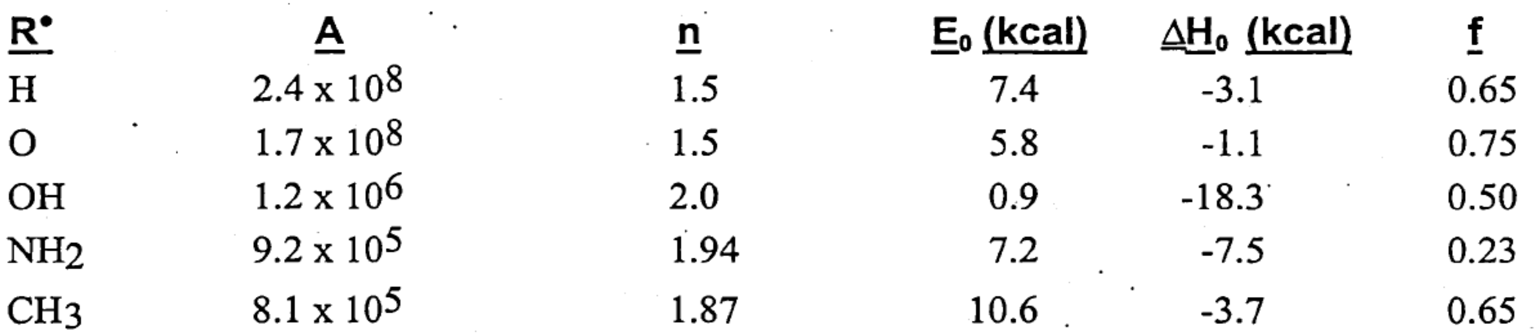
Correlation for H-abstractions on a C-atom or a N-atom (Dean and Bozzelli, 1999)

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

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

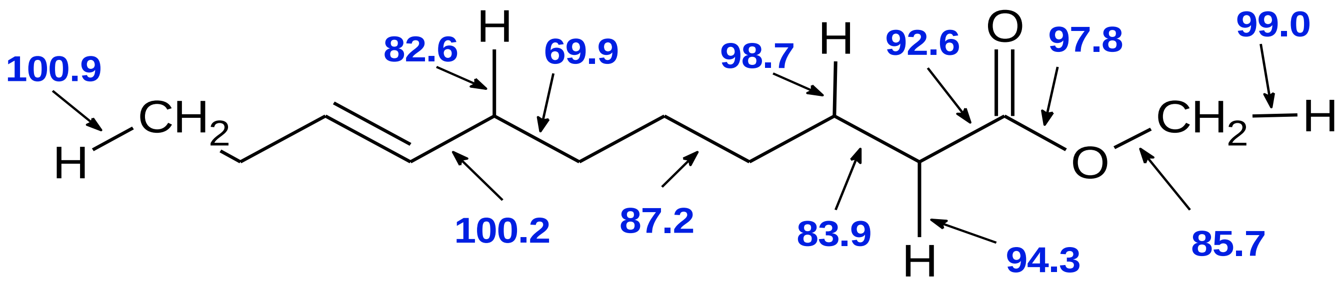
n_H number of equivalent abstractable H-atoms

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



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

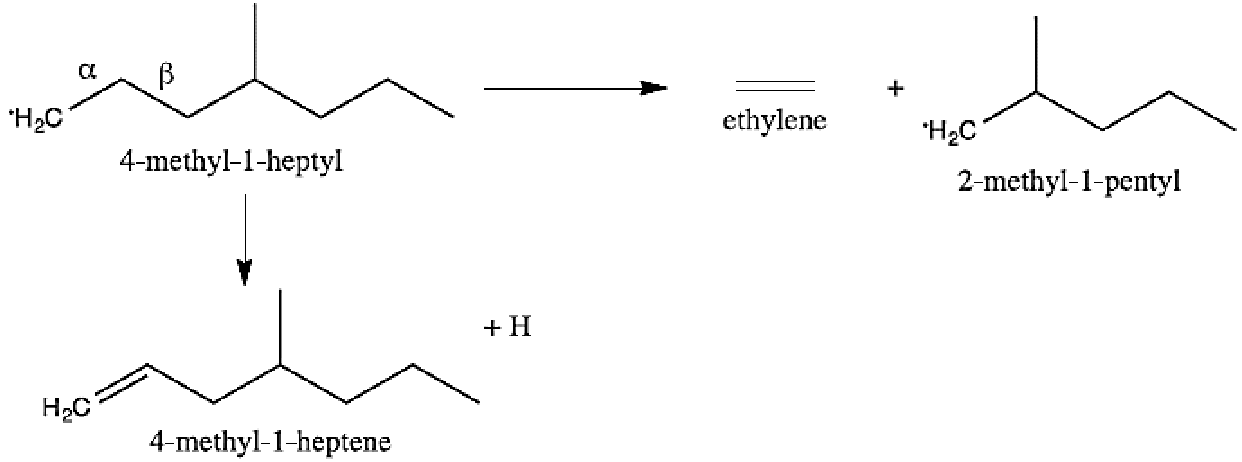
Importance of thermo data and BDE



Courtesy of Dr. Pierre-Alexandre Glaude

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 radical.
- β-scissions of C–H bonds are negligible compared to C–C bond scission at $T \lesssim 2000$ K.
- How many β-scissions are possible?



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)

$^{\cdot}R \rightarrow {}^{\cdot}R' + \text{alkene}$

$^{\cdot}R \rightarrow {}^{\cdot}H + \text{alkene}$

$$E_a = 0.60\,\Delta_rH_0 + 14.3\ \text{kcal/mol}$$

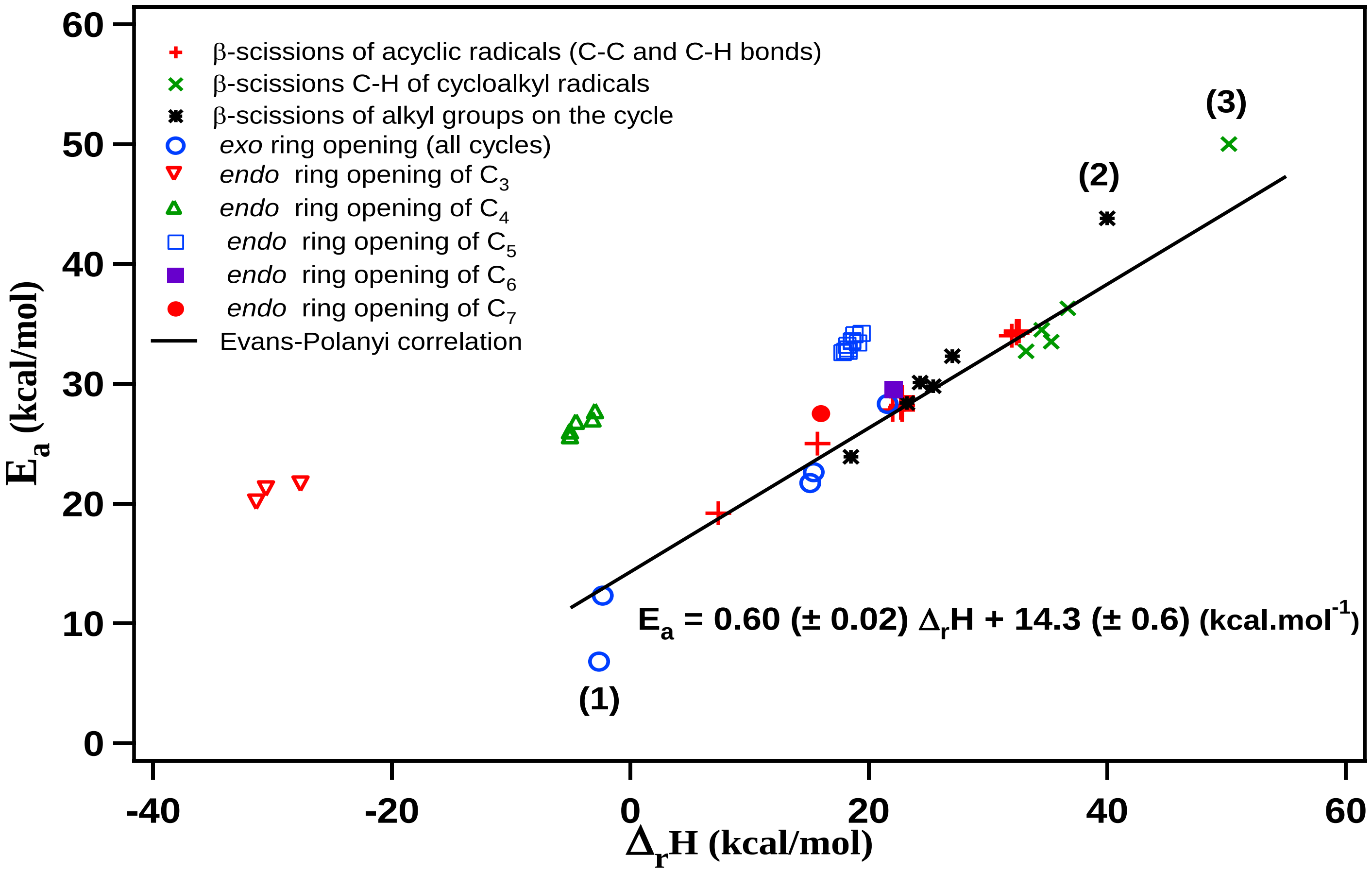
Reactions of acyclic radicals used to built the correlation

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

Courtesy of Dr. Pierre-Alexandre Glaude

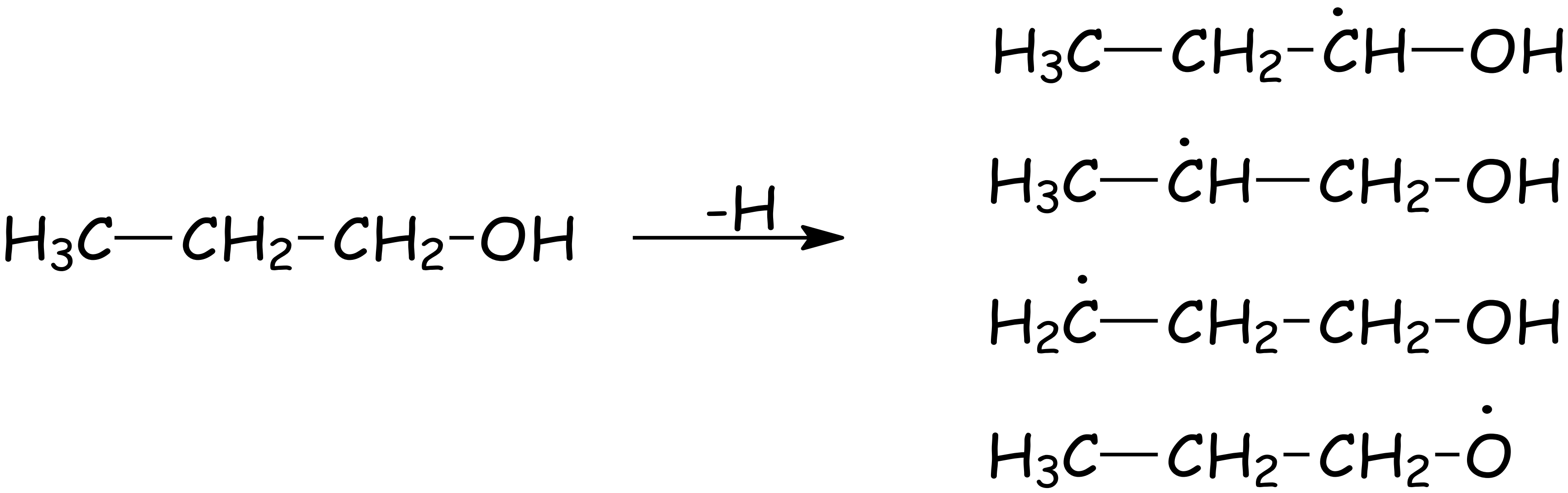
β-scission alkyl free radicals

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



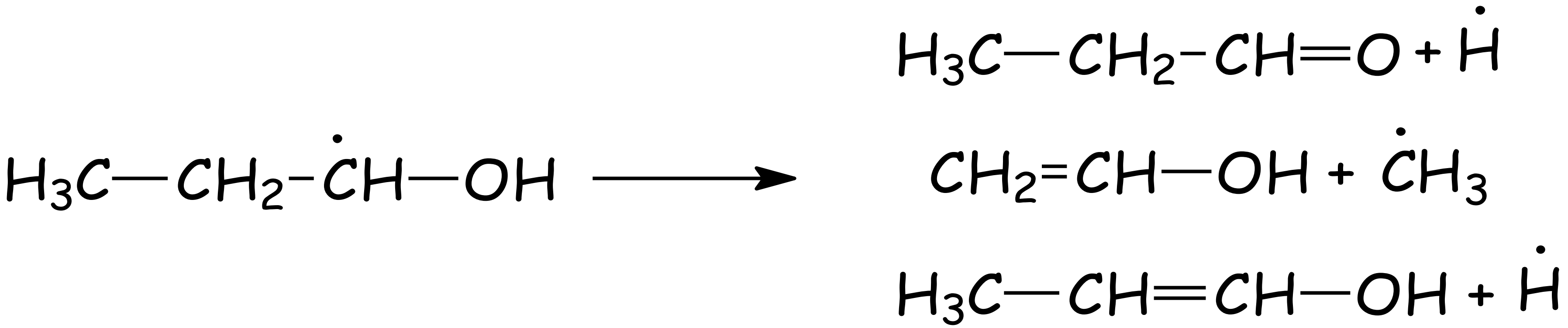
Courtesy of Dr. Pierre-Alexandre Glaude

Alkyl radical decomposition



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

n-Propanol α-radical decomposition



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

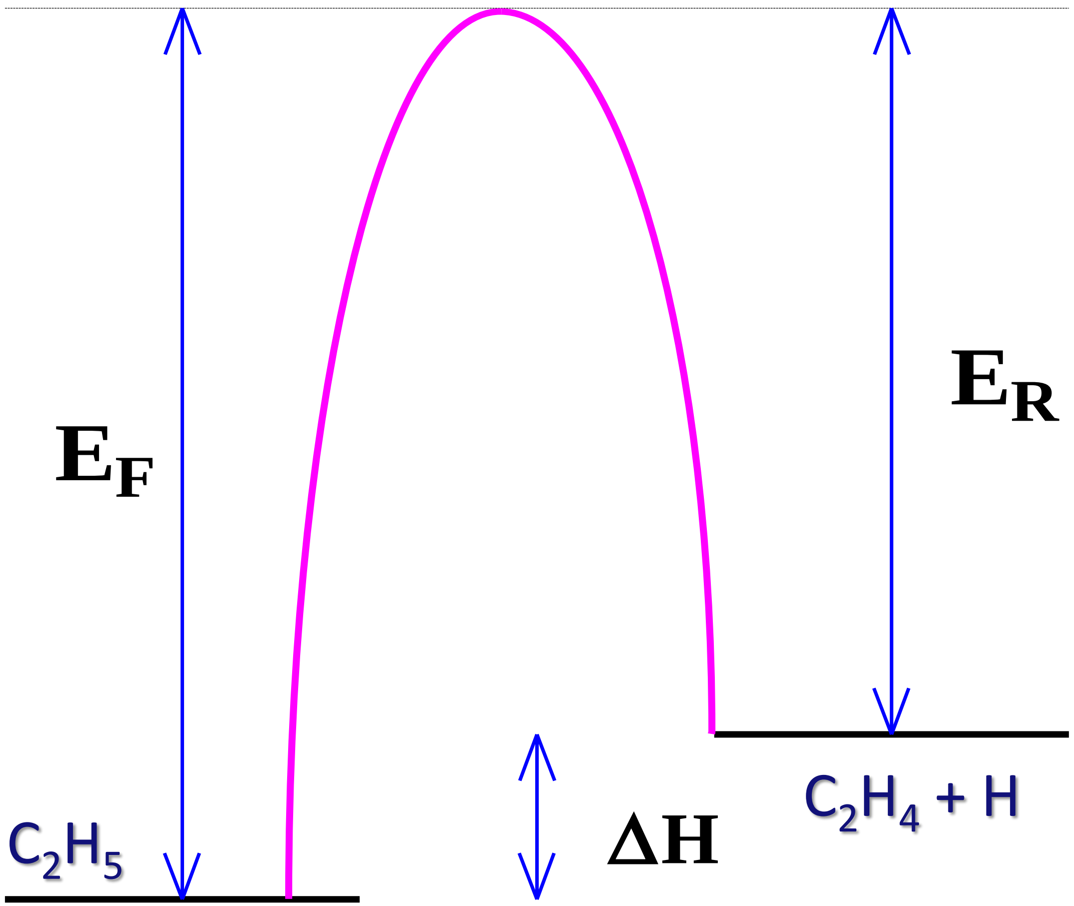
“Enols Are Common Intermediates in Hydrocarbon Oxidation”

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

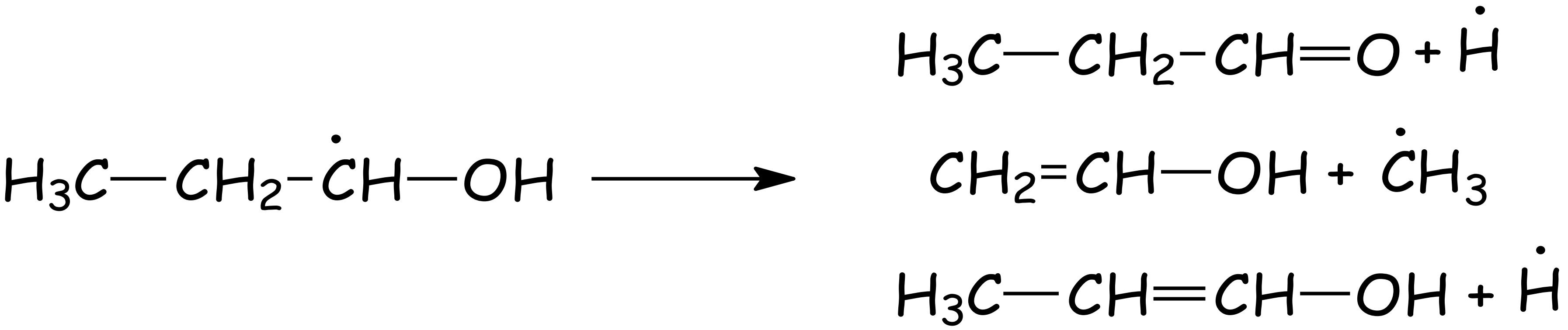
Photoionization mass spectrometry of flames

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

Alkyl radical decomposition



n-Propanol α-radical decomposition



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

Alkyl radical decomposition

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

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

Hydrogen addition

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

J.M. Simmie, H.J. Curran, J. Phys. Chem. A (2009) *113(27)* 7834–7845.

Methyl addition

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

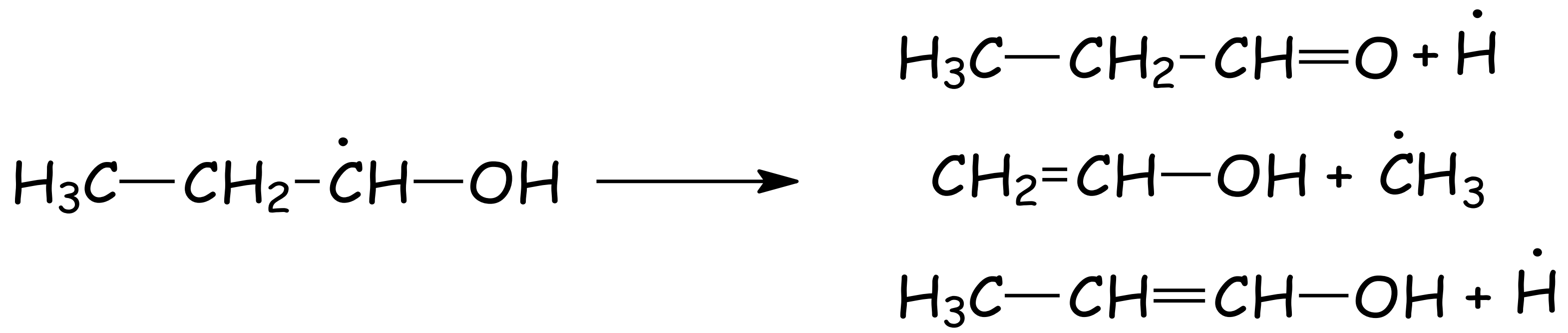
J.M. Simmie, H.J. Curran, J. Phys. Chem. A (2009) *113(27)* 7834–7845.

Ethyl addition

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

J.M. Simmie, H.J. Curran, J. Phys. Chem. A (2009) *113(27)* 7834–7845.

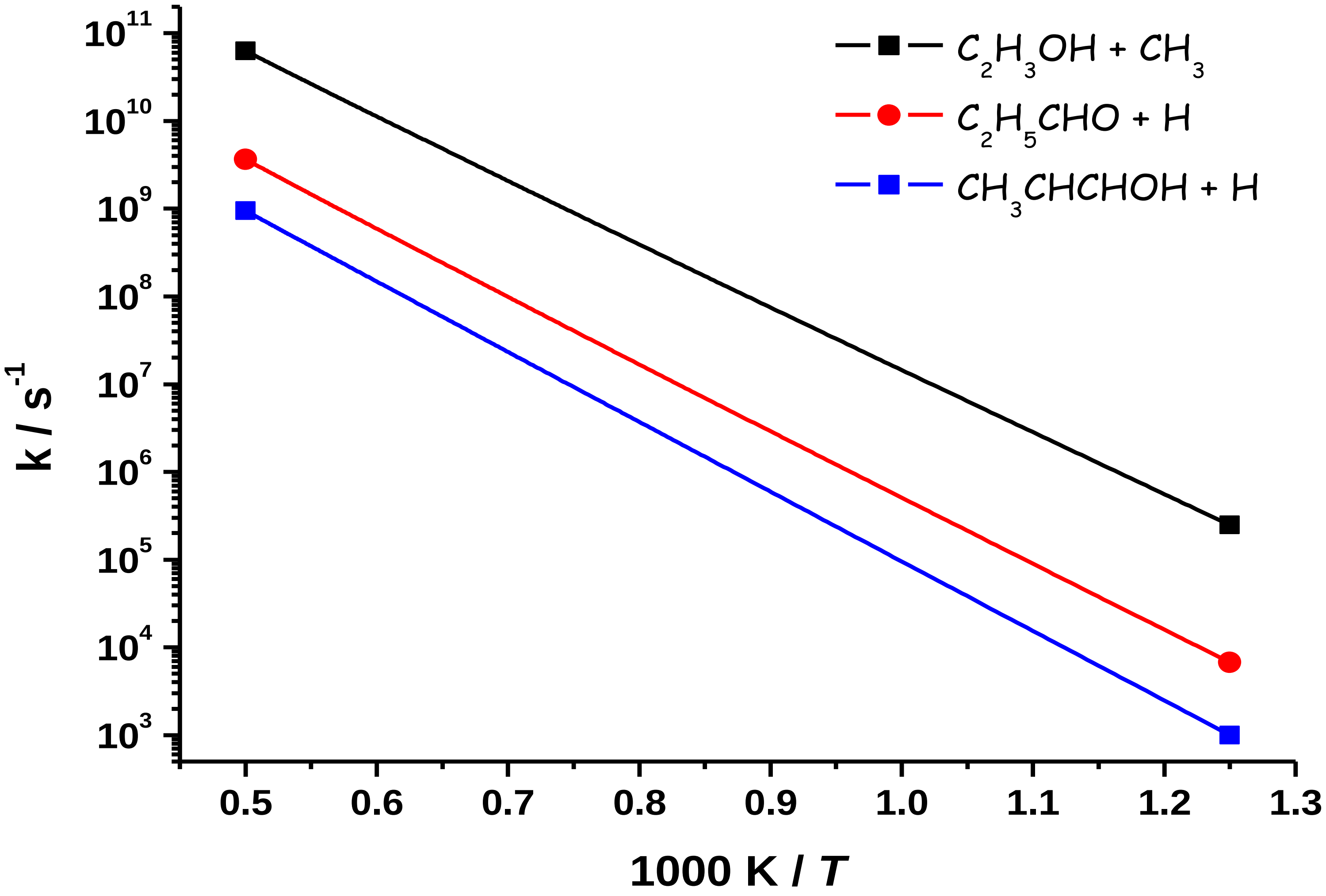
CH_3CH_2CHOH = products?



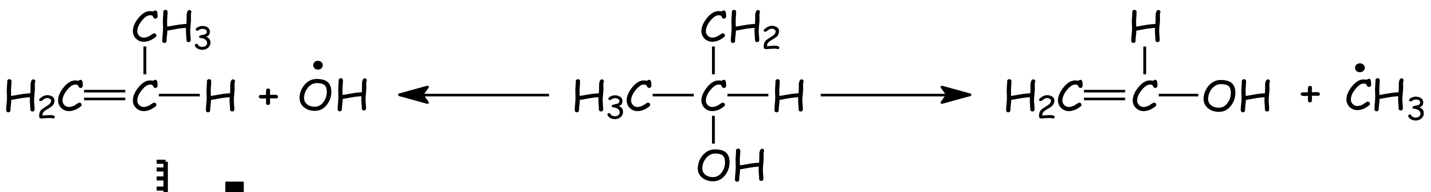
$$H_3C{-}CH_2{-}\dot{C}H{-}OH \longrightarrow \begin{cases} H_3C{-}CH_2{-}CH{=}O + \dot{H} \\ CH_2{=}CH{-}OH + \dot{C}H_3 \\ H_3C{-}CH{=}CH{-}OH + \dot{H} \end{cases}$$

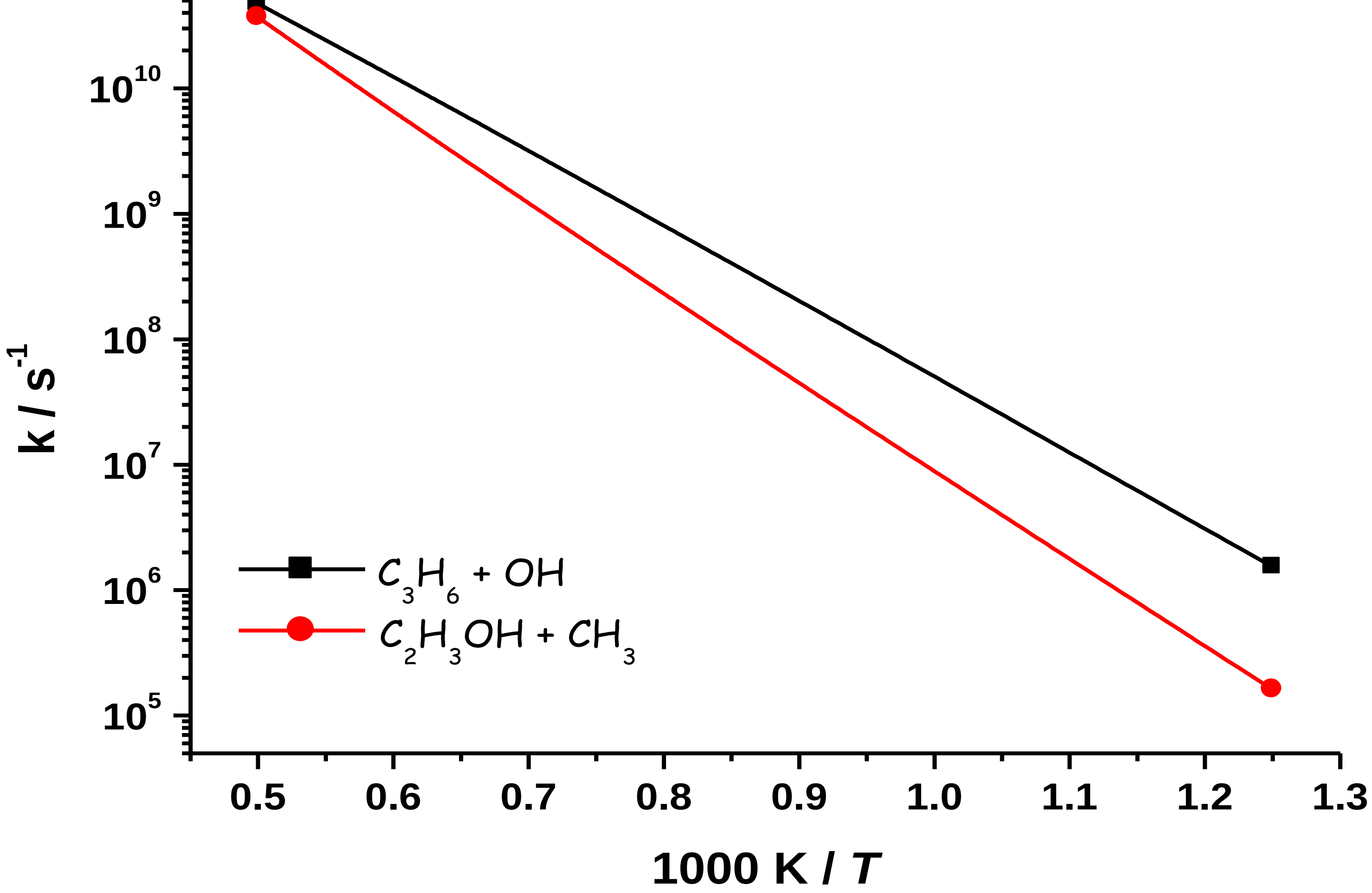
Reaction	A_r	n_r	Ea_r
$CH_3CH_2CH{=}O + H$	8.00×10^{12}	0.00	9500.
$CH_2{=}CHOH + CH_3$	1.76×10^{4}	2.48	6130.
$CH_3CH{=}CHOH + H$	2.50×10^{11}	0.51	2620.
	A_f	n_f	Ea_f
A	7.03×10^{09}	0.99	32590.
B	5.01×10^{10}	1.04	30450.
C	5.46×10^{11}	0.34	35630.

CH_3CH_2CHOH = products?



iC_3H_6OH = products?



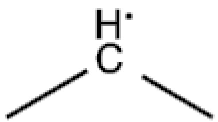


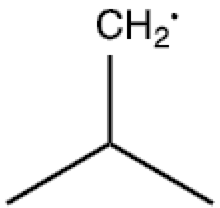
3: Alkyl radical decomposition

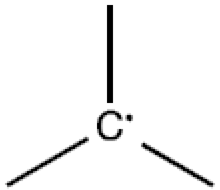
- Recombination rates for H-atom addition to an alkene (i.e., reverse of β-scission).

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


n-propyl


iso-propyl

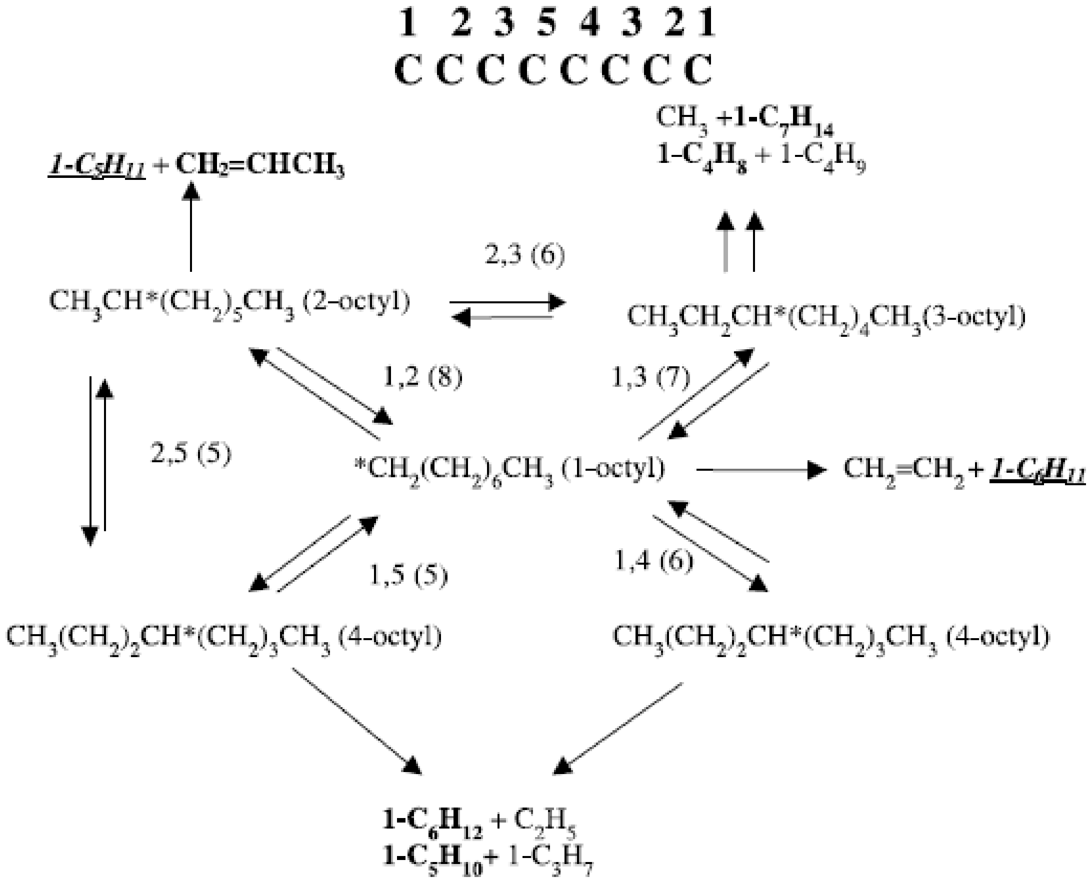

iso-butyl


tert-butyl

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

4: Alkyl radical isomerization

- Alkyl radical decompositions cannot be separated from radical isomerizations



1 2 3 5 4 3 2 1

C C C C C C C C

CH_3 + **1-C_7H_{14}**

1-C_4H_8 + 1-C_4H_9

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

2,3 (6)

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

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

1,2 (8)

1,3 (7)

2,5 (5)

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

CH_2=CH_2 + ***1-C_6H_{11}***

1,5 (5)

1,4 (6)

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

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

1-C_6H_{12} + C_2H_5

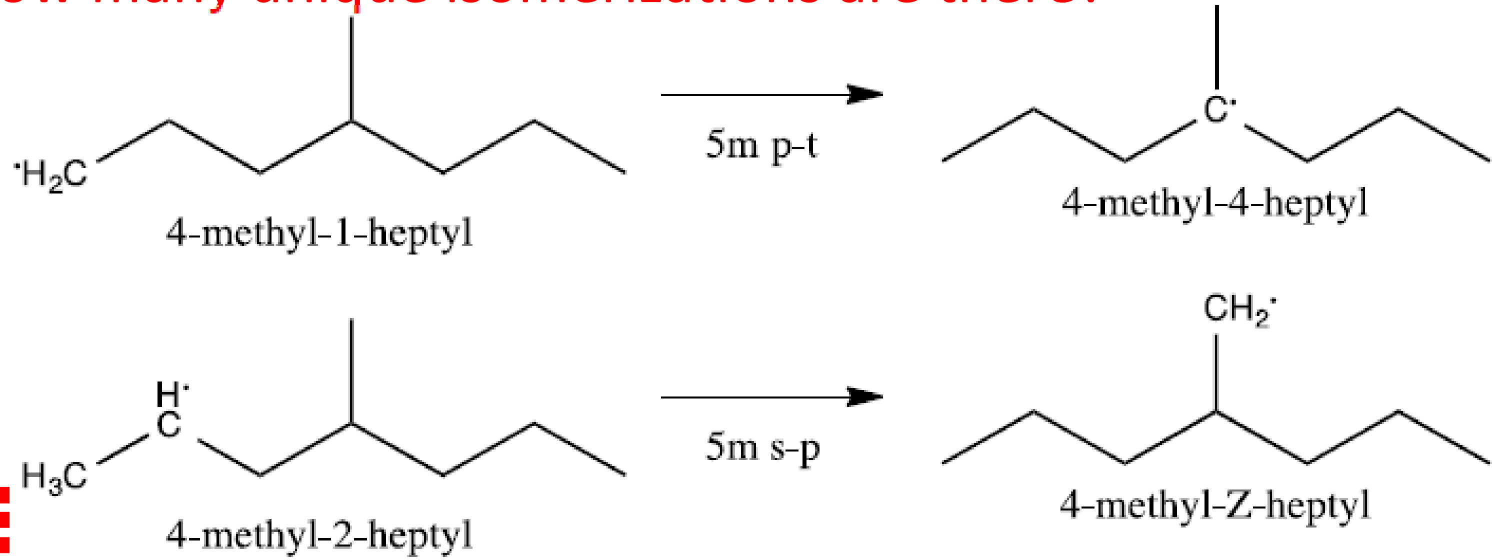
1-C_5H_{10}+ 1-C_3H_7

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

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

4: Alkyl radical isomerization

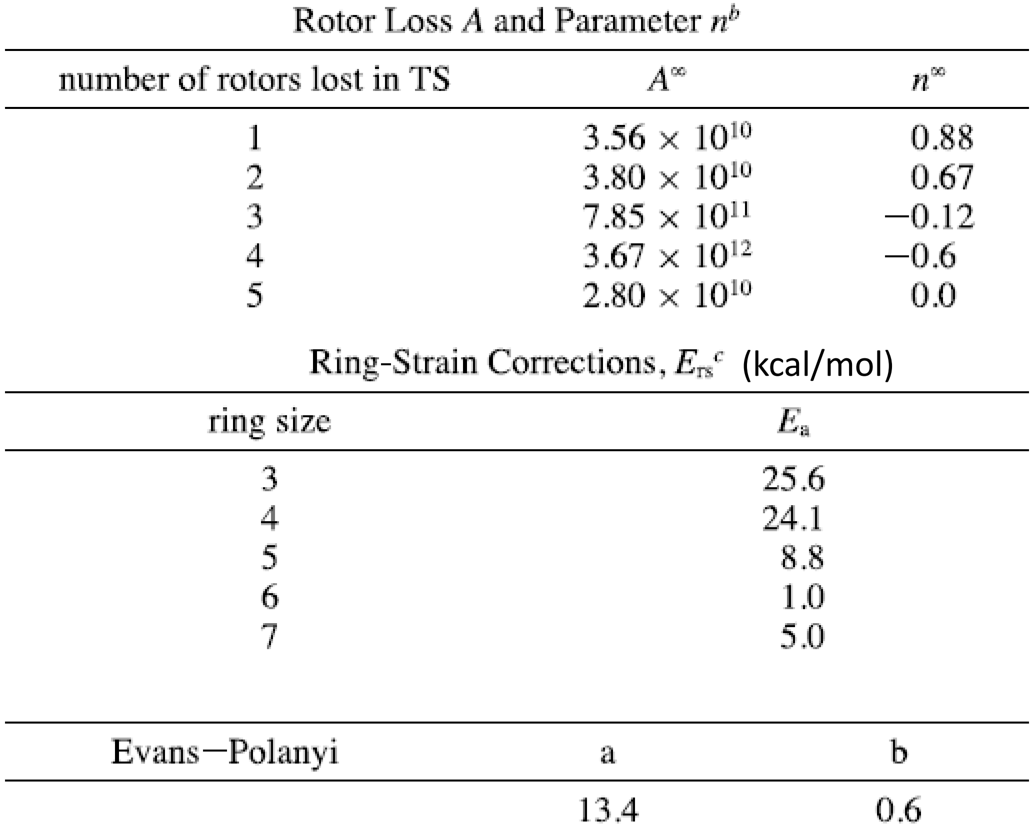
- The rate constant for these reactions depends on the nature of the broken C-H bond (i.e., primary, secondary, or tertiary) and on the ring strain energy barrier.
- Isomerization reactions involving 5-member, 6-member, and 7-member transition state ring are most important
- Radical isomerizations involving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



4: Alkyl radical isomerization

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

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



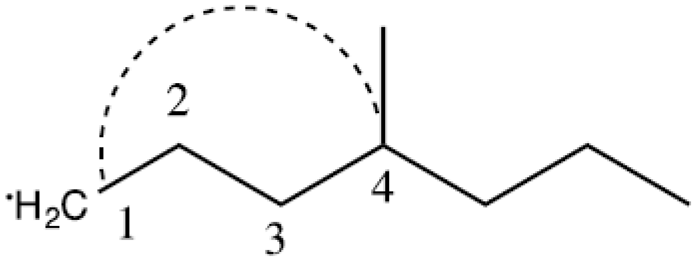
Rotor Loss A and Parameter n[b]

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

Ring-Strain Corrections, E_{rs}[c] (kcal/mol)

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

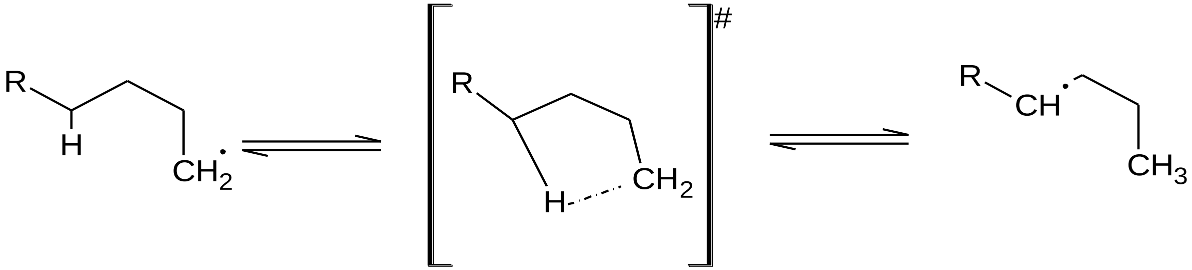
Evans−Polanyi	a	b
	13.4	0.6



1,4 isomerization ties up 3 rotors

D.M. Matheu, W.H. Green, J.M. Grenda, Intl. J. Chem. Kinet. 35 (2003) 95–119.

Isomerization of free radicals: activation energy



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

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

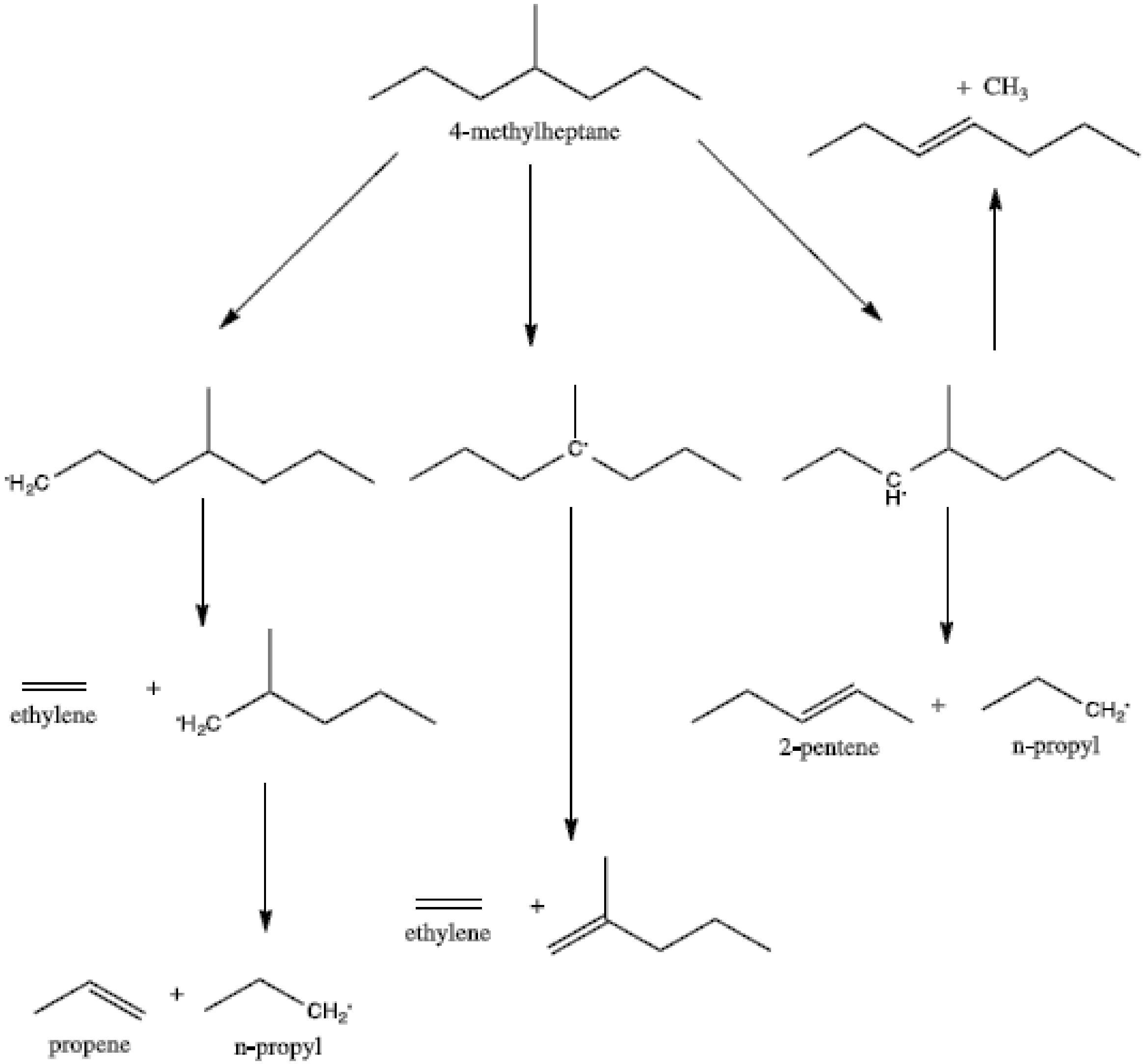
	H_p	H_s	H_t
E_{abstr} (kcal mol^{-1})	13500	11000	9000

Atoms in the cyclic TS	4	5	6	7	8	9
E_{ring} (kcal mol^{-1})	26000	6300	1000	6400	9900	12800

Courtesy of Dr. Pierre-Alexandre Glaude

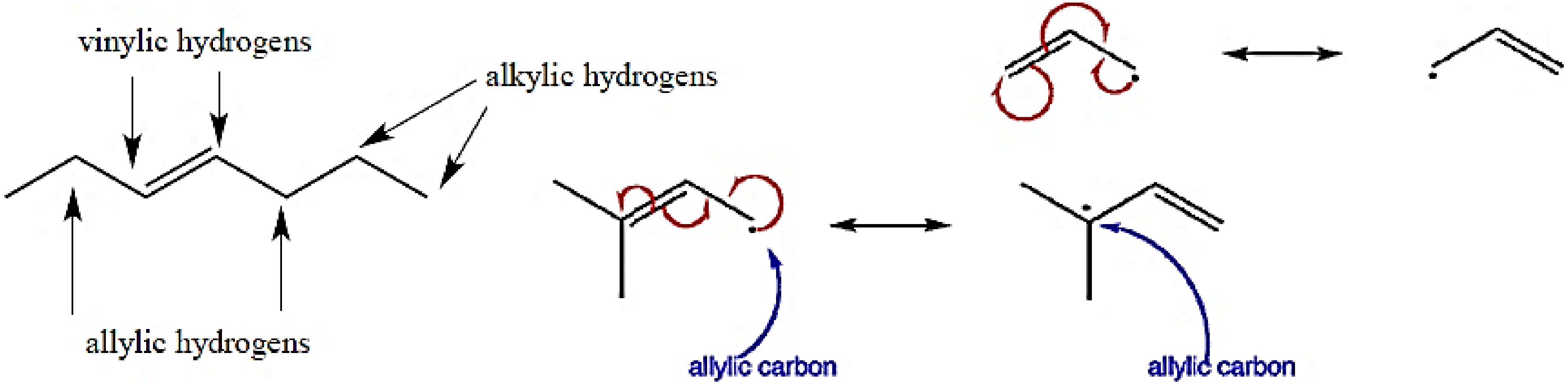
So where are we now?

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



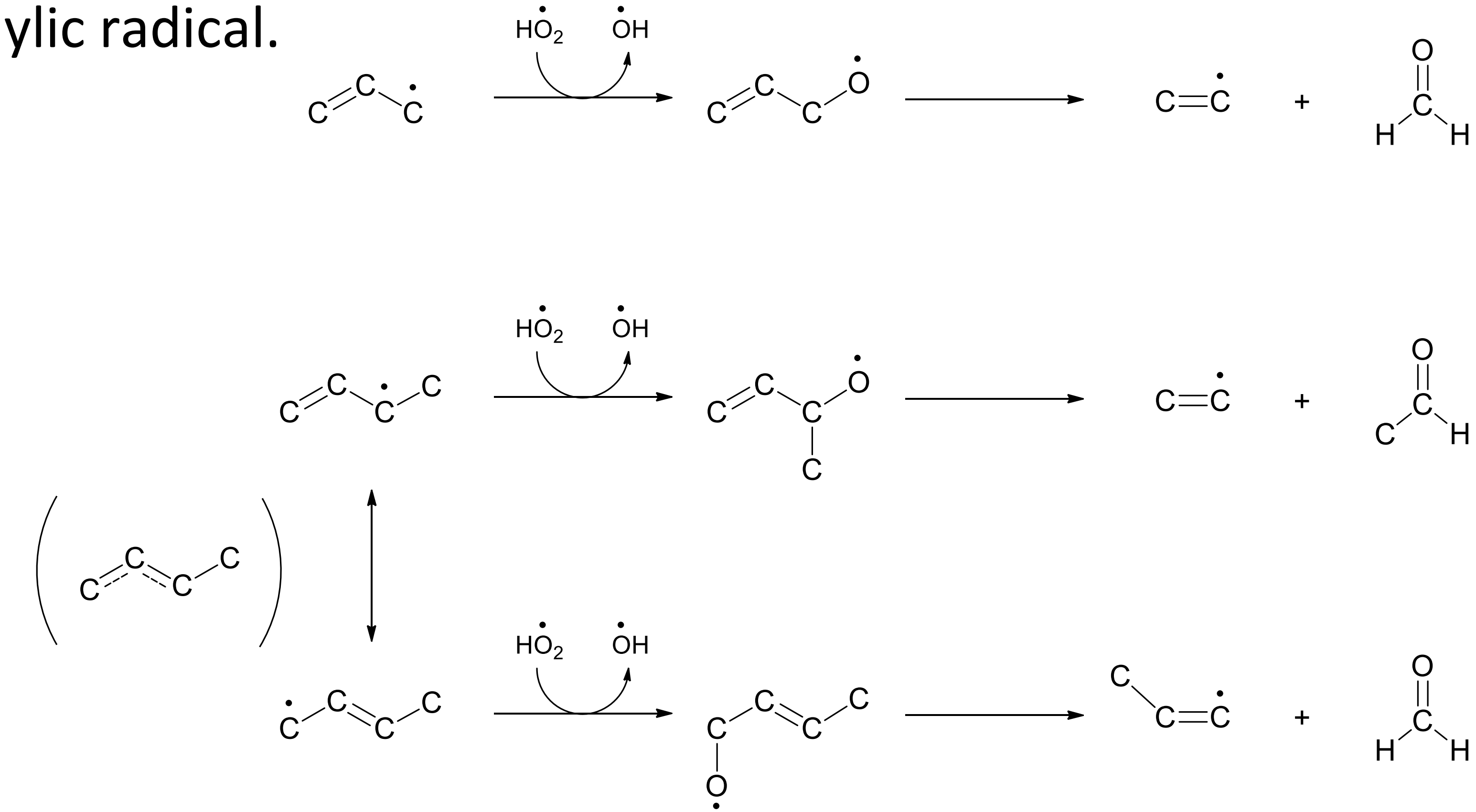
H atom abstraction from alkenes

- 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.

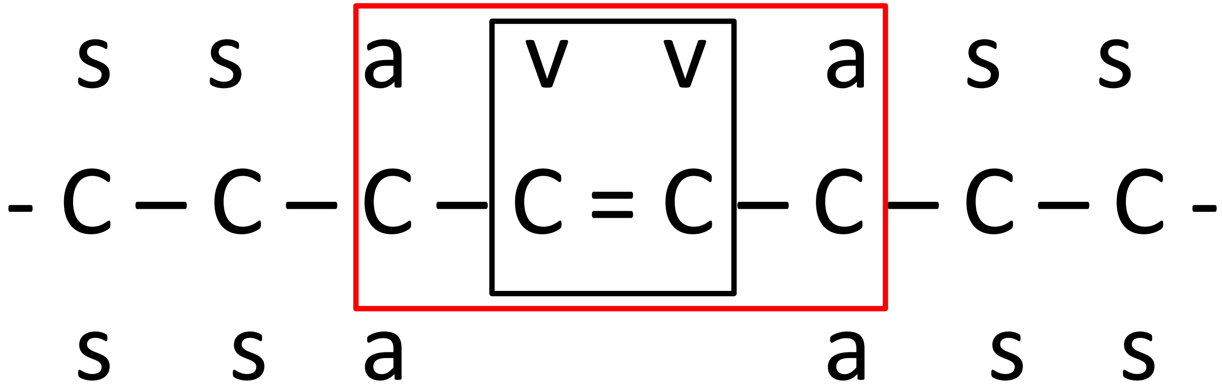


Allylic radical decomposition

- Allylic radicals either undergo β-scission or react with $H\dot{O}_2$ radicals to generate allyloxy and $\dot{O}H$ radicals.
- Allyloxy radicals decompose via β-scission to generate an aldehyde and a vinylic radical.

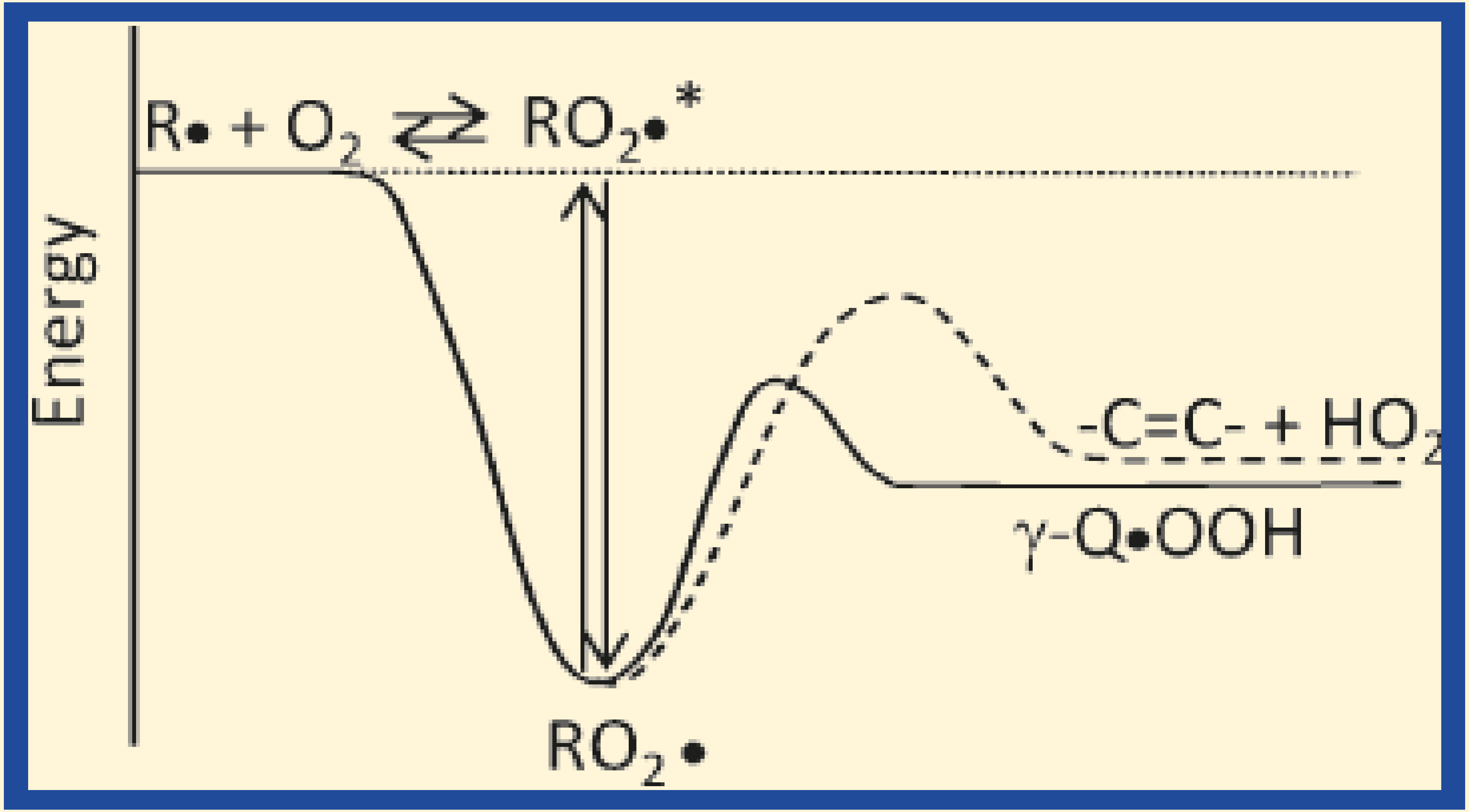


C = C double bonds reduce low T reactivity

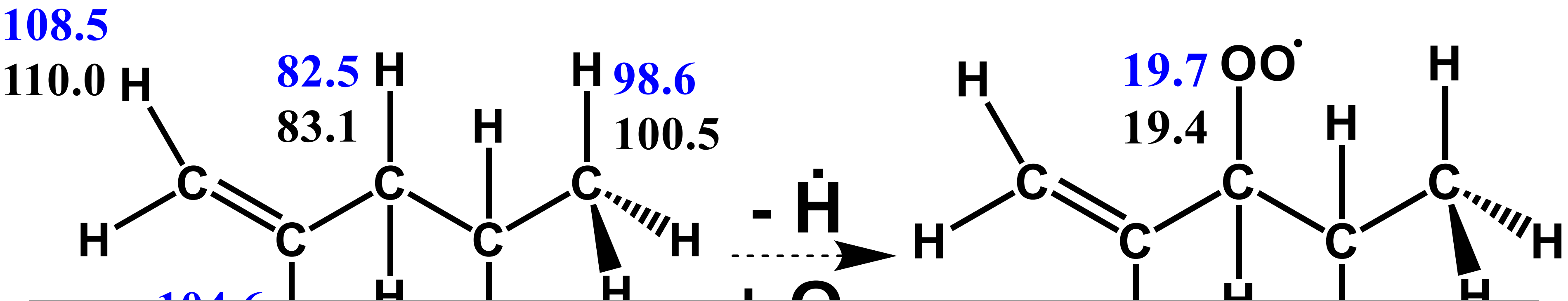


- Inserting one C=C double bonds changes the reactivity of 4 carbons atoms in the C chain
- Allylic C – H bond sites are weaker than most others
- Therefore they are preferentially abstracted by radicals
- O_2 is also very weakly bound at allylic sites and falls off rapidly, inhibiting low T reactivity

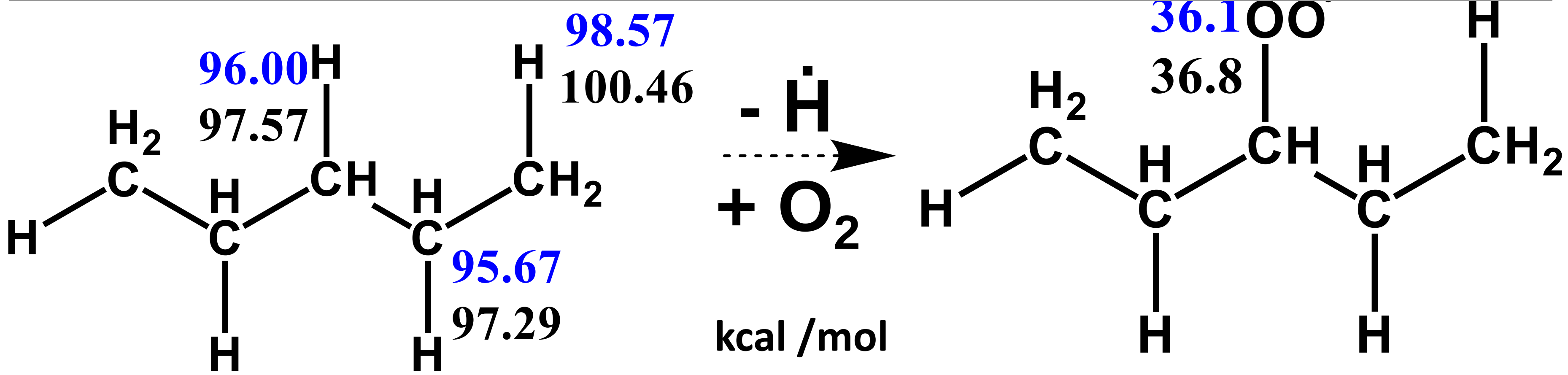
PES for $\dot{R} + O_2 \leftrightarrow R\dot{O}_2$



Structure Difference



Alkanes/Alkenes Different LTC

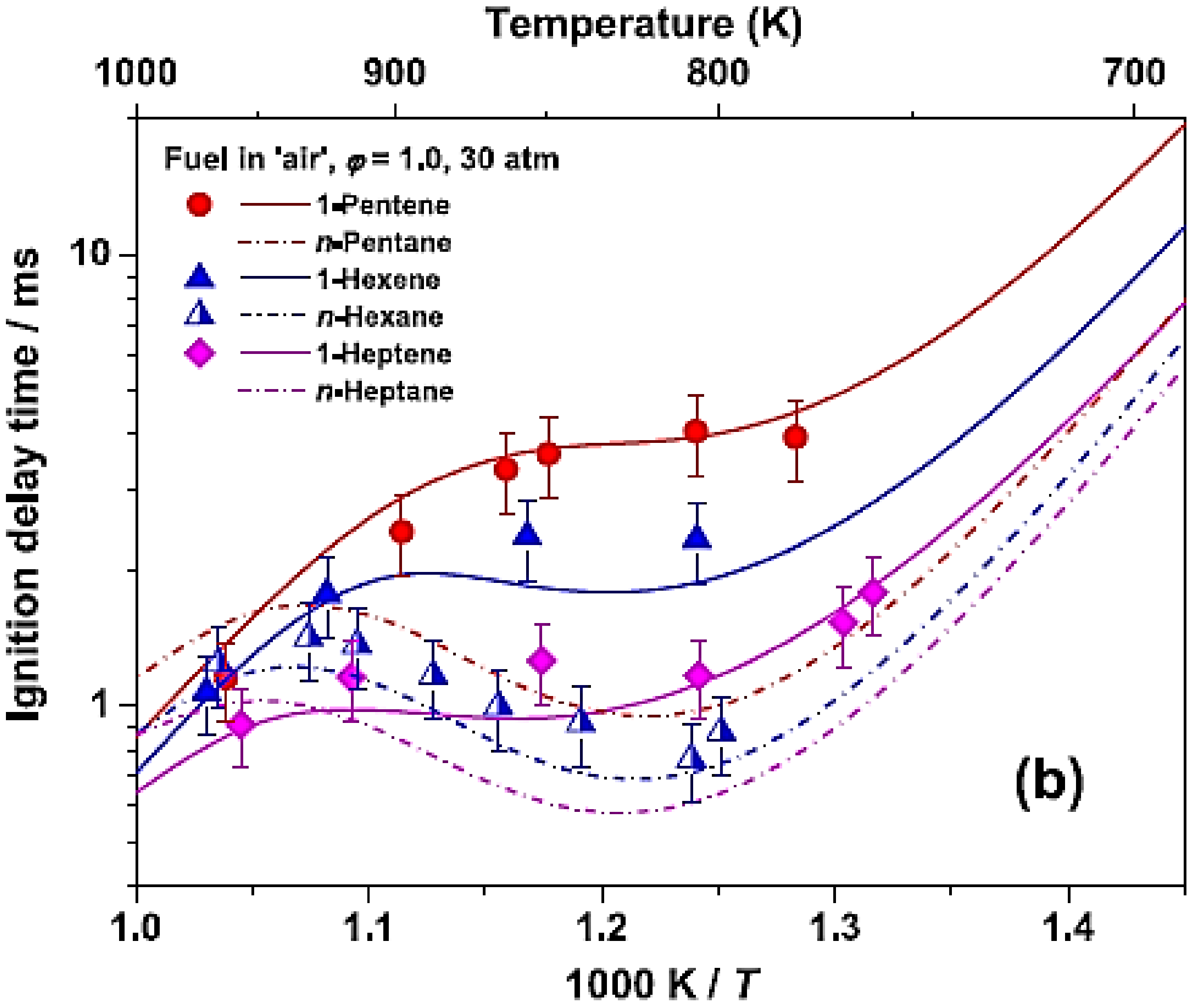


kcal /mol

G4

CBS-QB3

Alkane/Alkene different reactivity



S. Dong et al. Proc. Combust. Inst. 38 (2021) 611—619.

Observed reactivity effect in hexene fuels

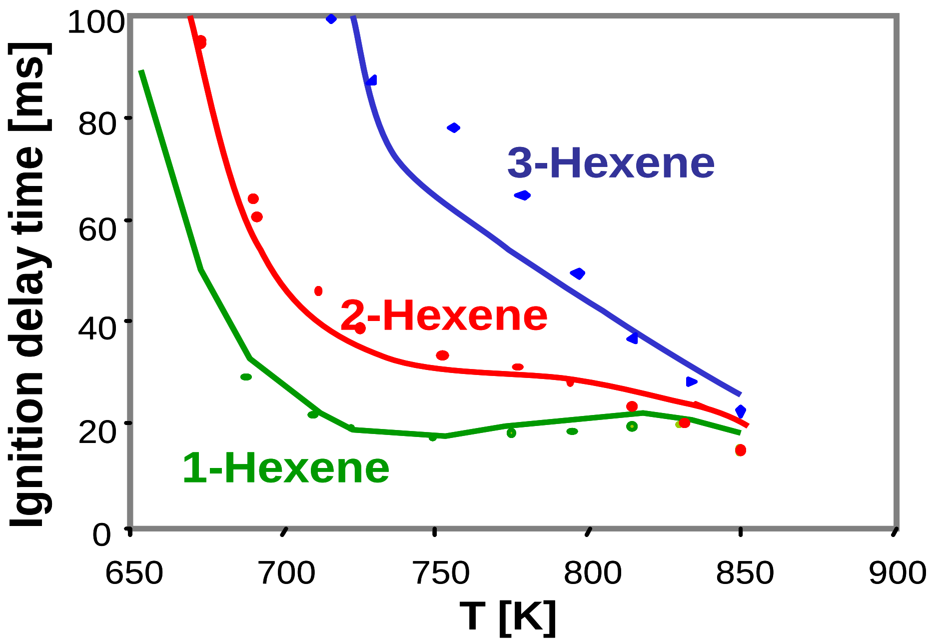
LLNL

C = C - C - C - C - C	1-hexene
C - C = C - C - C - C	2-hexene
C - C - C = C - C - C	3-hexene

RO_2 isomerization initiates low temperature reactivity

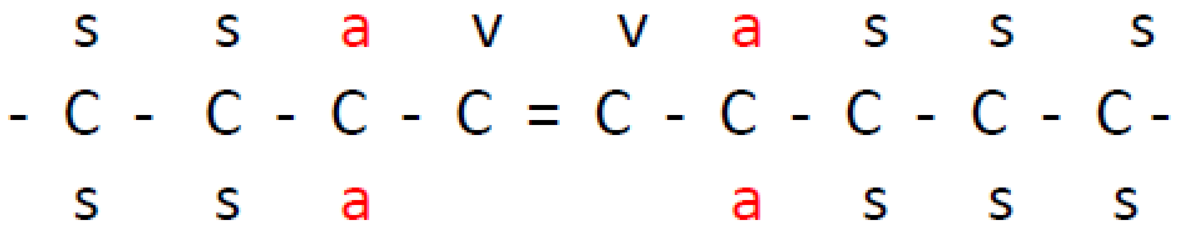
Moving the double bond towards the center of the molecule "inhibits" RO_2 kinetics

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



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

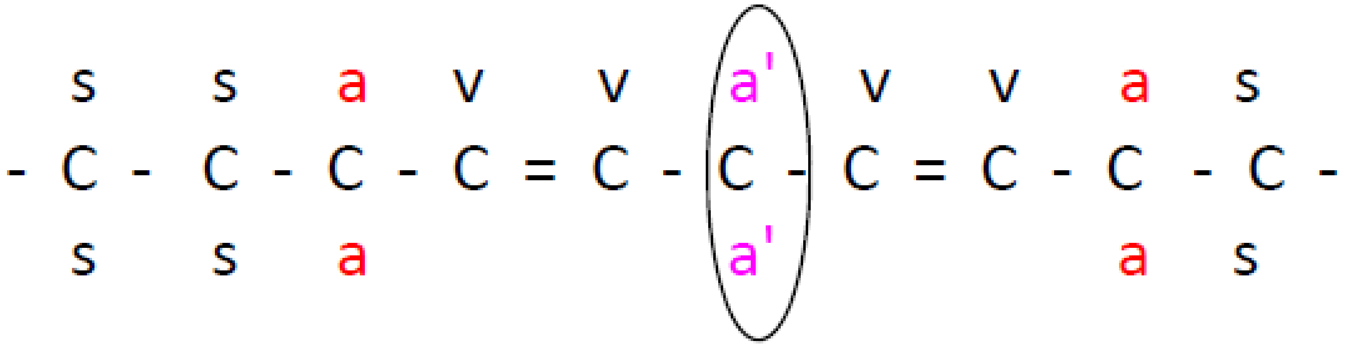
Two double bonds make a huge difference



s s a v v a s s s

- C - C - C - C = C - C - C - C - C -

s s a a s s s



s s a v v a' v v a s

- C - C - C - C = C - C - C = C - C - C -

s s a a' a s

C – H s site > C – H a site > C – H a′ site

Outlook

- Kinetic mechanisms for ever larger fuel molecules are being developed due to increasing computational ability
- Lack of focus on accurate thermochemistry. ATcT is a very good start but we need more than ΔH_f^0
- Experimental measurements and accurate quantum chemistry calculations of important reactions involved in the C_0–C_4 system are vital for accurate predictions of ALL fuels
- Rate rules are useful in building mechanisms for large molecular weight fuels
  - *k*s for larger molecules can be calculated with increasing accuracy due to increasing computational ability

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 = Cyclic Ether + $\dot{O}H$

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

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

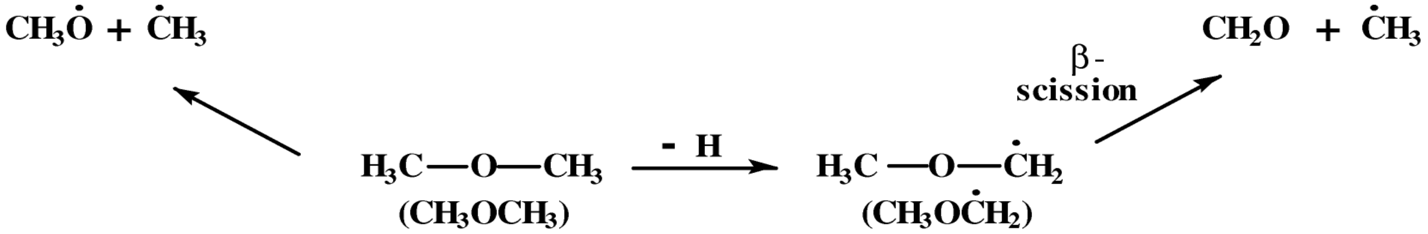
Reaction class 22: Addition of QOOH to molecular oxygen O_2

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 $H\dot{O}_2$

Courtesy of Dr. William Pitz, Lawrence Livermore National Laboratory


CH₃Ȯ + ĊH₃
H₃C—O—CH₃
(CH₃OCH₃)
- H
H₃C—O—ĊH₂
(CH₃OĊH₂)
β-scission
CH₂O + ĊH₃

Correlation 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

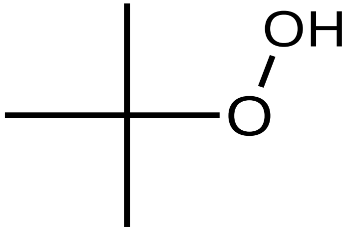
Decomposition of hydroperoxides: $ROOH \rightarrow R\dot{O} + \dot{O}H$

Weak O–O bond (43 kcal/mol)

Experimental measurement for tBuOOH (Sahetchian et al., Proc. Combust. Inst. 24 (1992) 637–643.)

Used for all ROOH molecules

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

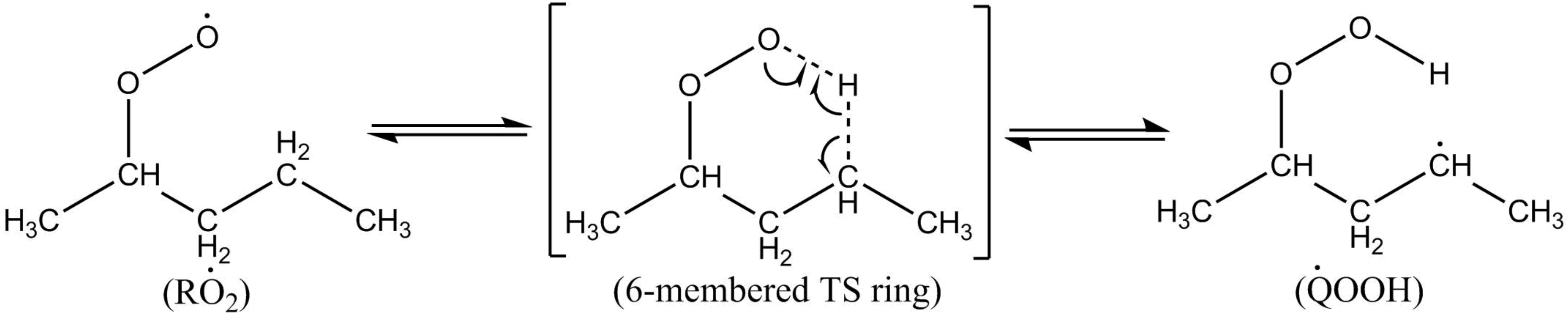


Courtesy of Dr. Pierre-Alexandre Glaude

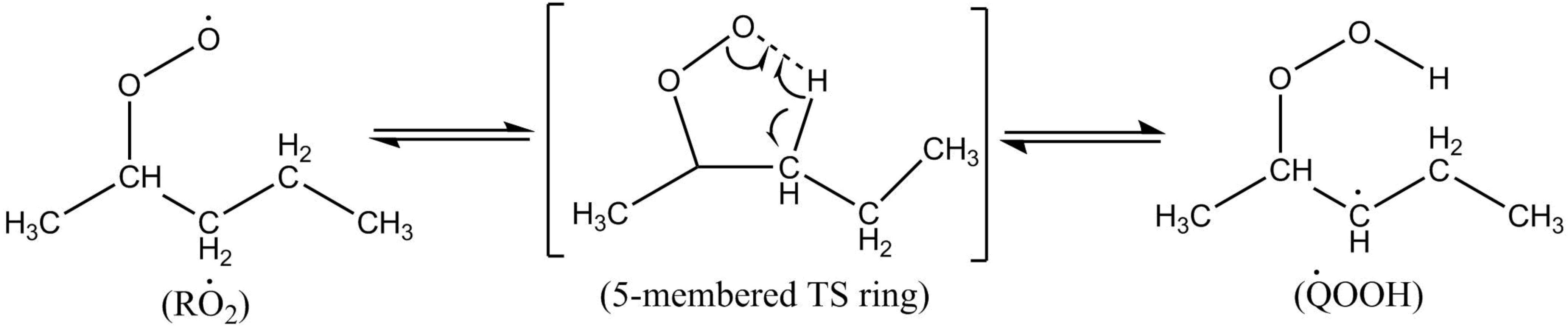
Low temperature chemistry: $RO\dot{O} \rightleftharpoons QOOH$ isomerizations

Class 12

6-membered ring isomerization: $k_6 = 2.5\times10^{10}\ \exp(-20450/RT)$



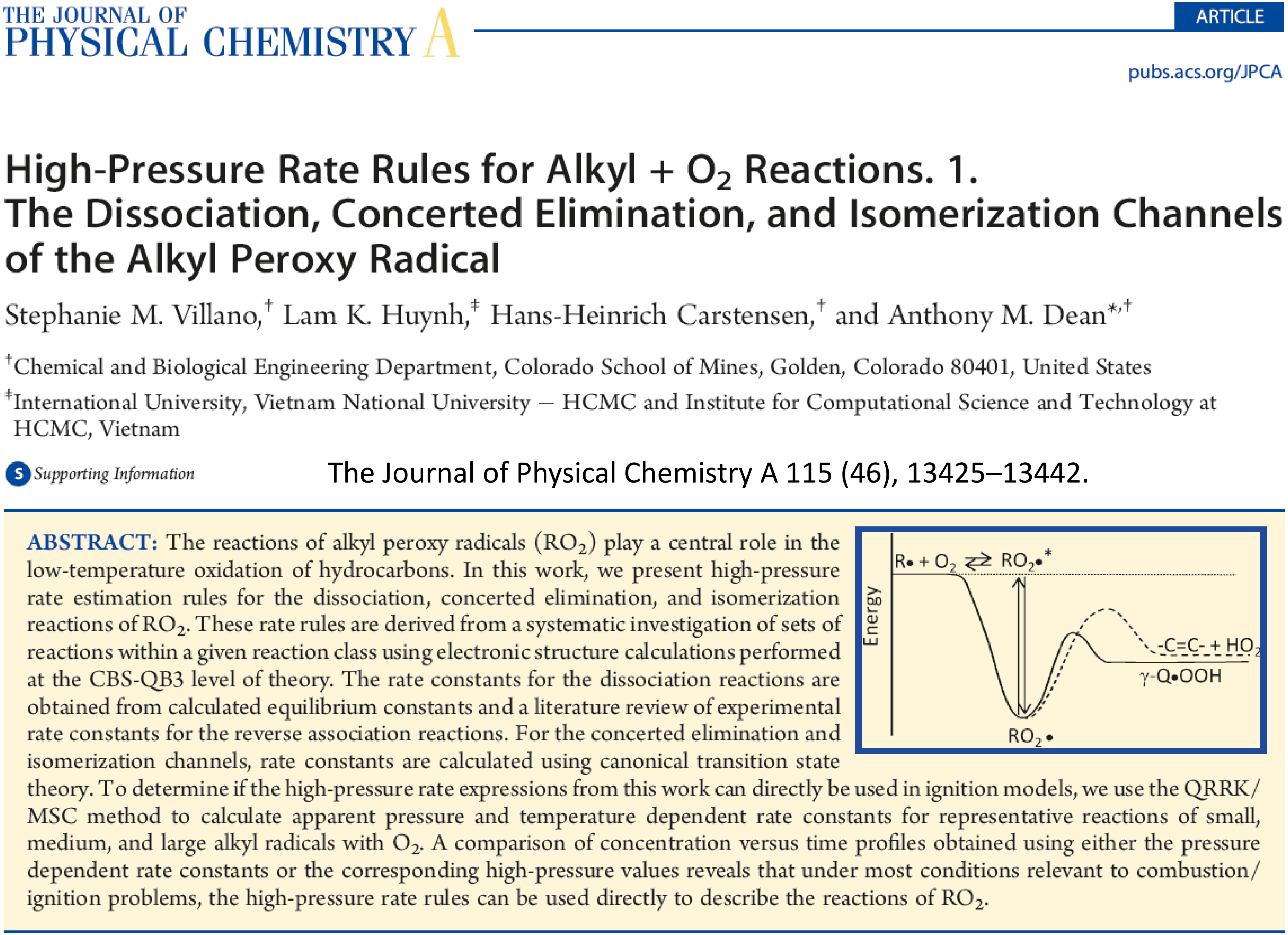
5-membered ring isomerization: $k_5 = 2.0\times10^{11}\ \exp(-26450/RT)$



$R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$

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.



THE JOURNAL OF
PHYSICAL CHEMISTRY A

ARTICLE

pubs.acs.org/JPCA

High-Pressure Rate Rules for Alkyl + O_2 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

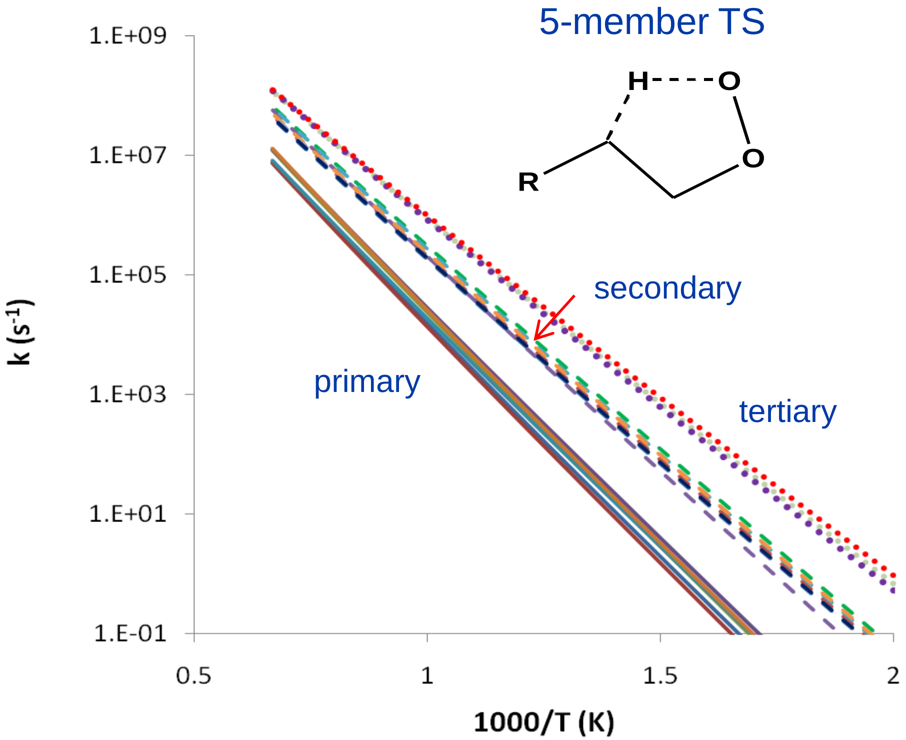
Supporting Information

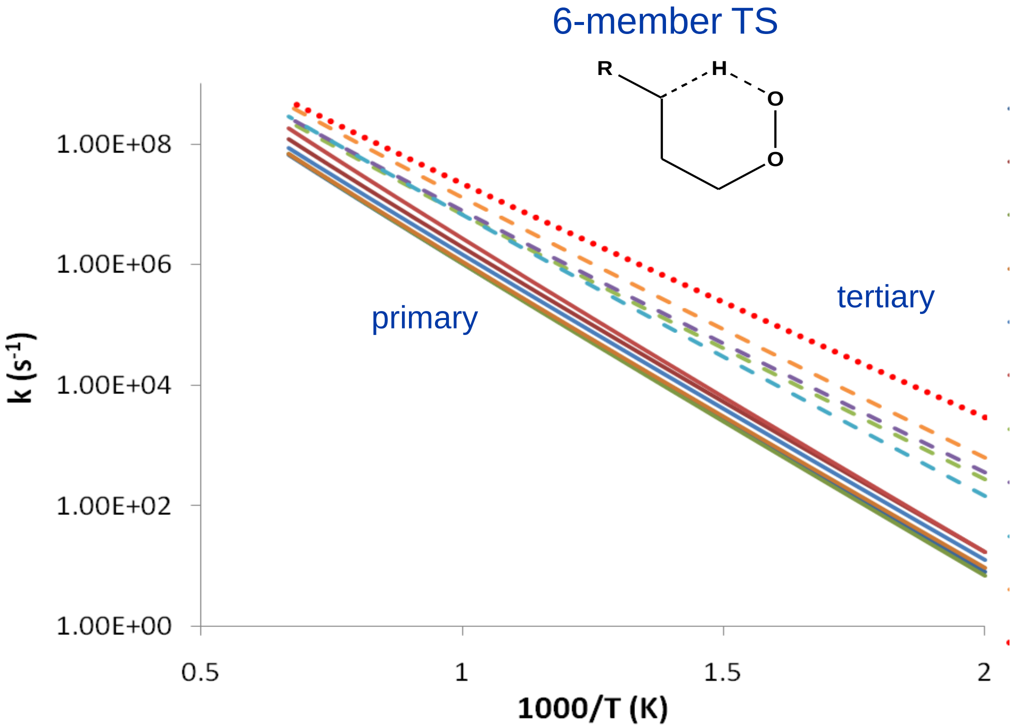
The Journal of Physical Chemistry A 115 (46), 13425–13442.

ABSTRACT: The reactions of alkyl peroxy radicals (RO_2) 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 RO_2. 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 O_2. 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 RO_2.

$R\dot{O}_2$ 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

Courtesy of Dr. William Pitz, Lawrence Livermore National Laboratory

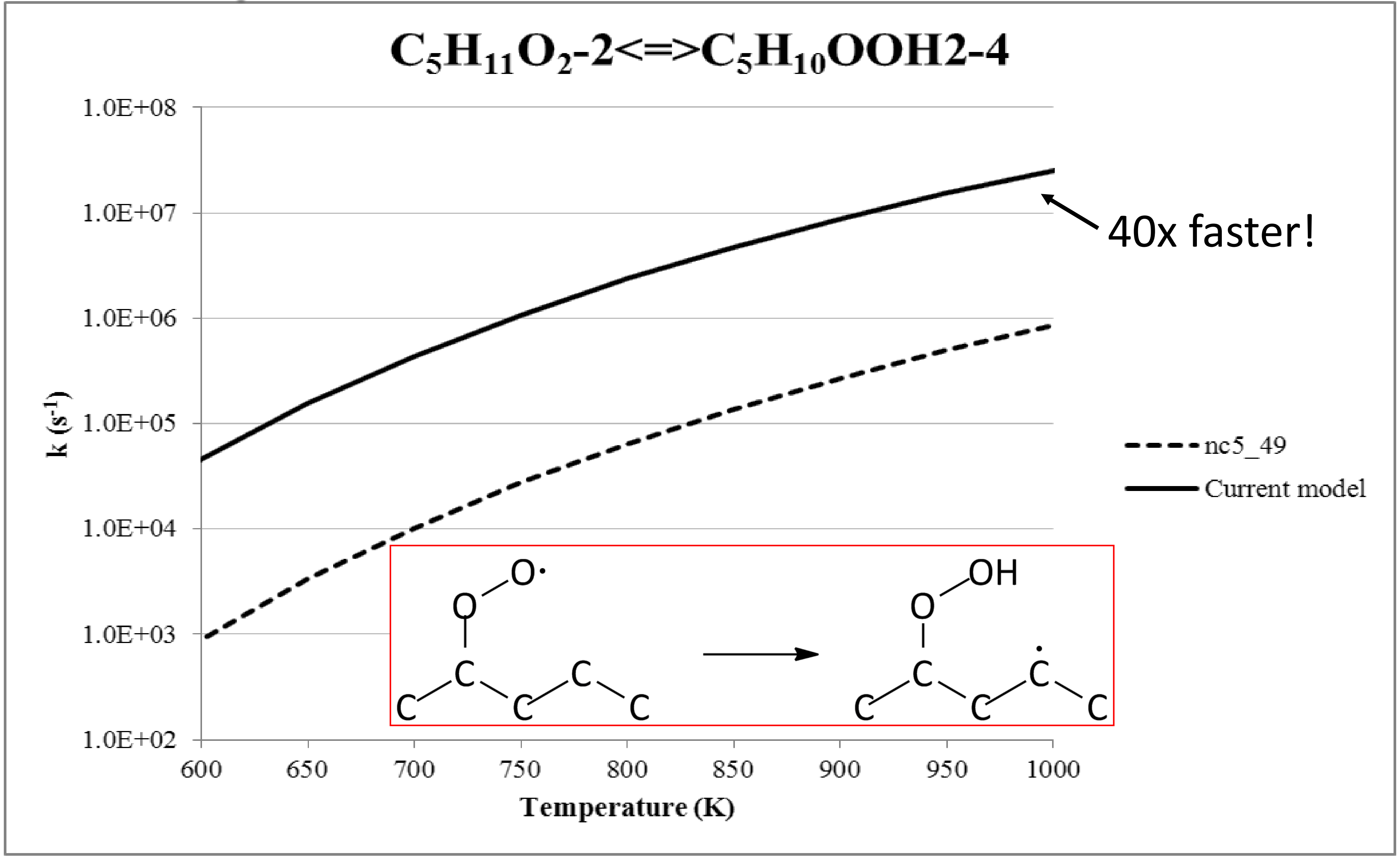
$R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$

		Curran *et al.*			Villano *et al.*		
Ring size	Site	*A*	*n*	*E*	*A*	*n*	*E*
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.

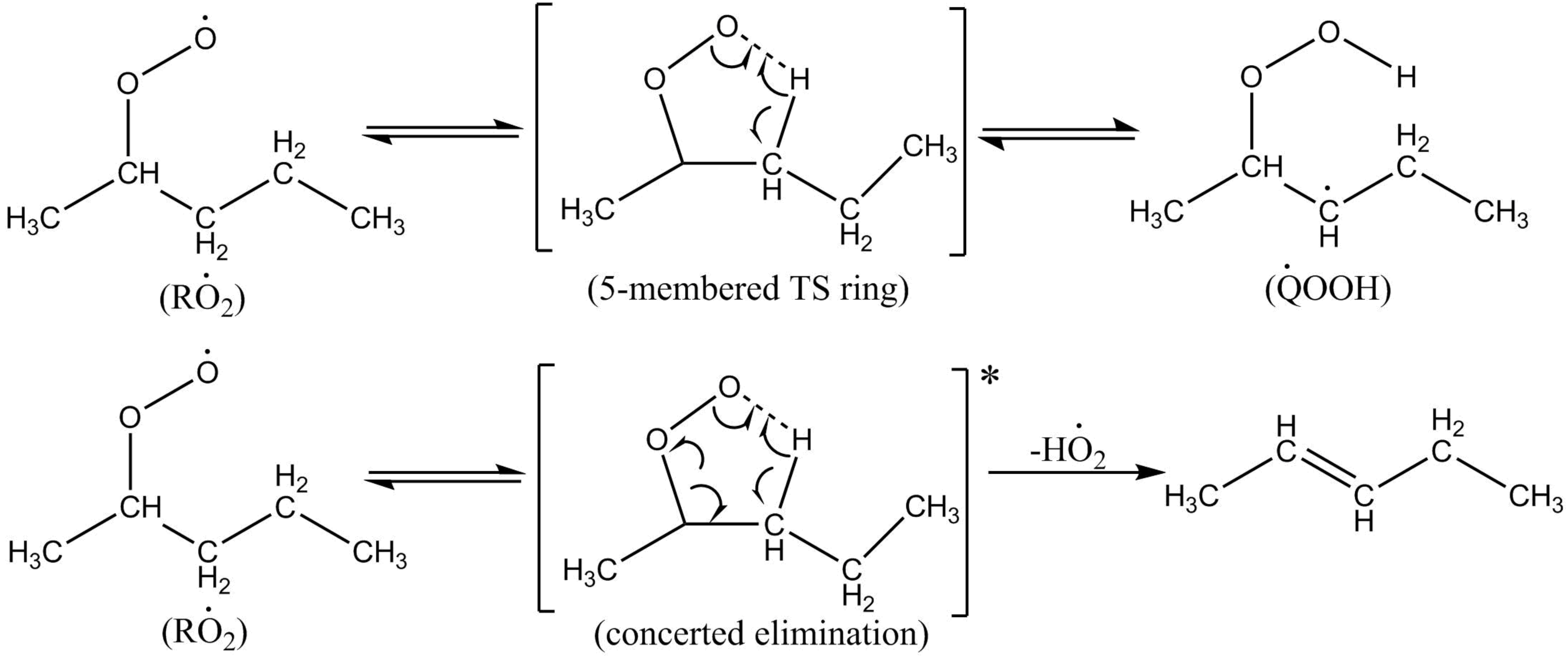
S. M. Villano, L. K. Huynh, H. -H. Carstensen, A. M. Dean
J. Phys. Chem. A **2011,** *115,* 13425–13442.

Comparison of rate coefficients

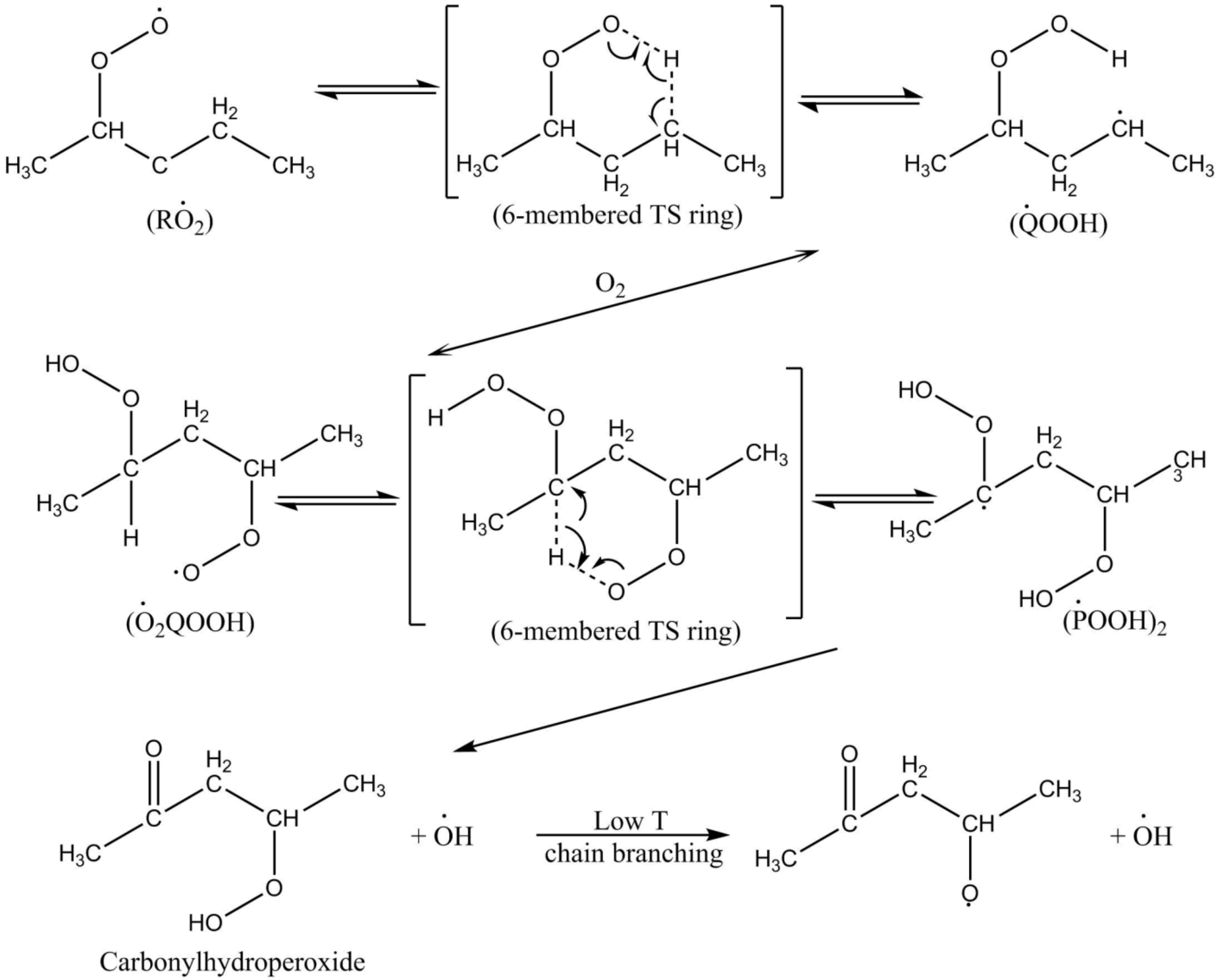

$C_5H_{11}O_2$-2<=>$C_5H_{10}OOH2$-4

40x faster!

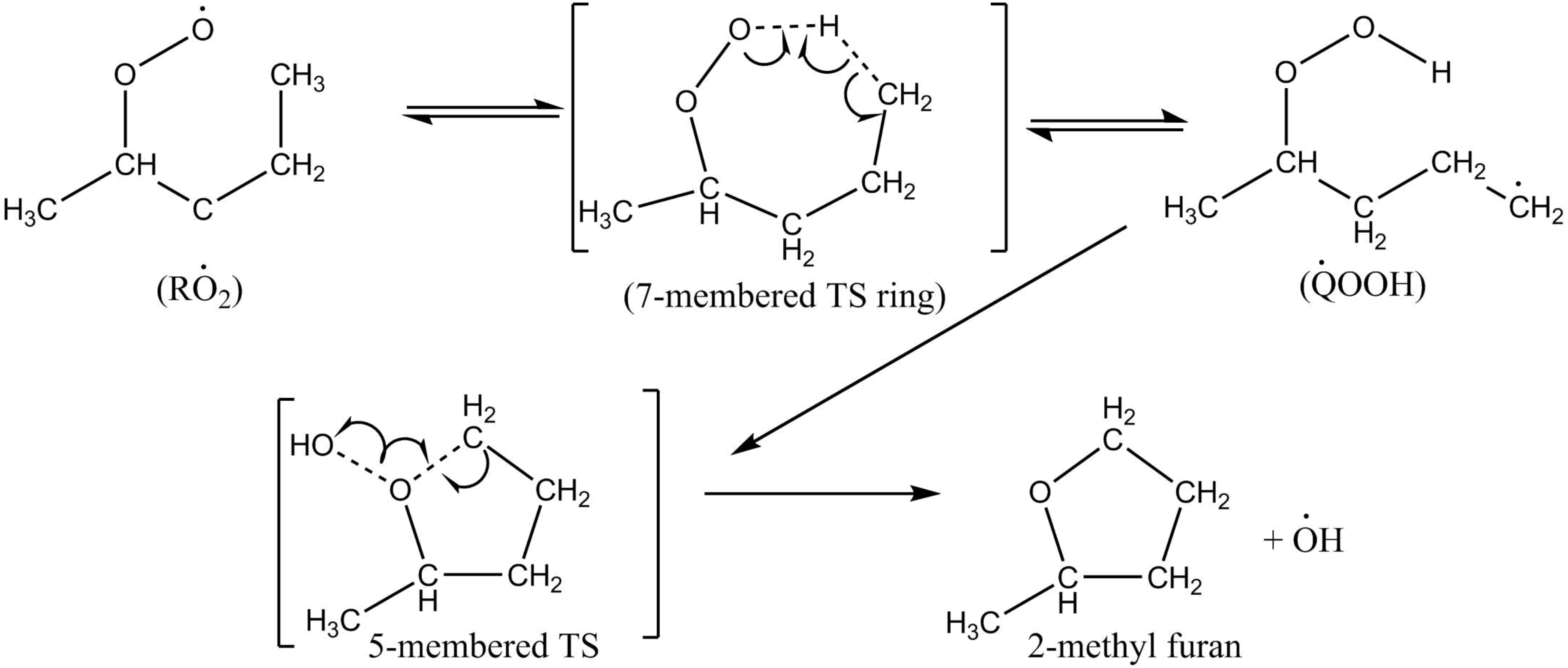
Fate of 5-membered TS Rings



Fate of 6-membered TS Rings



Fate of 7-membered TS Rings

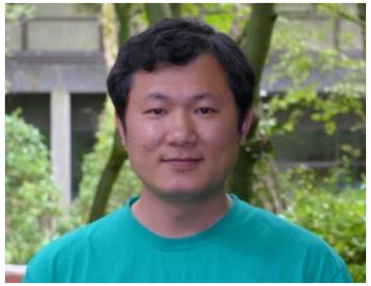


Developing Chemical Kinetic Mechanisms for fuel Oxidation at Low Temperatures and high Pressures

Prof Henry Curran

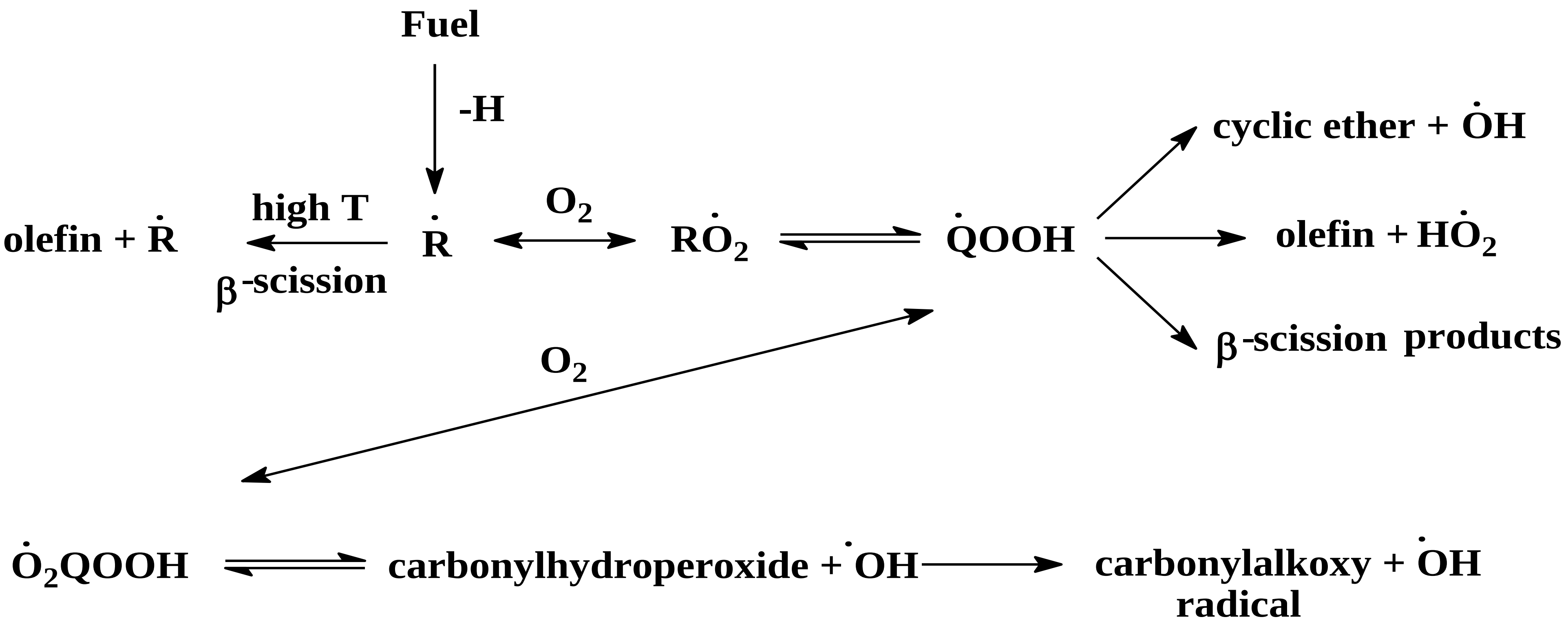
John Bugler, Kuiwen Zhang, Emma Silke

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 119(28) **(2015)** 7510–7527.

Old Generic Fuel Reaction Scheme



Fuel

-H

olefin + $\dot{R}$

high T

β-scission

$\dot{R}$

O_2

$R\dot{O}_2$

$\dot{Q}OOH$

cyclic ether + $\dot{O}H$

olefin + $H\dot{O}_2$

β-scission products

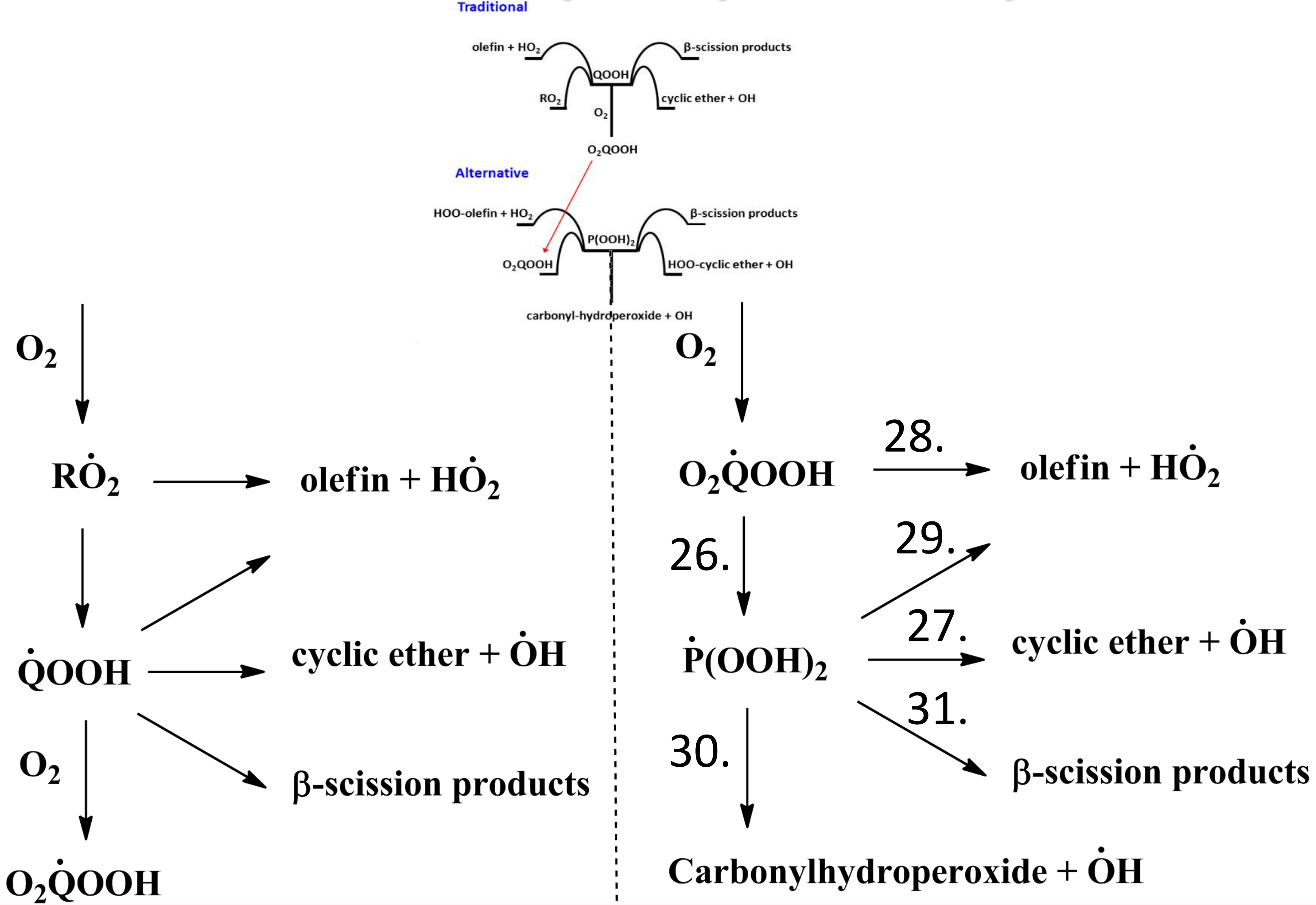
O_2

$\dot{O}_2QOOH$

carbonylhydroperoxide + $\dot{O}H$

carbonylalkoxy radical + $\dot{O}H$

Similarity of pathways



O_2

$R\dot{O}_2$ → olefin + $H\dot{O}_2$

$\dot{Q}OOH$ → cyclic ether + $\dot{O}H$

β-scission products

O_2

$O_2\dot{Q}OOH$

O_2

$O_2\dot{Q}OOH$ 28. → olefin + $H\dot{O}_2$

26.

29.

$\dot{P}(OOH)_2$ 27. → cyclic ether + $\dot{O}H$

31. β-scission products

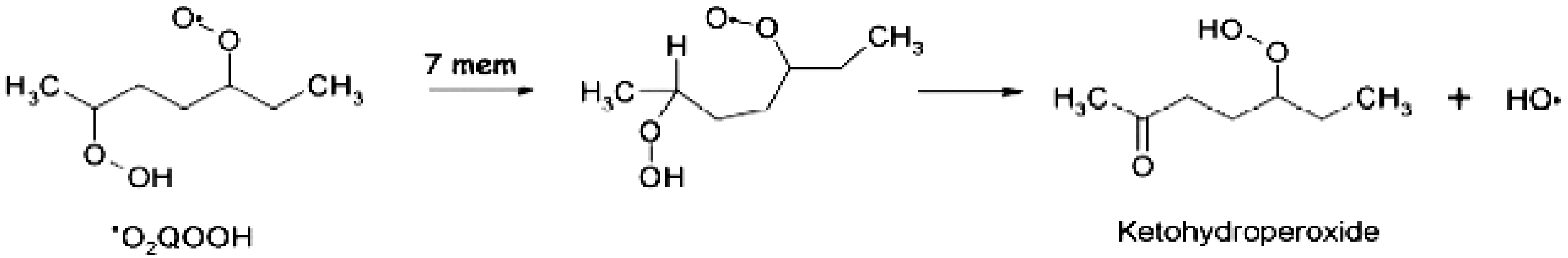
30.

Carbonylhydroperoxide + $\dot{O}H$

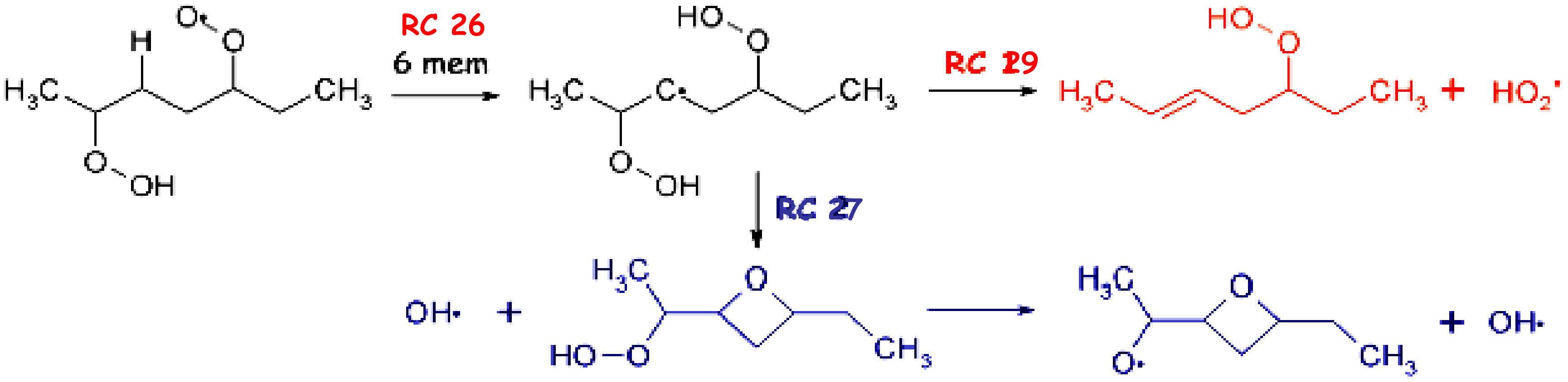
New reaction classes

- 26. $\dot{O}_2QOOH \rightleftharpoons$ alternative H-atom isomerisation
- 27. $\dot{P}(OOH)_2 \rightarrow$ cyclic ether + $\dot{O}H$
- 28. $\dot{O}_2QOOH \rightarrow$ olefin + $H\dot{O}_2$
- 29. $\dot{P}(OOH)_2 \rightarrow$ olefin + $H\dot{O}_2$
- 30. $\dot{O}_2QOOH \rightleftharpoons$ carbonylhydroperoxide + $\dot{O}H$
- 31. $\dot{P}(OOH)_2 \rightarrow$ β-scission products
- 32. QOOH intramolecular isomerisation
- 33. $R\dot{O}_2 \rightarrow$ Olefin + $H\dot{O}_2$ (concerted elimination)

$\dot{O}_2QOOH \rightleftharpoons$ alternative isomerisation



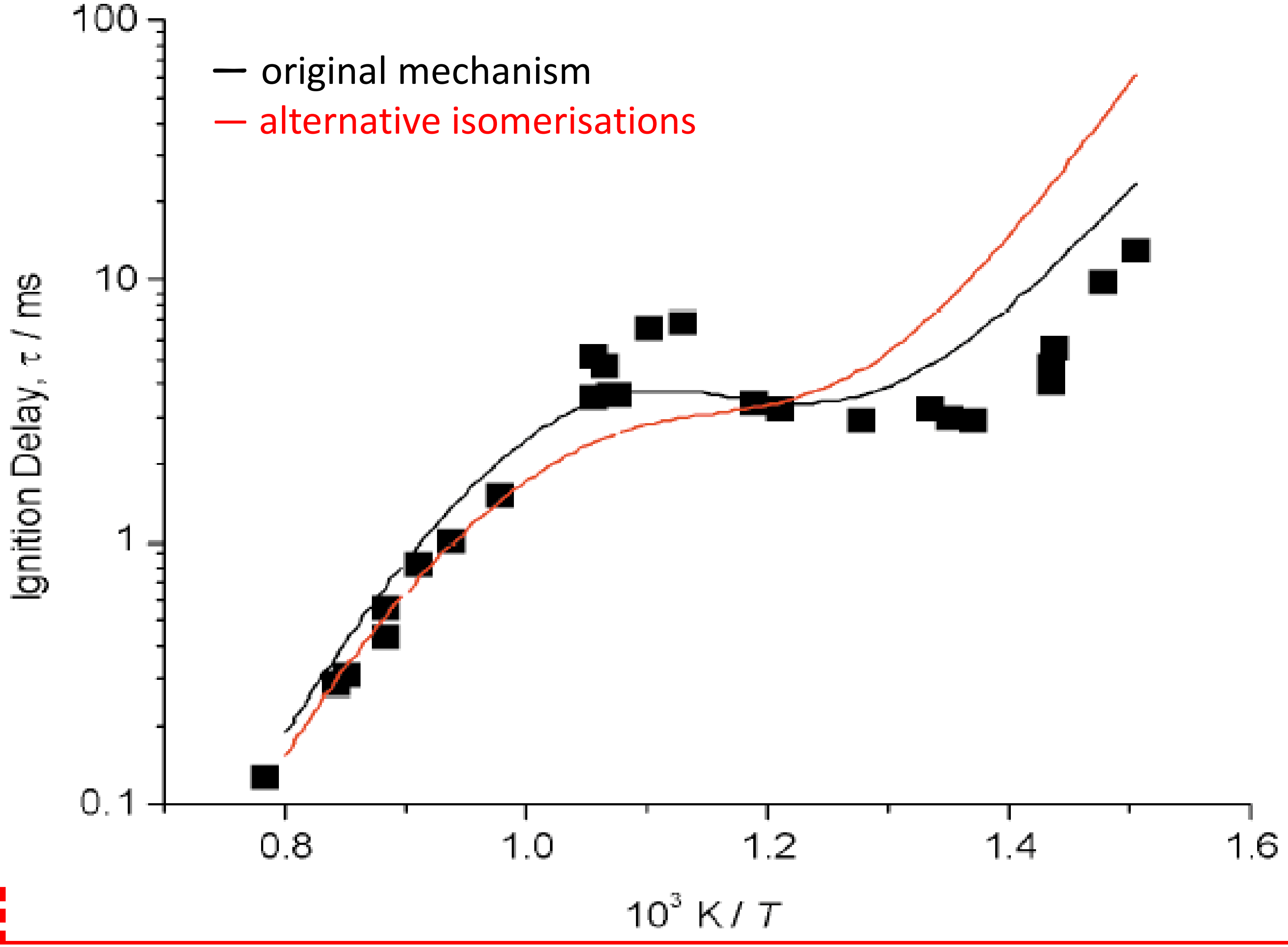
Conventional chemistry



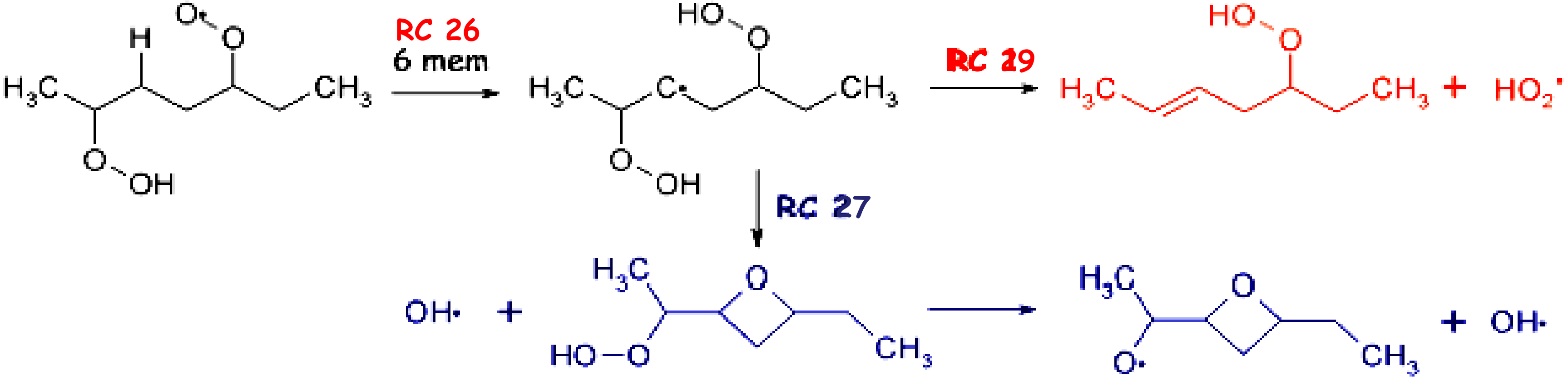
Alternative chemistry

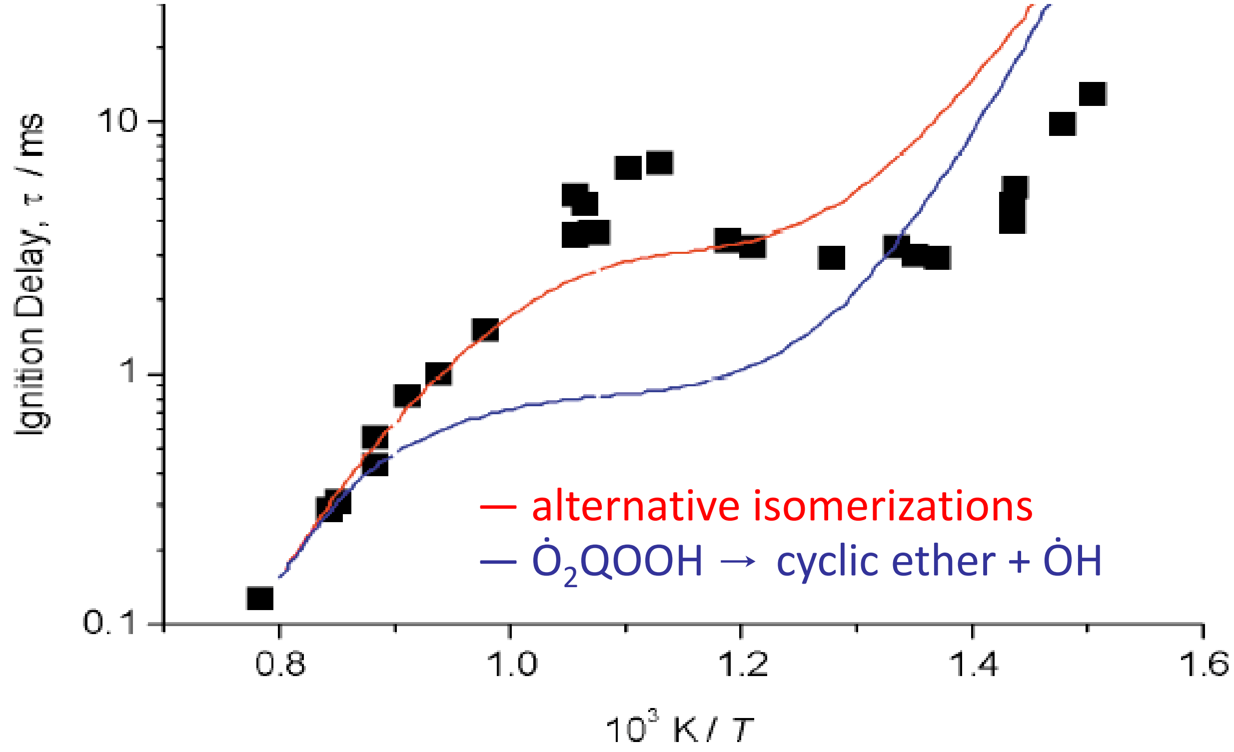
$\dot{O}_2QOOH \rightleftharpoons$ alternative isomerization

1.0% nC_7H_{16}, ϕ = 1.0 in ‘air’, P = 13.5 bar



$\dot{O}_2QOOH \rightarrow$ cyclic ether + $\dot{O}H$



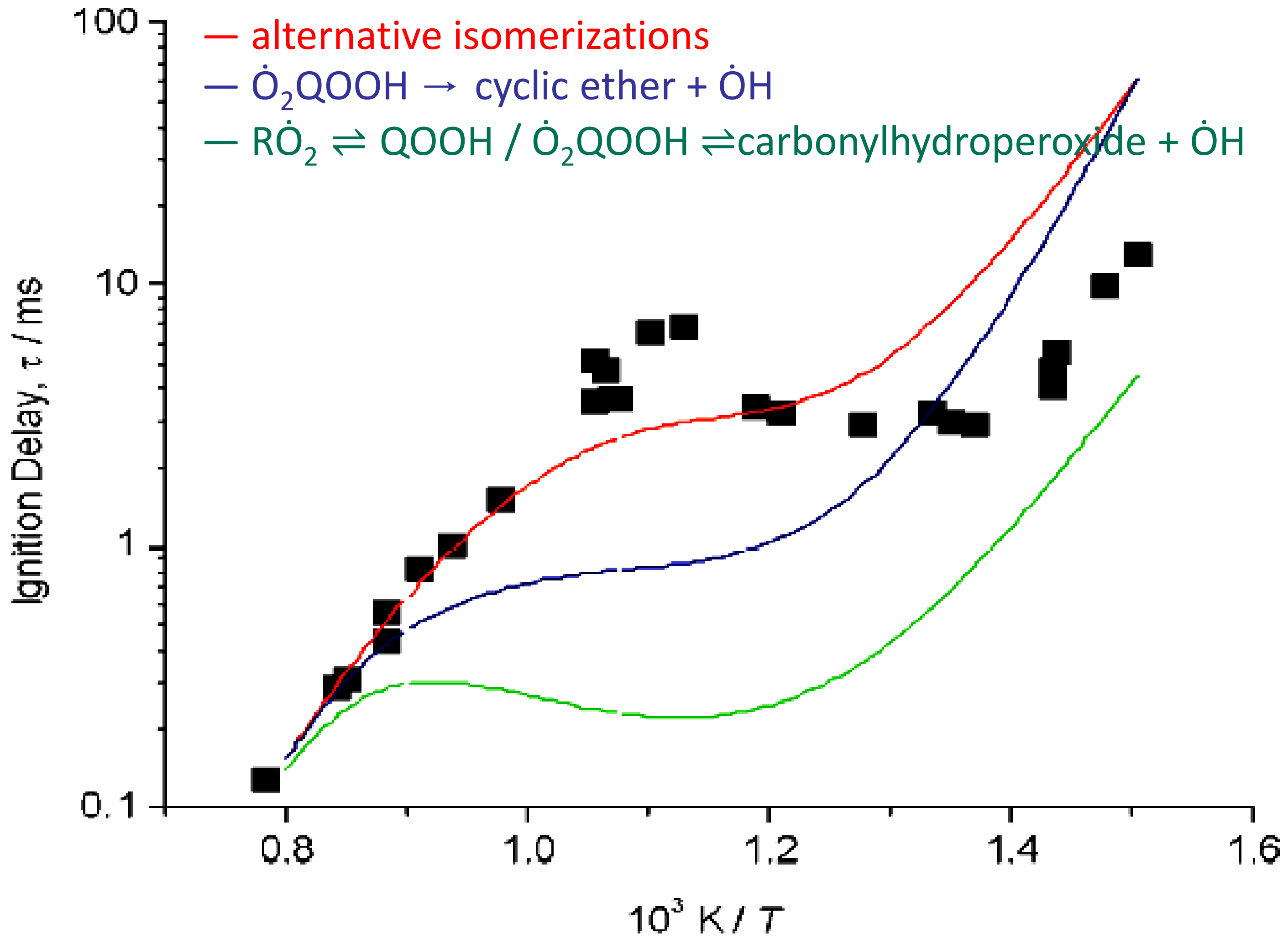


$R\dot{O}_2 \rightleftharpoons QOOH$
$\dot{O}_2QOOH \rightleftharpoons$ carbonylhydroperoxide + $\dot{O}H$

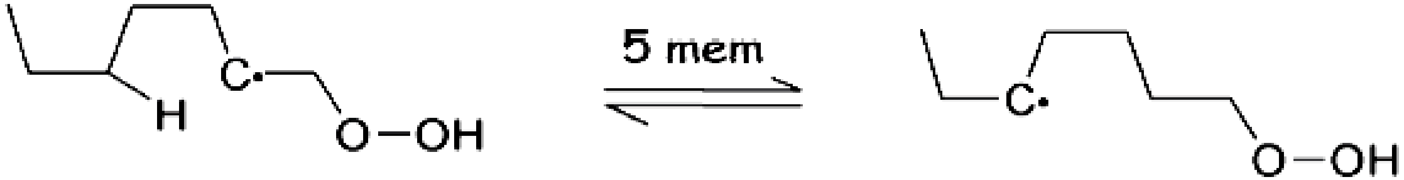
- R. Sumathi and W.H. Green
  - *ab-initio* calculations at the CBS-QB3 level

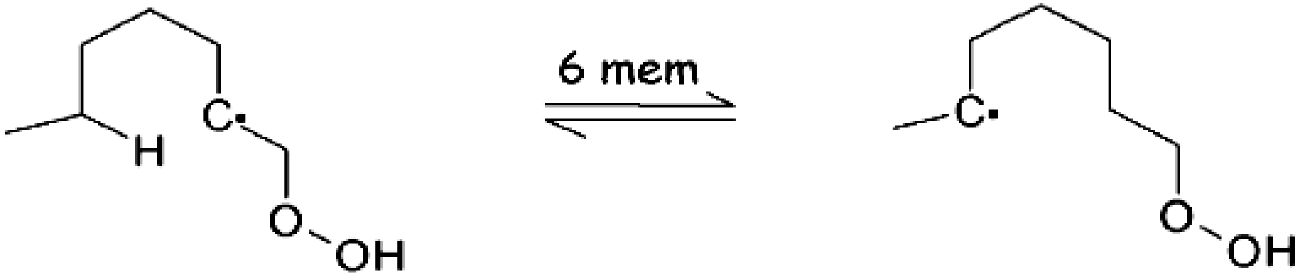
- Rate constants for isomerization significantly faster (x 10) than Curran recommendations

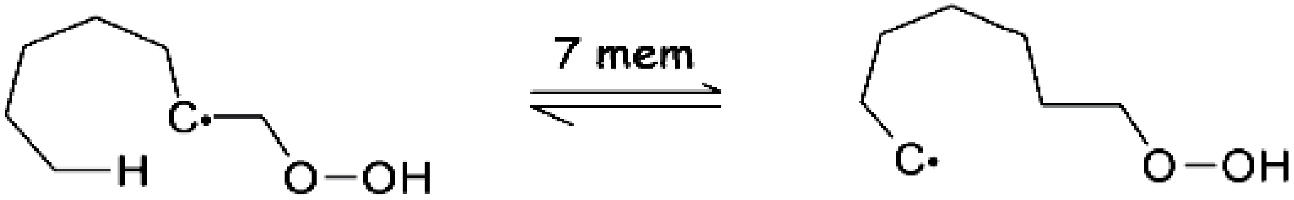
$\mathrm{R\dot{O}_2 \rightleftharpoons QOOH}$
$\mathrm{\dot{O}_2QOOH \rightleftharpoons carbonylhydroperoxide + \dot{O}H}$



QOOH Intramolecular isomerisation







QOOH Intramolecular isomerisation

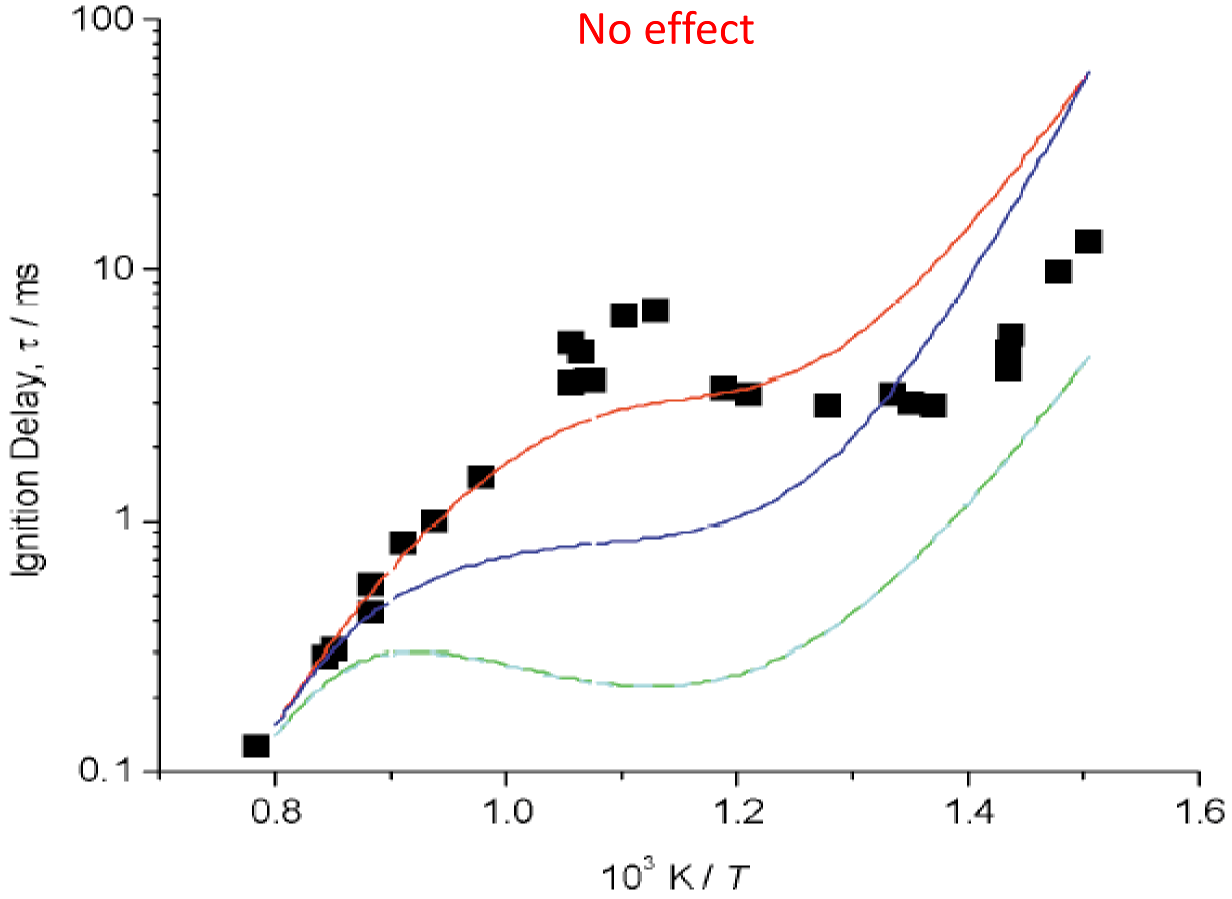
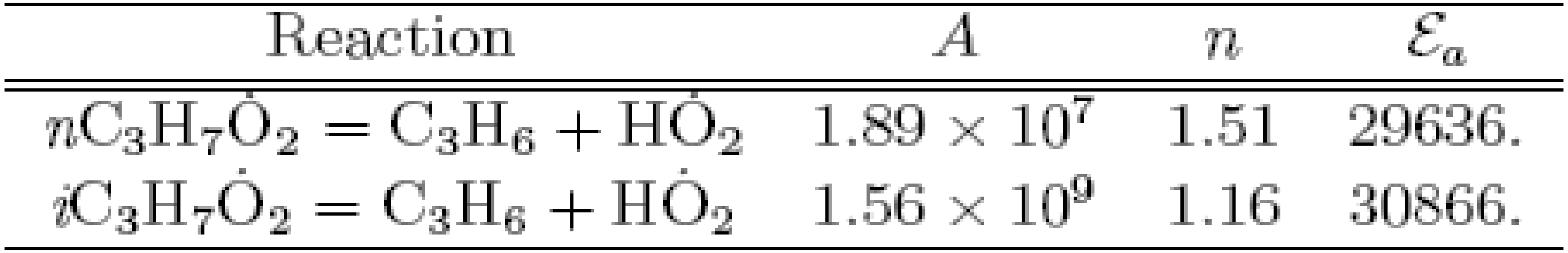


Figure 5.13: *n*-Heptane, $\phi = 1.0$ and ~ 13.5 bar: ■ Ciezki *et al* [58], — *this study* plus reaction class 1, — reaction class 1 *and* 2, — reaction class 1, 2, 5 and 6, - - - reaction class 1, 2, 5, 6 *and* 7.

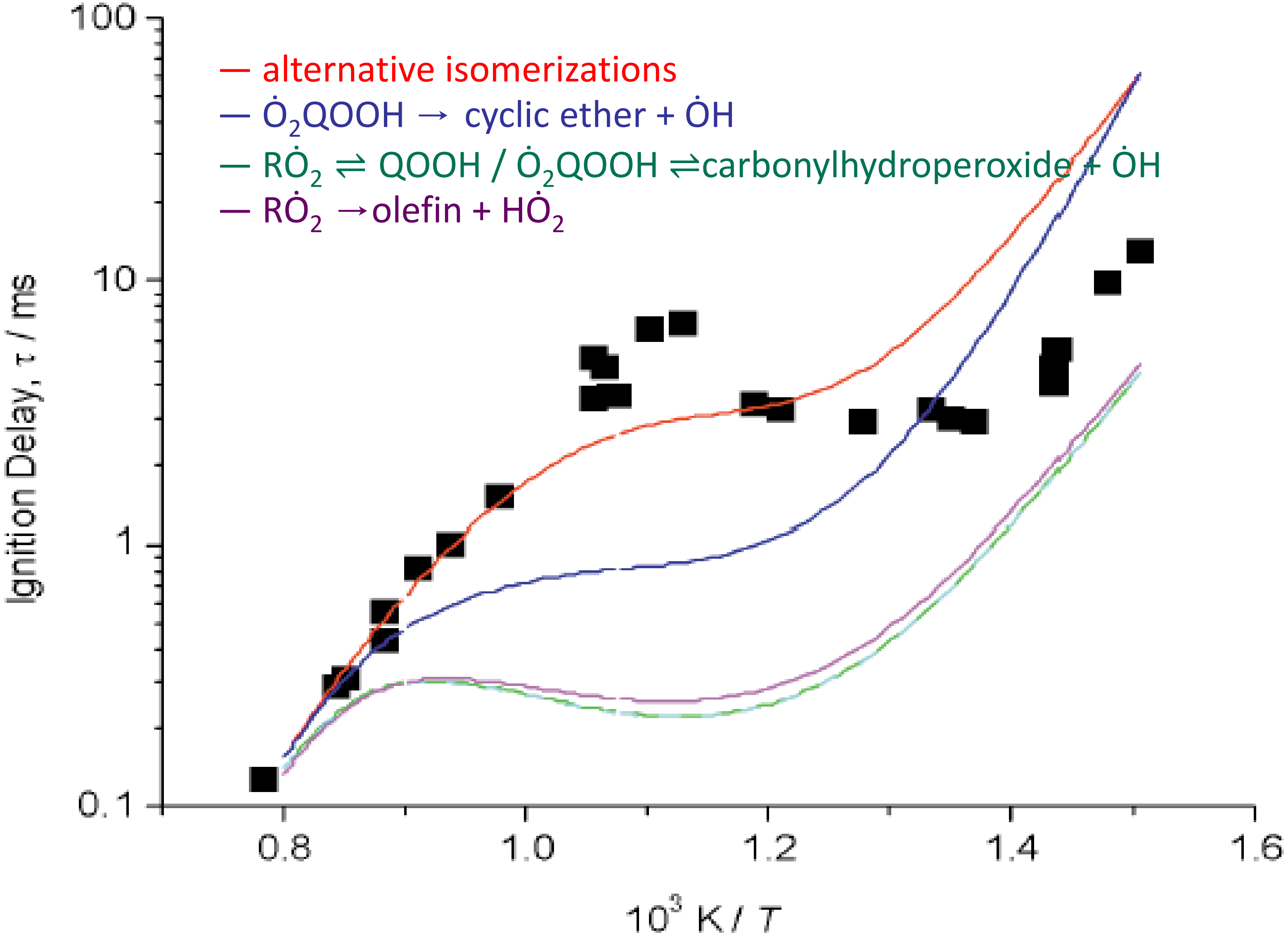
$R\dot{O}_2 \rightarrow \mathrm{olefin} + H\dot{O}_2$



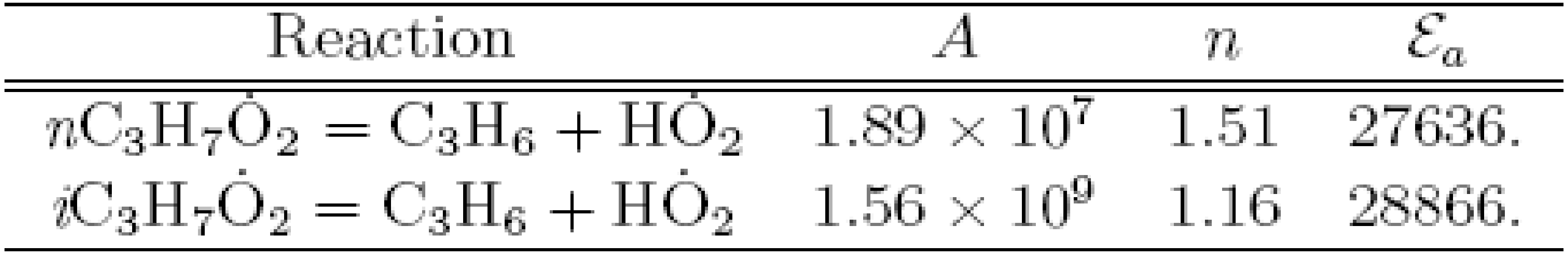
Reaction	A	n	$\mathcal{E}_a$
$n\mathrm{C_3H_7\dot{O}_2} = \mathrm{C_3H_6} + \mathrm{H\dot{O}_2}$	1.89×10^7	1.51	29636.
$i\mathrm{C_3H_7\dot{O}_2} = \mathrm{C_3H_6} + \mathrm{H\dot{O}_2}$	1.56×10^9	1.16	30866.

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.

$R\dot{O}_2 \rightarrow$ olefin + $H\dot{O}_2$



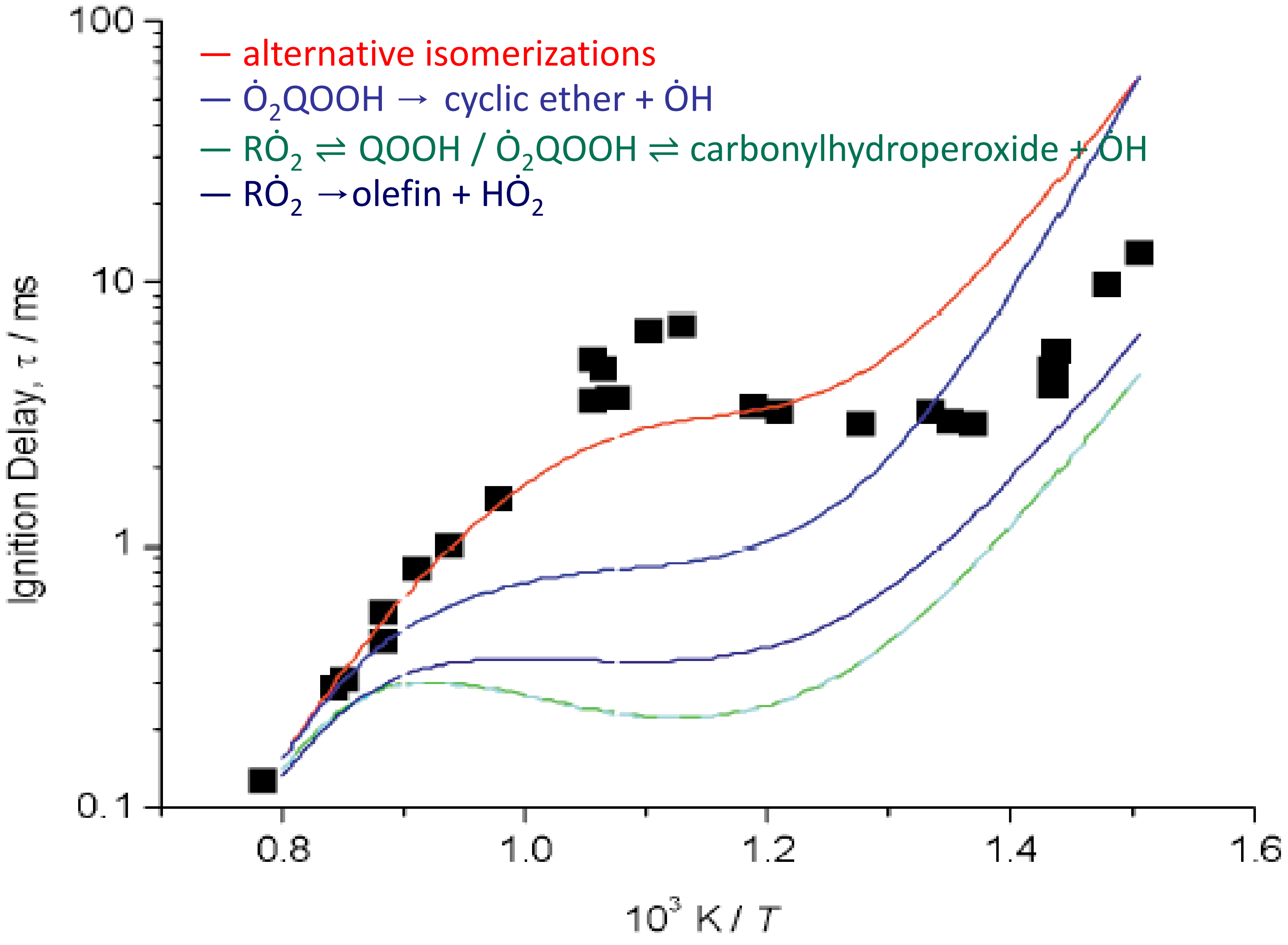
$R\dot{O}_2 \rightarrow$ olefin + $H\dot{O}_2$



Reaction	A	n	$\mathcal{E}_a$
$n\mathrm{C_3H_7\dot{O}_2} = \mathrm{C_3H_6} + \mathrm{H\dot{O}_2}$	1.89×10^7	1.51	27636.
$i\mathrm{C_3H_7\dot{O}_2} = \mathrm{C_3H_6} + \mathrm{H\dot{O}_2}$	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.

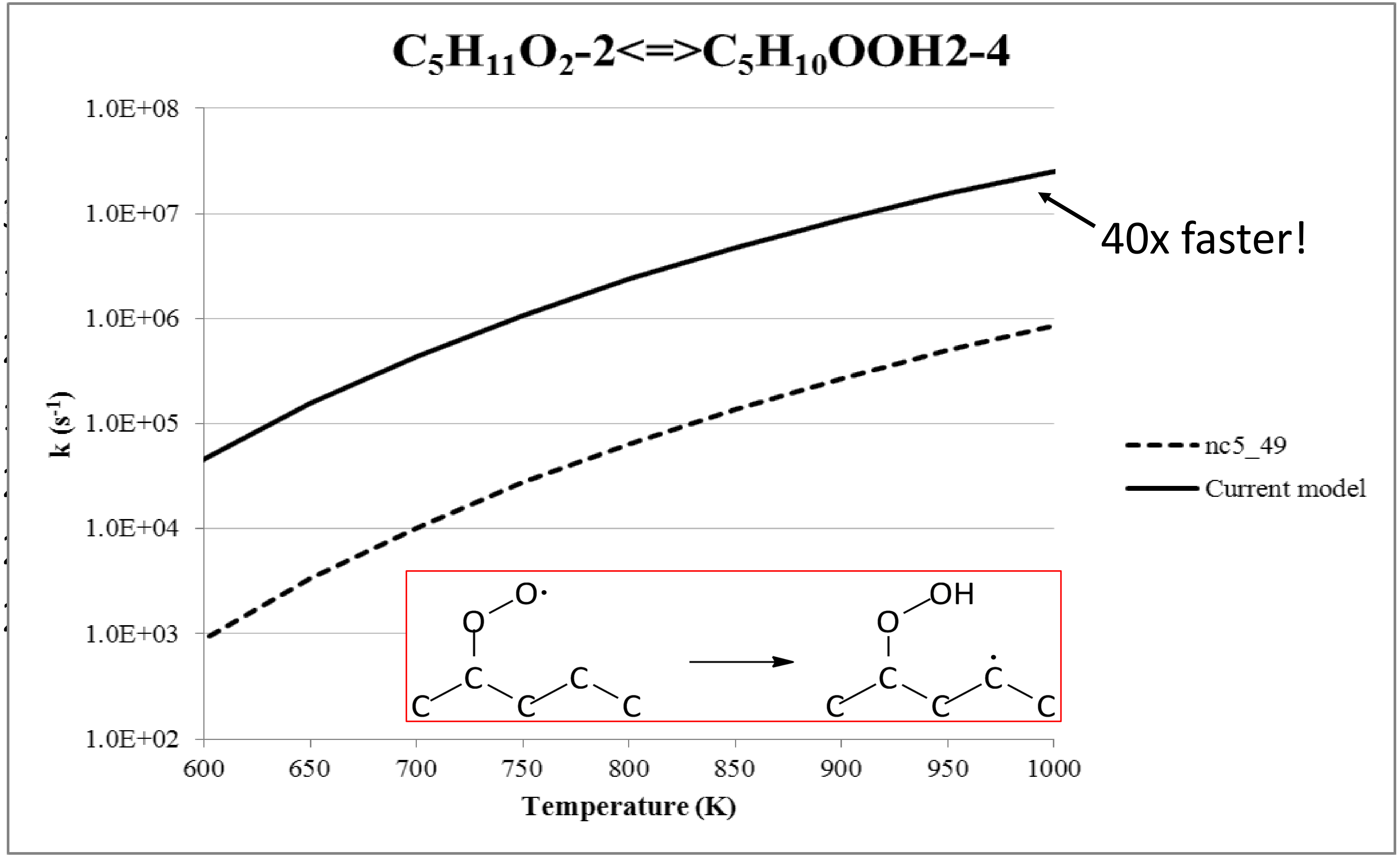
$R\dot{O}_2 \rightarrow$ olefin + $H\dot{O}_2$



Updates to *n*-Pentane mechanism

All solid lines in graphs represent constant volume simulations

Updates to Kinetics

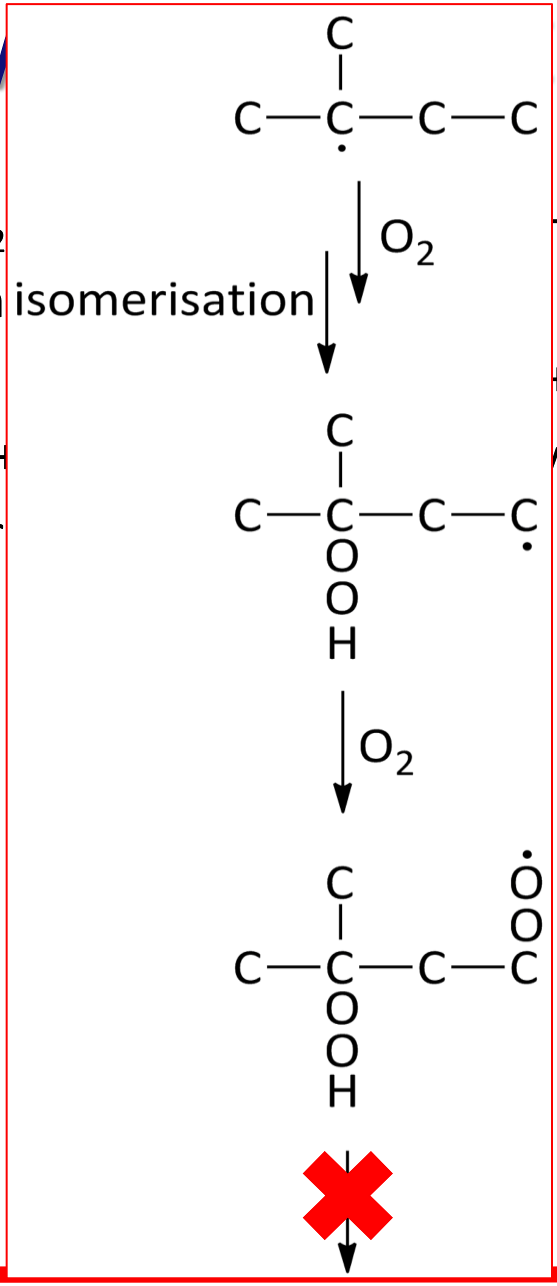


$C_5H_{11}O_2$-2<=>$C_5H_{10}OOH2$-4

40x faster!

New lasses

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

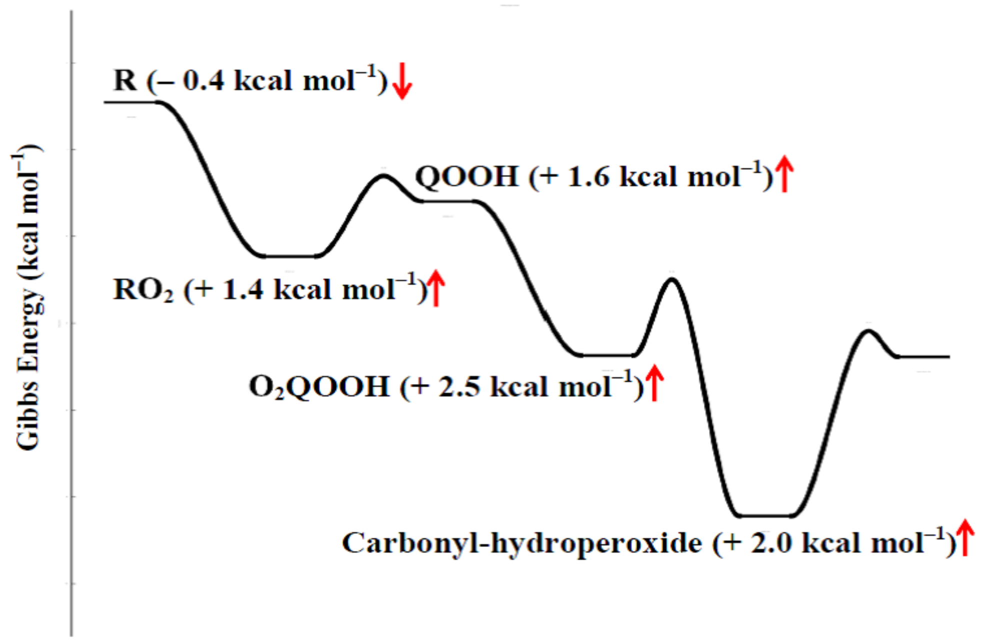


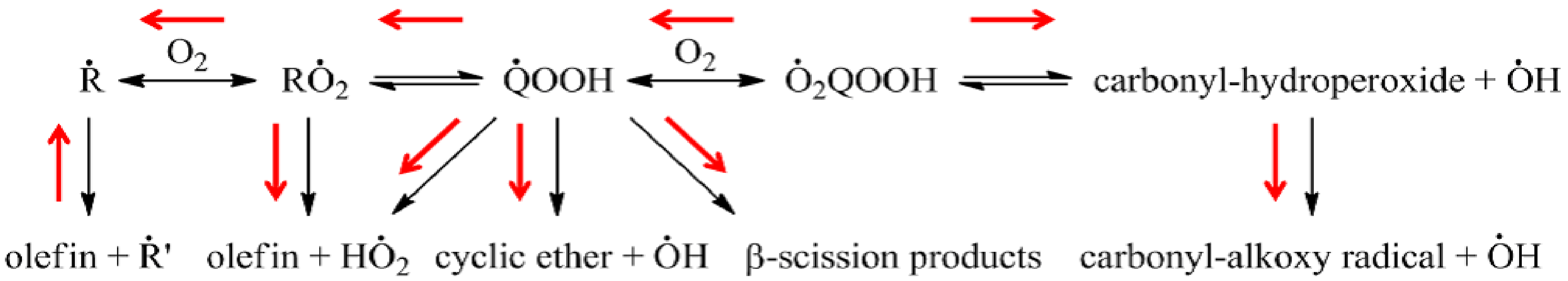
Effect of thermochemistry

- Thermochemistry updated from Burke et al.

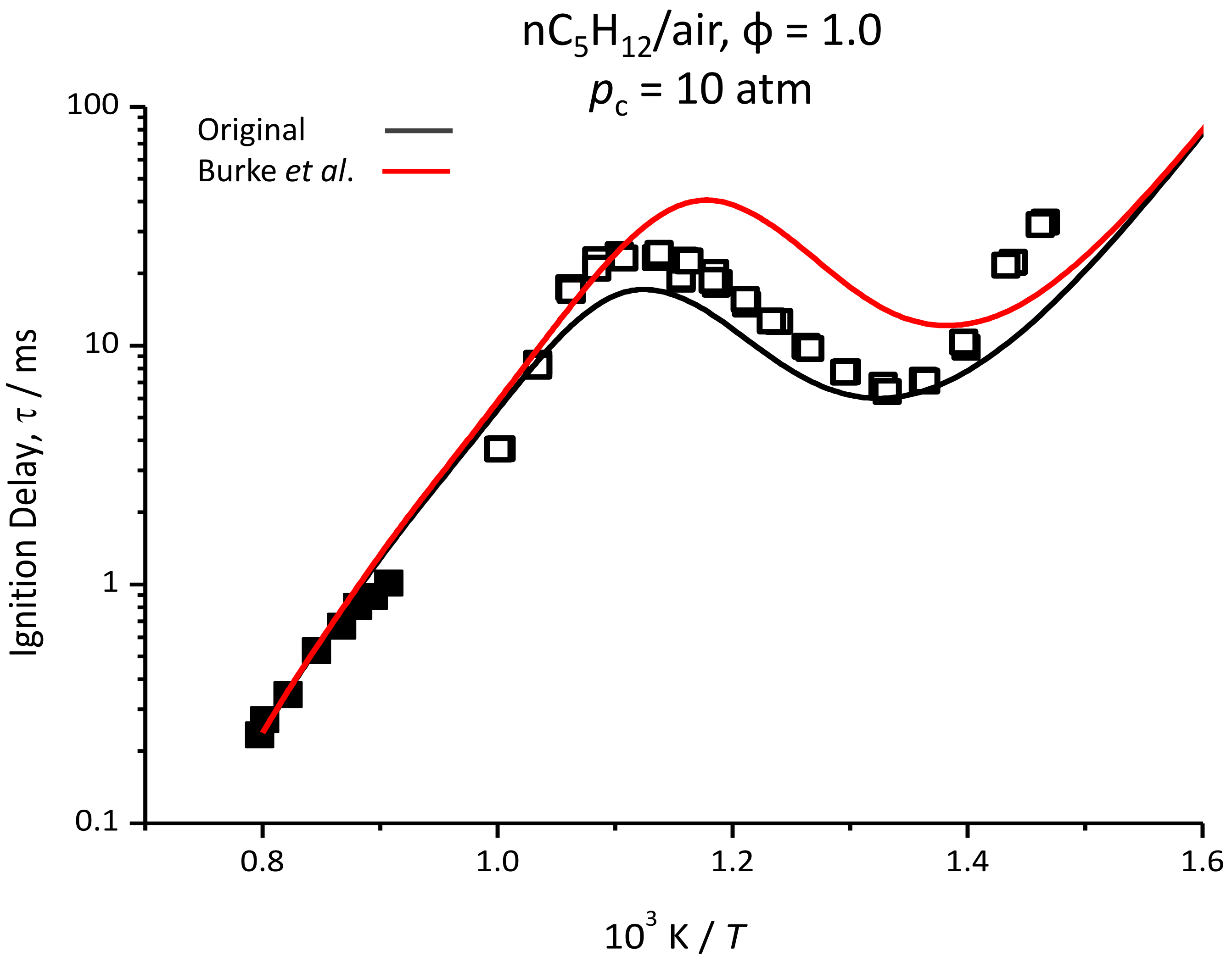
S. Burke, J. M. Simmie, H. J. Curran
J. Phys. Chem. Ref. Data **2015,** *44,* 013101.

Effect of thermochemistry



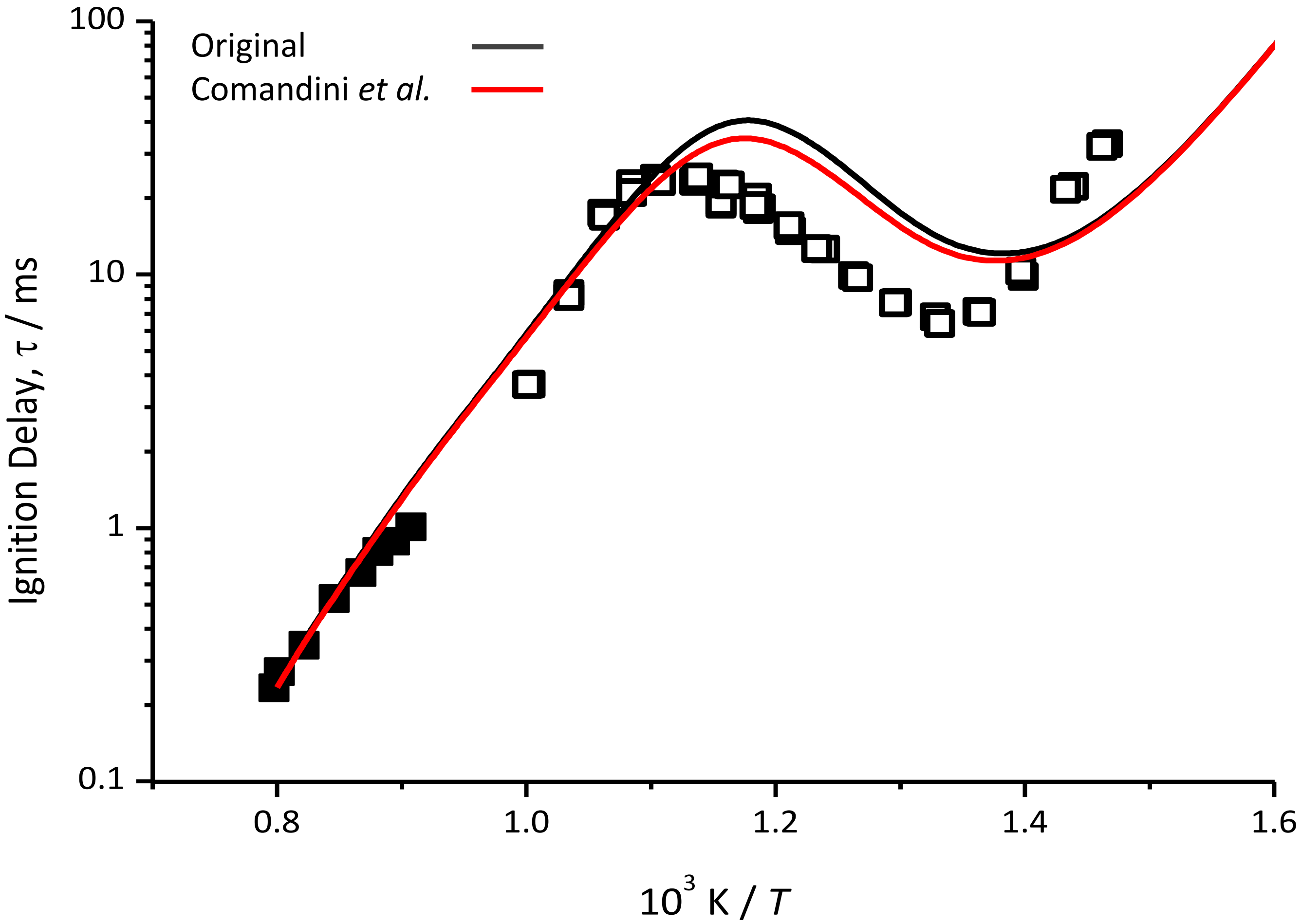


Effect of Thermochemistry



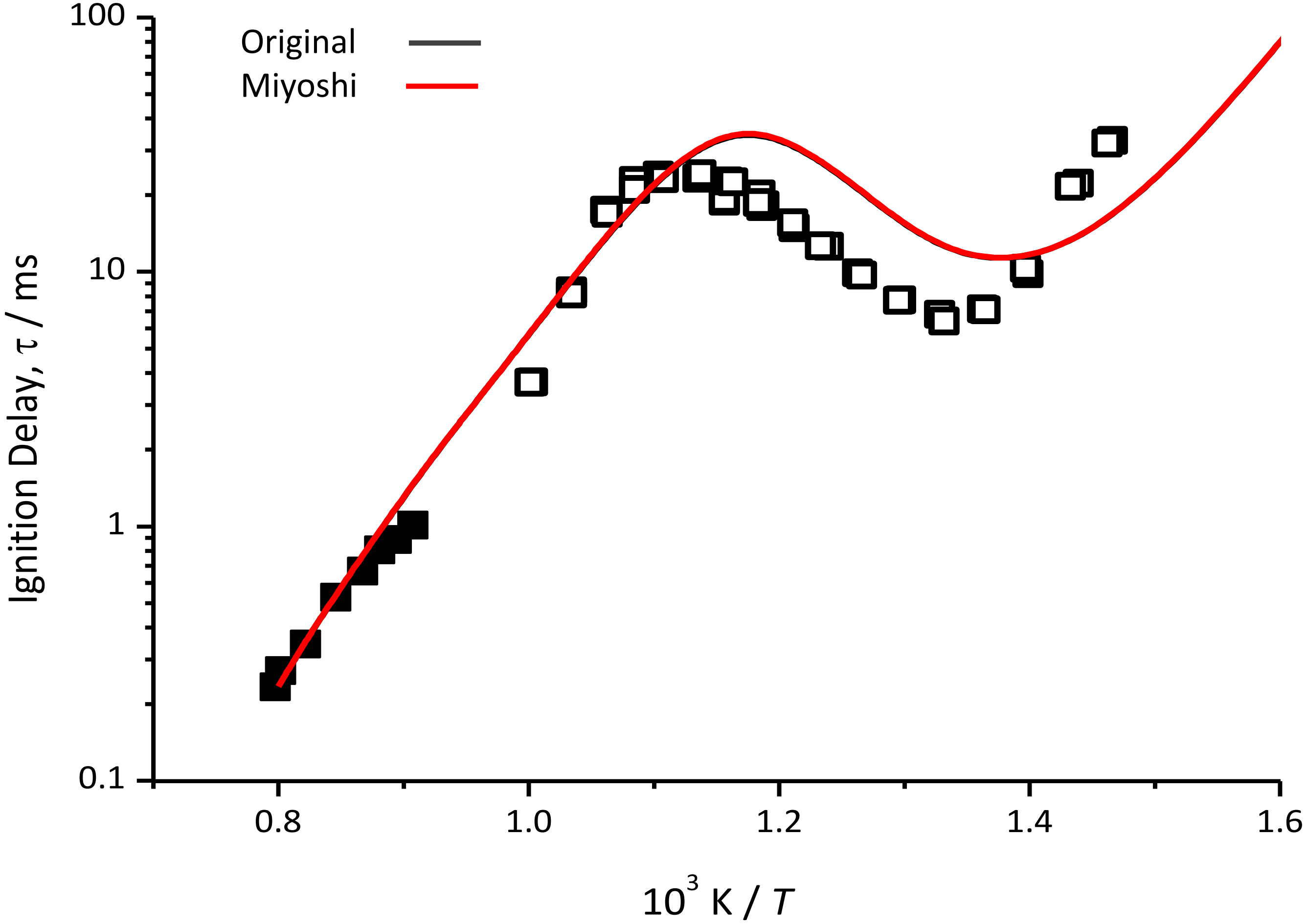
S. Burke, J. M. Simmie, H. J. Curran *J. Phys. Chem. Ref. Data* **2015,** *44,* 013101.

$\dot{R} \longleftrightarrow \text{olefin} + \dot{R}'$



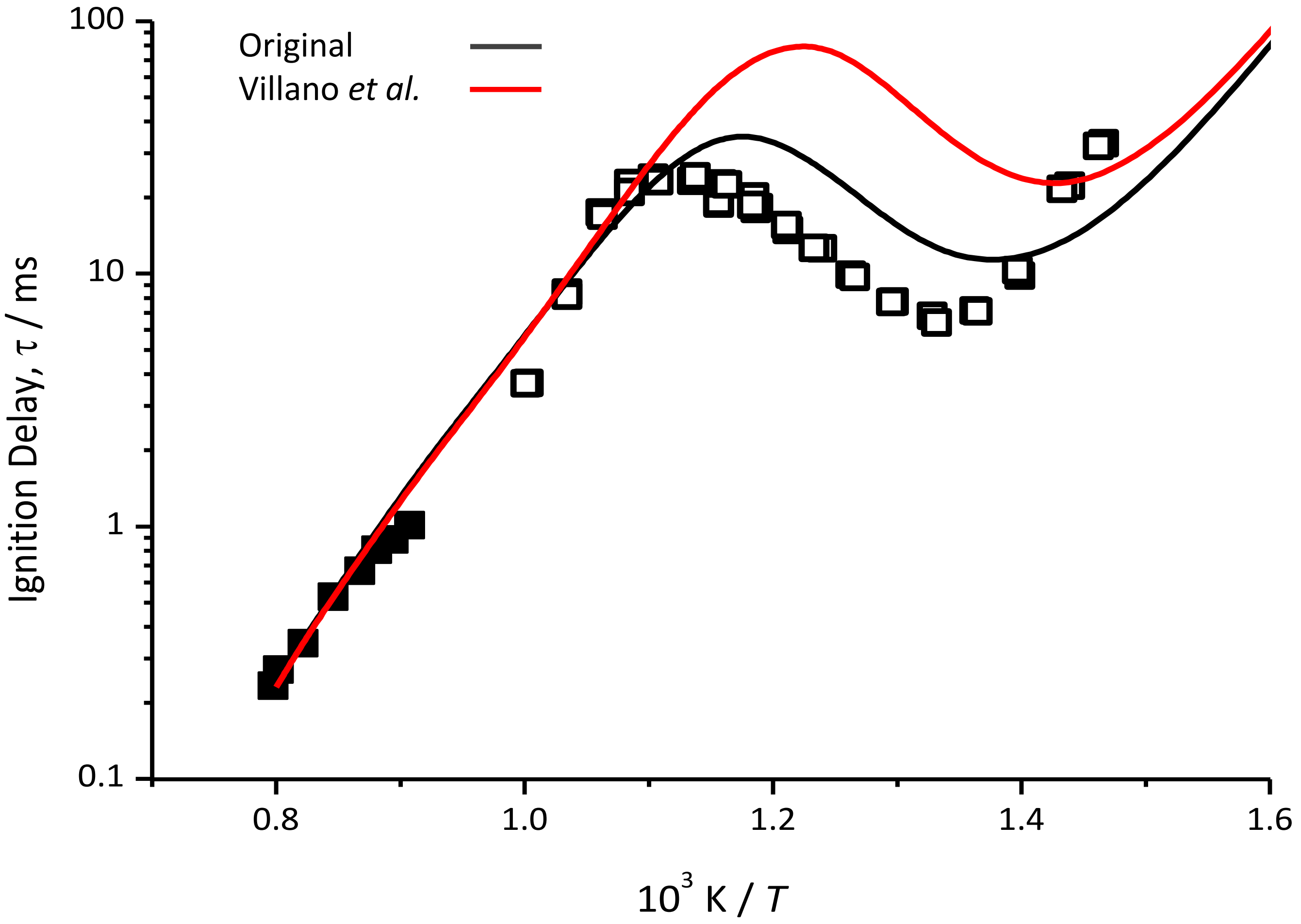
A. Comandini, I. A. Awan, J. A. Manion *Chem. Phys. Lett.* **2012**, *552*, 20–26.

$\dot{R} + O_2 \leftrightarrow R\dot{O}_2$



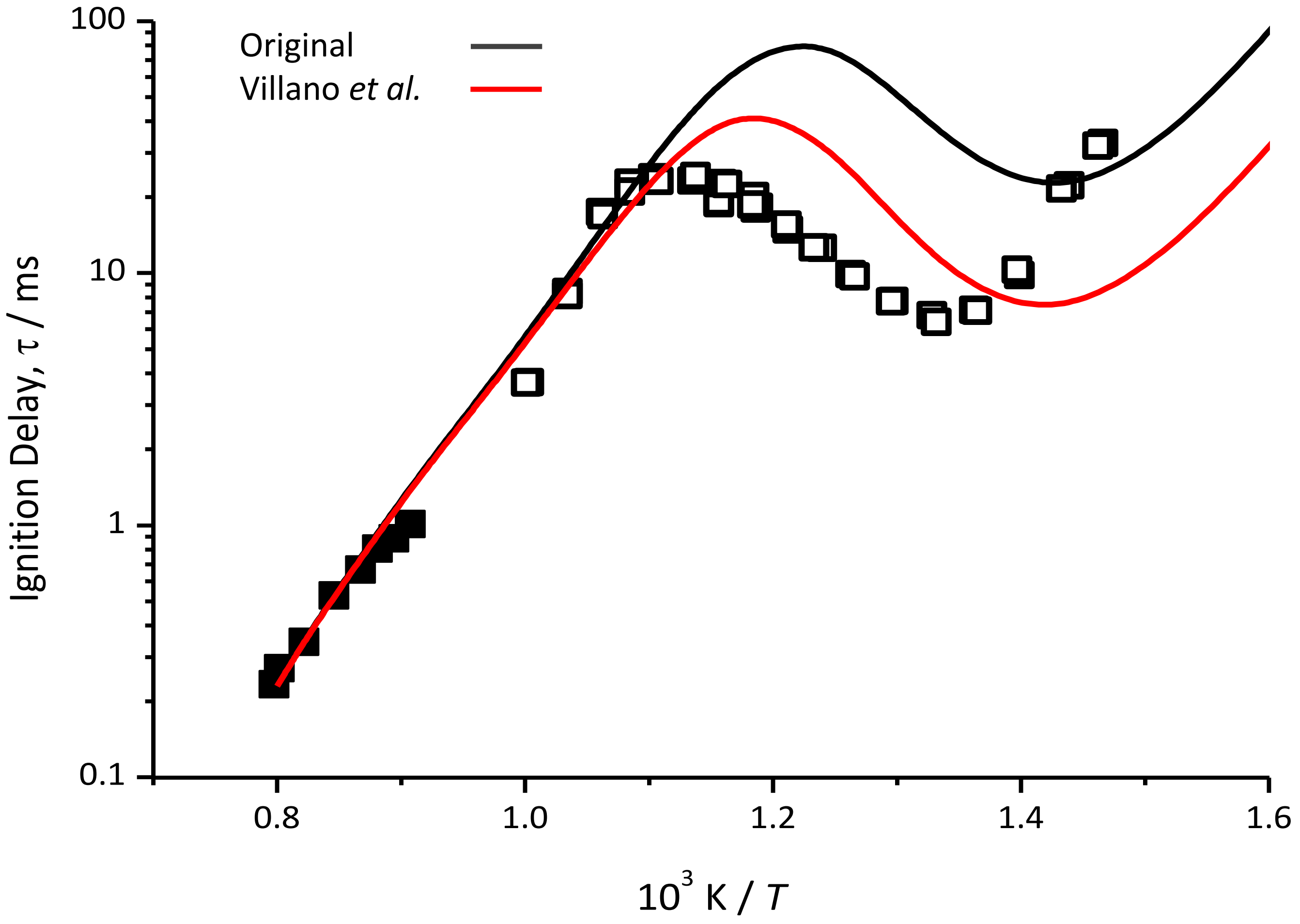
A. Miyoshi *Int. J. Chem. Kin.* **2012**, 44, 59–74.

$R\dot{O}_2 \longleftrightarrow \text{olefin} + H\dot{O}_2$



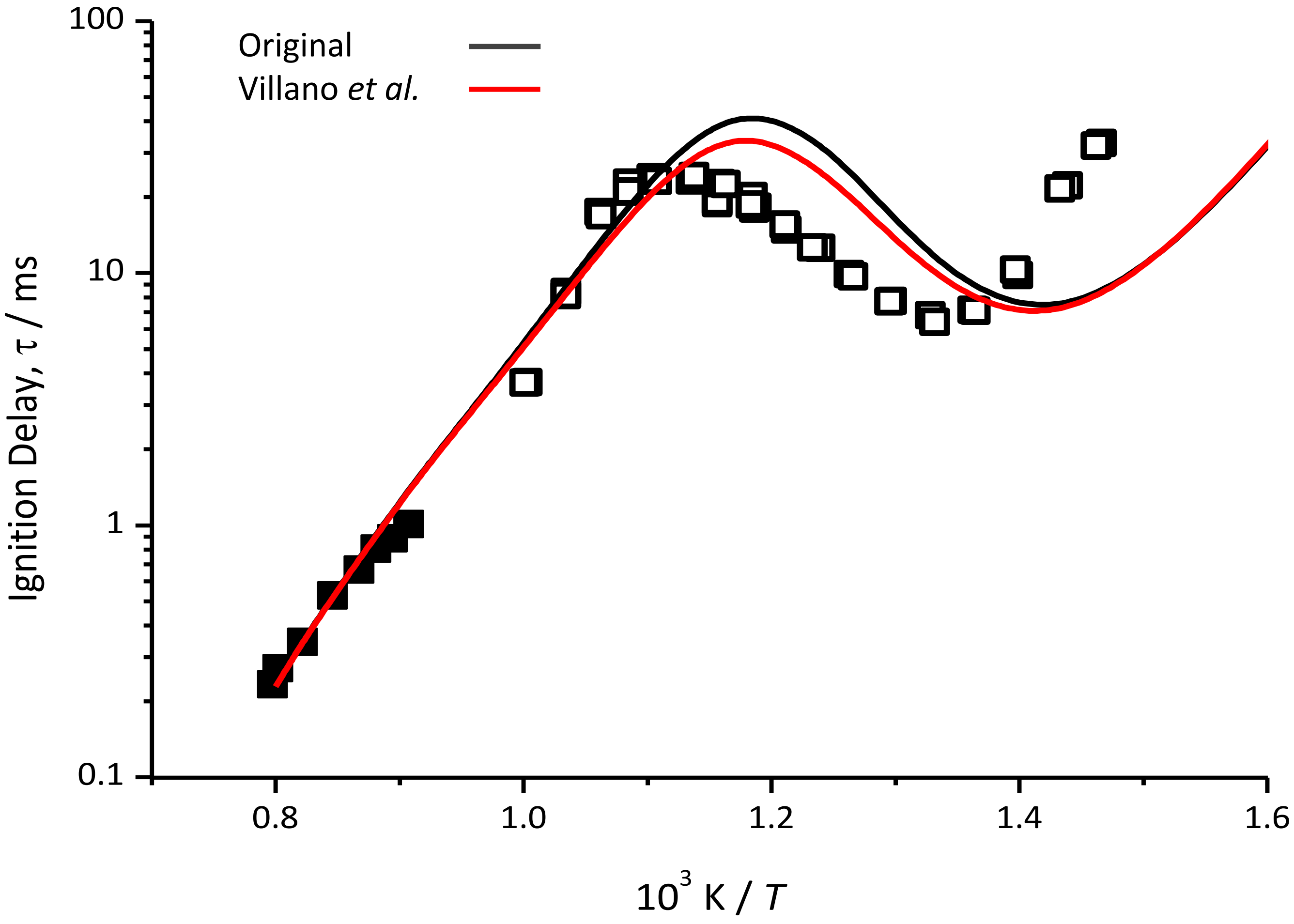
S. M. Villano, L. K. Huynh, H. –H. Carstensen, A. M. Dean *J. Phys. Chem. A* **2011**, *115*, 13425–13442

$R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$



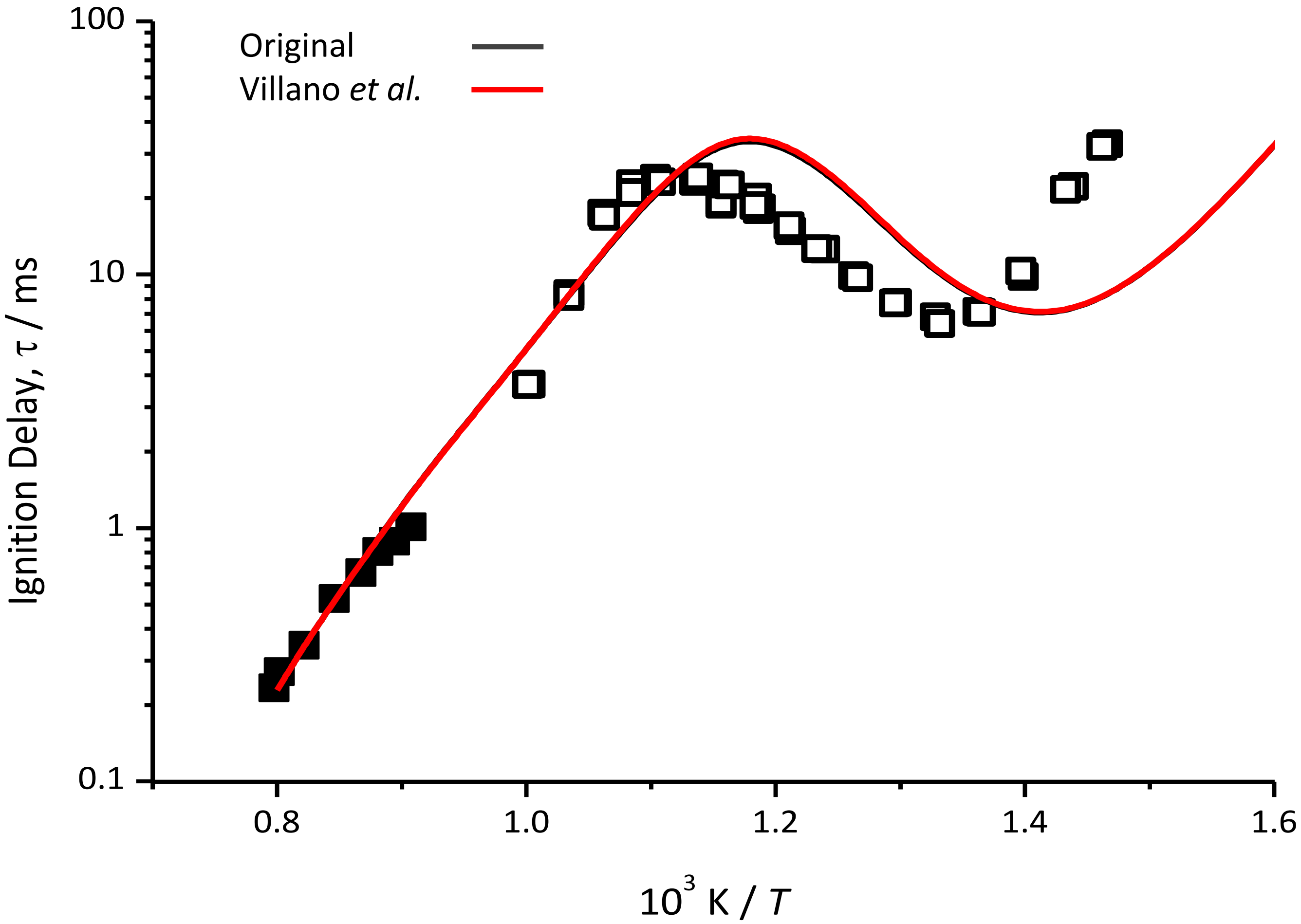
S. M. Villano, L. K. Huynh, H. –H. Carstensen, A. M. Dean *J. Phys. Chem. A* **2011**, *115*, 13425–13442

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



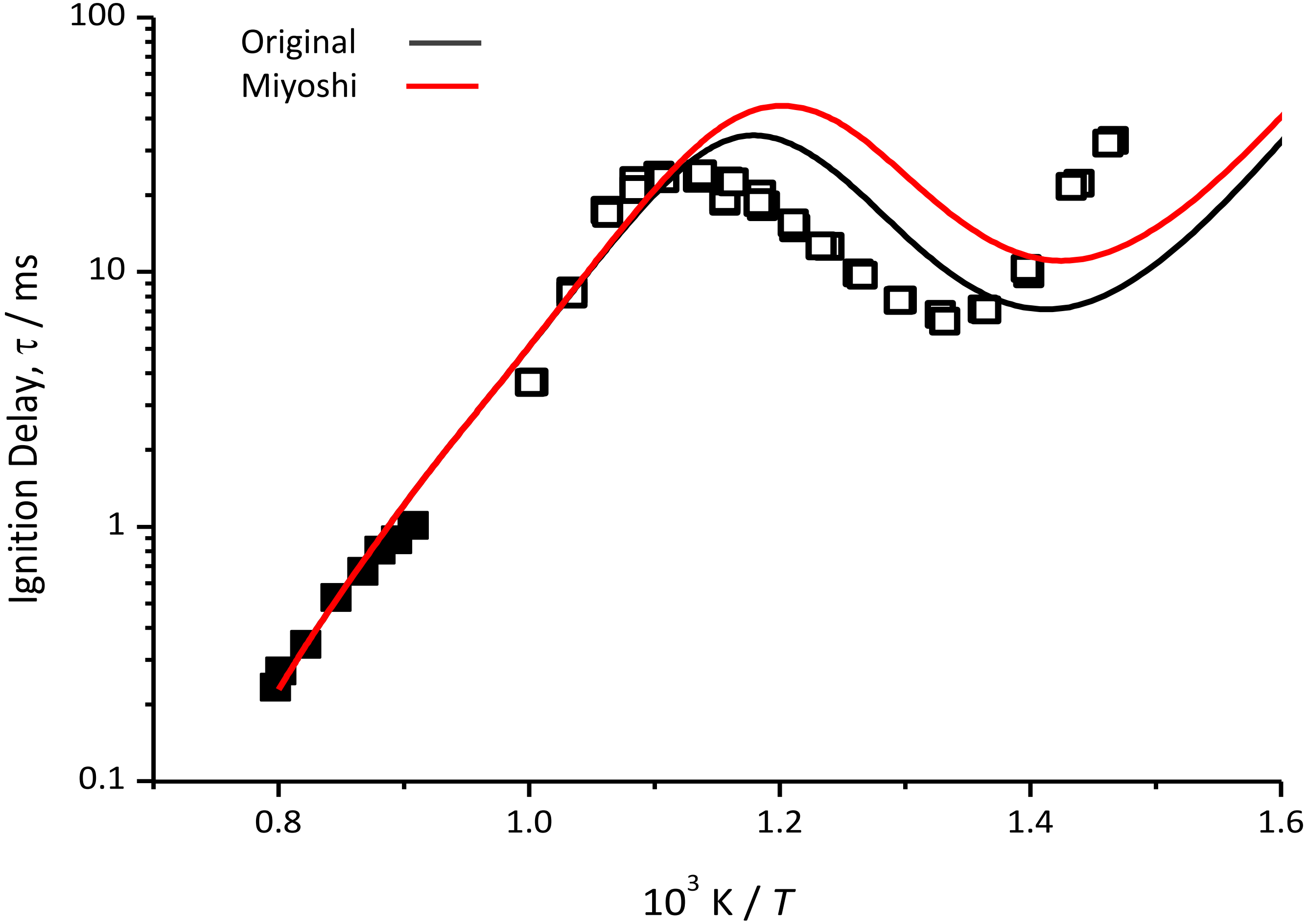
S. M. Villano, L. K. Huynh, H. –H. Carstensen, A. M. Dean *J. Phys. Chem. A* **2012**, *116*, 5068–5089

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



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

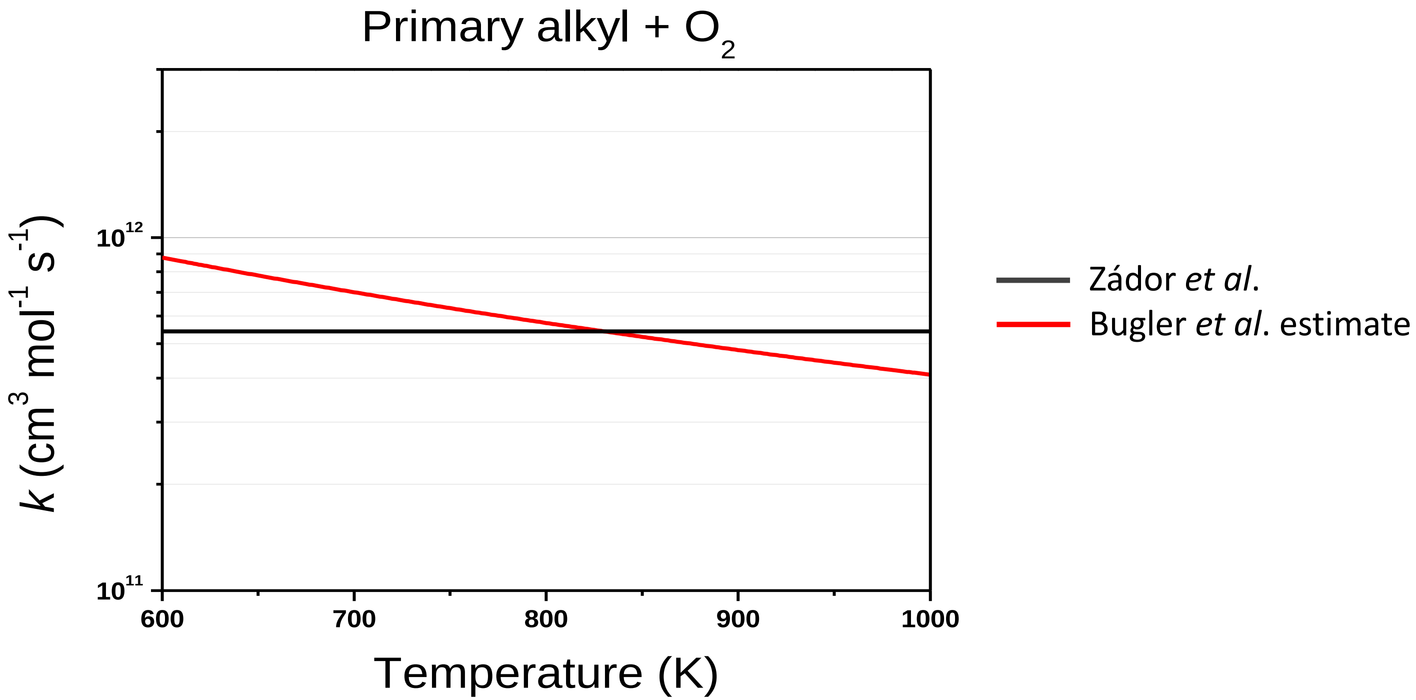
$\dot{Q}OOH + O_2 \rightleftharpoons \dot{O}_2QOOH$



Analogy to $\dot{R} + O_2 \rightleftharpoons R\dot{O}_2$

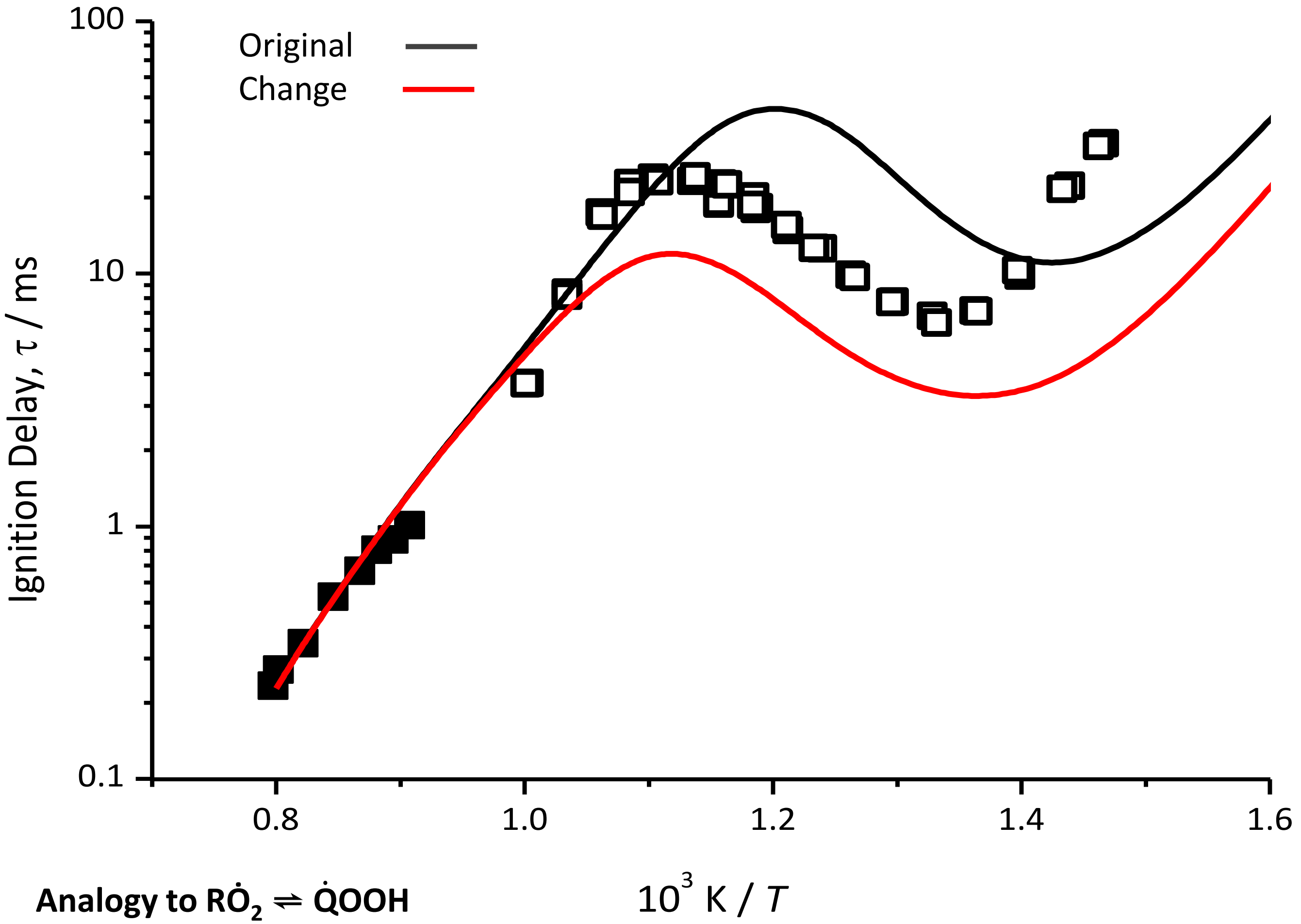
$\dot{Q}OOH + O_2 \rightleftharpoons \dot{O}_2QOOH$

- Rate constants estimated by analogy to $\dot{R} + O_2$
- Reduced by approximately factor of 2
- Good agreement with recent experimental and theoretical determinations from Sandia National Laboratories[1]



[1] **J. Zádor, H. Huang, O. Welz, J. Zetterberg, D. L. Osborn, C. A. Taatjes** *Phys. Chem. Chem. Phys.* **2013**, *15*, 10753–10760.

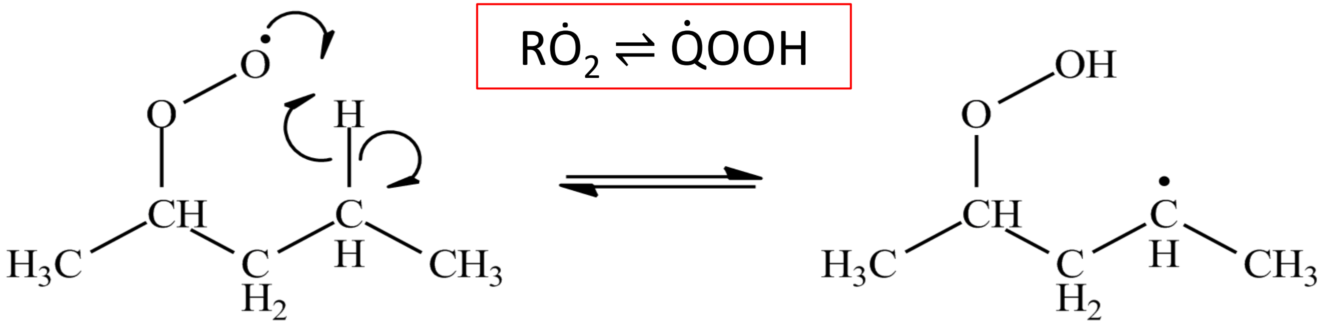
$\dot{O}_2QOOH \rightleftharpoons$ Carbonylhydroperoxide + $\dot{O}H$



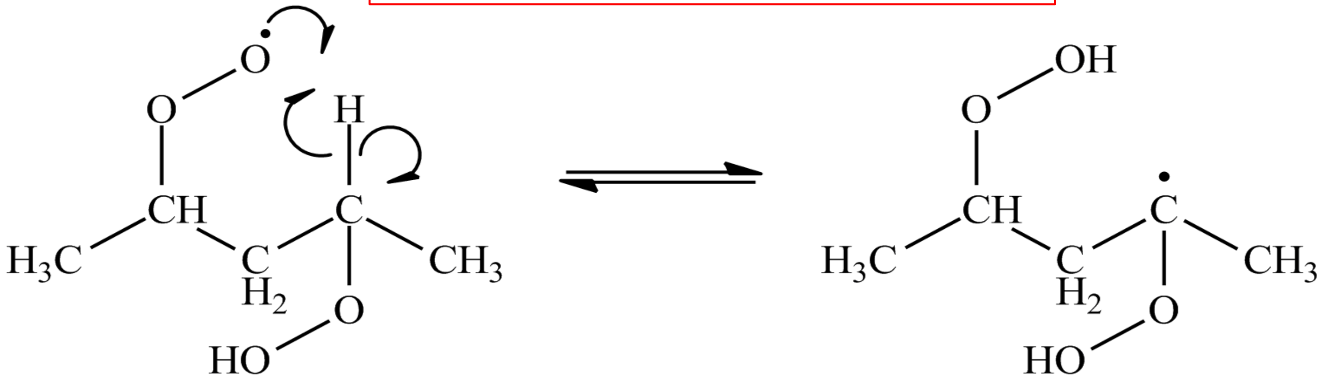
Analogy to $R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$
Ea: –3 kcal mol⁻¹

1st and 2nd Isomerisations

$R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$

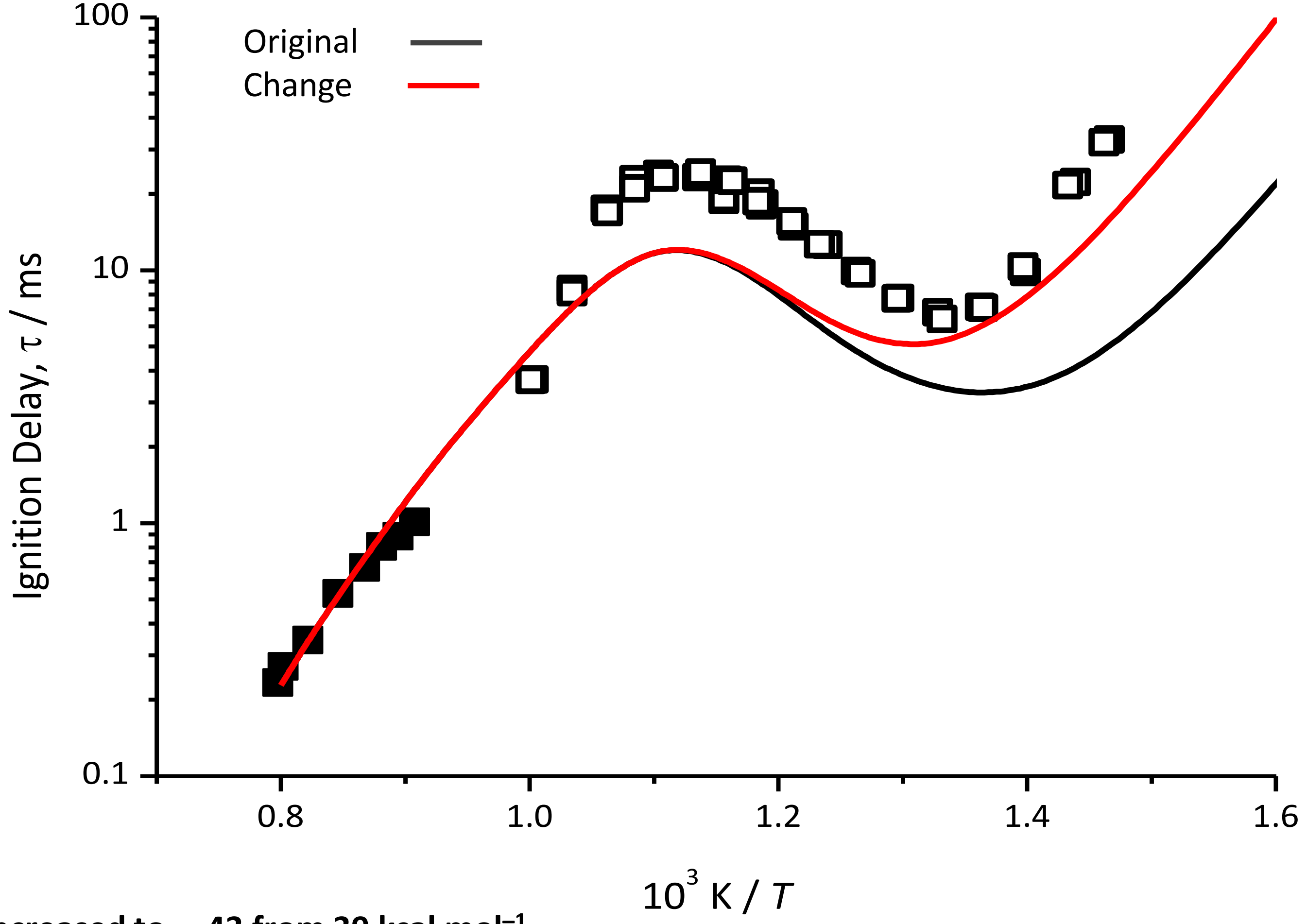


$\dot{O}_2QOOH \rightleftharpoons$ intermediate



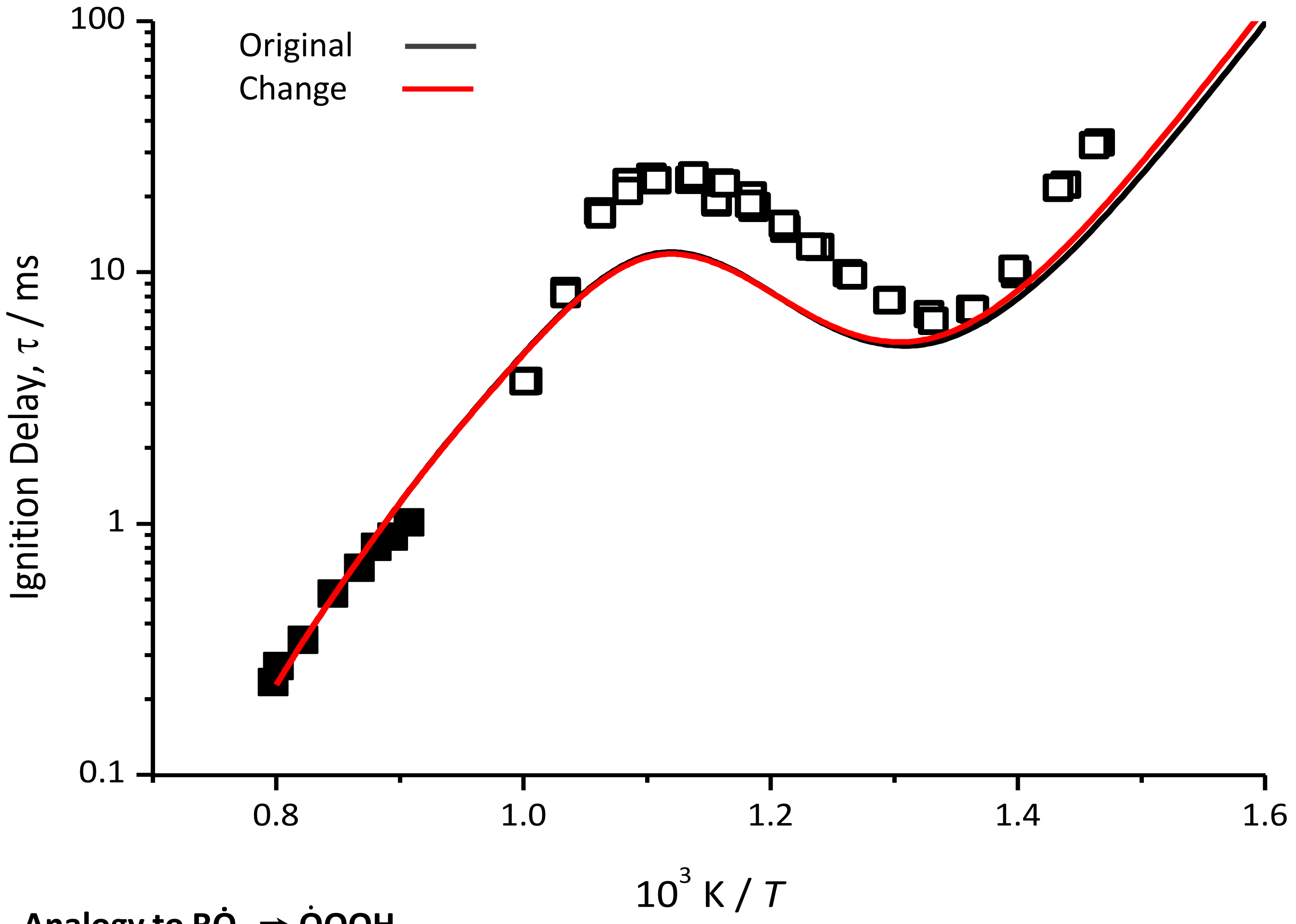
Activation energy:
-3 kcal mol^{-1} relative to $R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$

Carbonylhydroperoxide → Ȯ-R=O + ȮH



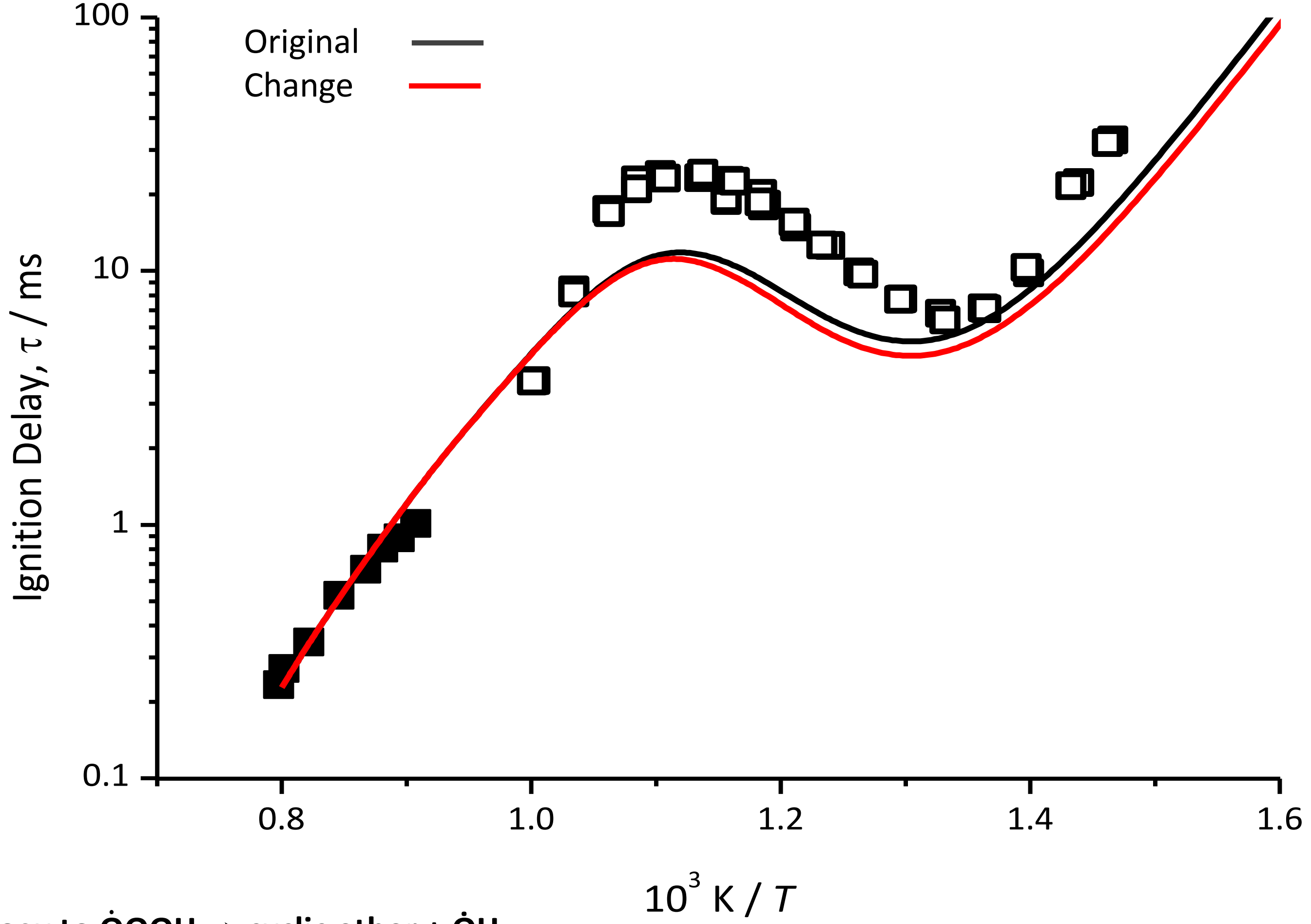
Ea: increased to ~ 43 from 39 kcal mol^{-1}

$\dot{O}_2QOOH \rightleftharpoons \dot{P}(OOH)_2$



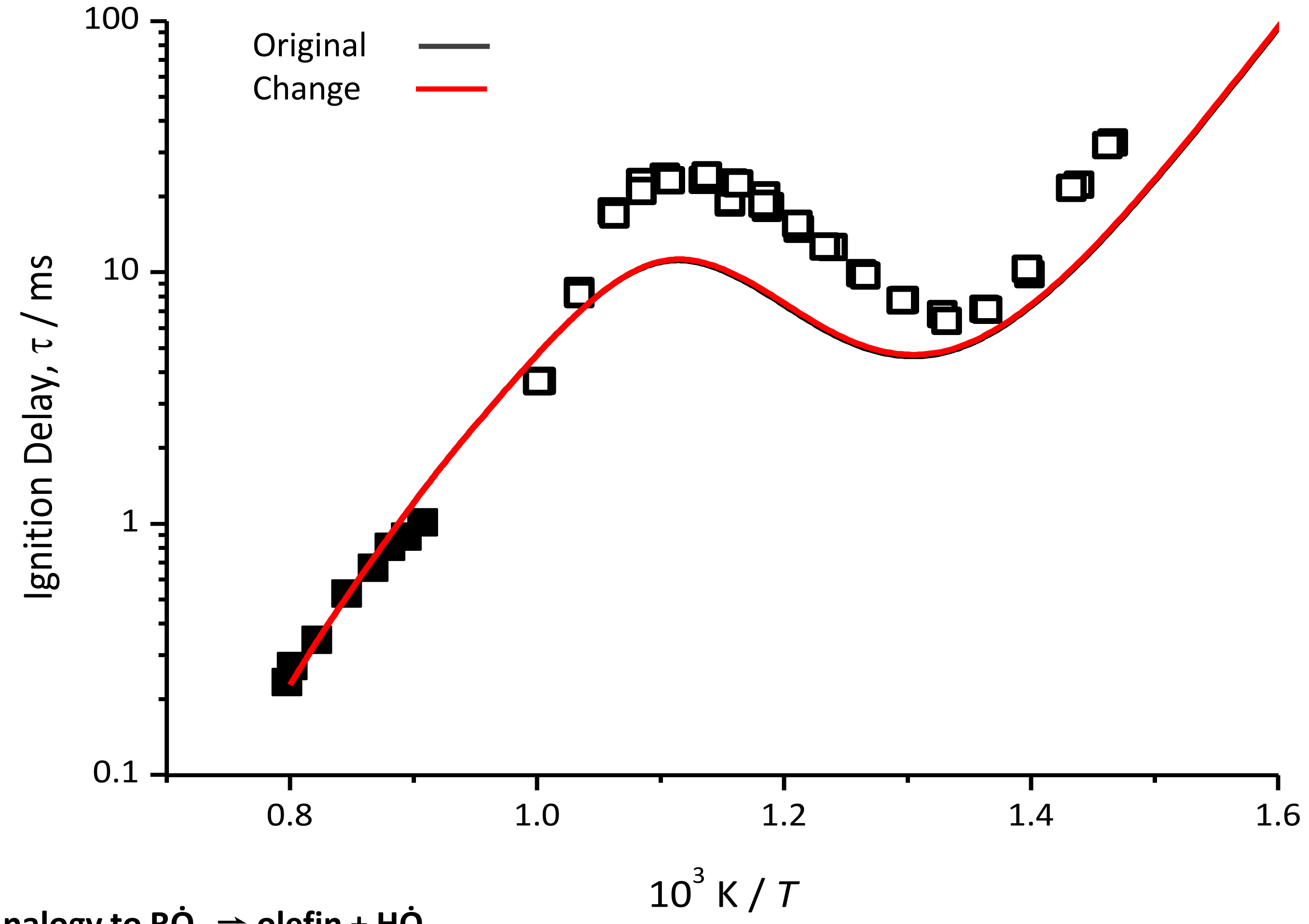
Analogy to $R\dot{O}_2 \rightleftharpoons \dot{Q}OOH$

$\dot{P}(OOH)_2 \rightleftharpoons$ cyclic ether + $\dot{O}H$



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

$\dot{O}_2QOOH \rightleftharpoons$ olefin + $H\dot{O}_2$



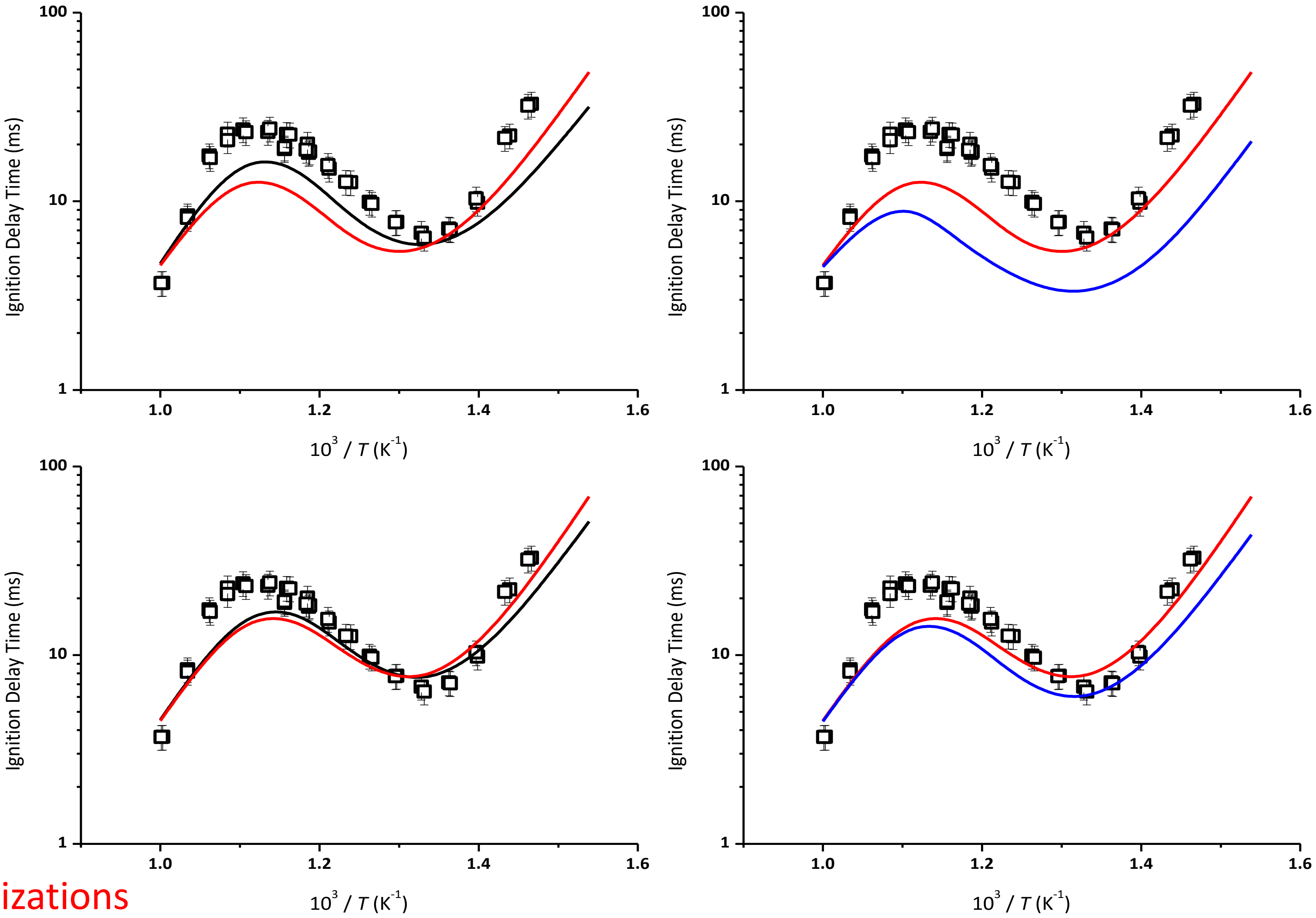
Analogy to $R\dot{O}_2 \rightleftharpoons$ olefin + $H\dot{O}_2$

Effect of Alternative Pathways

nc5_49

Healy *et al.*
JPCA 2010 24:1521

Current mechanism

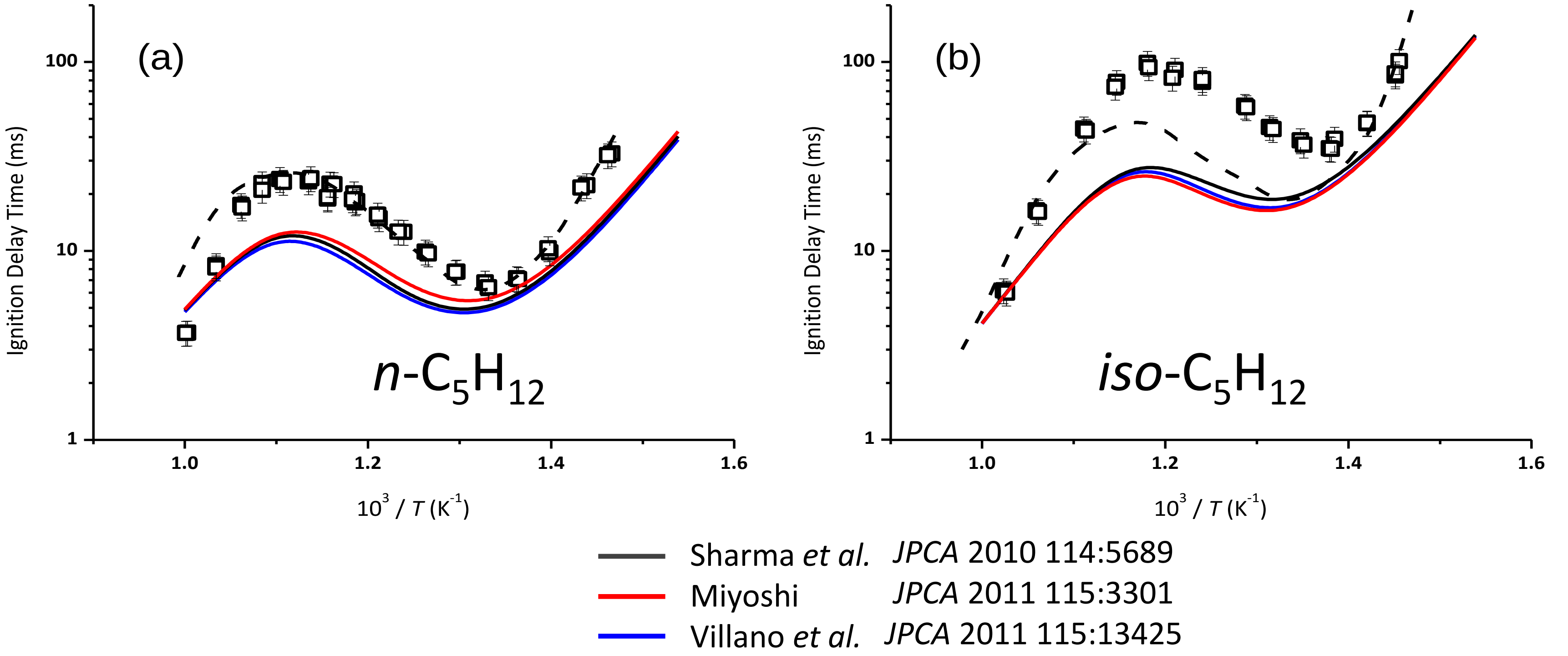


— alternative isomerizations

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

$\dot{O}_2QOOH \rightleftharpoons$ Carbonyl-hydroperoxide + $\dot{O}H$

Fuel/'air', ϕ = 1.0, 10 atm

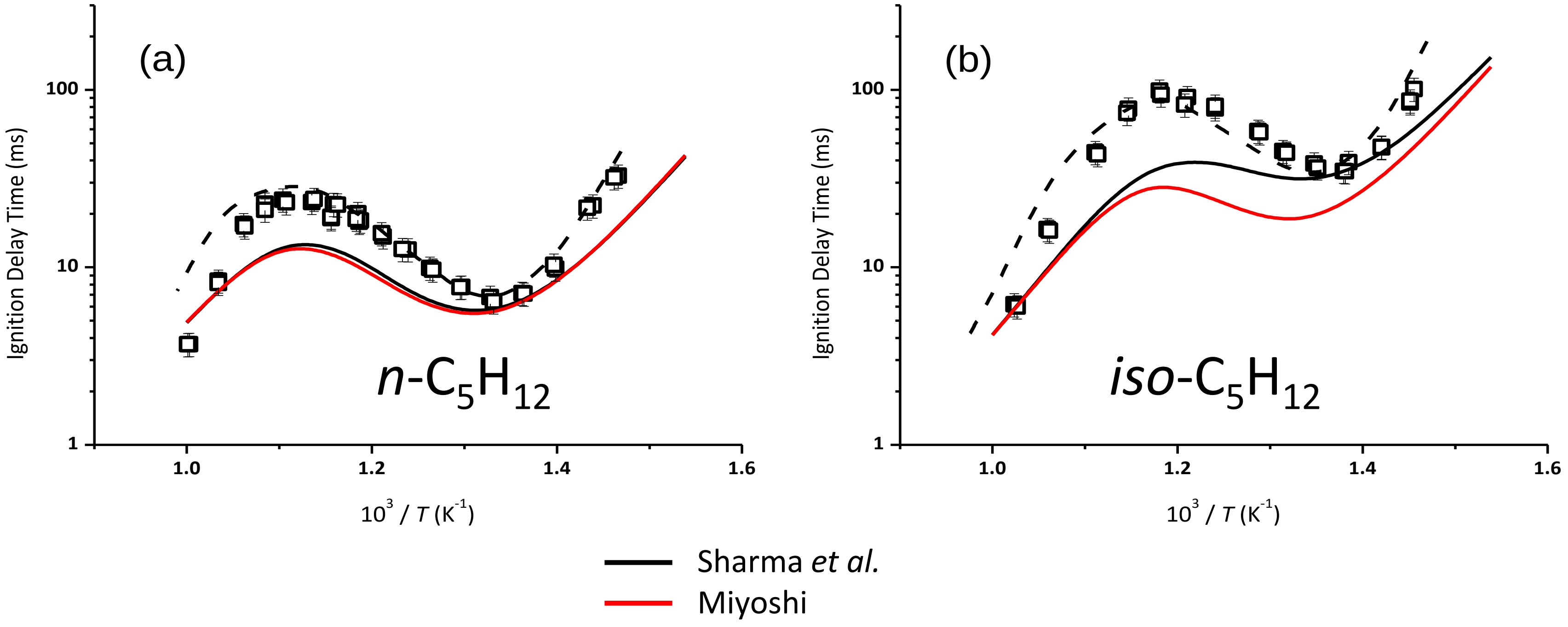


$R\dot{O}_2$ = $\dot{Q}OOH$: TST calculations

$\dot{O}_2QOOH$ = Carbonyl-hydroperoxide + $\dot{O}H$: analogy to $R\dot{O}_2$ = $\dot{Q}OOH$ (E_a: –3 kcal mol^{-1})

$\dot{O}_2QOOH \rightleftharpoons$ Carbonyl-hydroperoxide + $\dot{O}H$

Fuel/'air', ϕ = 1.0, 10 atm



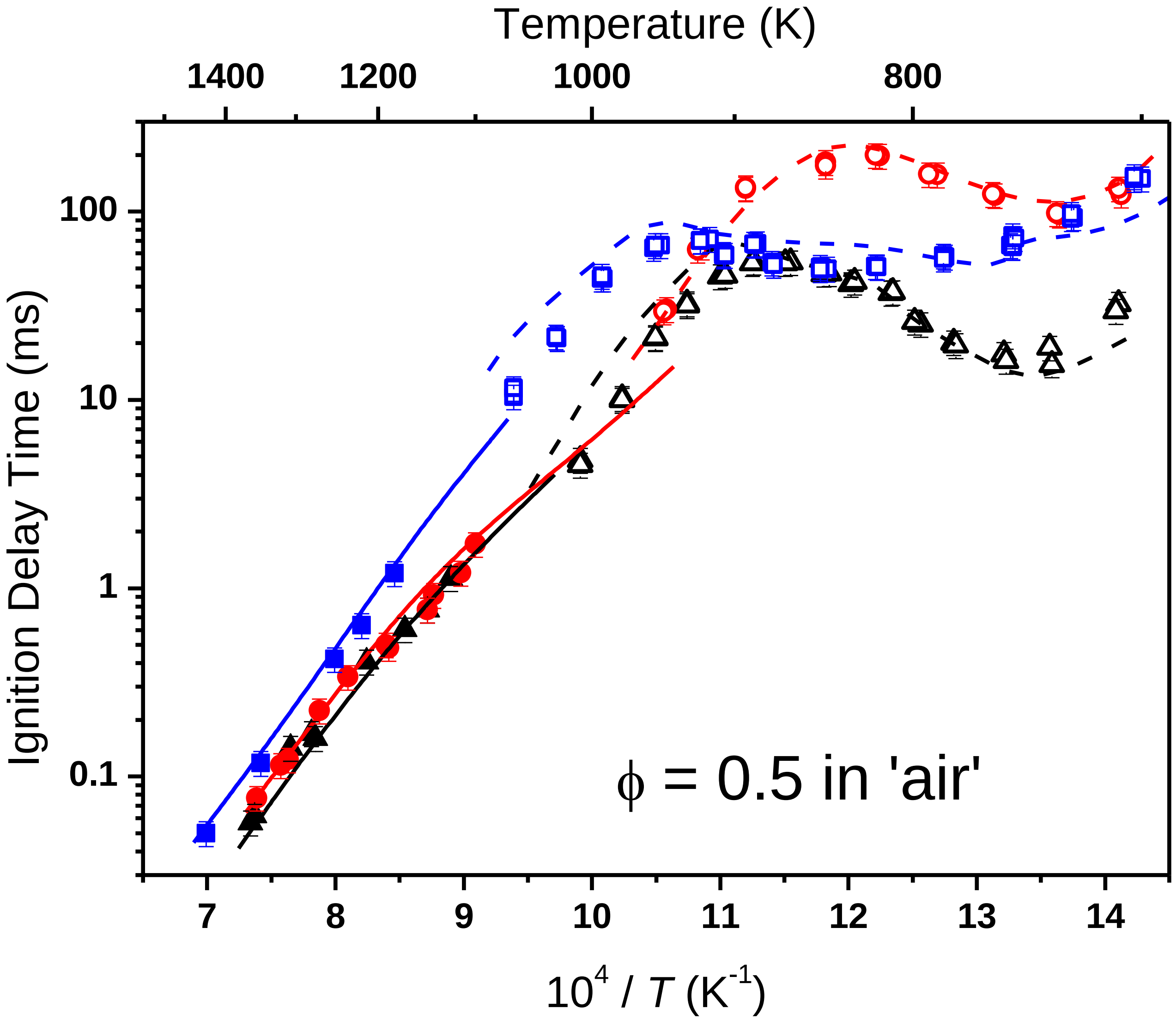
$R\dot{O}_2 = \dot{Q}OOH$: TST calculations
$\dot{O}_2QOOH$ = Carbonyl-hydroperoxide + $\dot{O}H$: TST calculations

Sharma *et al.* *JPCA* 2010 114:5689
Miyoshi *JPCA* 2011 115:3301

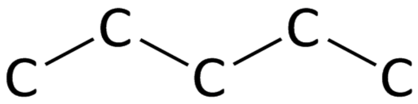
1st and 2nd Isomerisations

- Curran *et al.* recommends E_a –3 kcal mol^{-1} independent of ring size
- Sharma *et al.* calculations:
  - 5-membered TS rings: ~ – 3.3 kcal mol^{-1} ↑*k*
  - 6-membered TS rings: ~ – 1.7 kcal mol^{-1} ↓*k*
  - 7-membered TS rings: ~ – 0.4 kcal mol^{-1} ↓*k*
- Isomerisations through 6-membered transition state rings still dominate

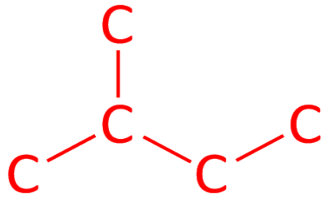
Model vs Experiments



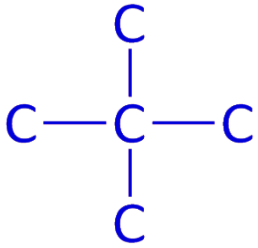
***n*-Pentane**



***iso*-Pentane**

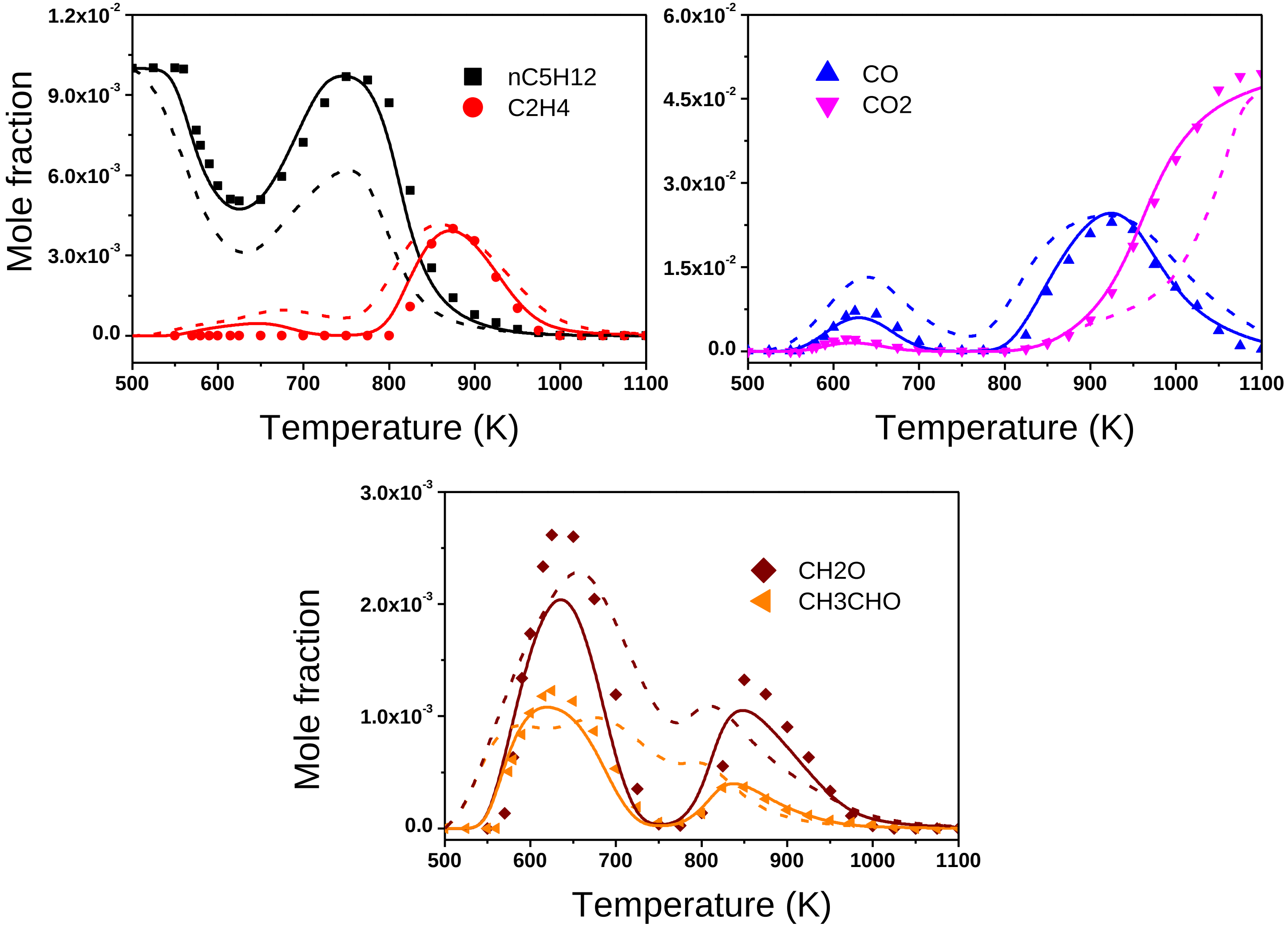


***neo*-Pentane**



Speciation data

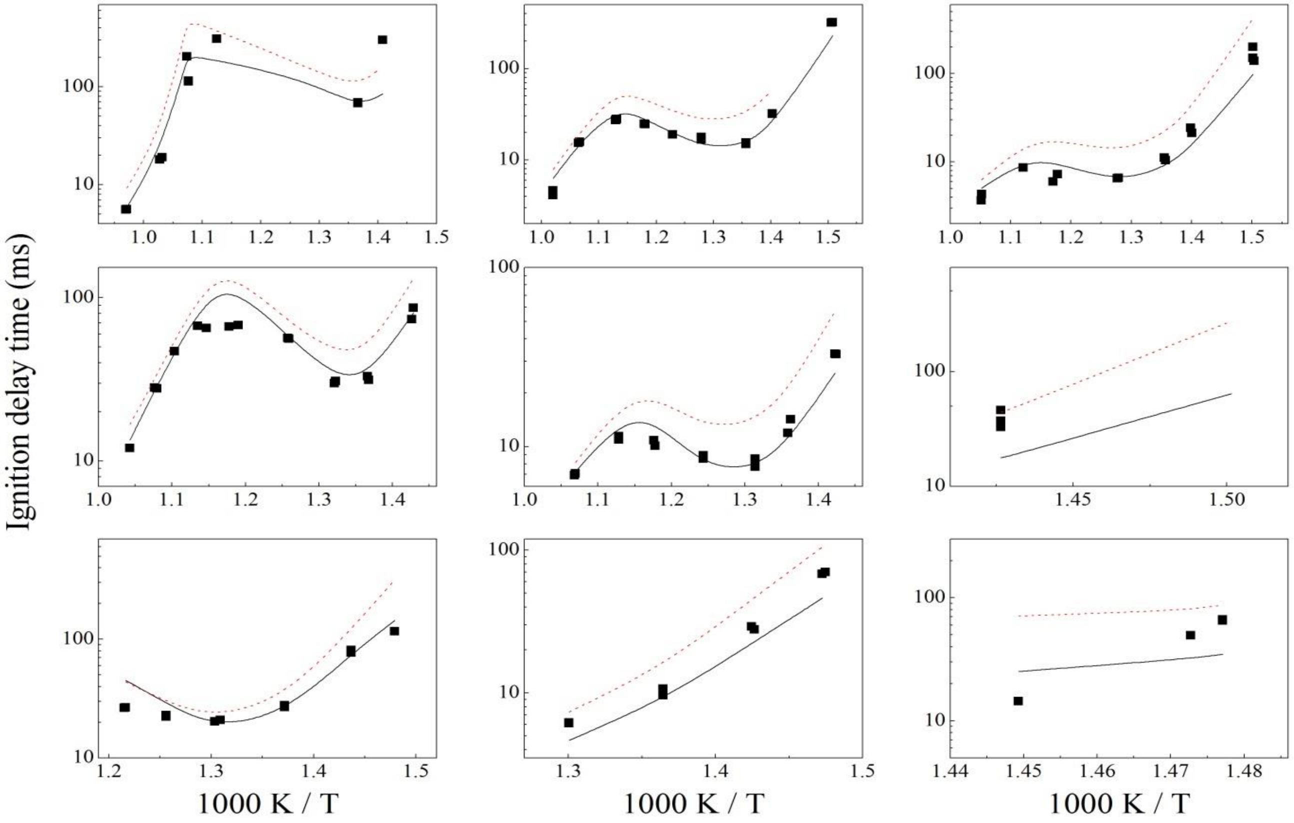
Jet-stirred reactor data: 1% n-C_5H_{12}, 16% O_2, 83% N_2, p = 1 atm



J. Bugler et al. Proc. Combust. Inst. *36(1)* (2017) 441–448.

Improvement in C_4 chemistry

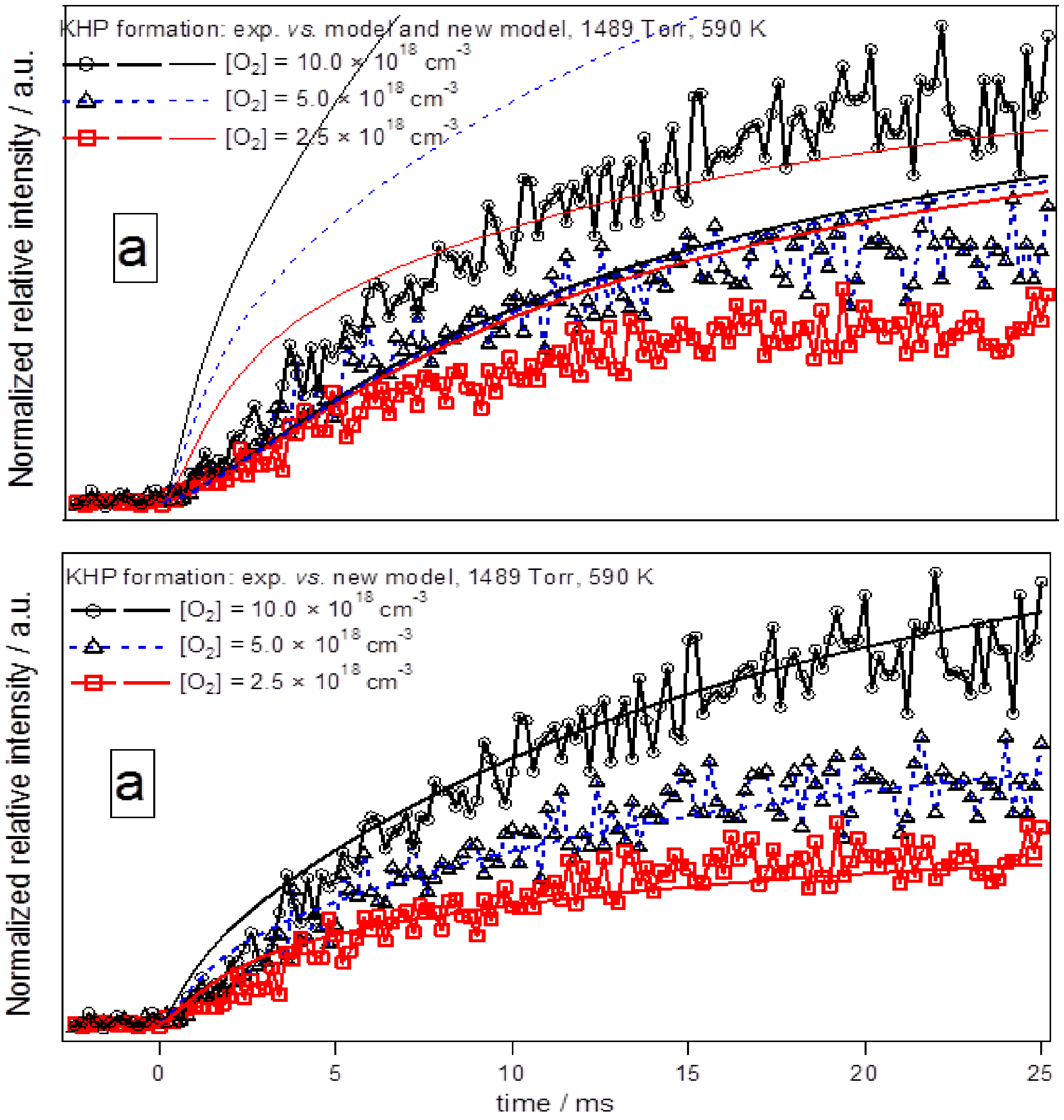
- n-butane ignition delay time in RCM under ϕ = 0.5, 1.0 and 2.0 (rows); p = 10, 20 and 30 atm (columns)



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

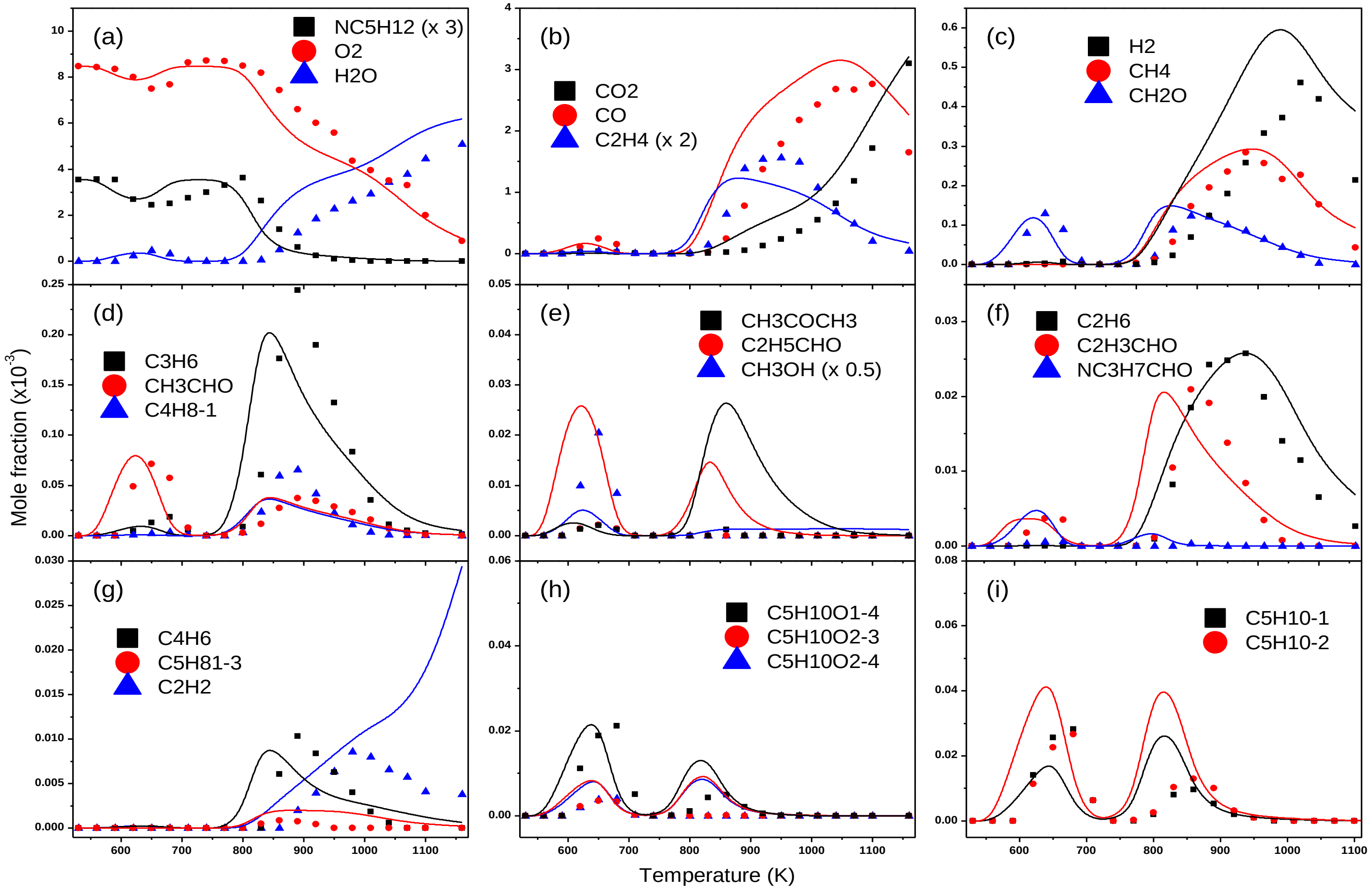
Black solid line: current mechanism
Red dashed line: Aramco 1.3 mech

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

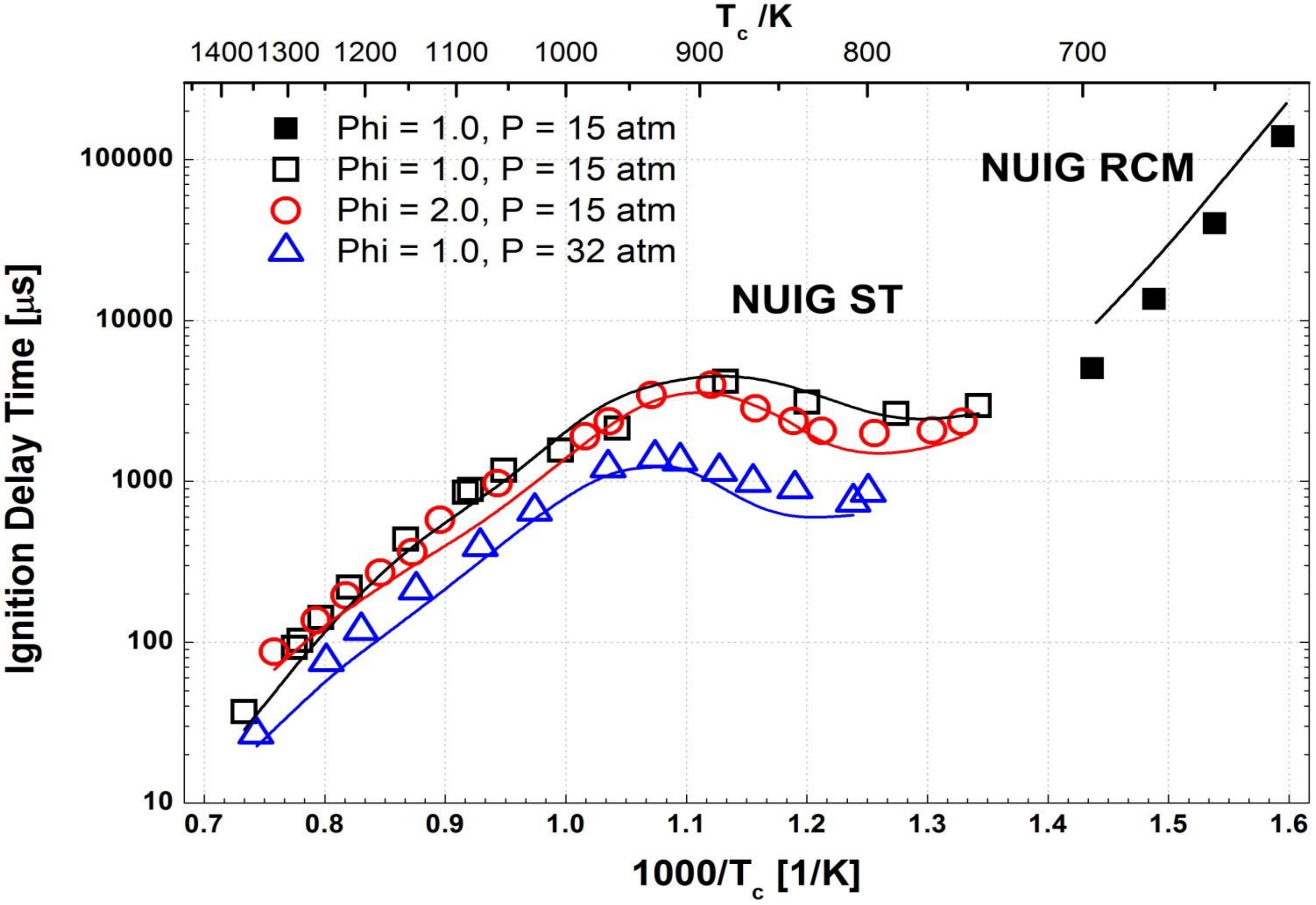
Validation: n-Pentane



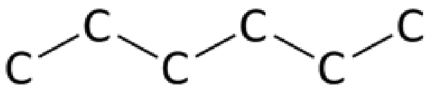
JSR experiment from Philippe Dagaut at Orléans
φ = 1.0, τ = 0.7 s, 10 atm, 0.1% fuel

J. Bugler et al. Proc. Combust. Inst. *36(1)* (2017) 441–448.

Validation: n-Hexane

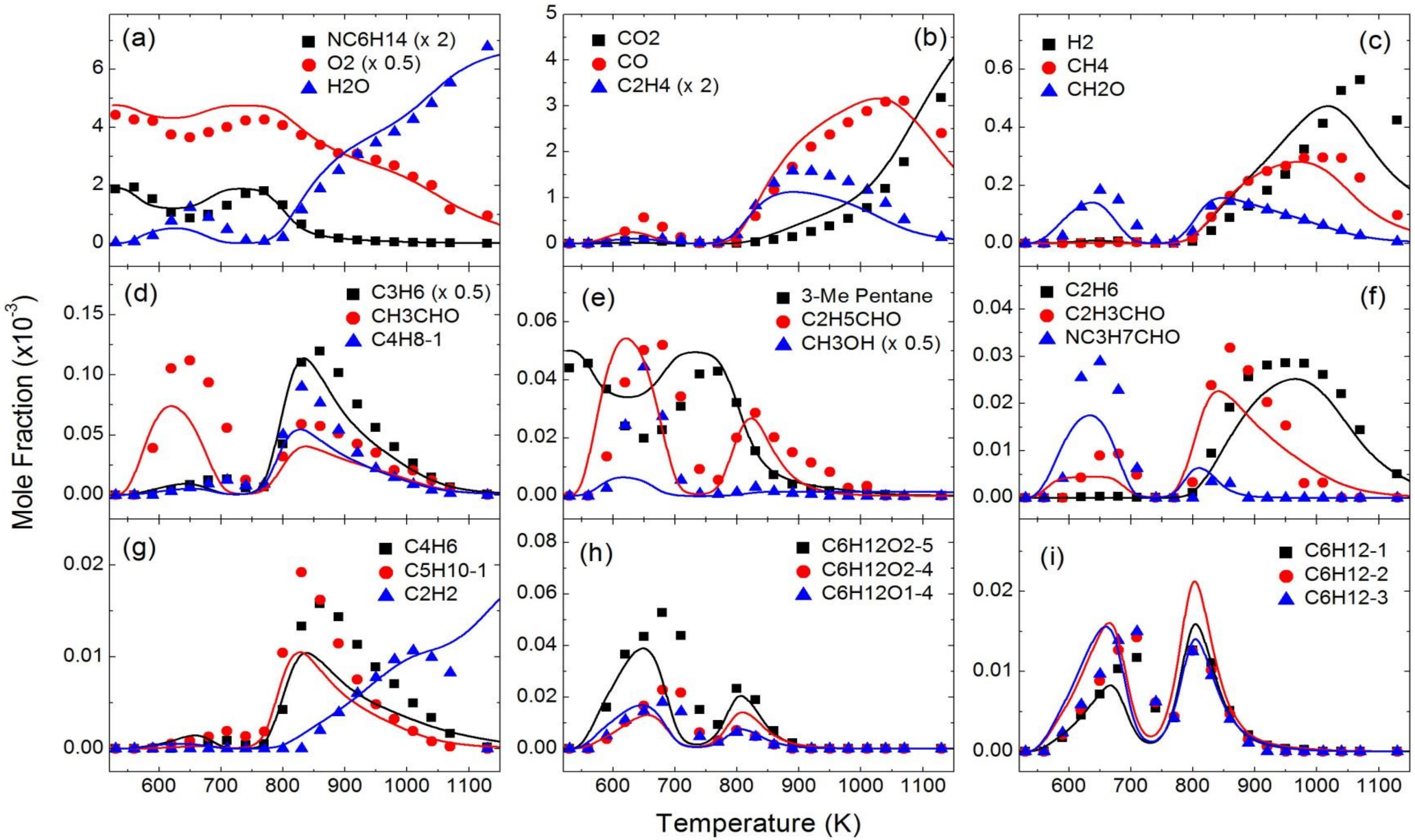


***n*-Hexane**



K. Zhang et al. Combust. Flame *162* (2015) 4194–4207.

Validation: n-Hexane

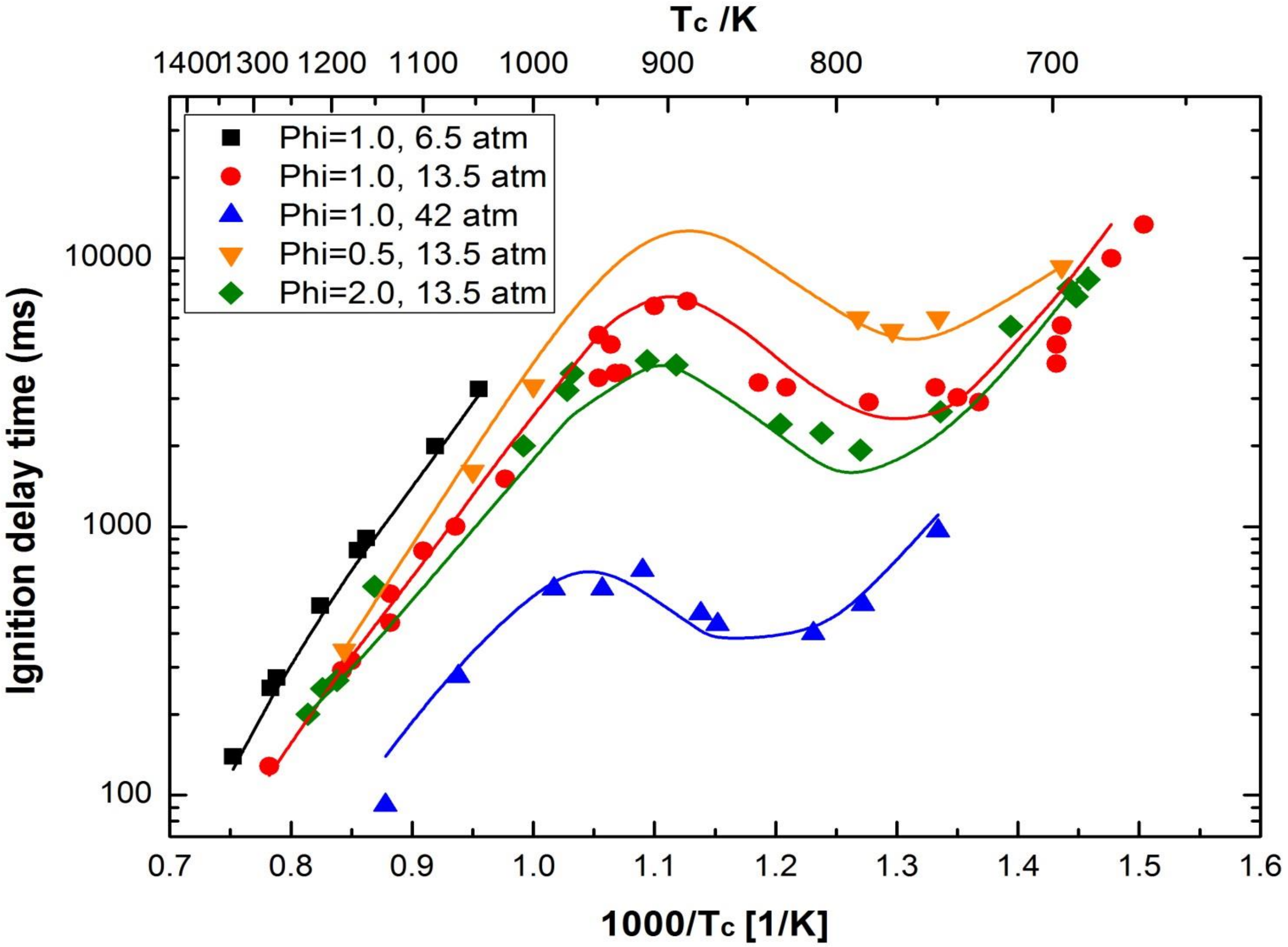


JSR experiment Philippe Dagaut at Orléans

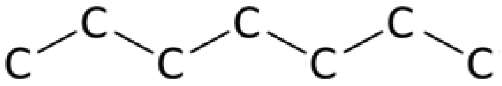
φ = 1.0, τ = 0.7 s, 10 atm, 0.1% fuel

K. Zhang et al. Combust. Flame *162* (2015) 4194–4207.

Validation: n-Heptane

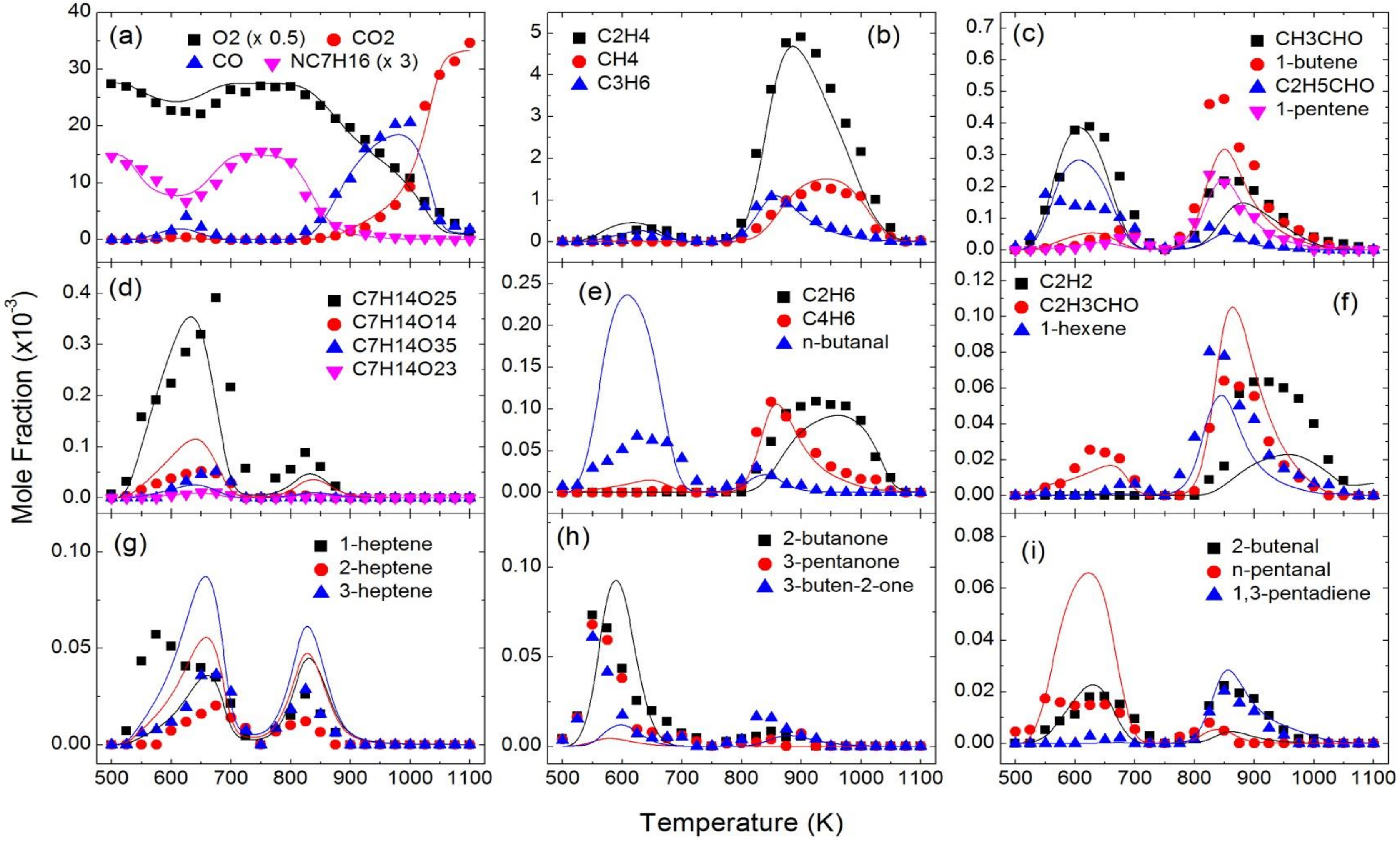


***n*-Heptane**



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

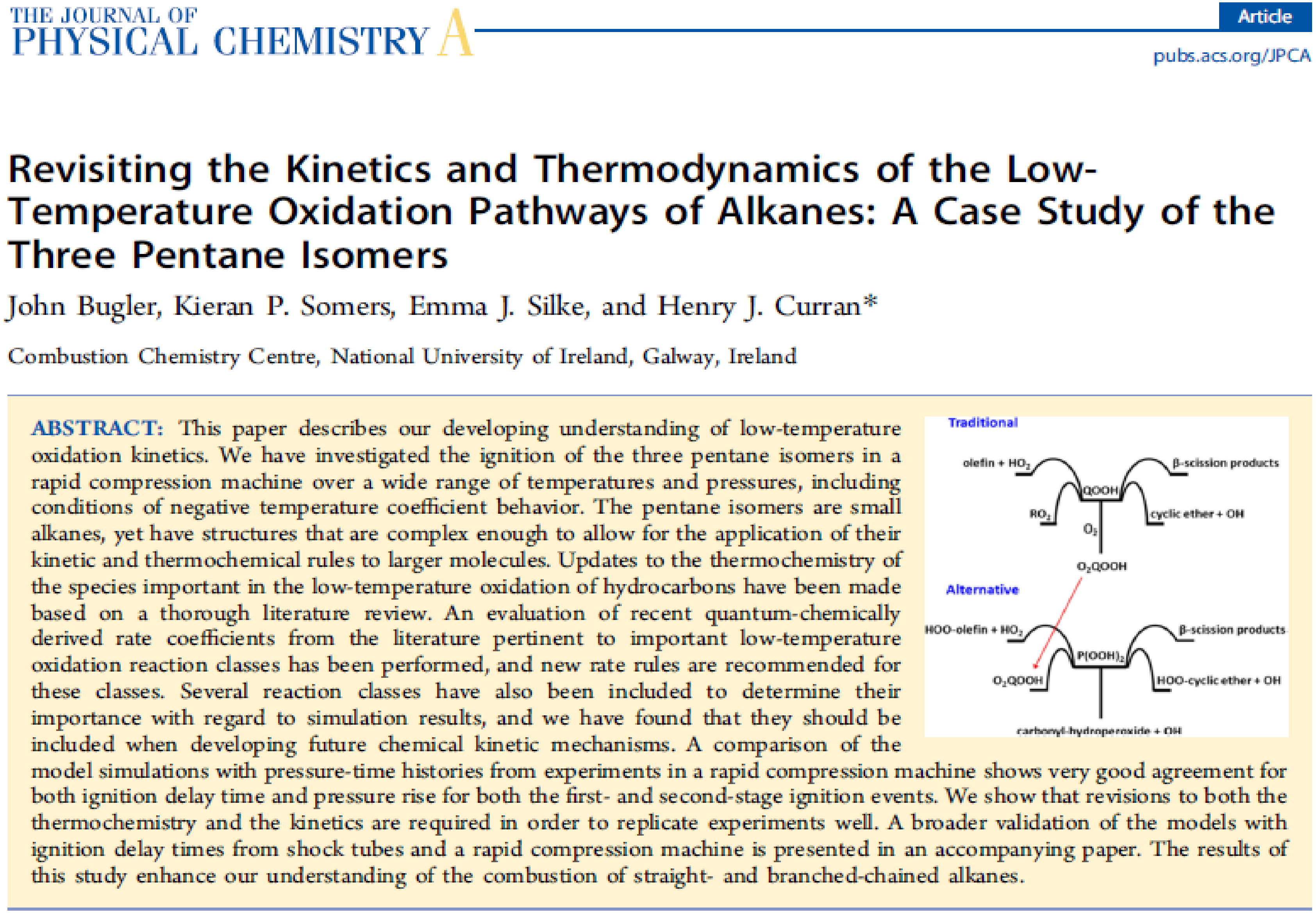
Validation: n-Heptane



φ = 1.0, τ = 2.0 s, 1.06 bar, 0.5% fuel

Herbinet et al. Combust. Flame 159 (2012) 3455–3471.

Pentane Isomers



THE JOURNAL OF
PHYSICAL CHEMISTRY A

Article

pubs.acs.org/JPCA

Revisiting the Kinetics and Thermodynamics of the Low-Temperature Oxidation Pathways of Alkanes: A Case Study of the Three Pentane Isomers

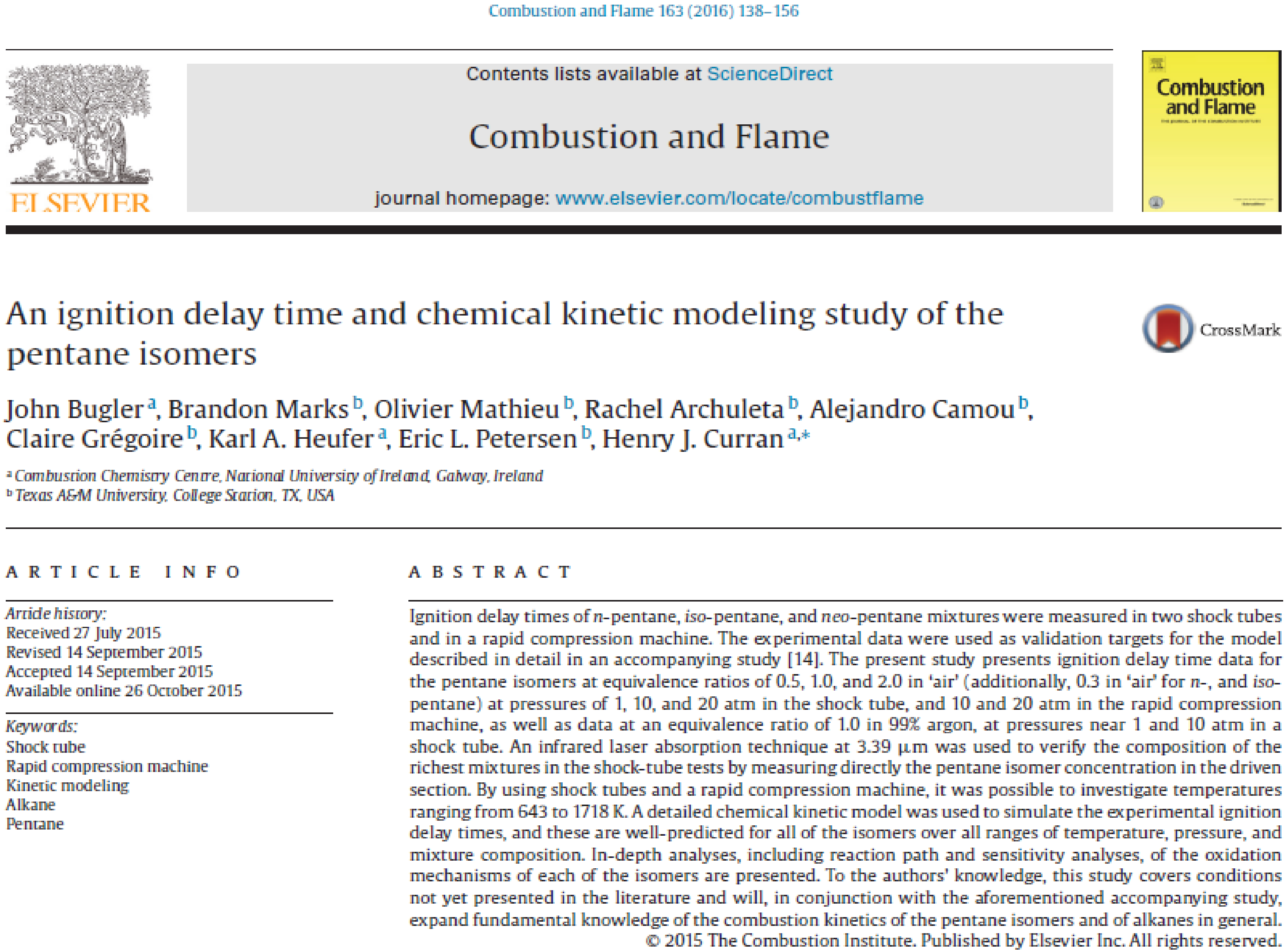
John Bugler, Kieran P. Somers, Emma J. Silke, and Henry J. Curran*

Combustion Chemistry Centre, National University of Ireland, Galway, Ireland

ABSTRACT: This paper describes our developing understanding of low-temperature oxidation kinetics. We have investigated the ignition of the three pentane isomers in a rapid compression machine over a wide range of temperatures and pressures, including conditions of negative temperature coefficient behavior. The pentane isomers are small alkanes, yet have structures that are complex enough to allow for the application of their kinetic and thermochemical rules to larger molecules. Updates to the thermochemistry of the species important in the low-temperature oxidation of hydrocarbons have been made based on a thorough literature review. An evaluation of recent quantum-chemically derived rate coefficients from the literature pertinent to important low-temperature oxidation reaction classes has been performed, and new rate rules are recommended for these classes. Several reaction classes have also been included to determine their importance with regard to simulation results, and we have found that they should be included when developing future chemical kinetic mechanisms. A comparison of the model simulations with pressure-time histories from experiments in a rapid compression machine shows very good agreement for both ignition delay time and pressure rise for both the first- and second-stage ignition events. We show that revisions to both the thermochemistry and the kinetics are required in order to replicate experiments well. A broader validation of the models with ignition delay times from shock tubes and a rapid compression machine is presented in an accompanying paper. The results of this study enhance our understanding of the combustion of straight- and branched-chained alkanes.

Journal of Physical Chemistry A 119(28) (2015) 7510–7527.

Pentane Isomers



Combustion and Flame 163 (2016) 138–156

Contents lists available at ScienceDirect

Combustion and Flame

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

An ignition delay time and chemical kinetic modeling study of the pentane isomers

John Bugler[a], Brandon Marks[b], Olivier Mathieu[b], Rachel Archuleta[b], Alejandro Camou[b], Claire Grégoire[b], Karl A. Heufer[a], Eric L. Petersen[b], Henry J. Curran[a,*]

[a] Combustion Chemistry Centre, National University of Ireland, Galway, Ireland
[b] Texas A&M University, College Station, TX, USA

ARTICLE INFO

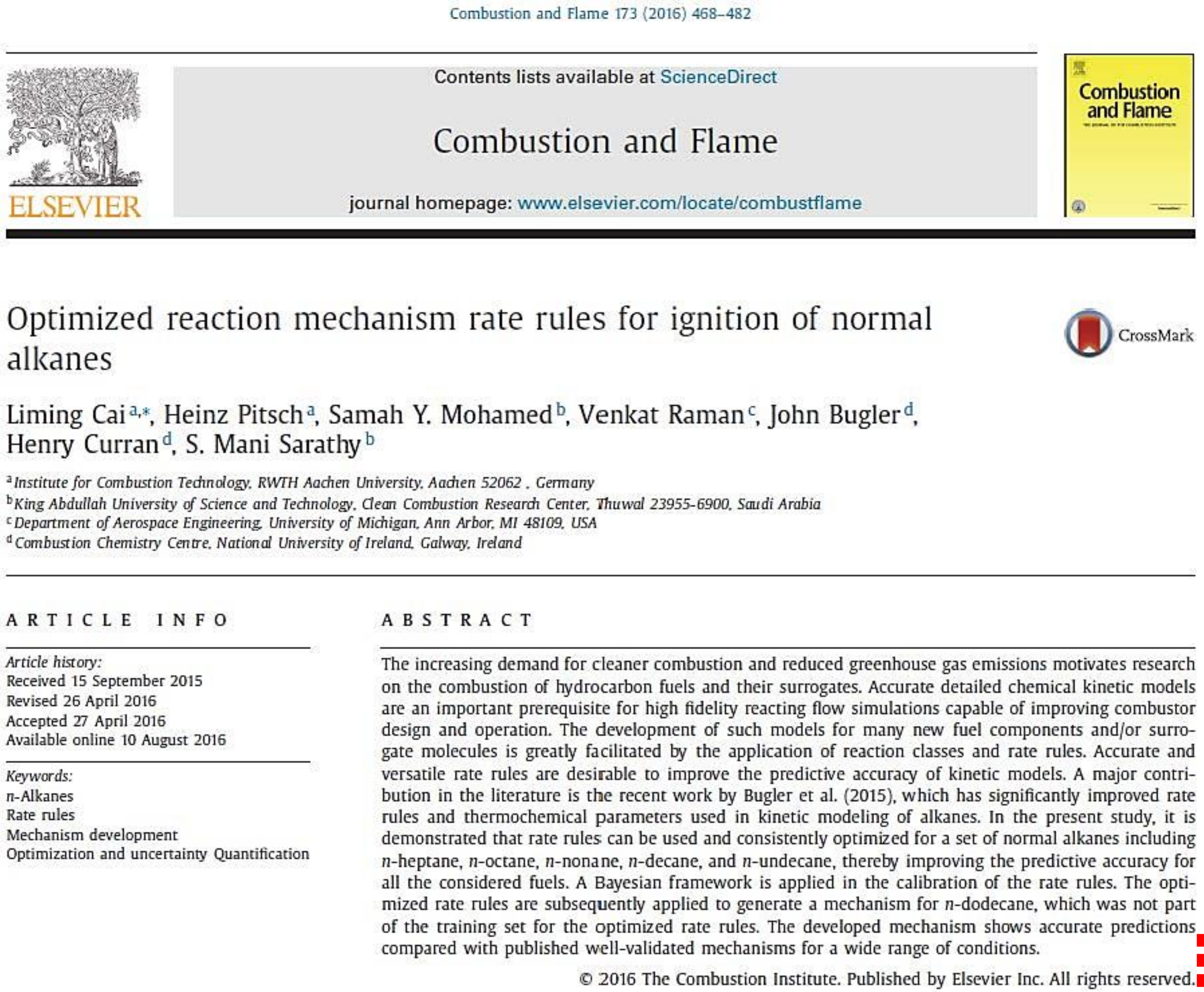
Article history:
Received 27 July 2015
Revised 14 September 2015
Accepted 14 September 2015
Available online 26 October 2015

Keywords:
Shock tube
Rapid compression machine
Kinetic modeling
Alkane
Pentane

ABSTRACT

Ignition delay times of *n*-pentane, *iso*-pentane, and *neo*-pentane mixtures were measured in two shock tubes and in a rapid compression machine. The experimental data were used as validation targets for the model described in detail in an accompanying study [14]. The present study presents ignition delay time data for the pentane isomers at equivalence ratios of 0.5, 1.0, and 2.0 in 'air' (additionally, 0.3 in 'air' for *n*-, and *iso*-pentane) at pressures of 1, 10, and 20 atm in the shock tube, and 10 and 20 atm in the rapid compression machine, as well as data at an equivalence ratio of 1.0 in 99% argon, at pressures near 1 and 10 atm in a shock tube. An infrared laser absorption technique at 3.39 μm was used to verify the composition of the richest mixtures in the shock-tube tests by measuring directly the pentane isomer concentration in the driven section. By using shock tubes and a rapid compression machine, it was possible to investigate temperatures ranging from 643 to 1718 K. A detailed chemical kinetic model was used to simulate the experimental ignition delay times, and these are well-predicted for all of the isomers over all ranges of temperature, pressure, and mixture composition. In-depth analyses, including reaction path and sensitivity analyses, of the oxidation mechanisms of each of the isomers are presented. To the authors' knowledge, this study covers conditions not yet presented in the literature and will, in conjunction with the aforementioned accompanying study, expand fundamental knowledge of the combustion kinetics of the pentane isomers and of alkanes in general.

Rate rules for C_7—C_{12} *n*-alkanes



Combustion and Flame 173 (2016) 468–482

Contents lists available at ScienceDirect

Combustion and Flame

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

Optimized reaction mechanism rate rules for ignition of normal alkanes

Liming Cai[a,*], Heinz Pitsch[a], Samah Y. Mohamed[b], Venkat Raman[c], John Bugler[d], Henry Curran[d], S. Mani Sarathy[b]

[a] *Institute for Combustion Technology, RWTH Aachen University, Aachen 52062 , Germany*
[b] *King Abdullah University of Science and Technology, Clean Combustion Research Center, Thuwal 23955-6900, Saudi Arabia*
[c] *Department of Aerospace Engineering, University of Michigan, Ann Arbor, MI 48109, USA*
[d] *Combustion Chemistry Centre, National University of Ireland, Galway, Ireland*

ARTICLE INFO

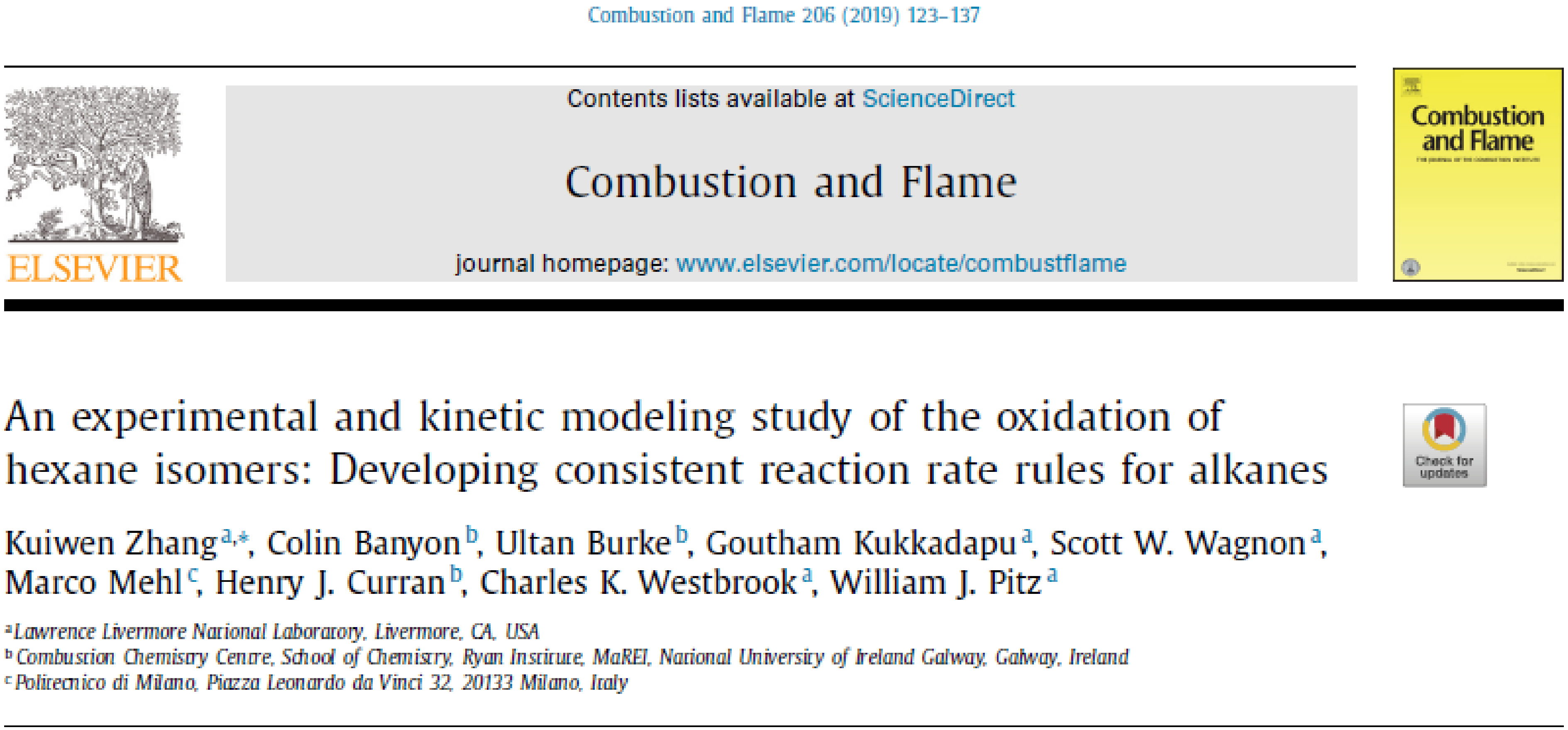
Article history:
Received 15 September 2015
Revised 26 April 2016
Accepted 27 April 2016
Available online 10 August 2016

Keywords:
n-Alkanes
Rate rules
Mechanism development
Optimization and uncertainty Quantification

ABSTRACT

The increasing demand for cleaner combustion and reduced greenhouse gas emissions motivates research on the combustion of hydrocarbon fuels and their surrogates. Accurate detailed chemical kinetic models are an important prerequisite for high fidelity reacting flow simulations capable of improving combustor design and operation. The development of such models for many new fuel components and/or surrogate molecules is greatly facilitated by the application of reaction classes and rate rules. Accurate and versatile rate rules are desirable to improve the predictive accuracy of kinetic models. A major contribution in the literature is the recent work by Bugler et al. (2015), which has significantly improved rate rules and thermochemical parameters used in kinetic modeling of alkanes. In the present study, it is demonstrated that rate rules can be used and consistently optimized for a set of normal alkanes including *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, and *n*-undecane, thereby improving the predictive accuracy for all the considered fuels. A Bayesian framework is applied in the calibration of the rate rules. The optimized rate rules are subsequently applied to generate a mechanism for *n*-dodecane, which was not part of the training set for the optimized rate rules. The developed mechanism shows accurate predictions compared with published well-validated mechanisms for a wide range of conditions.

Rate rules for C_6 alkane isomers



Combustion and Flame 206 (2019) 123–137

Contents lists available at ScienceDirect

Combustion and Flame

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

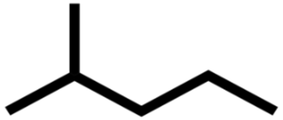
An experimental and kinetic modeling study of the oxidation of hexane isomers: Developing consistent reaction rate rules for alkanes

Kuiwen Zhang[a,*], Colin Banyon[b], Ultan Burke[b], Goutham Kukkadapu[a], Scott W. Wagnon[a], Marco Mehl[c], Henry J. Curran[b], Charles K. Westbrook[a], William J. Pitz[a]

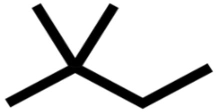
[a] Lawrence Livermore National Laboratory, Livermore, CA, USA
[b] Combustion Chemistry Centre, School of Chemistry, Ryan Institute, MaREI, National University of Ireland Galway, Galway, Ireland
[c] Politecnico di Milano, Piazza Leonardo da Vinci 32, 20133 Milano, Italy

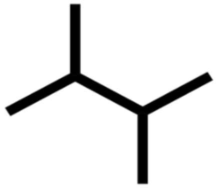
Hexane Isomer Work


24.8 RON


73.4 RON


74.5 RON


91.8 RON


104.3 RON

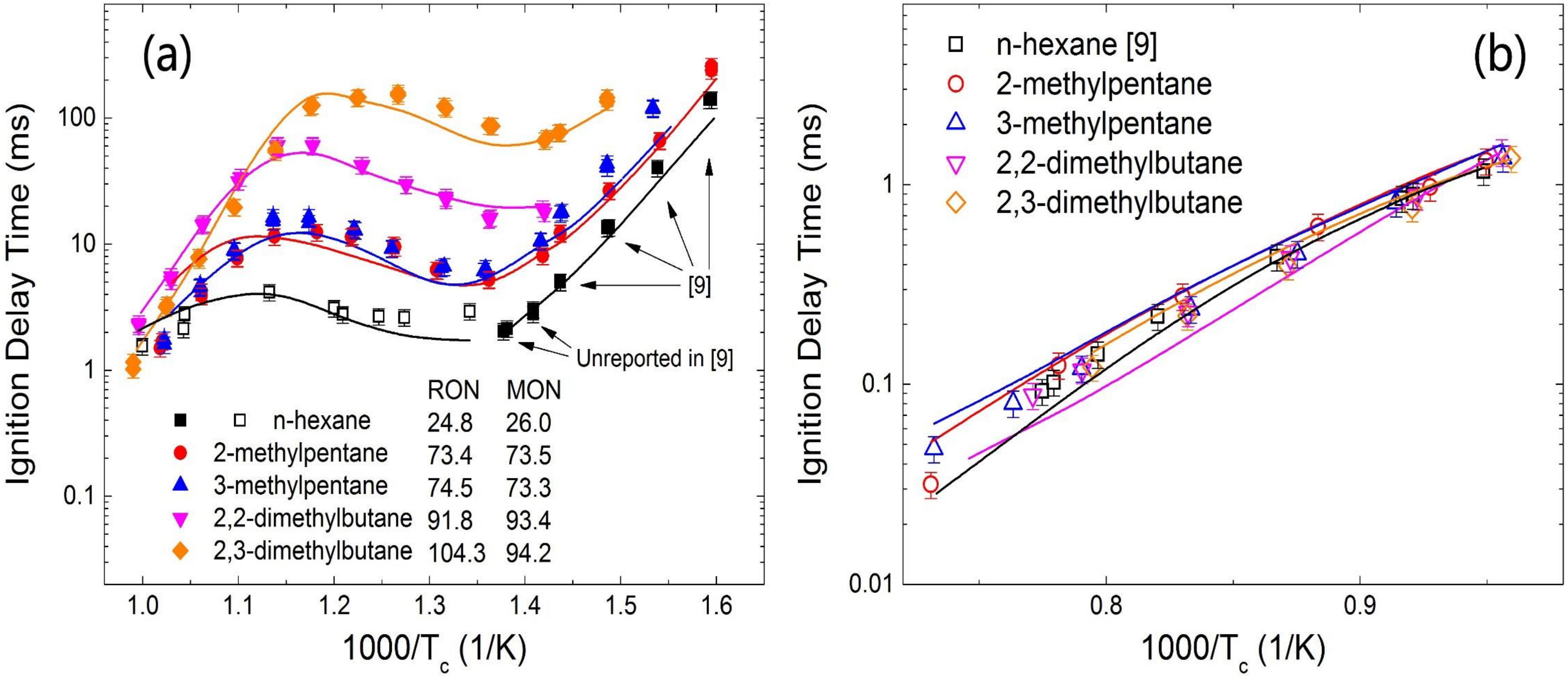
Colin Banyon

31/03/2016, Galway

K. Zhang et al. Combust. Flame *206* (2019) 123–137.

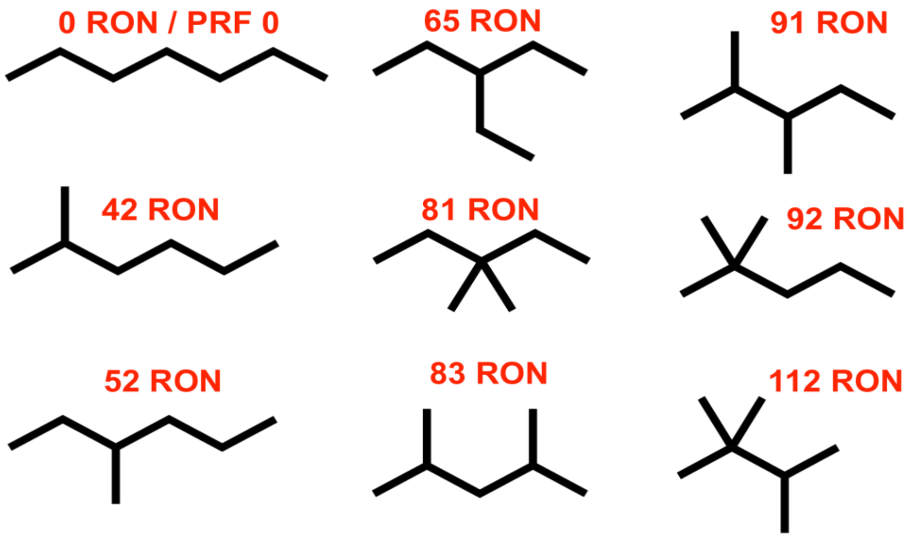
Hexane isomers

- Φ =1.0 in air at 15 bar



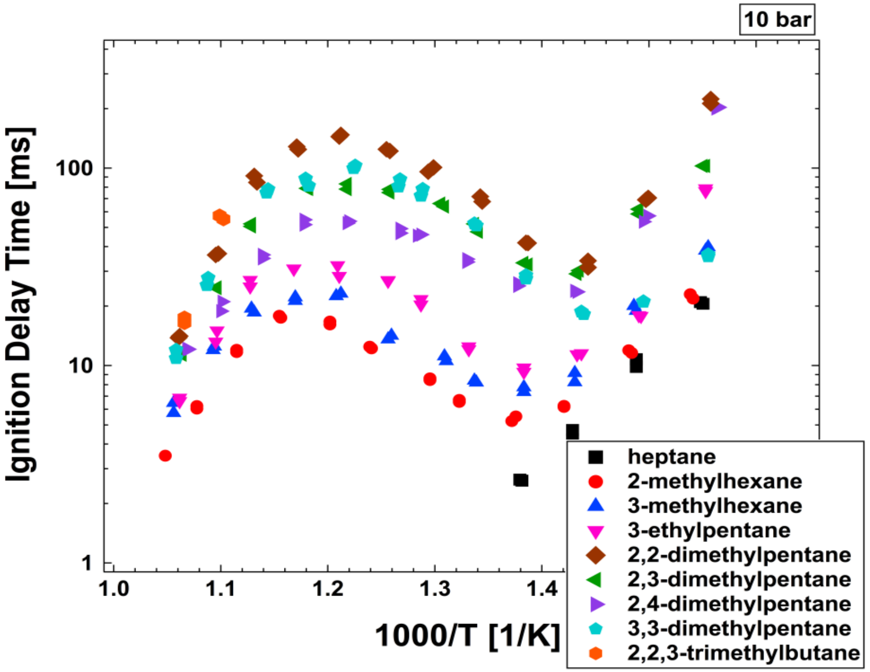
K. Zhang et al. Combust. Flame *206* (2019) 123–137.

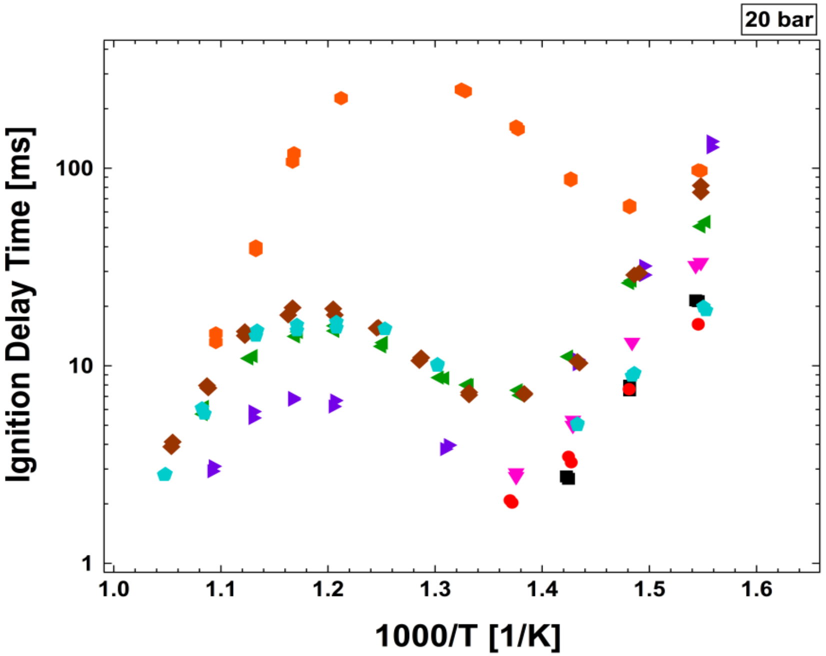
Heptane Isomer Work



Colin Banyon

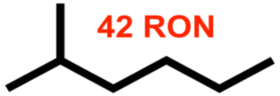
31/03/2016, Galway



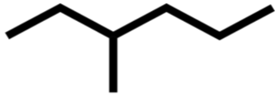


0 RON / PRF 0

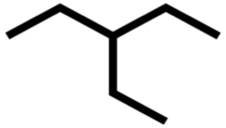
42 RON



52 RON

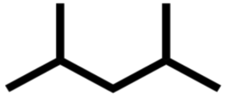


65 RON

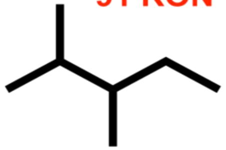


81 RON

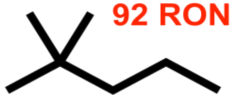
83 RON



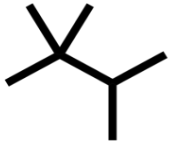
91 RON



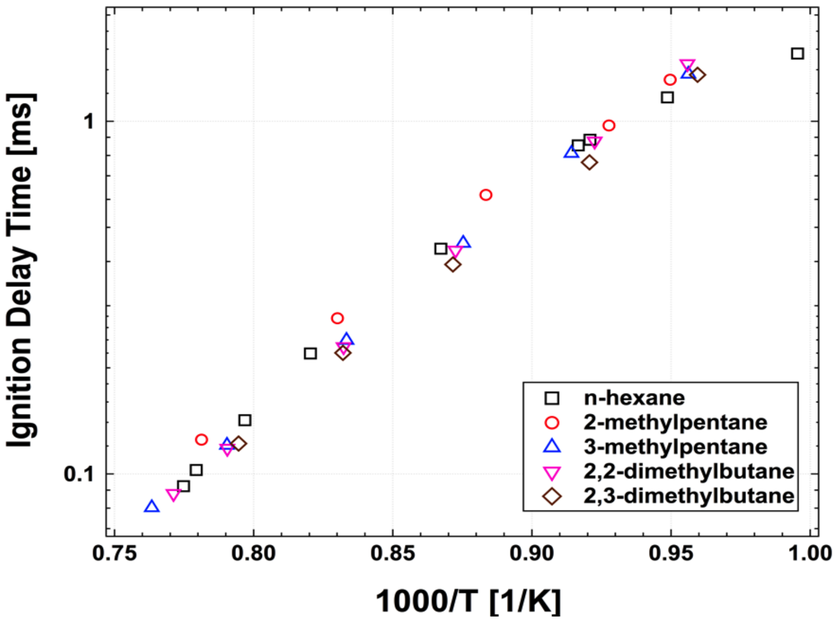
92 RON

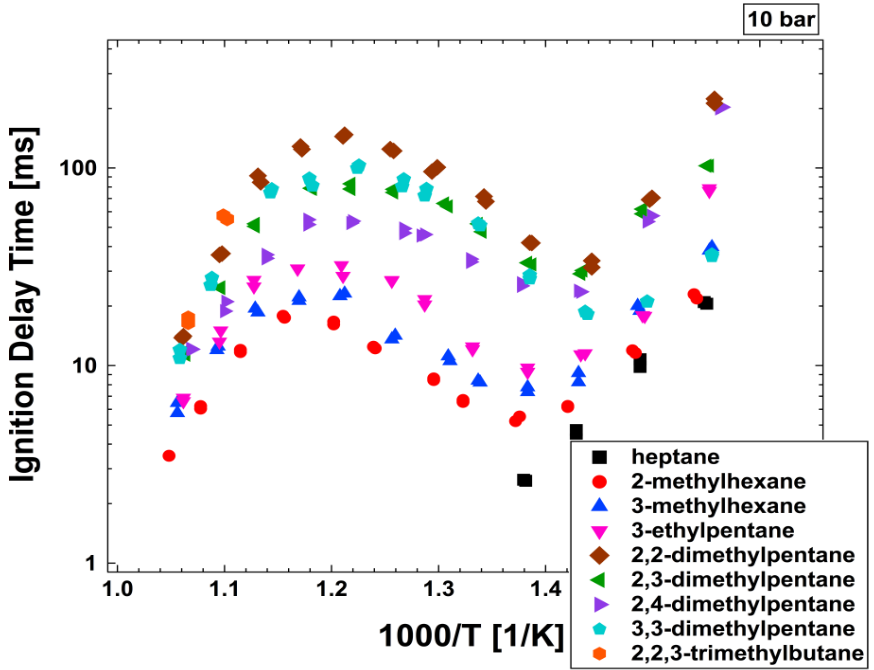


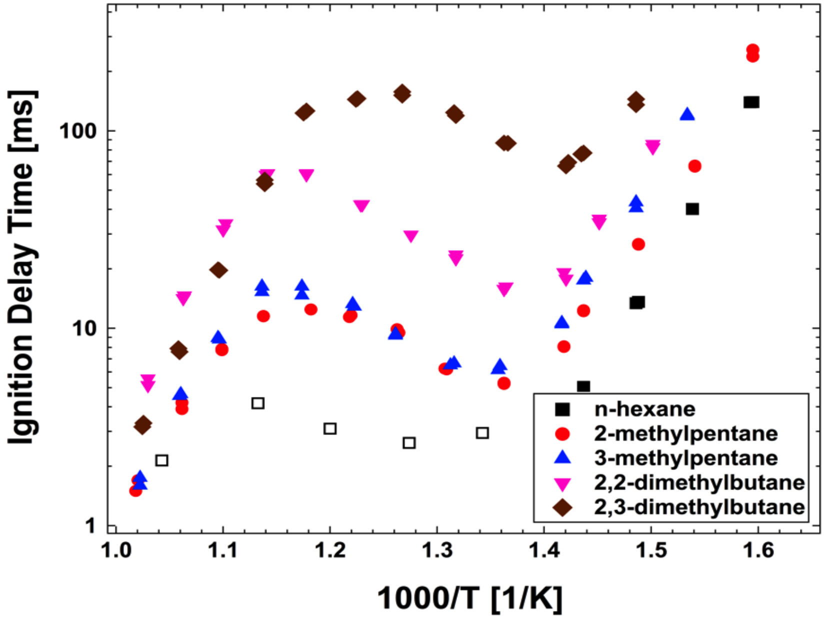
112 RON

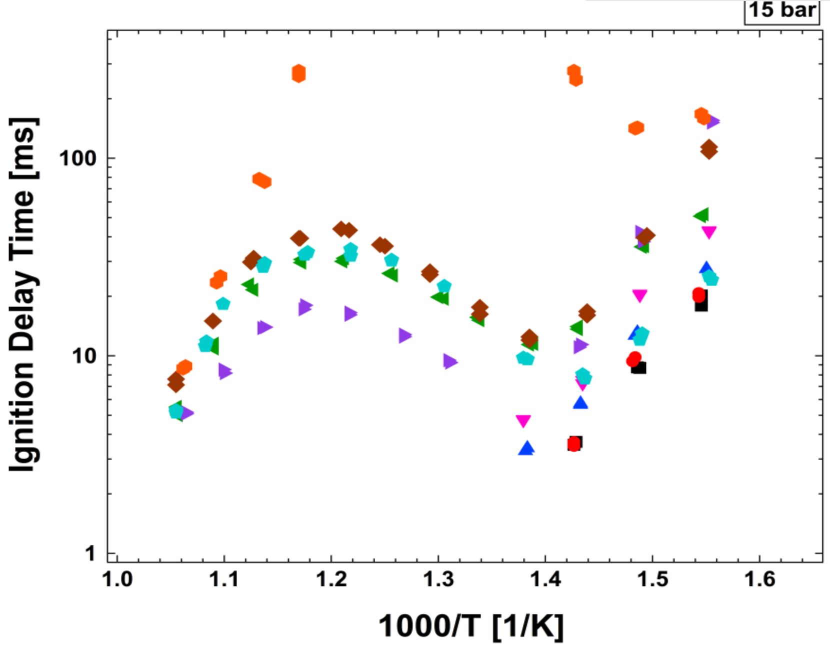


Φ =1.0 in air at 15 bar









Conclusions

- Re-evaluated our understanding of low-temperature oxidation of alkanes
- Developed rate rules for reaction classes important in low-temperature regime
- “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

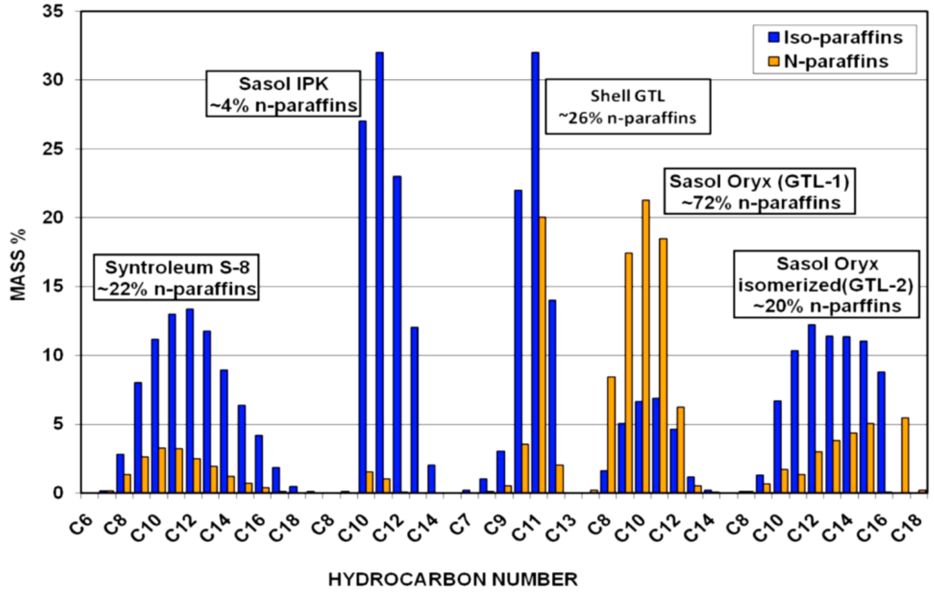
- Wind power
- Solar radiation
- Geothermal power
- Sea waves
- Nuclear power
- Fusion reactors
- Any others ? Probably
- But combustion is a big contributor

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?

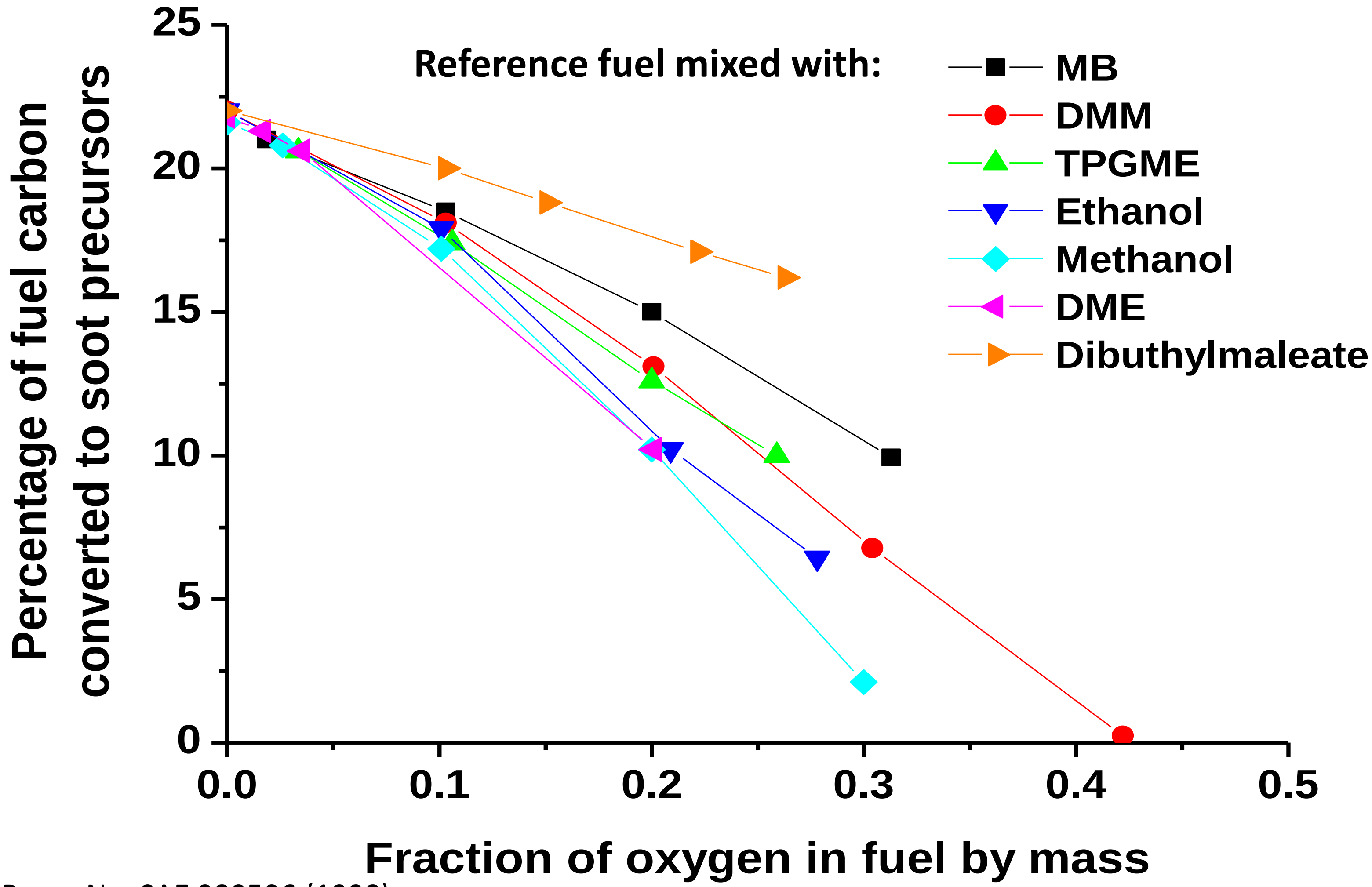
- Oxygenated fuel ⇒ cleaner burning
  - Renewable, “Carbon neutral” fuel
  - Some can be used with existing diesel engines & distribution systems

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



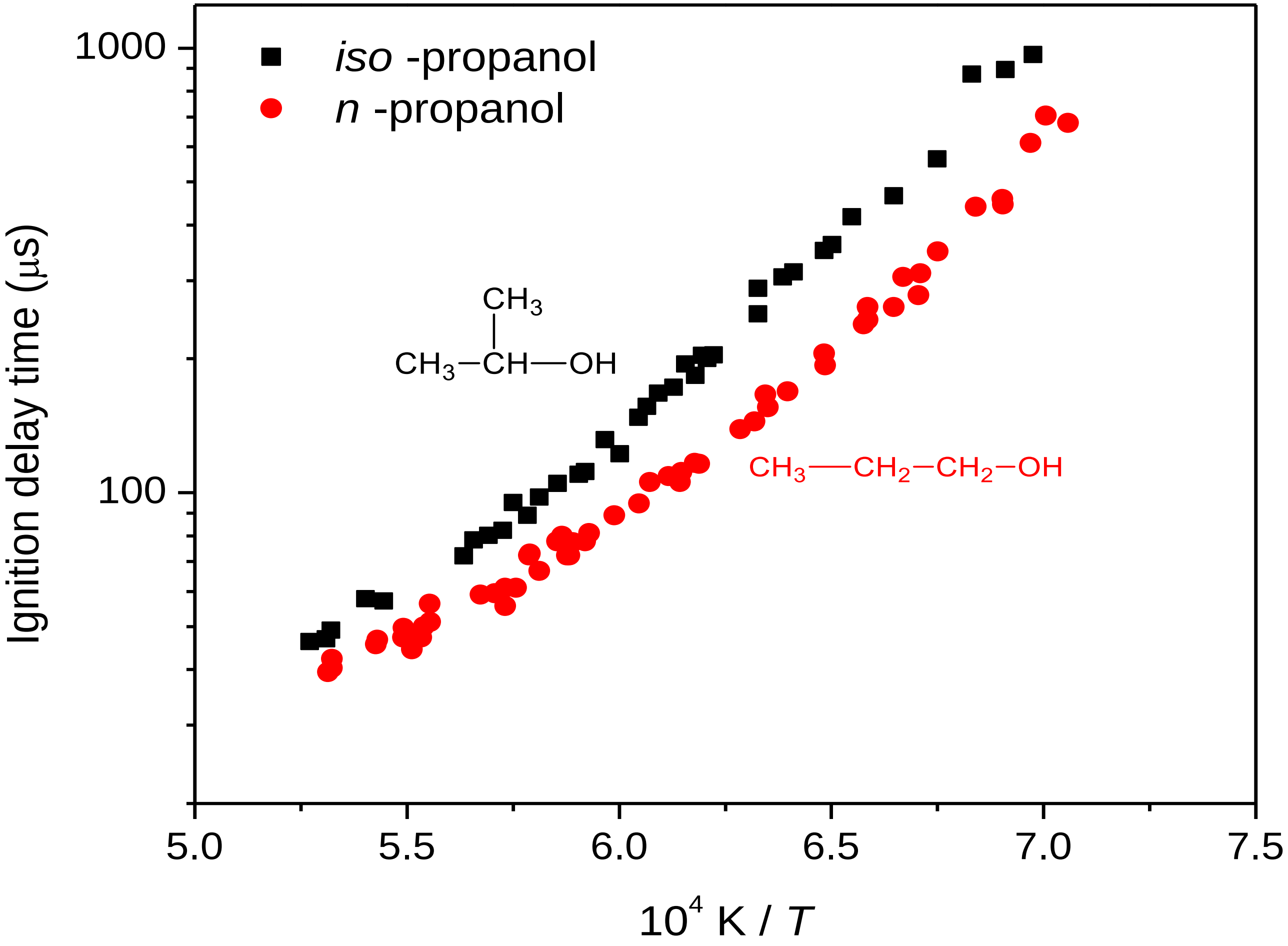
Miyamoto *et al.* Paper No. SAE 980506 (1998).
Westbrook *et al.* J. Phys. Chem. A (2006) *110:* 6912–6922.

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)

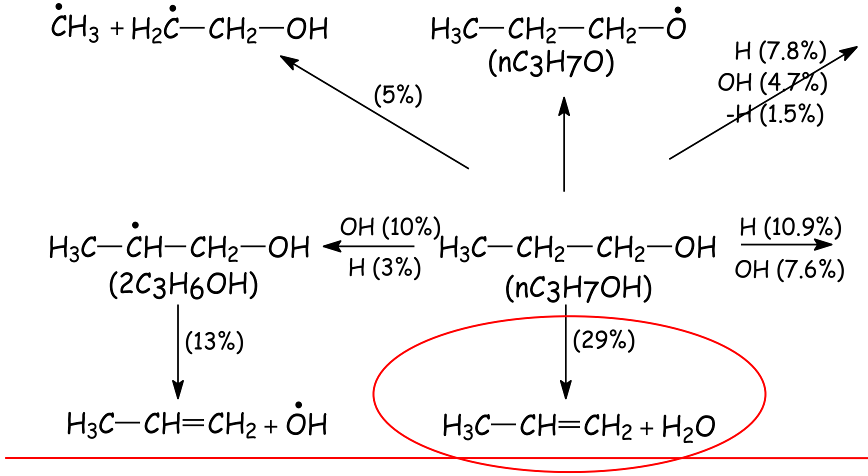
Propanol isomers – shock tube study
Comparison of reactivity of the isomers

0.5% fuel, 2.25% O_2, $\phi = 1.0$, P = 1 atm



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

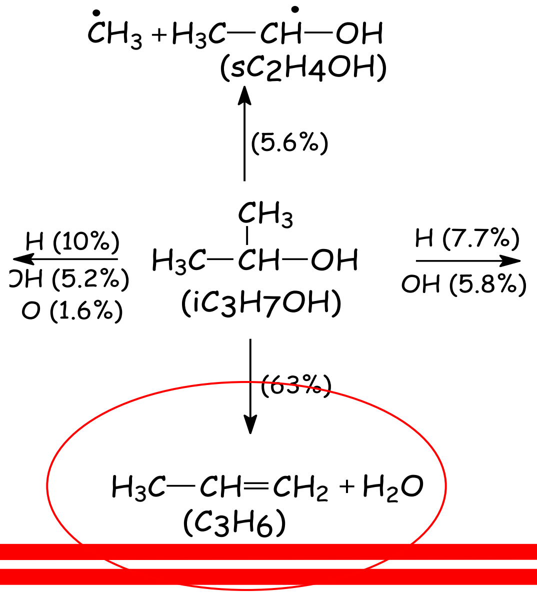
Water elimination is much more important for iso-propanol



0.5% *n*-propanol

$\phi = 1.0$, $T = 1600$ K

30% fuel consumed



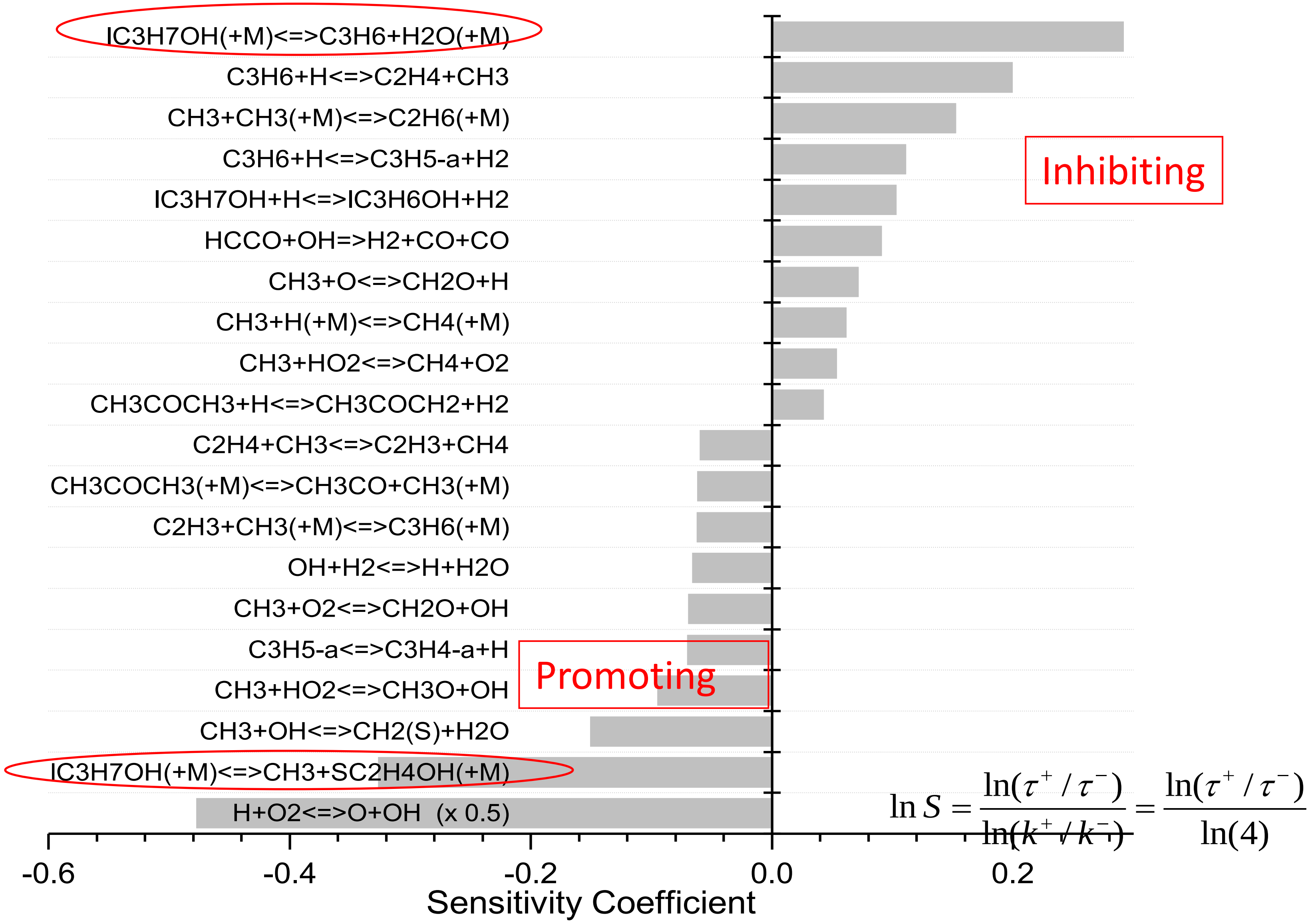
0.5% *iso*-propanol

$\phi = 1.0$, $T = 1600$ K

30% fuel consumed

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

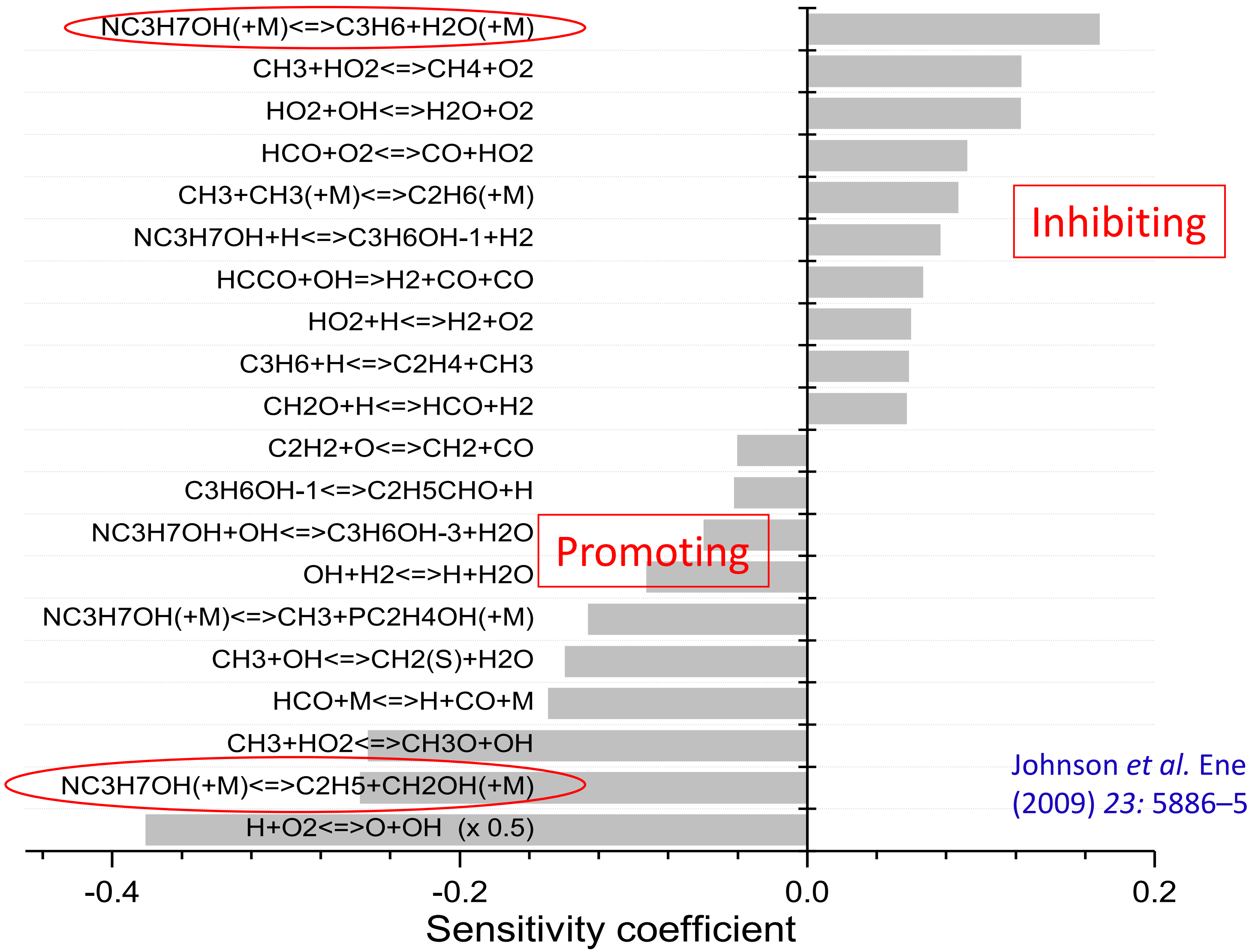
iso-propanol –Sensitivity analysis in ST



$$\ln S = \frac{\ln(\tau^+/\tau^-)}{\ln(k^+/k^-)} = \frac{\ln(\tau^+/\tau^-)}{\ln(4)}$$

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

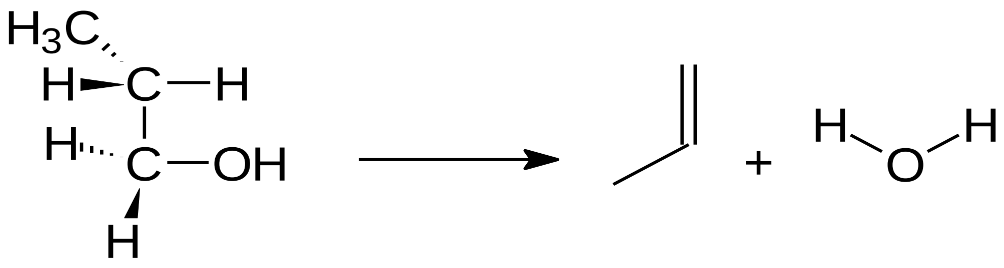
n-propanol –Sensitivity analysis in ST



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

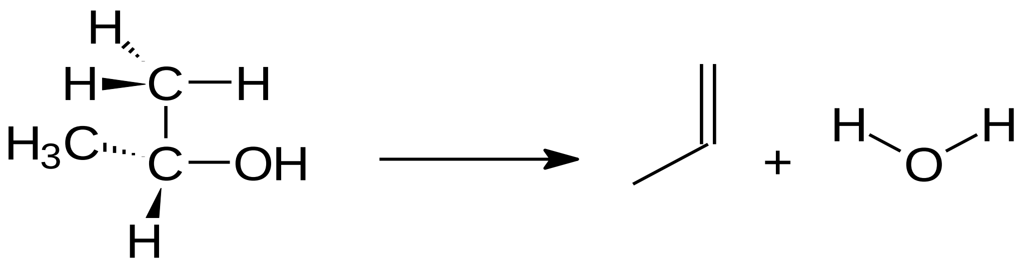
Johnson *et al.* Energy & Fuels (2009) *23:* 5886–5898.

Alcohol molecular elimination



n-propanol propene + water

k = 3.52 x 10^{13} exp(-67300/RT) s^{-1}



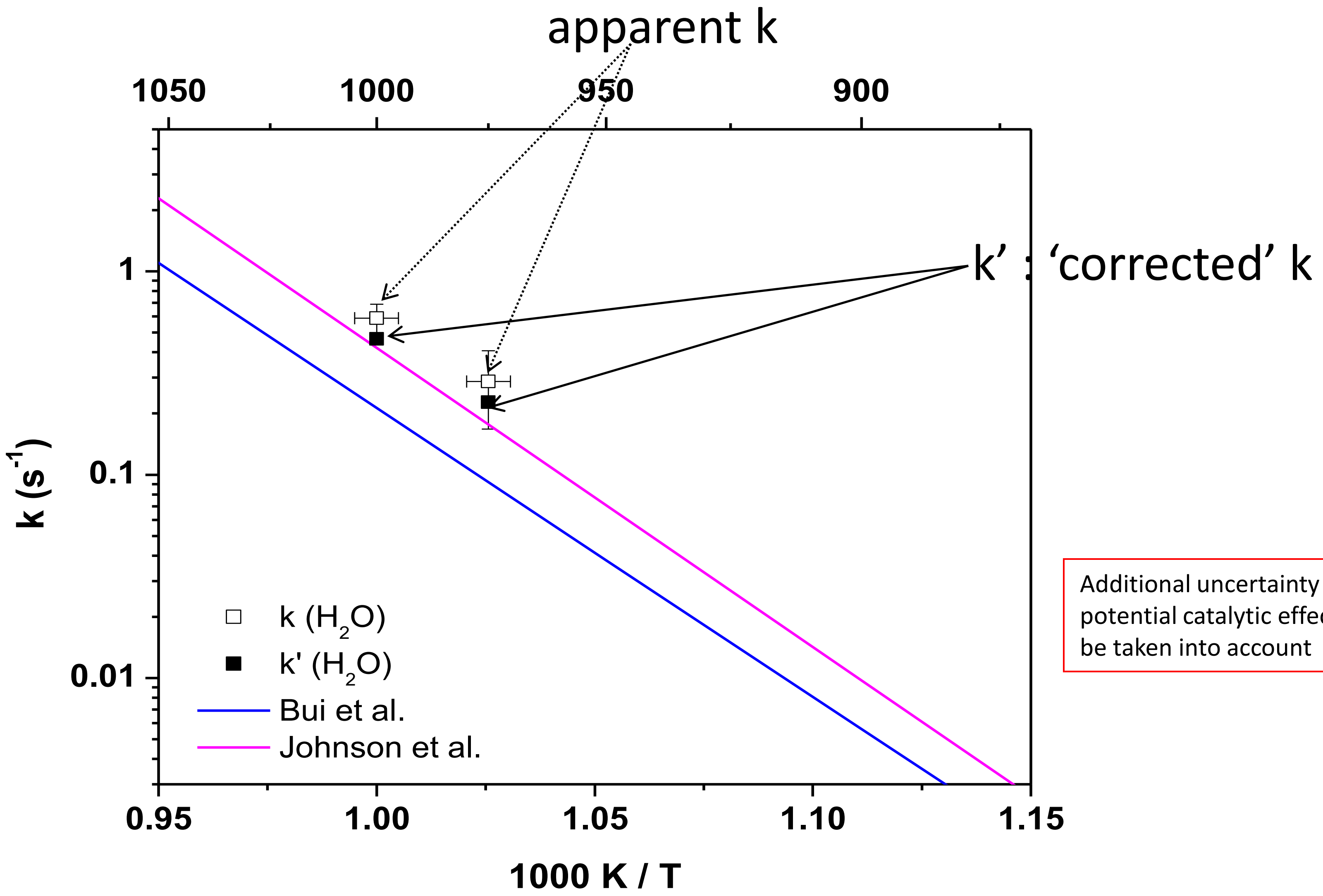
iso-propanol propene + water

k = 2.11 x 10^{14} exp(-67300/RT) s^{-1}

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

iso-propanol – Flow Reactor Study

Rate constant of molecular elimination

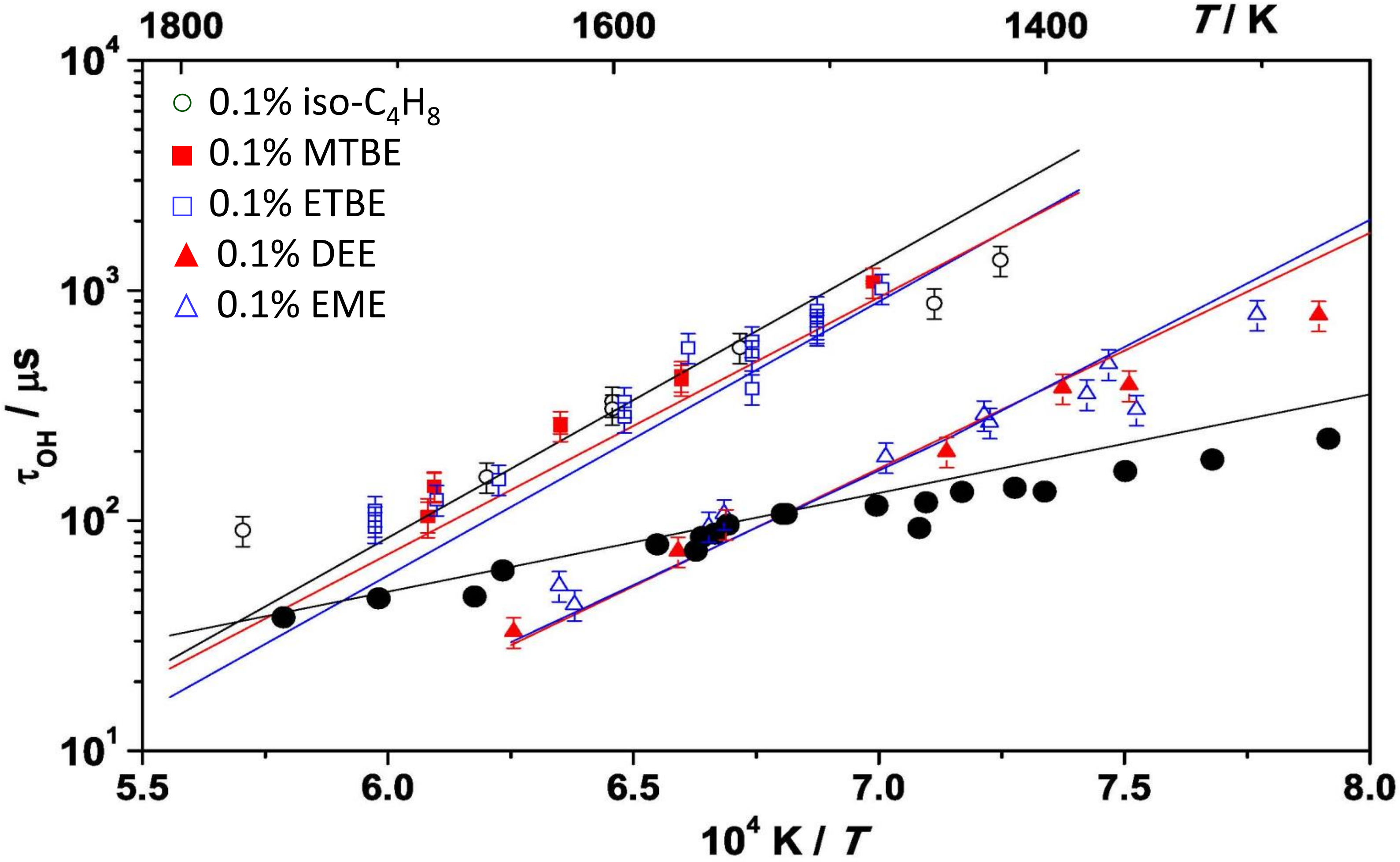


Additional uncertainty caused by potential catalytic effects; needs to be taken into account

J.S. Heyne et al. Zeitschrift Fur Physikalische Chemie–Intl. J. Research Phys. Chem. Chem. Phys. 229(6) (2015) 881–907.

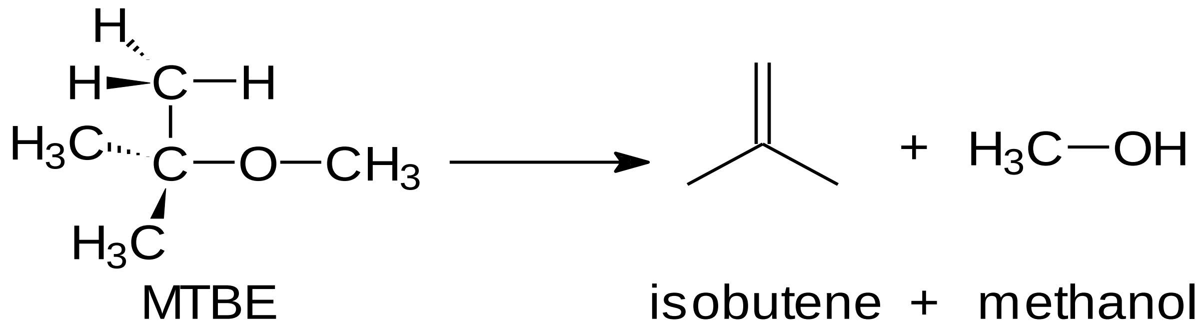
Reactivity of ethers

● 1% H_2, 1% O_2 in Ar, p_5 = 1.4–2.6 atm

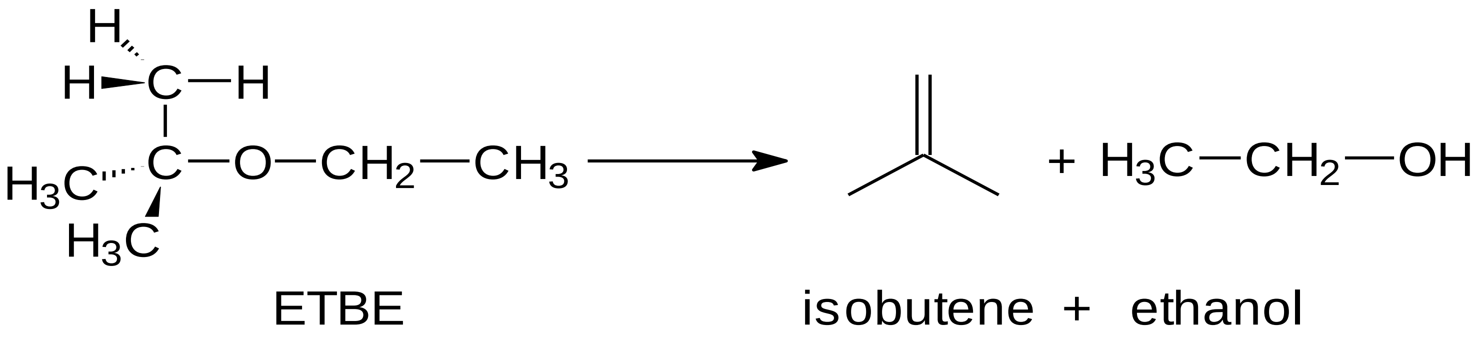


Yasunaga *et al.* Comb. Flame (2011) *158:* 1032–1036.

Ether molecular elimination



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

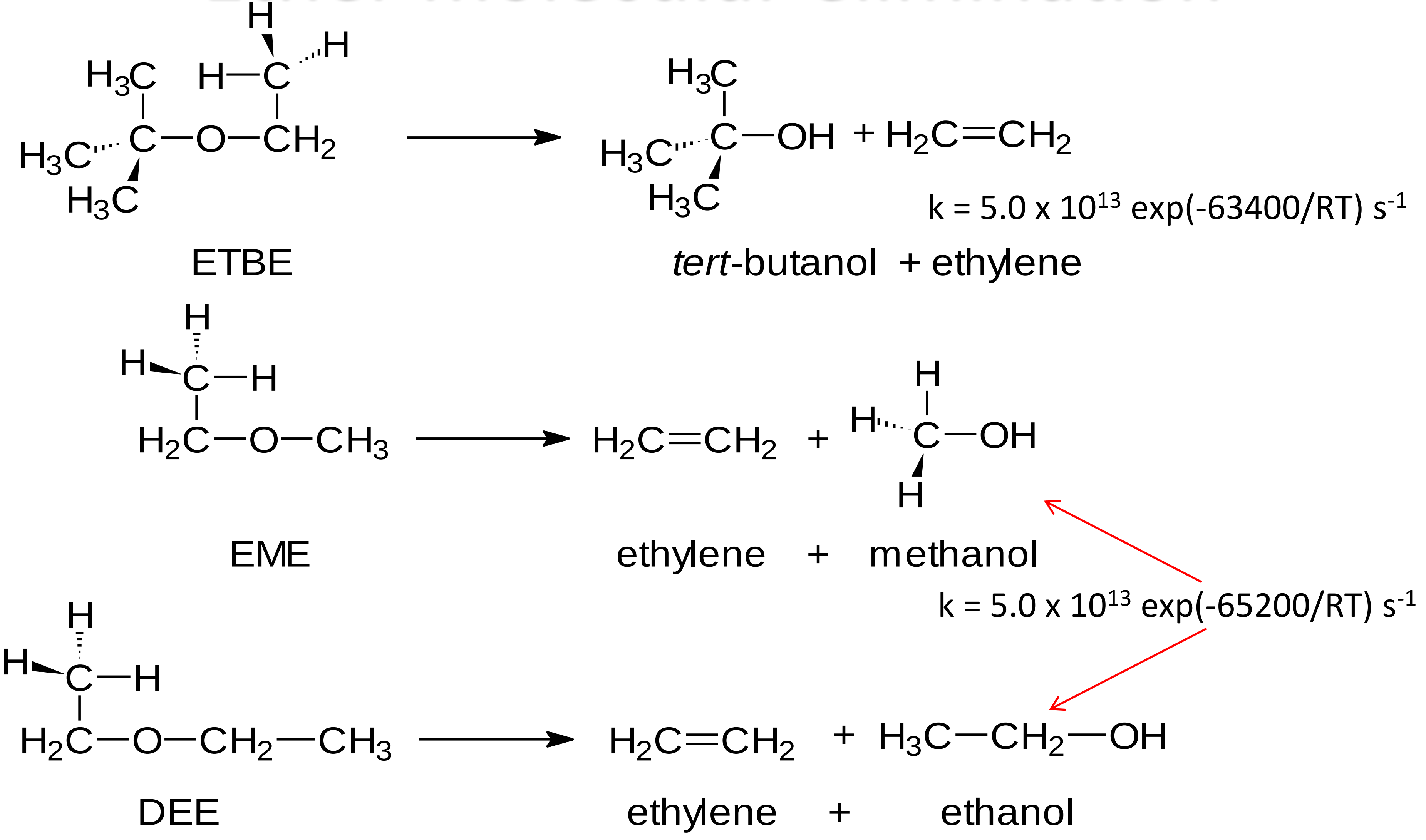


$k = 1.70 \times 10^{14} \exp(-60600/RT)\ s^{-1}$

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

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

Ether molecular elimination



ETBE → *tert*-butanol + ethylene

$k = 5.0 \times 10^{13} \exp(-63400/RT)\ s^{-1}$

EME → ethylene + methanol

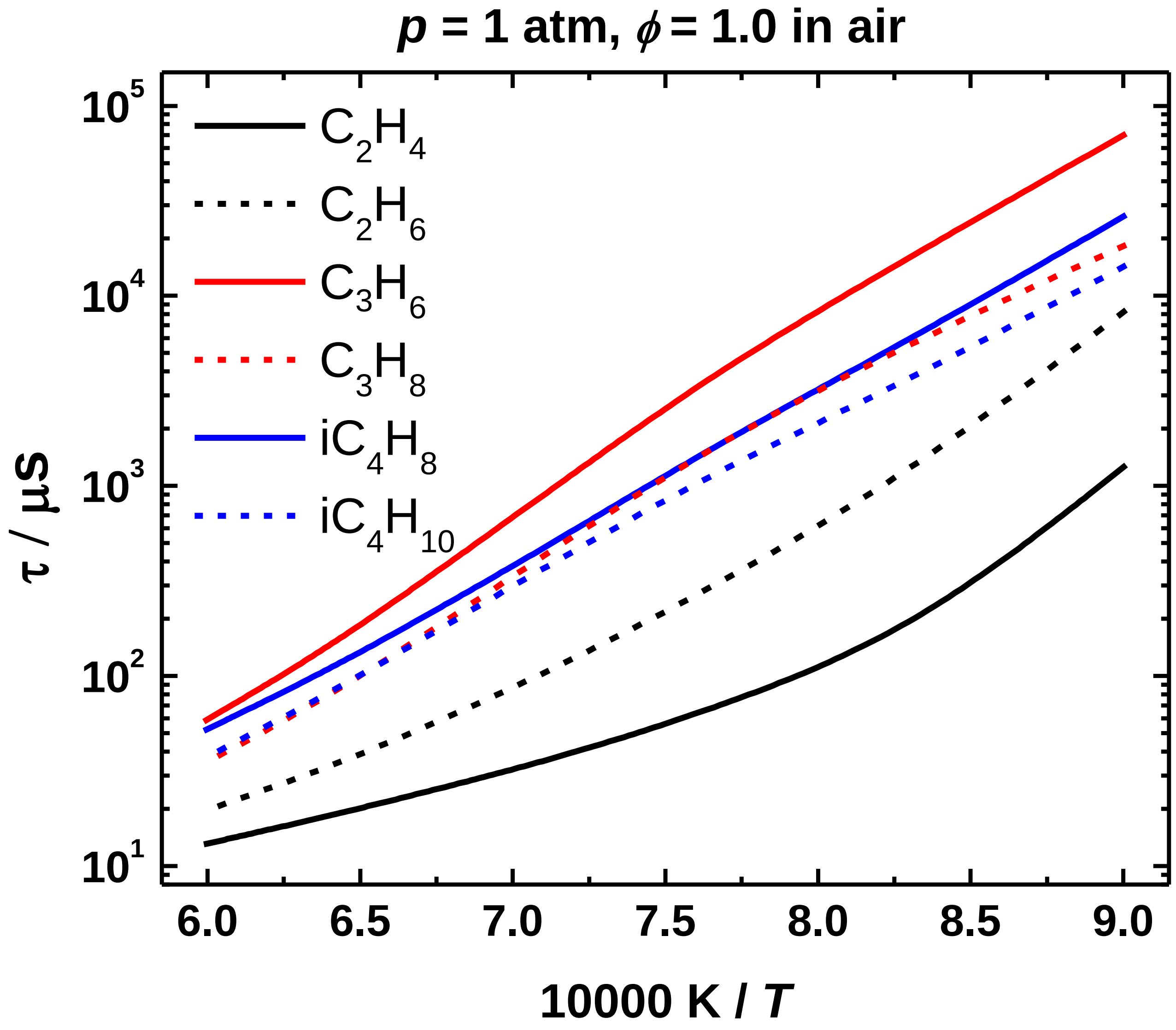
$k = 5.0 \times 10^{13} \exp(-65200/RT)\ s^{-1}$

DEE → ethylene + ethanol

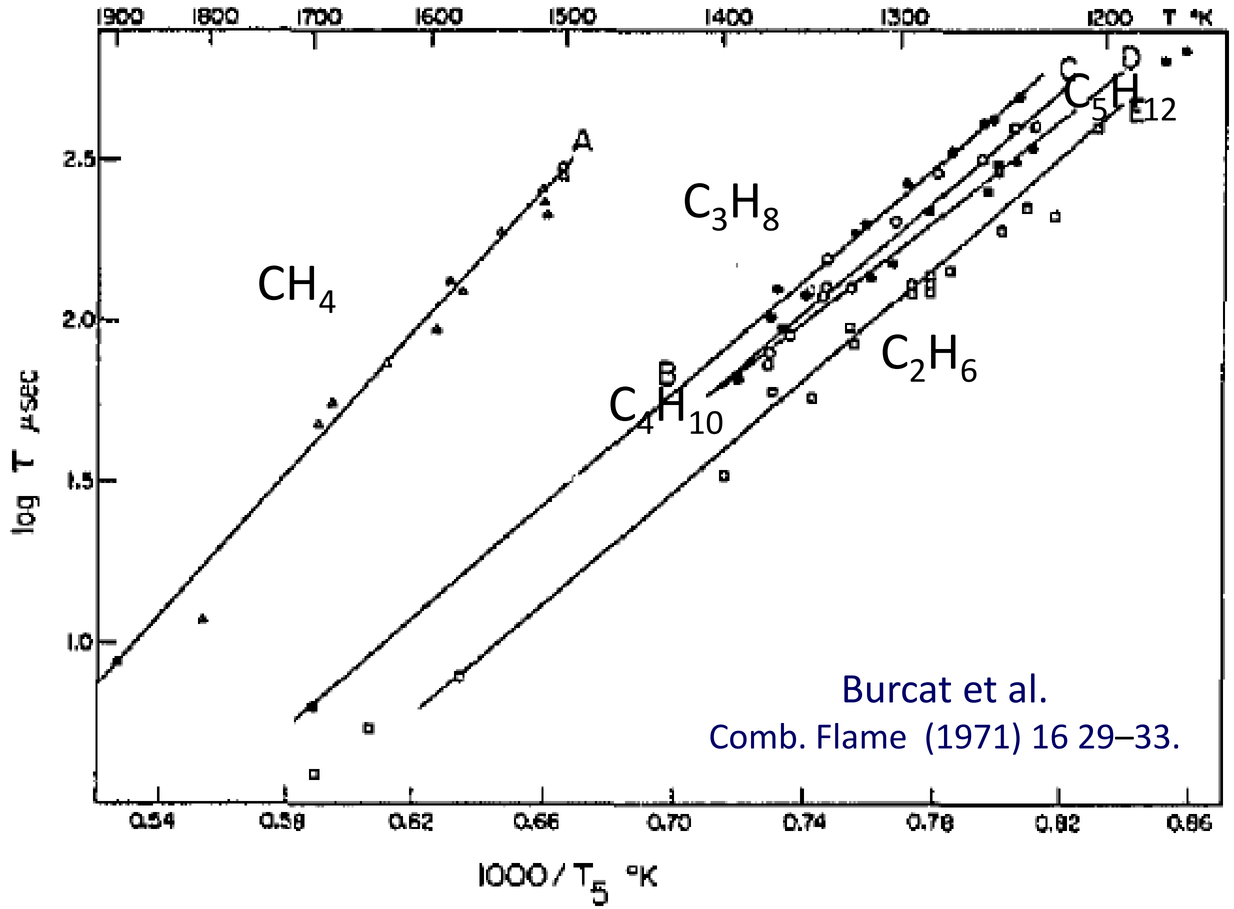
MP4/cc-pVTZ//MP2/cc-pVTZ level of theory with zero point corrections

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

Ethylene is very fast to ignite



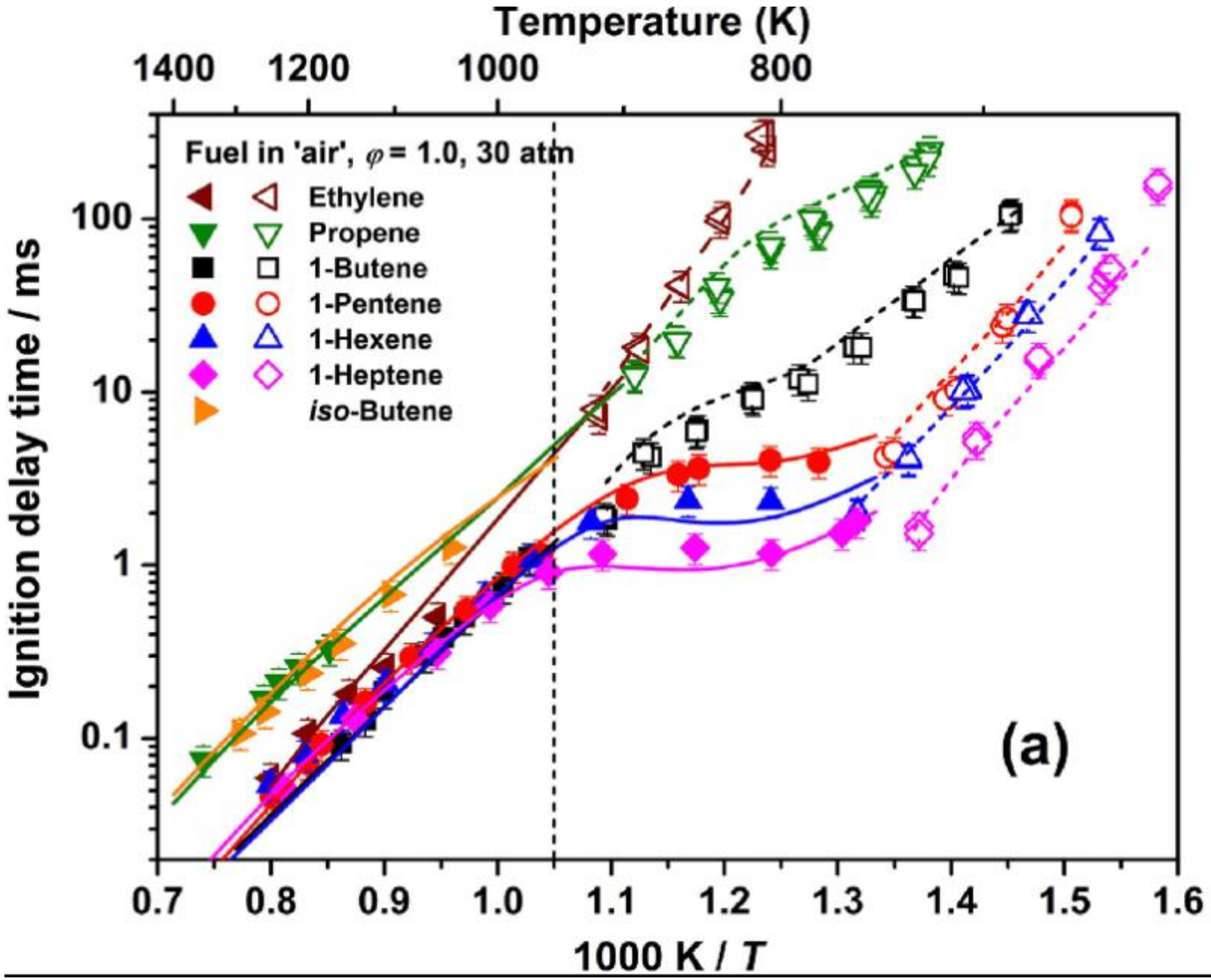
Relative reactivity of fuels



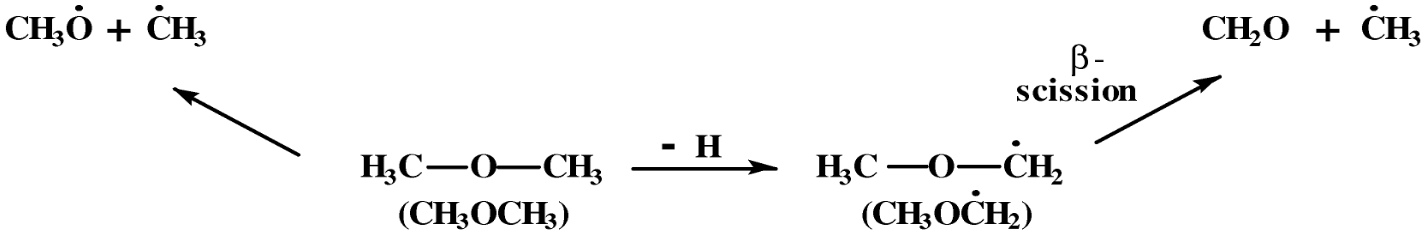
Burcat et al.
Comb. Flame (1971) 16 29–33.

Figure 1. A plot of log τ 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.

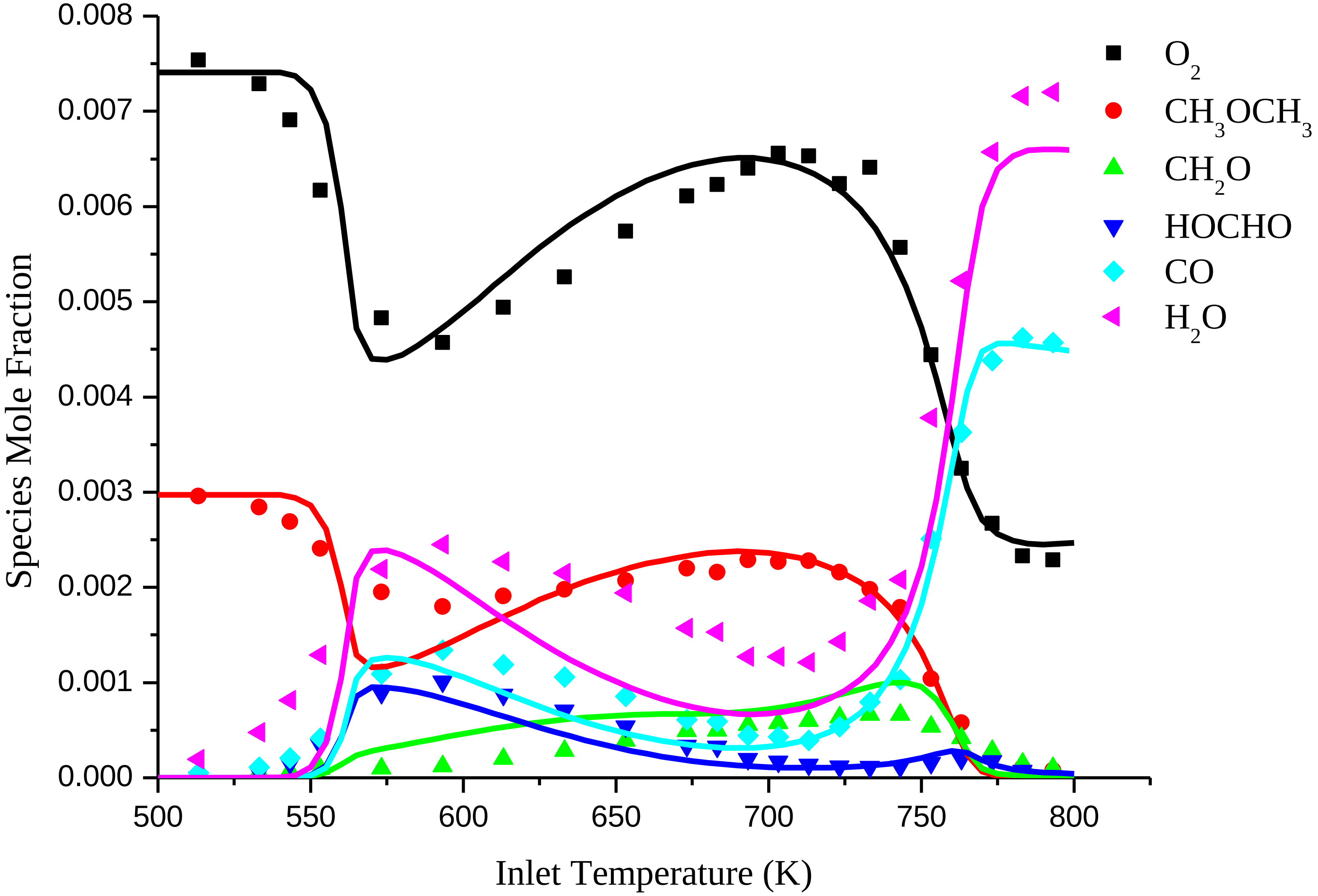
Comparison of alkene reactivity at high *p*



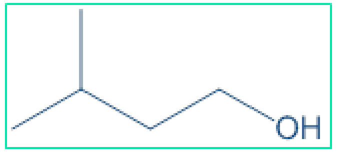
Dong *et al.* Proc. Combust. Inst. 38 (2021) 611–619.


$CH_3\dot{O} + \dot{C}H_3$
$H_3C—O—CH_3$
(CH_3OCH_3)
- H
$H_3C—O—\dot{C}H_2$
$(CH_3O\dot{C}H_2)$
β-
scission
$CH_2O + \dot{C}H_3$

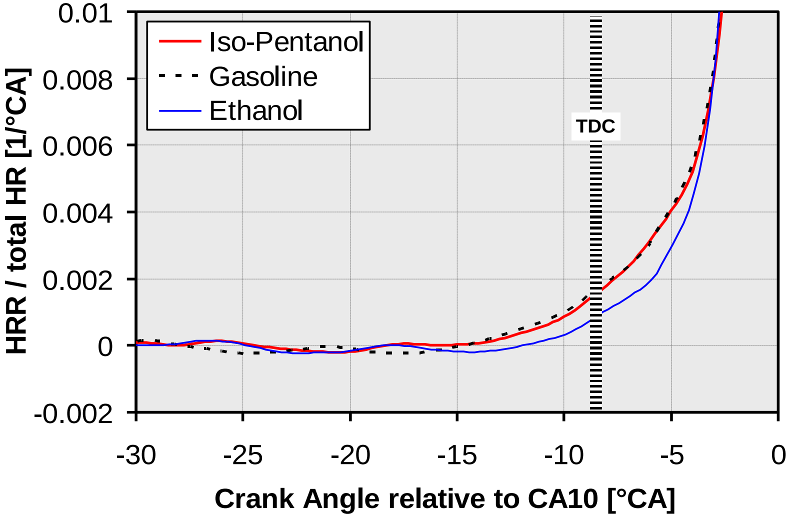
3030 ppm DME, ϕ = 1.19, *p* = 12.5 atm, τ = 1.8 s.



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)



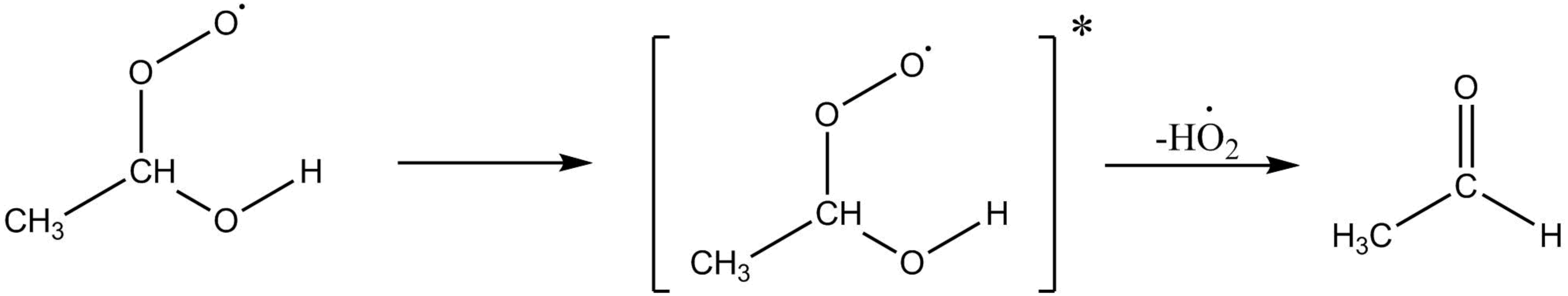
Isopentanol shows ITHR similar to gasoline

- 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*

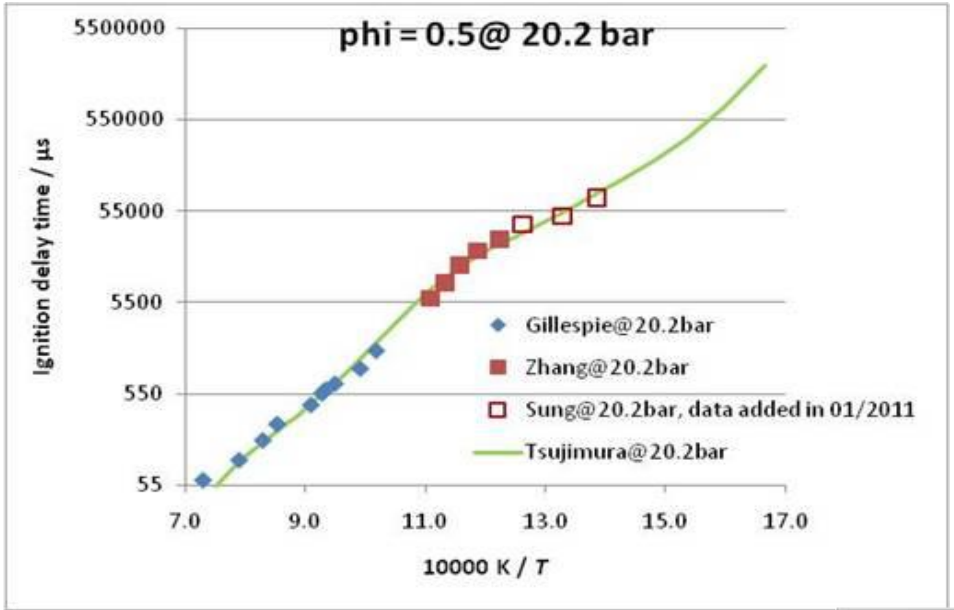
Alcohols are less reactive than their corresponding alkane

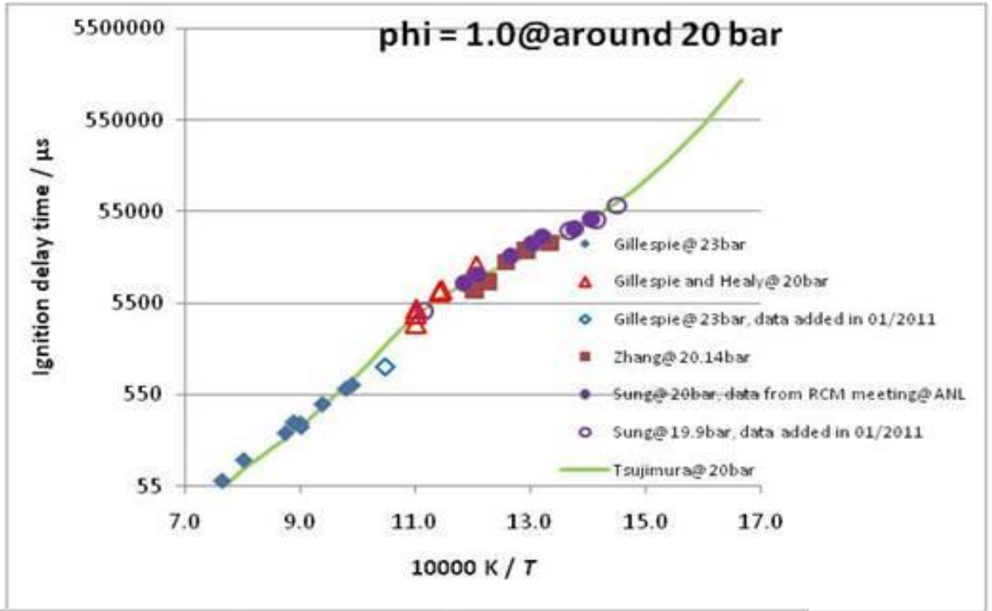
- ☐ Isopentanol (RON = 113) slower to ignite compared to *iso*-pentane (RON = 92.3)
- ☐ Carbon alpha to –OH alcohol functional group is weakest
- ☐ Da Silva et al.[1] showed concerted elimination reaction Ea = 11.4 kcal mol^{-1}



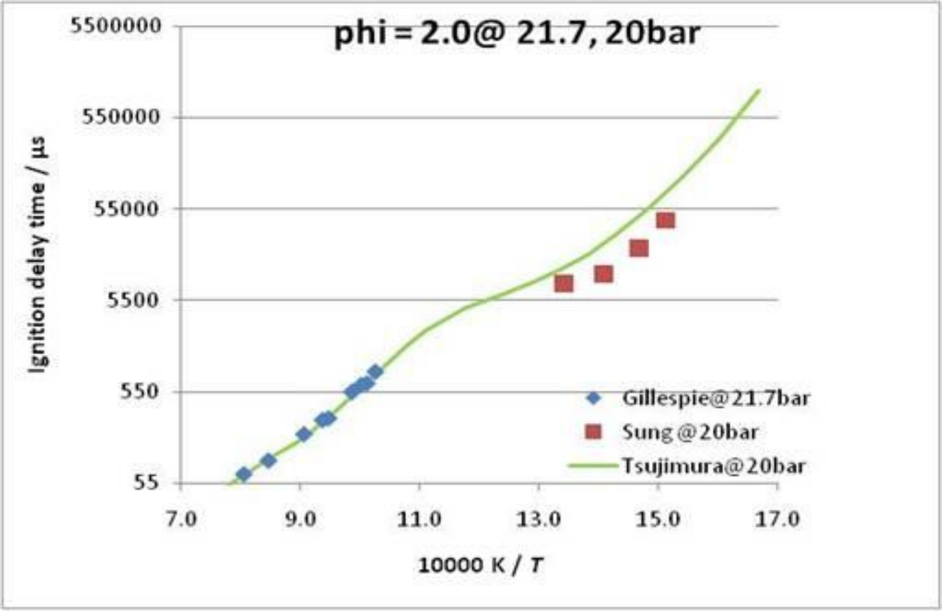
[1] **G. da Silva, J.W. Bozzelli, L. Liang, J.T. Farrell,** J. Phys. Chem. A 113 (2009) 8923–8933.

Isopentanol Oxidation

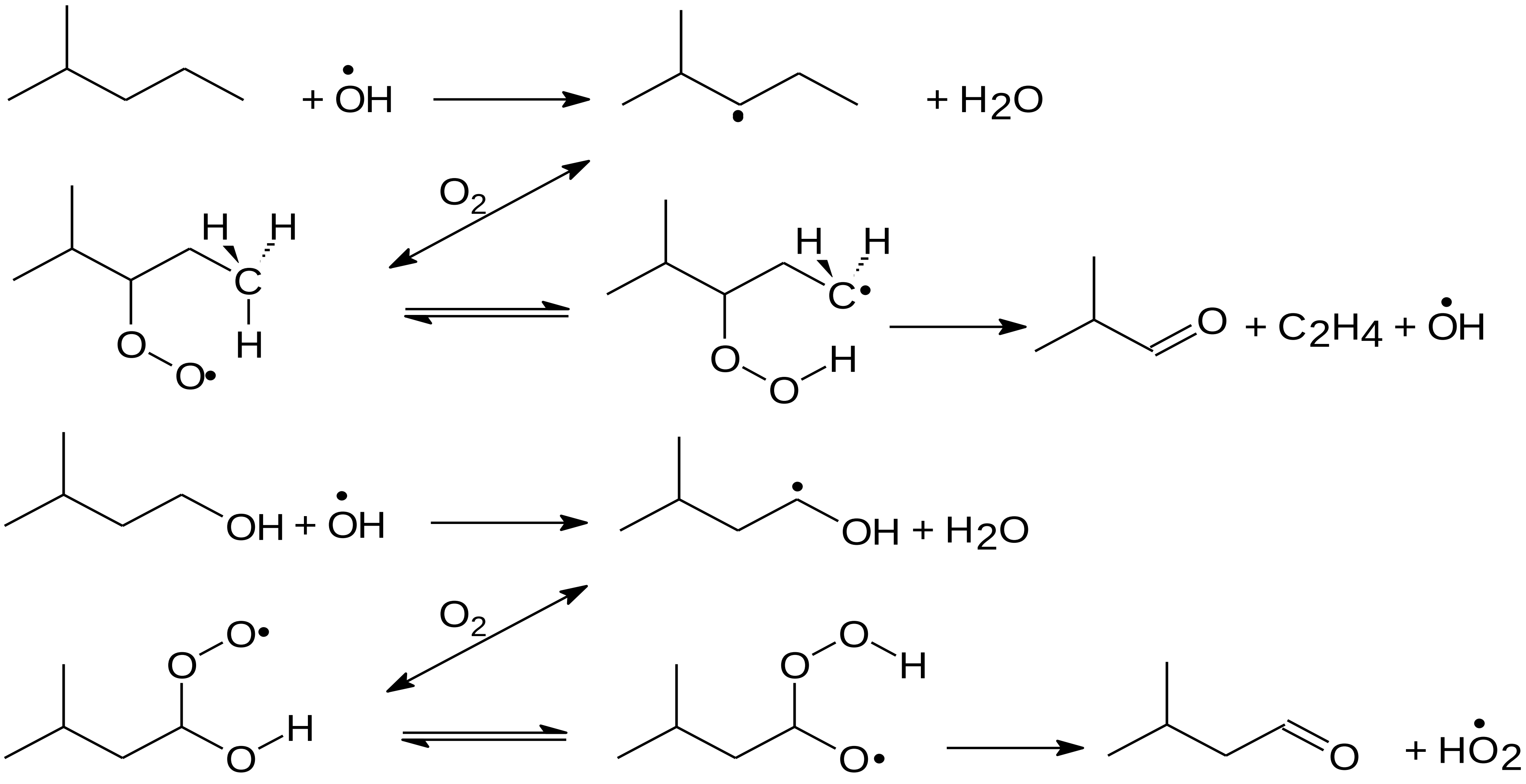




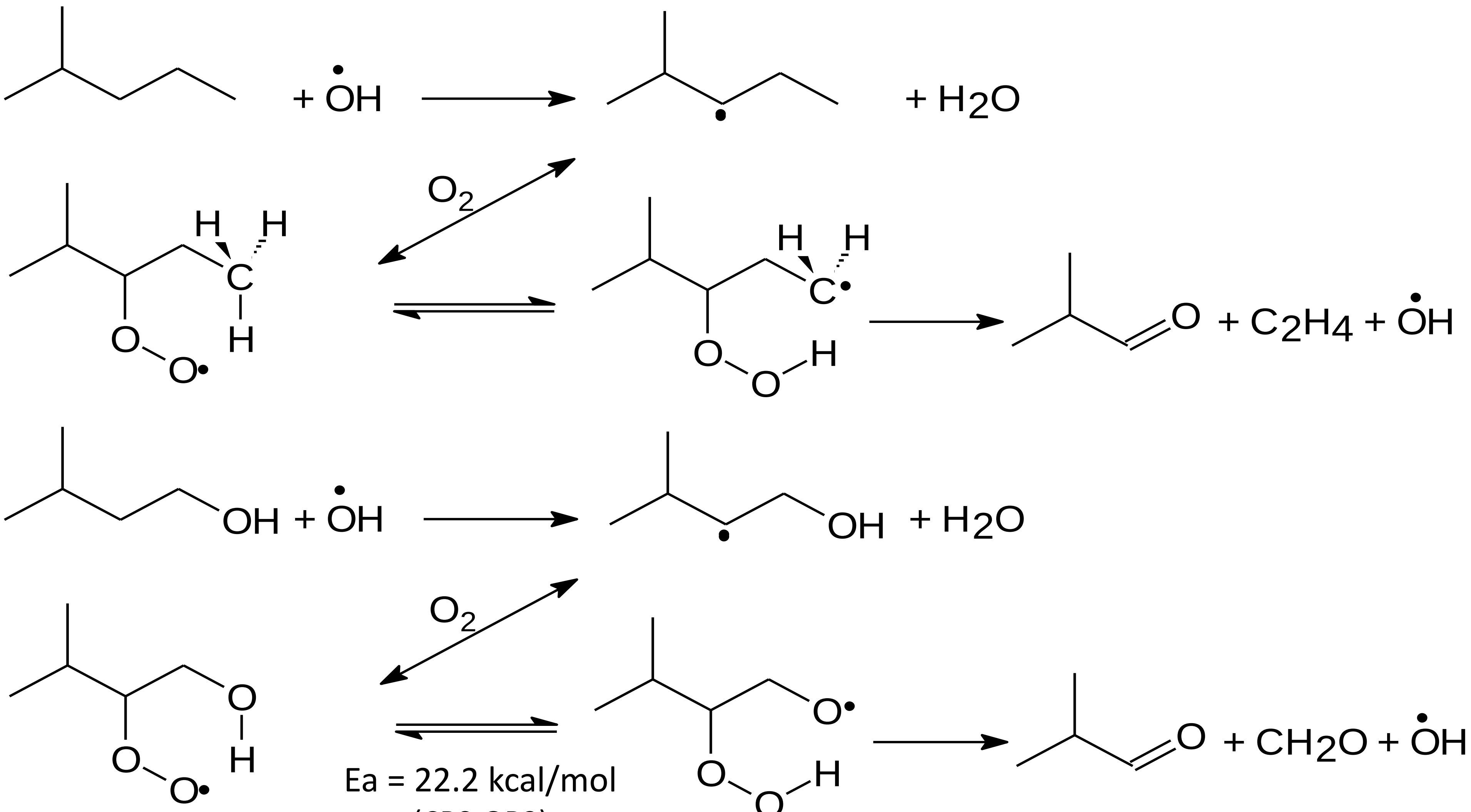
T. Tsujimura, W.J. Pitz, F. Gillespie, H.J. Curran, B.W. Weber, Y. Zhang, C-J. Sung, “Development of *iso*-Pentanol Reaction Mechanism Reproducing Autoignition Character at High and Low Temperatures”, Energy Fuels (2012) 26(8) 4871–4886.



Isopentanol Oxidation

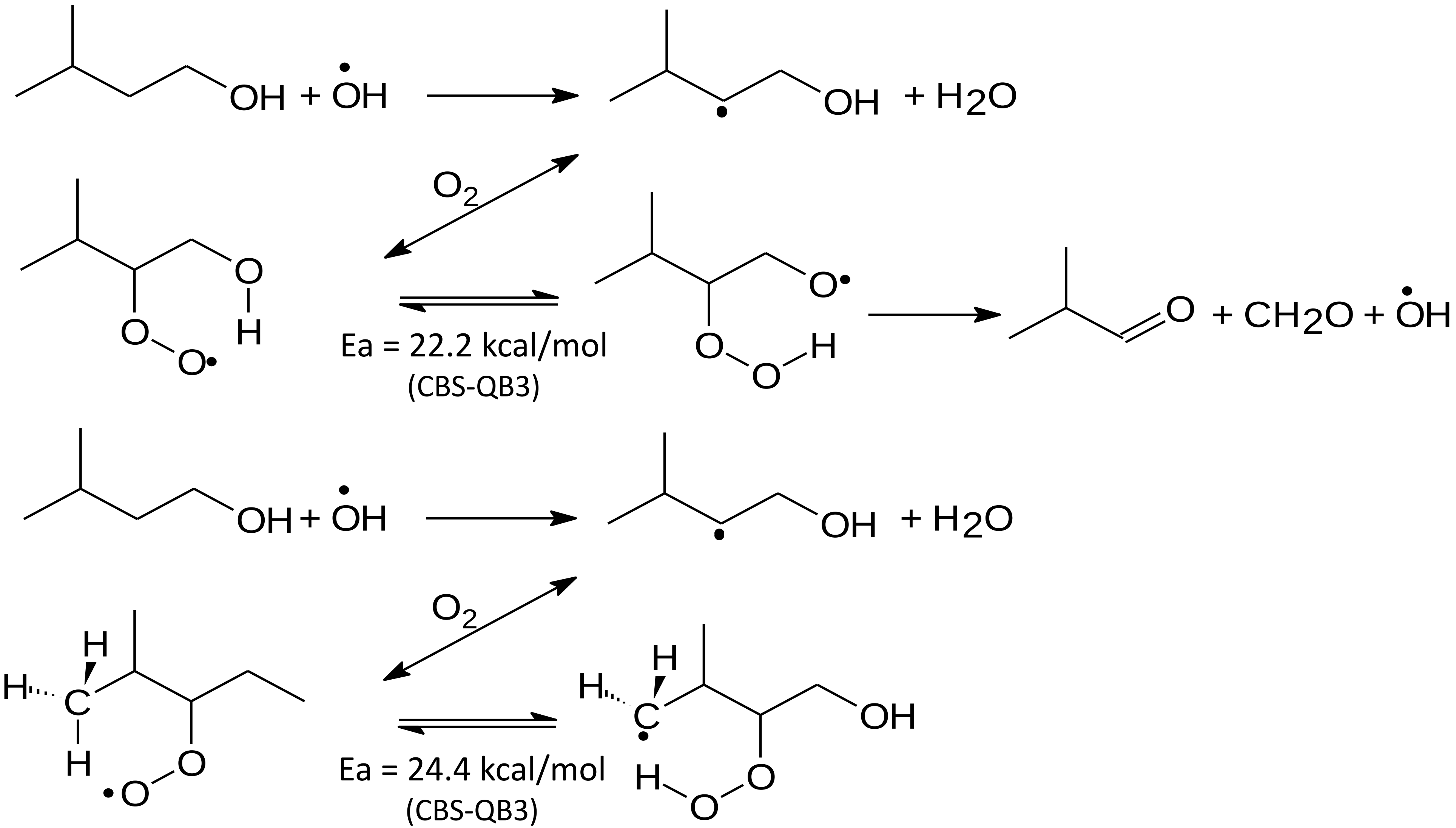


Isopentanol Oxidation



Ea = 22.2 kcal/mol
(CBS-QB3)

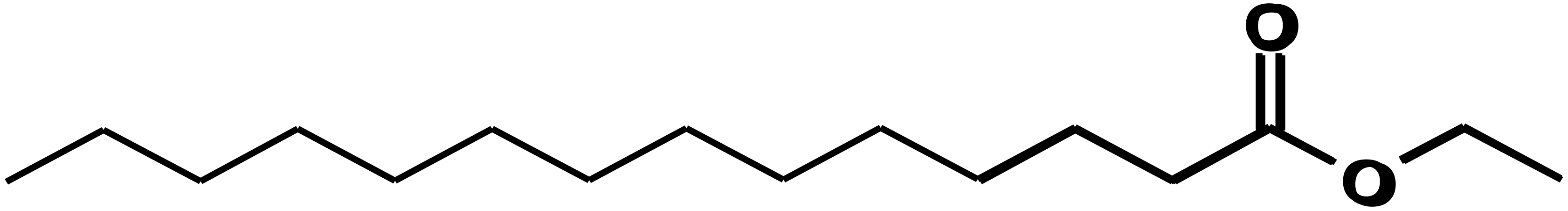
Isopentanol Oxidation



Ea = 22.2 kcal/mol
(CBS-QB3)

Ea = 24.4 kcal/mol
(CBS-QB3)

Combustion of Model Biodiesels

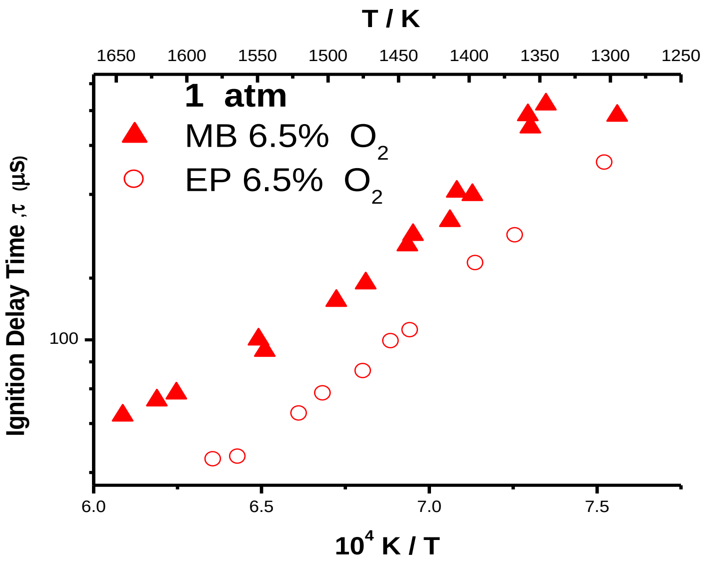


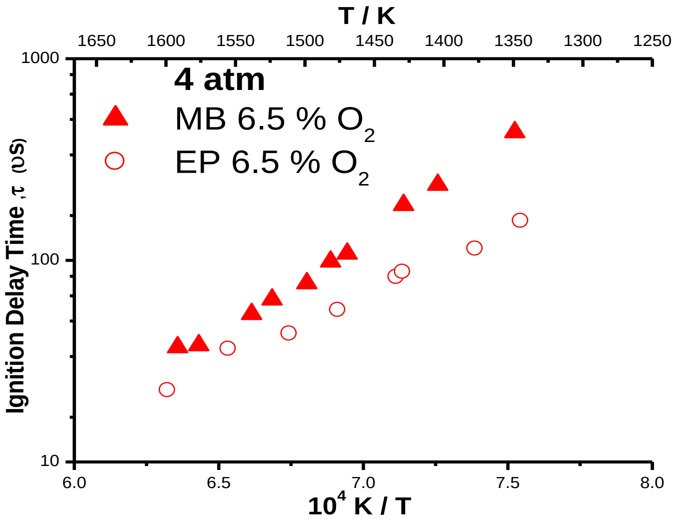
Ethyl tetradecanoate

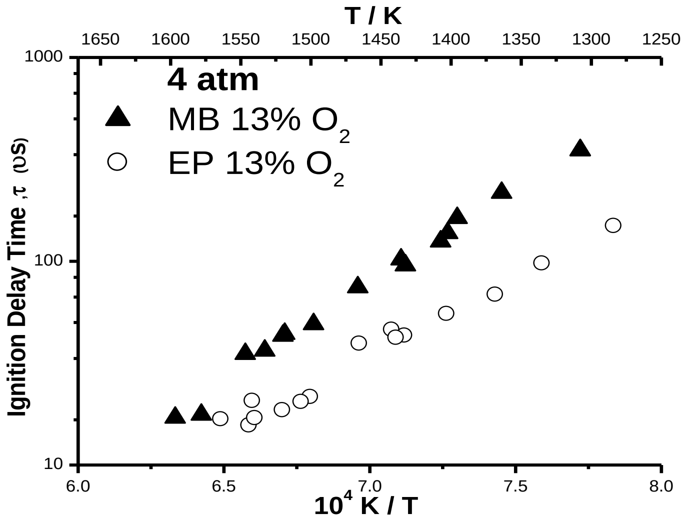
$C_5H_{10}O_2$

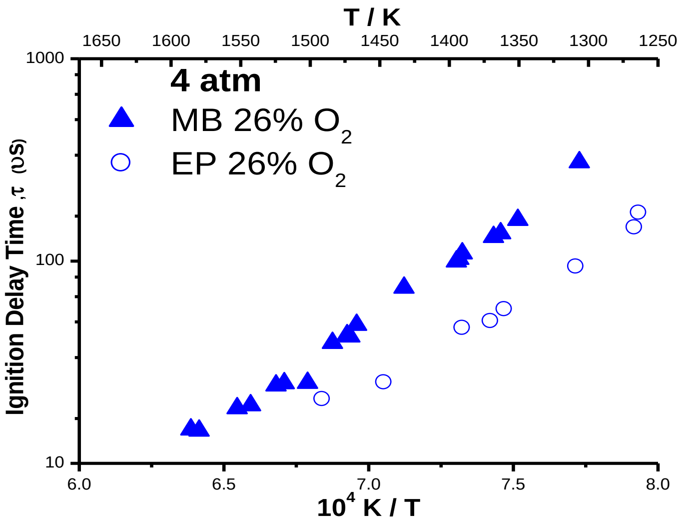
methyl butanoate (MB) **ethyl propanoate (EP)**

Comparison – MB vs EP





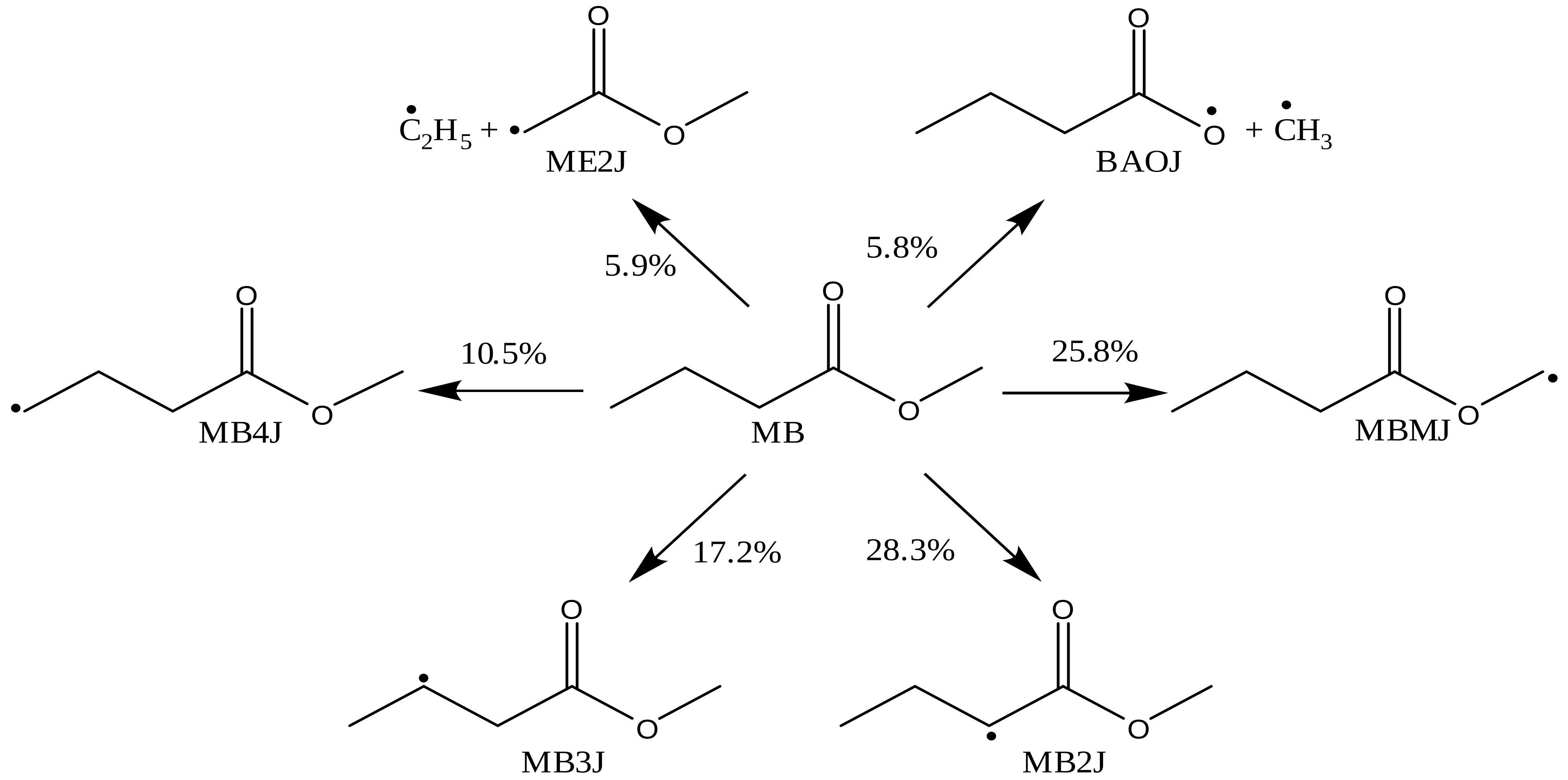




Dooley *et al.* Comb. Flame (2008) *153:* 2–32.
Metcalfe *et al.* Comb. Flame (2009) *159:* 250–260.

MB Consumption

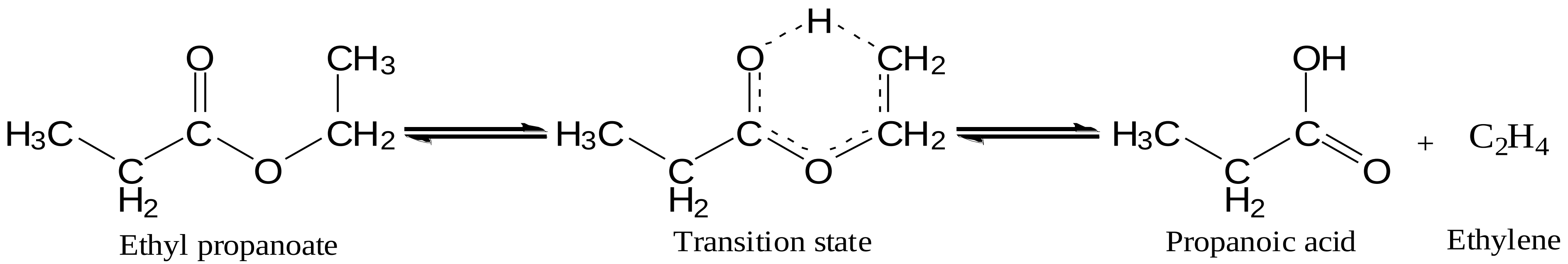
1.0 % MB 6.5% O_2 1600 K , 1 atm ⇒ 50 % MB consumed



Dooley *et al.* Comb. Flame (2008) *153:* 2–32.
Metcalfe *et al.* Comb. Flame (2009) *159:* 250–260.

EP decomposition

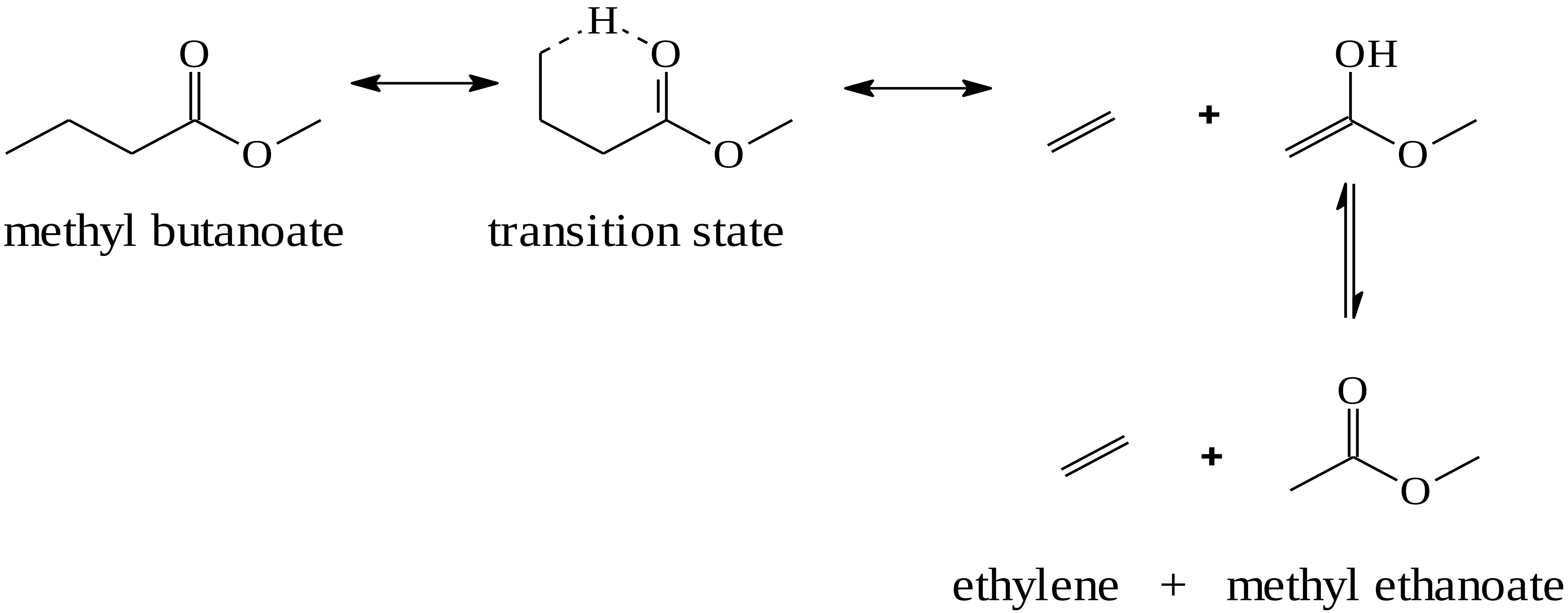
1.0 % EP 6.5% O_2 1600 K , 1 atm ⇒ 50 % EP consumed



$$k = 1.60 \times 10^{13} \exp(-50000/RT)\ s^{-1}$$

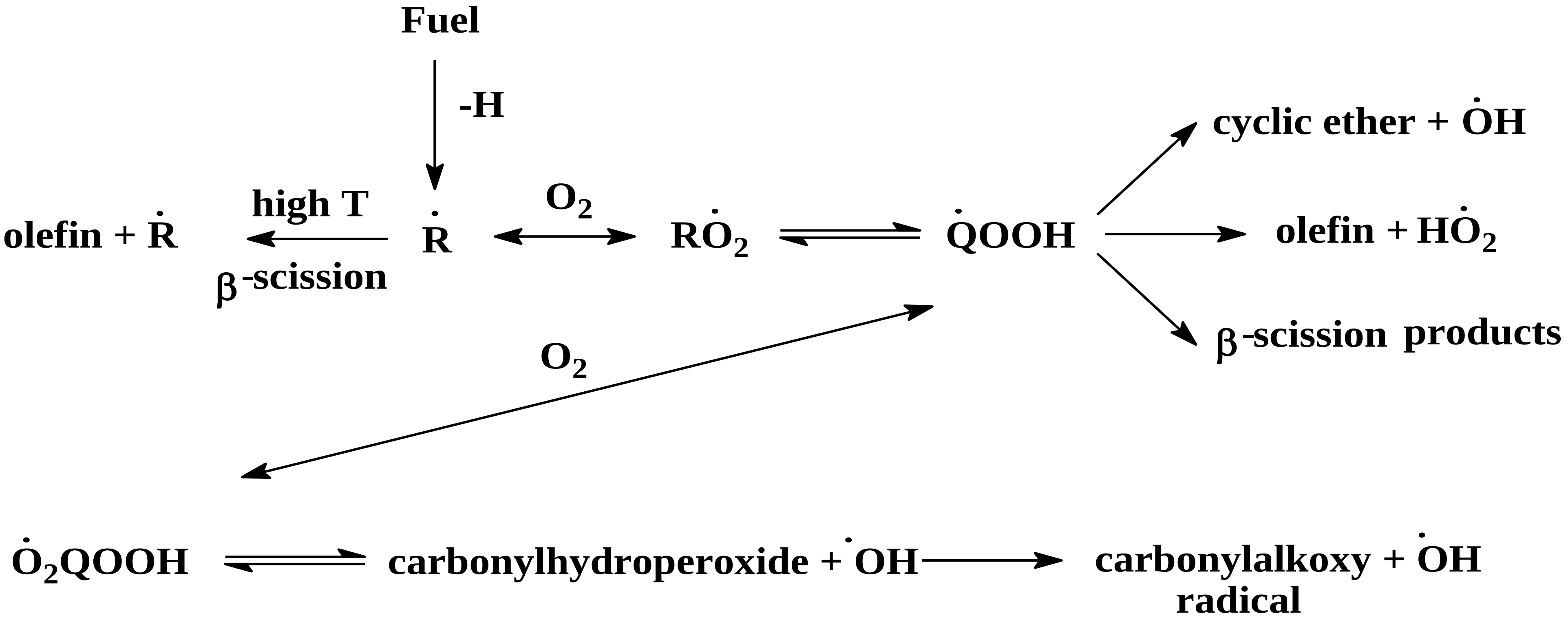
Dooley *et al.* Comb. Flame (2008) *153:* 2–32.
Metcalfe *et al.* Comb. Flame (2009) *159:* 250–260.

MB decomposition



Dooley *et al.* Comb. Flame (2008) *153:* 2–32.
Metcalfe *et al.* Comb. Flame (2009) *159:* 250–260.

Low Temperature Reaction Scheme



$$\text{Fuel} \xrightarrow{-\text{H}} \dot{\text{R}}$$

$$\dot{\text{R}} \xrightarrow[\beta\text{-scission}]{\text{high T}} \text{olefin} + \dot{\text{R}}$$

$$\dot{\text{R}} \xleftrightarrow{\text{O}_2} \text{R}\dot{\text{O}}_2 \rightleftharpoons \dot{\text{Q}}\text{OOH}$$

$$\dot{\text{Q}}\text{OOH} \rightarrow \text{cyclic ether} + \dot{\text{O}}\text{H}$$

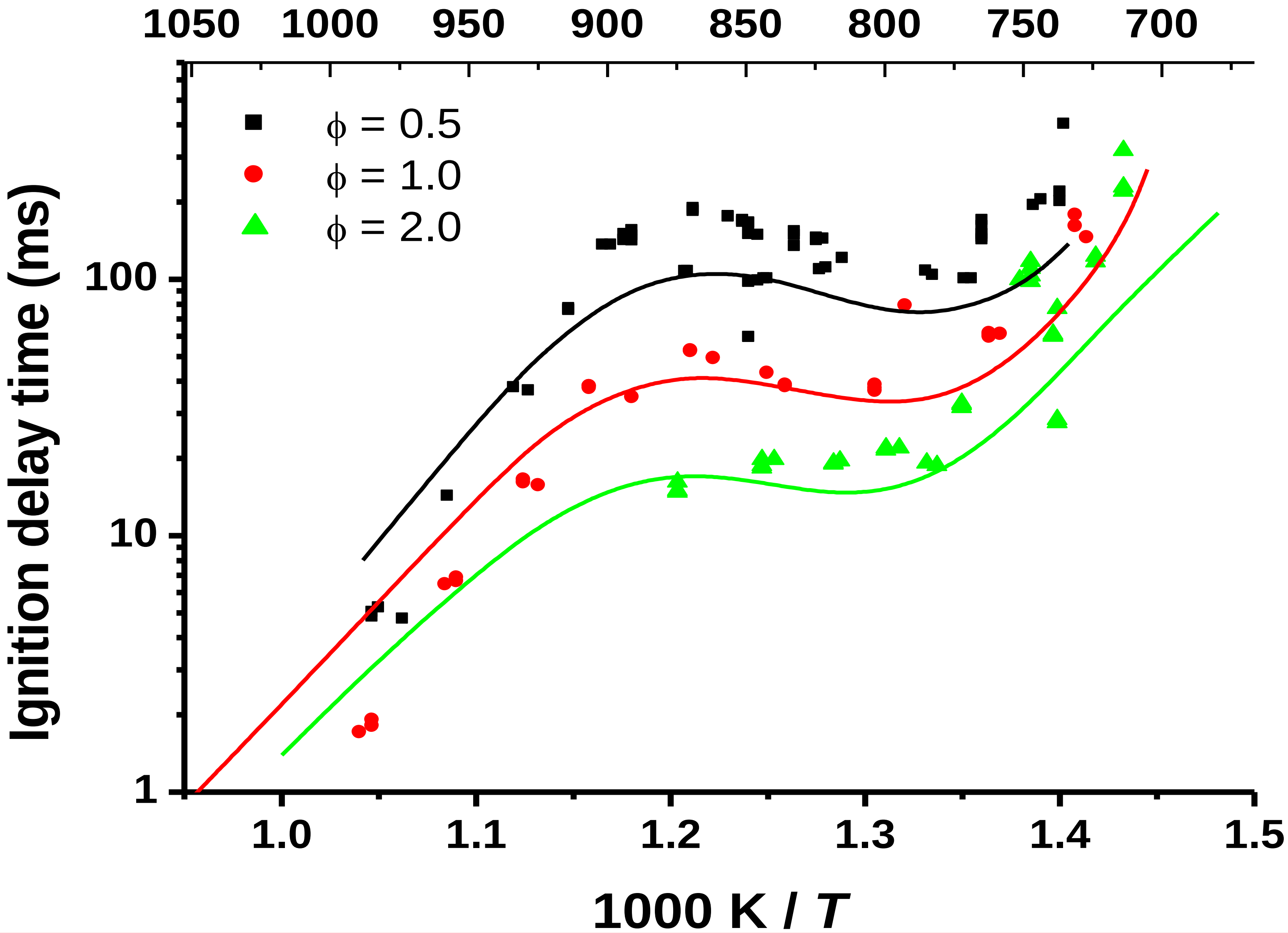
$$\dot{\text{Q}}\text{OOH} \rightarrow \text{olefin} + \text{H}\dot{\text{O}}_2$$

$$\dot{\text{Q}}\text{OOH} \rightarrow \beta\text{-scission products}$$

$$\dot{\text{Q}}\text{OOH} \xleftrightarrow{\text{O}_2} \dot{\text{O}}_2\text{QOOH}$$

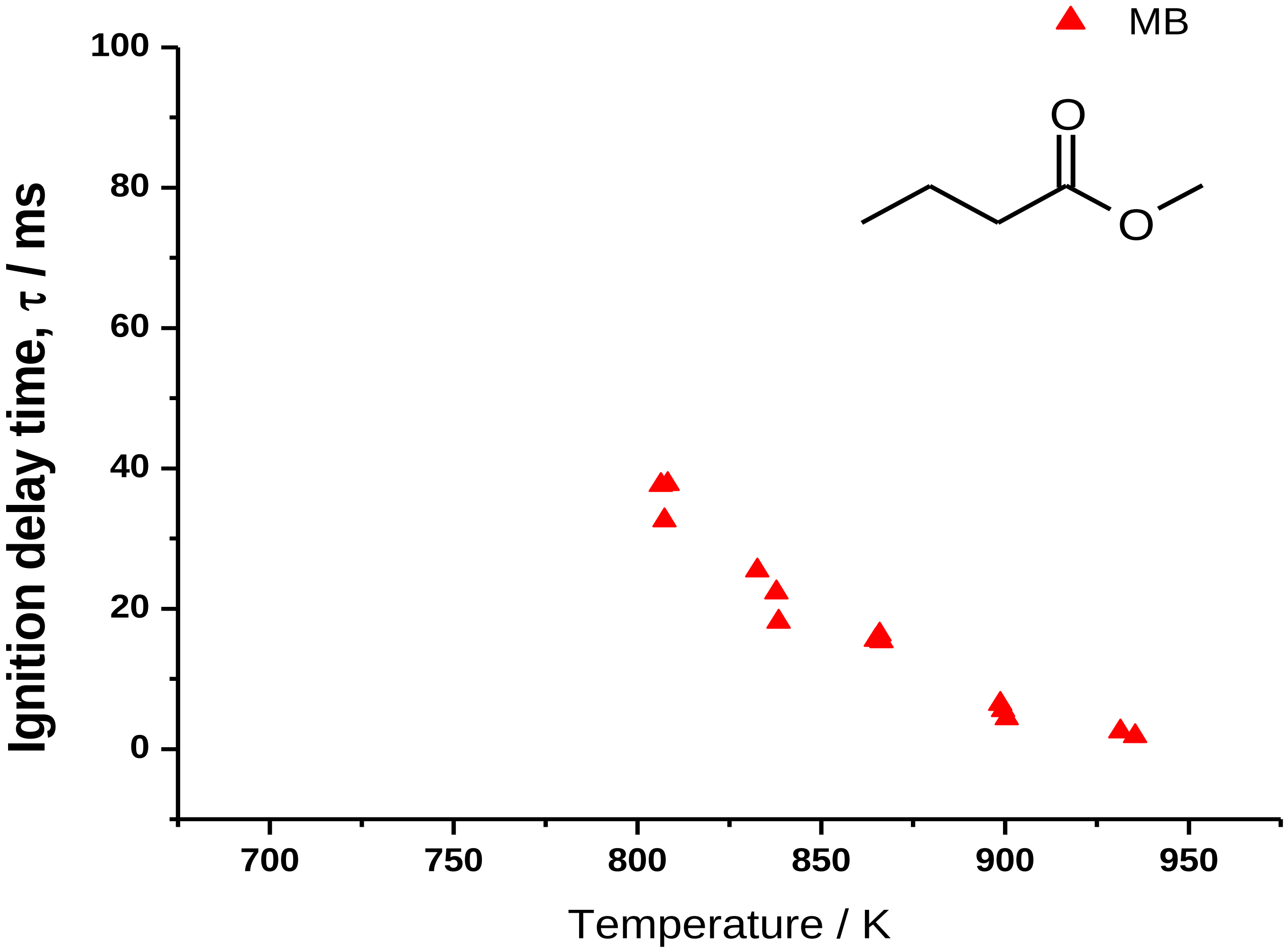
$$\dot{\text{O}}_2\text{QOOH} \rightleftharpoons \text{carbonylhydroperoxide} + \dot{\text{O}}\text{H} \longrightarrow \text{carbonylalkoxy radical} + \dot{\text{O}}\text{H}$$

C_3H_8 in "air", P_C = 30 atm



MB versus *n*-butane

RCM, Fuel/O_2/Diluent : 0.0313/0.2034/0.7653, ϕ = 1.0 at 10 atm



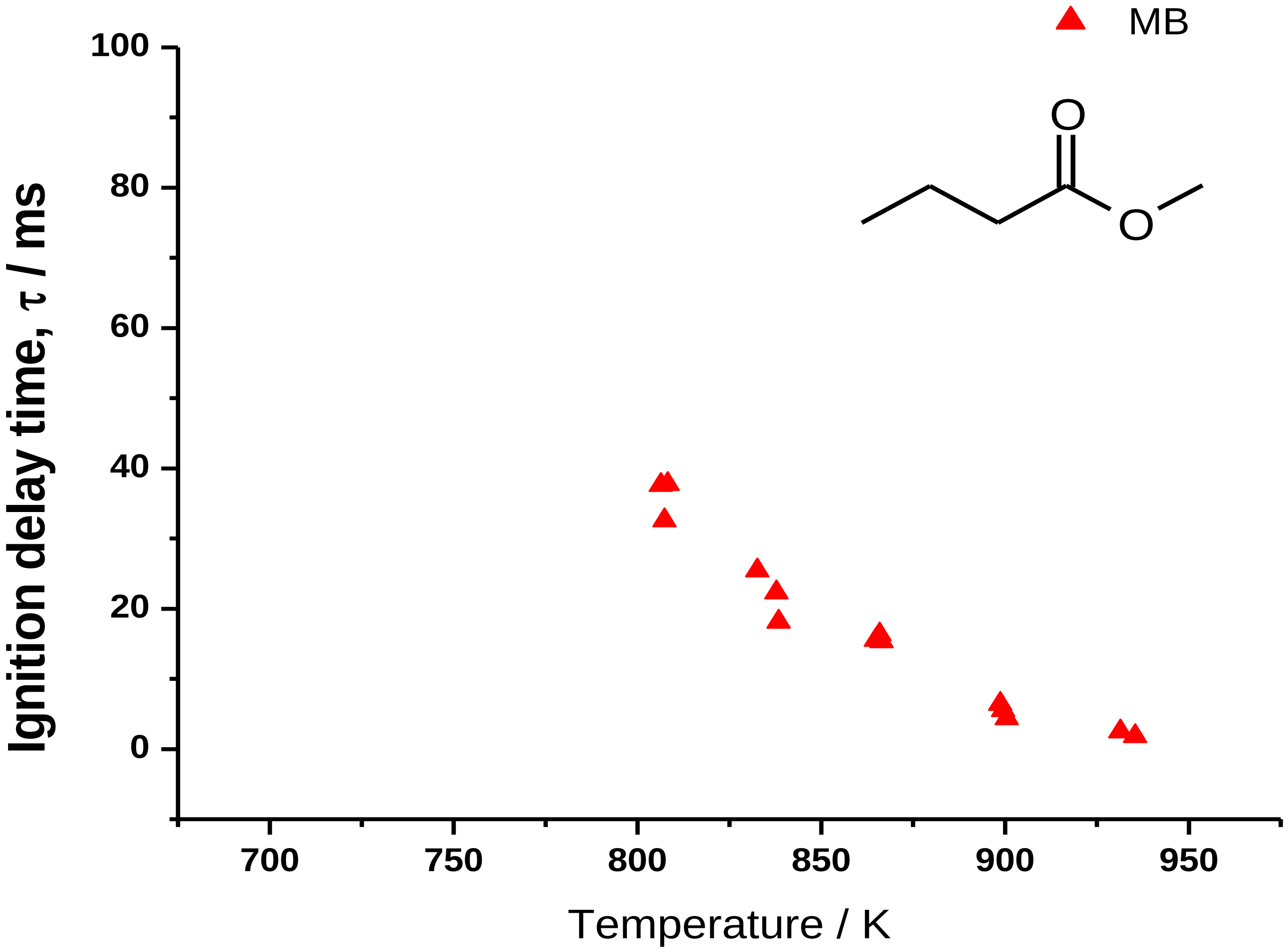
- No NTC behaviour observed for MB
- Compare to n-Butane as ϕ is common

$$C_5H_{10}O_2 + 6\tfrac{1}{2}\ O_2 \Leftrightarrow 5CO_2 + 5H_2O$$

$$nC_4H_{10} + 6\tfrac{1}{2}\ O_2 \Leftrightarrow 4CO_2 + 5H_2O$$

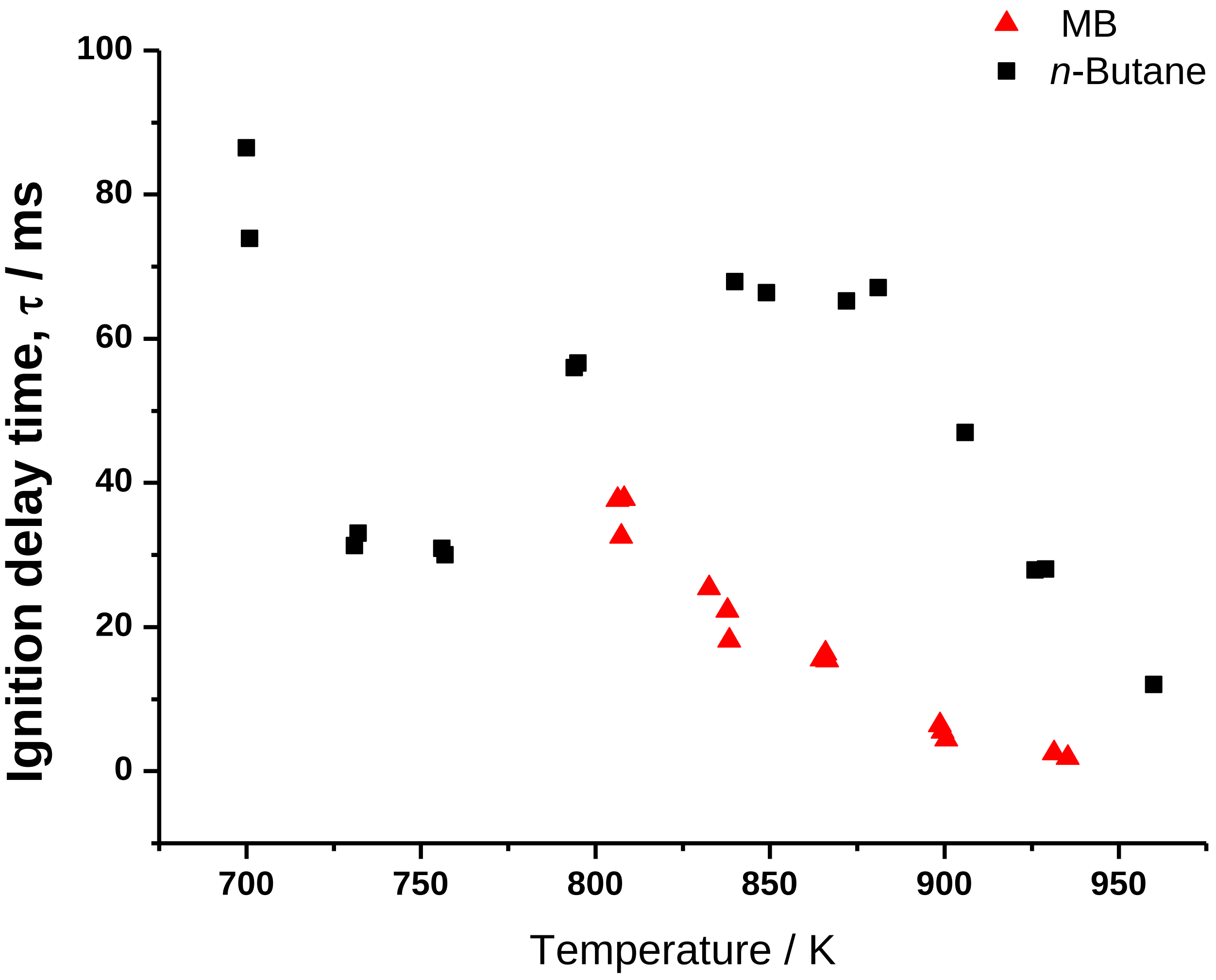
MB versus *n*-butane

RCM, Fuel/O_2/Diluent : 0.0313/0.2034/0.7653, ϕ = 1.0 at 10 atm

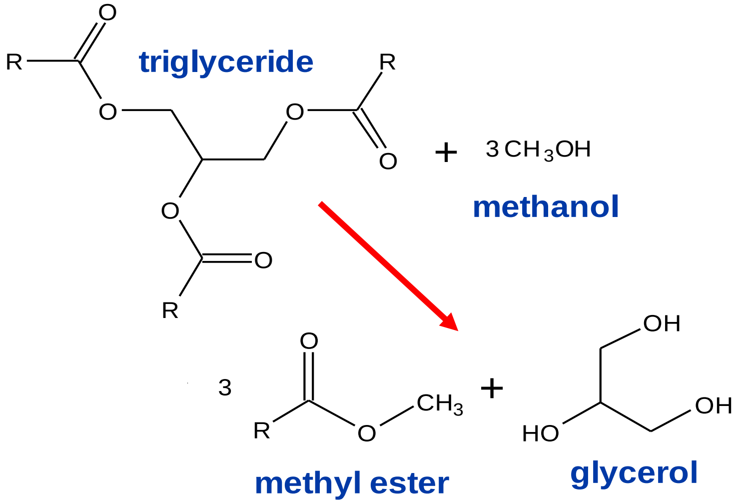


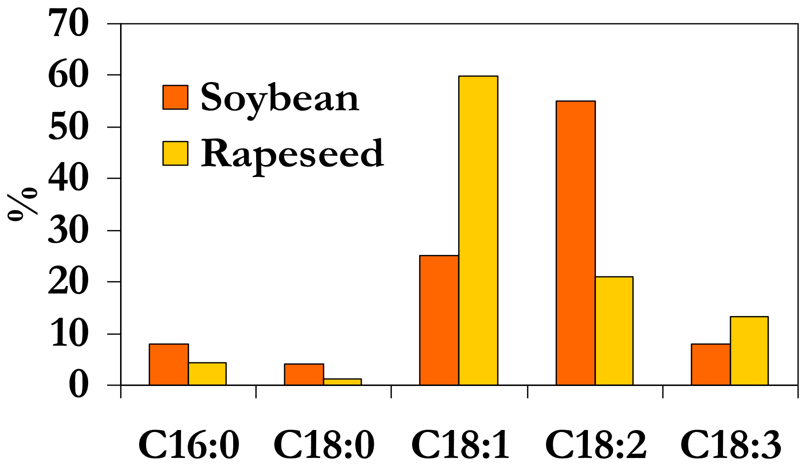
MB versus *n*-butane

RCM, Fuel/O_2/Diluent : 0.0313/0.2034/0.7653, ϕ = 1.0 at 10 atm



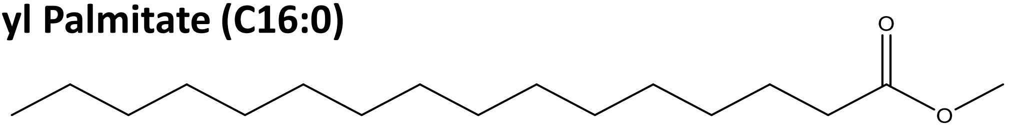
Soybean and rapeseed derived biodiesels have only 5 principal components



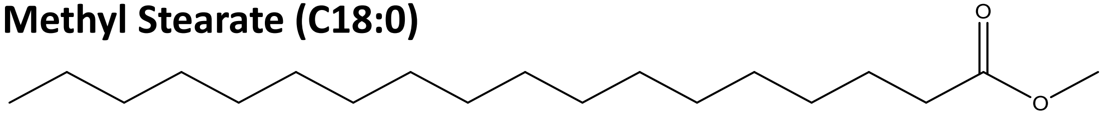


Fatty acid methyl esters (FAMEs):

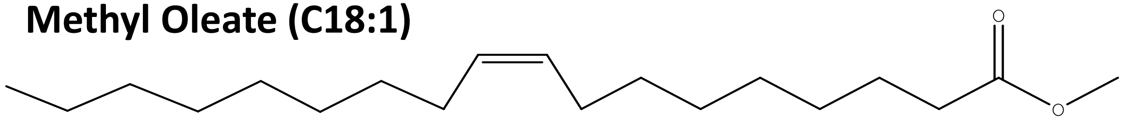
Methyl Palmitate (C16:0)



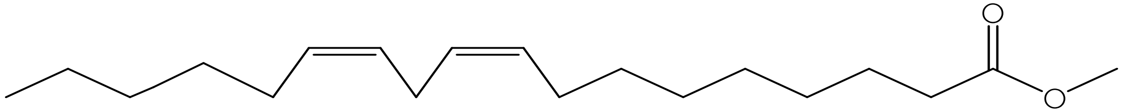
Methyl Stearate (C18:0)



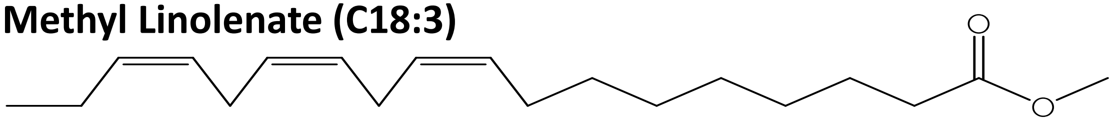
Methyl Oleate (C18:1)



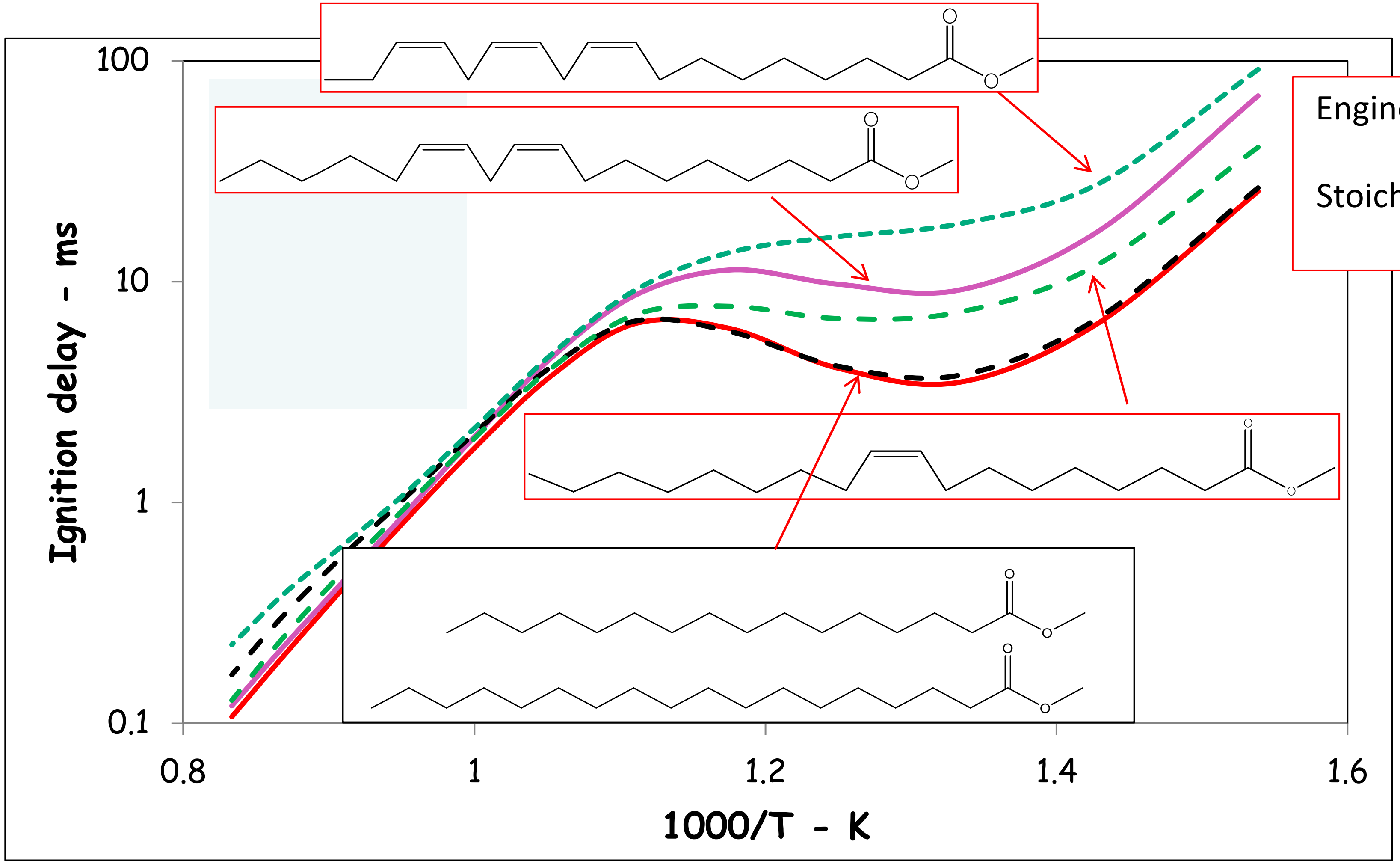
Methyl Linoleate (C18:2)



Methyl Linolenate (C18:3)

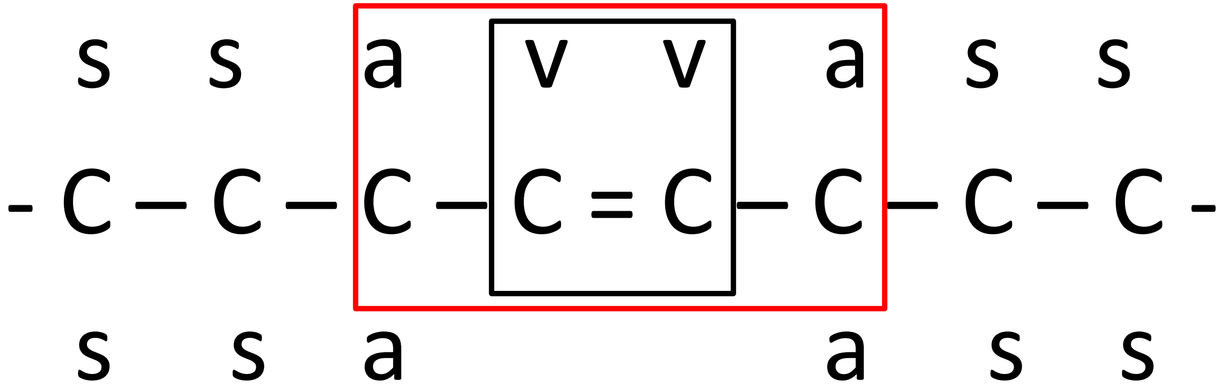


Biodiesel components ignite in order of number of double bonds

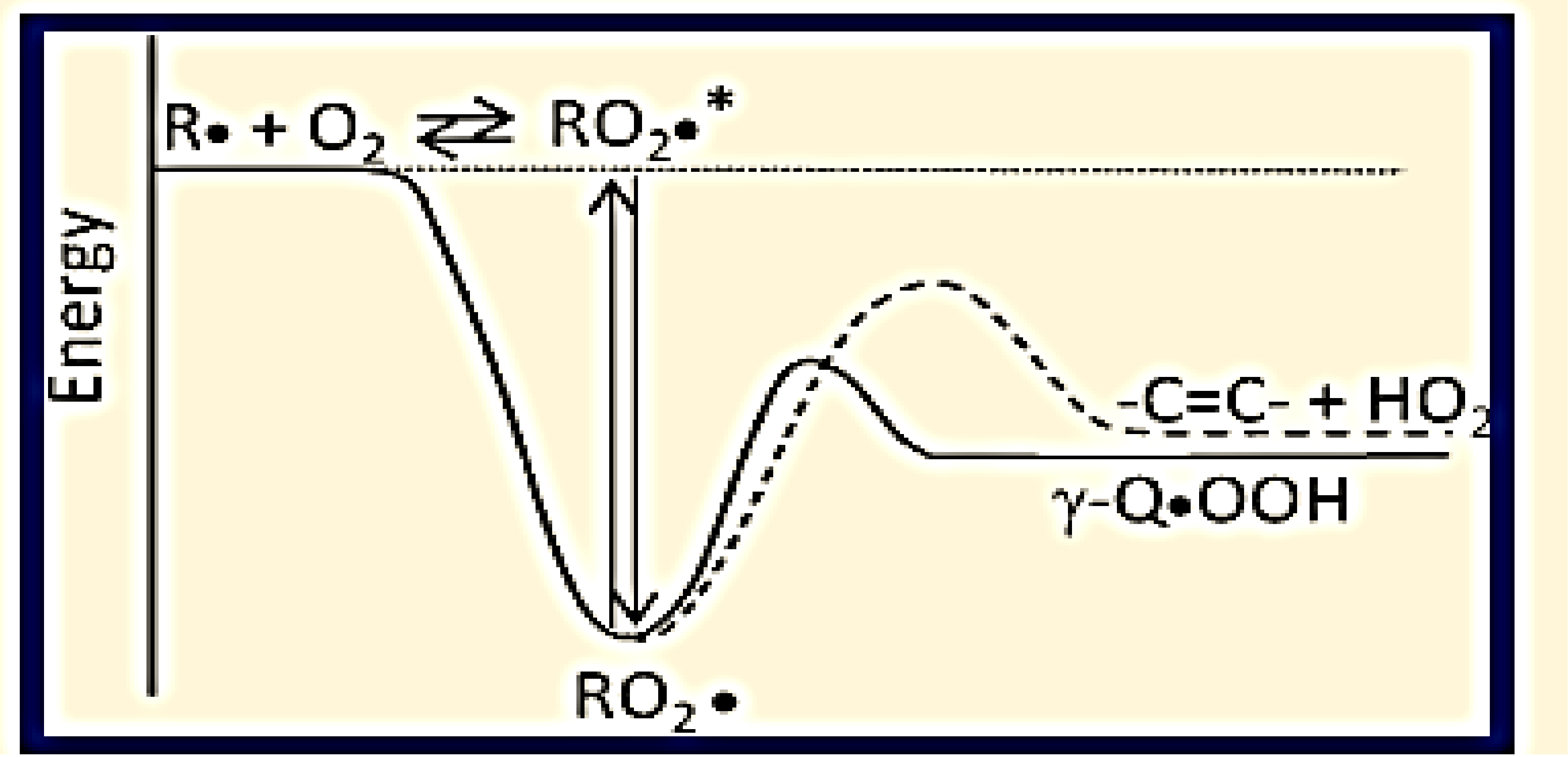


Engine-like conditions:
13.5 bar
Stoichiometric fuel/air
mixtures

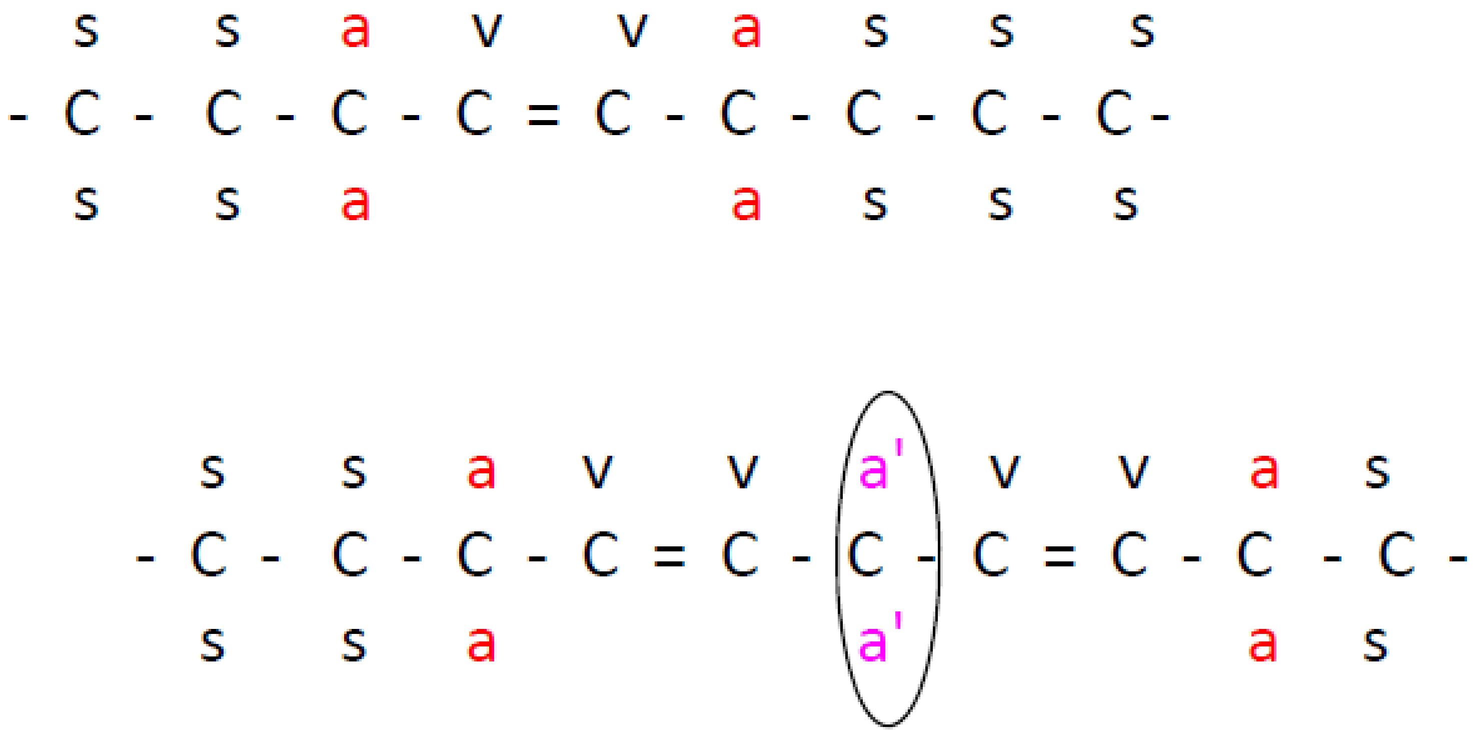
C = C double bonds reduce low T reactivity



- 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
- O_2 is also very weakly bound at allylic sites and falls off rapidly, inhibiting low T reactivity


R• + O$_2$ ⇄ RO$_2$•*
Energy
-C=C- + HO$_2$
γ-Q•OOH
RO$_2$•

Two double bonds make a huge difference



$$-\overset{s}{\underset{s}{C}}-\overset{s}{\underset{s}{C}}-\overset{a}{\underset{a}{C}}-\overset{v}{C}=\overset{v}{C}-\overset{a}{\underset{a}{C}}-\overset{s}{\underset{s}{C}}-\overset{s}{\underset{s}{C}}-\overset{s}{\underset{s}{C}}-$$

$$-\overset{s}{\underset{s}{C}}-\overset{s}{\underset{s}{C}}-\overset{a}{\underset{a}{C}}-\overset{v}{C}=\overset{v}{C}-\boxed{\overset{a'}{\underset{a'}{C}}}-\overset{v}{C}=\overset{v}{C}-\overset{a}{\underset{a}{C}}-\overset{s}{\underset{s}{C}}-$$

$$C-H\ \ \underline{s}\ \text{site} > C-H\ \ \underline{a}\ \text{site} > C-H\ \ \underline{a'}\ \text{site}$$

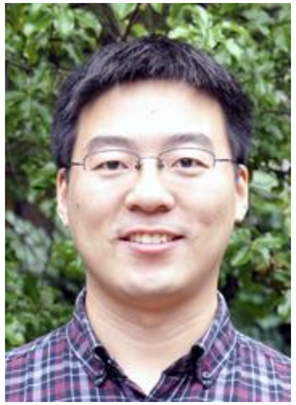
Inter-dependence/overlap of fuel chemistry

The picture can't be displayed.

NH_3 Chemistry Acknowledgements

Mr. Yuxiang Zhu

Dr. Chong-Wen Zhou



Dr. Shijun Dong

Dr. Ahmed Mohamed

Dr. Mohamed Hamdy

Dr. Snehasish Panigrahy

Dr. Amrit Sahu

High-T reaction classes highlighted

Hydrocarbon

- *High temperature mechanism*
  - Reaction class 1: Unimolecular fuel decomposition:
  - Reaction class 2: H atom abstraction from the fuel
  - Reaction class 3: Alkyl radical consumption:
  - Reaction class 4: Alkyl radical + O_2 = olefin + $H\dot{O}_2$
  - 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

Ammonia

- *High temperature mechanism*
  - $NH_3 + M = \dot{N}H_2 + \dot{H} + M$
  - $NH_3 + \dot{R} = \dot{N}H_2 + RH = NH + RH = N + RH$
  - $\dot{N}H_2 + NO = NNH + \dot{O}H / N_2 + H_2O$
  - $\dot{N}H_2 + NH = N_2H_2 + \dot{H}$
  - $N_2H_2 (+M) = NNH + \dot{H} (+M); N_2H_2 + \dot{R} = NNH + RH$
  - $\dot{N}H_2 + \ddot{O} = HNO + \dot{H}$
  - $HNO (+M) = NO + \dot{H} (+M); HNO + \dot{R} = NO + RH$
  - $\dot{N}H_2 + O_2 = H_2NO + \ddot{O} / HNO + \dot{O}H$
  - $H_2NO + \dot{R} = HNO + RH$

High-T reaction classes highlighted

Hydrocarbon

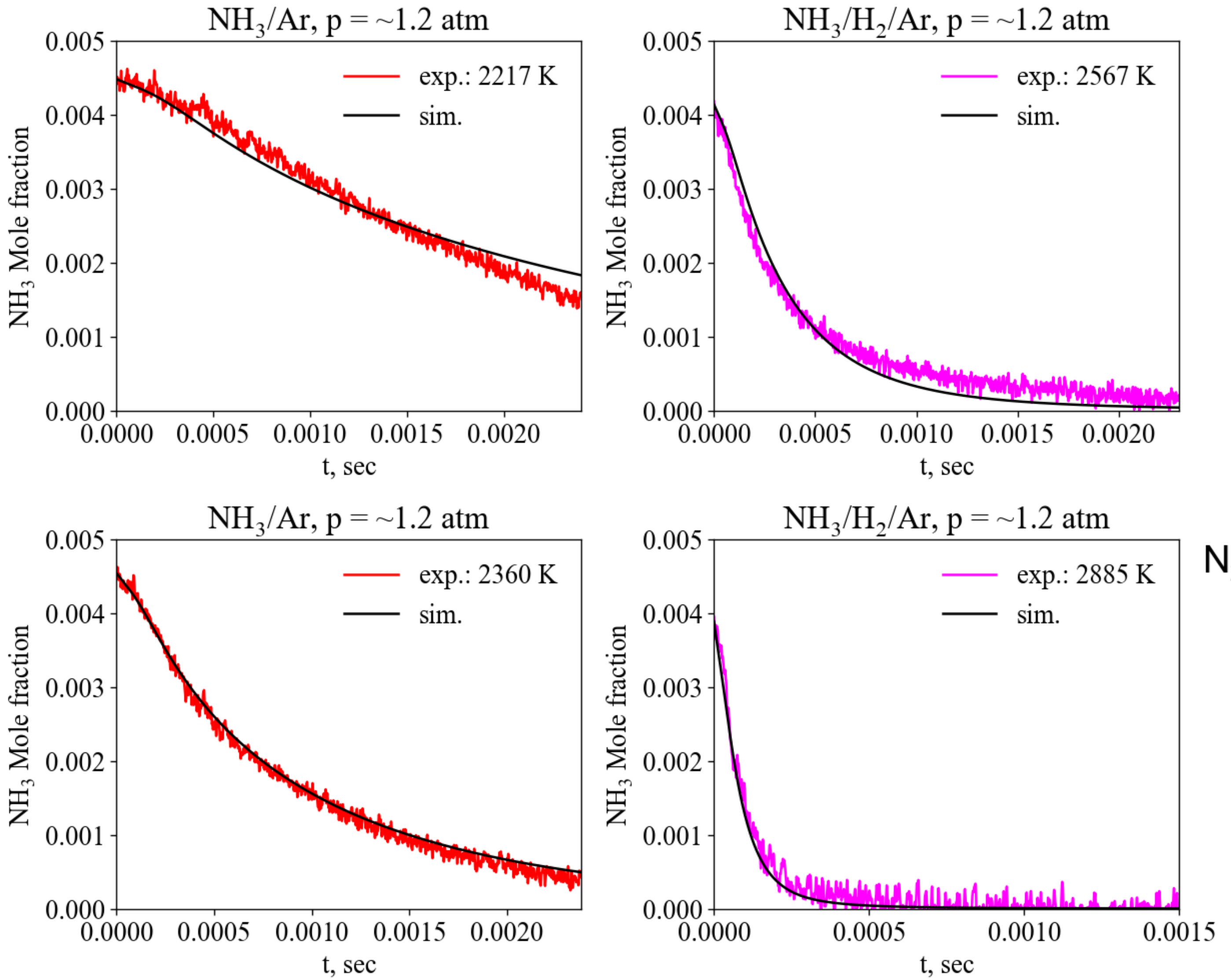
- *High temperature mechanism*
  - Reaction class 1: Unimolecular fuel decomposition:
  - Reaction class 2: H atom abstraction from the fuel
  - Reaction class 3: Alkyl radical consumption:
  - Reaction class 4: Alkyl radical + O_2 = olefin + $H\dot{O}_2$
  - Reaction class 5: Alkyl radical isomerization
  - 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

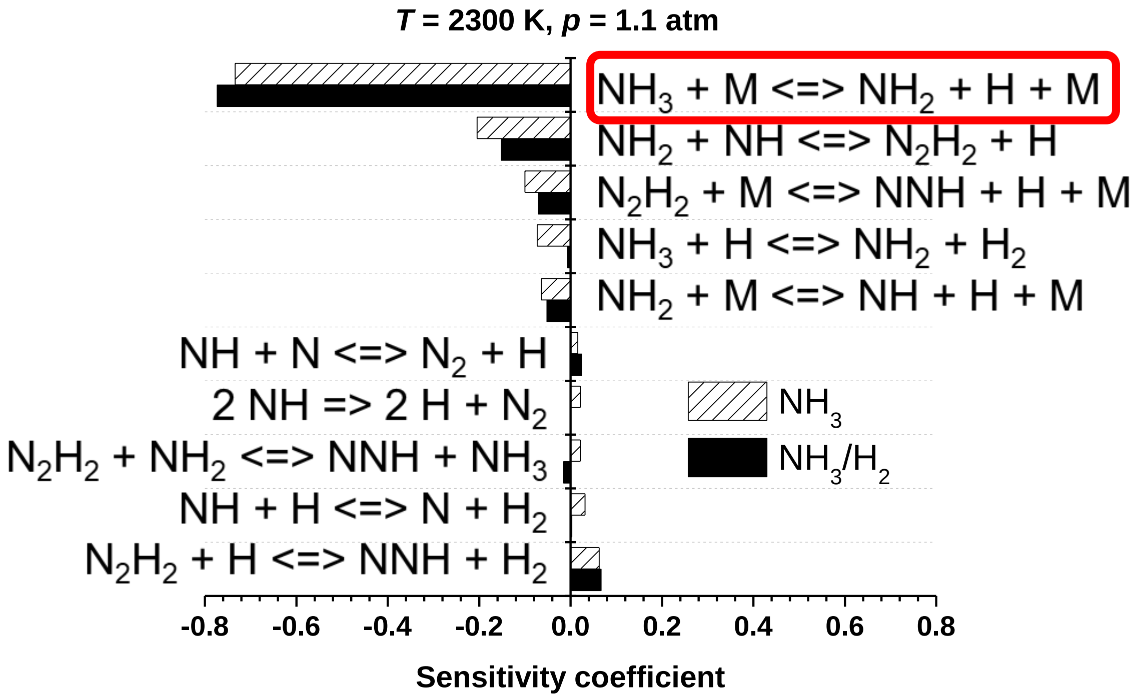
Ammonia

- *High temperature mechanism*
  - $NH_3 + M = \dot{N}H_2 + \dot{H} + M$
  - $NH_3 + \dot{R} = \dot{N}H_2 + RH = NH + RH = N + RH$
  - $\dot{N}H_2 + NO = NNH + \dot{O}H$ / $N_2 + H_2O$
  - $\dot{N}H_2 + NH = N_2H_2 + \dot{H}$
  - N_2H_2 (+M) = $NNH + \dot{H}$ (+M); $N_2H_2 + \dot{R} = NNH + RH$
  - $\dot{N}H_2 + \ddot{O} = HNO + \dot{H}$
  - HNO (+M) = $NO + \dot{H}$ (+M); $HNO + \dot{R} = NO + RH$
  - $\dot{N}H_2 + O_2 = H_2NO + \ddot{O}$ / $HNO + \dot{O}H$
  - $H_2NO + \dot{R} = HNO + RH$

NH_3 unimolecular decomposition

- Sensitivity for $[NH_3]_t$ under pyrolysis conditions



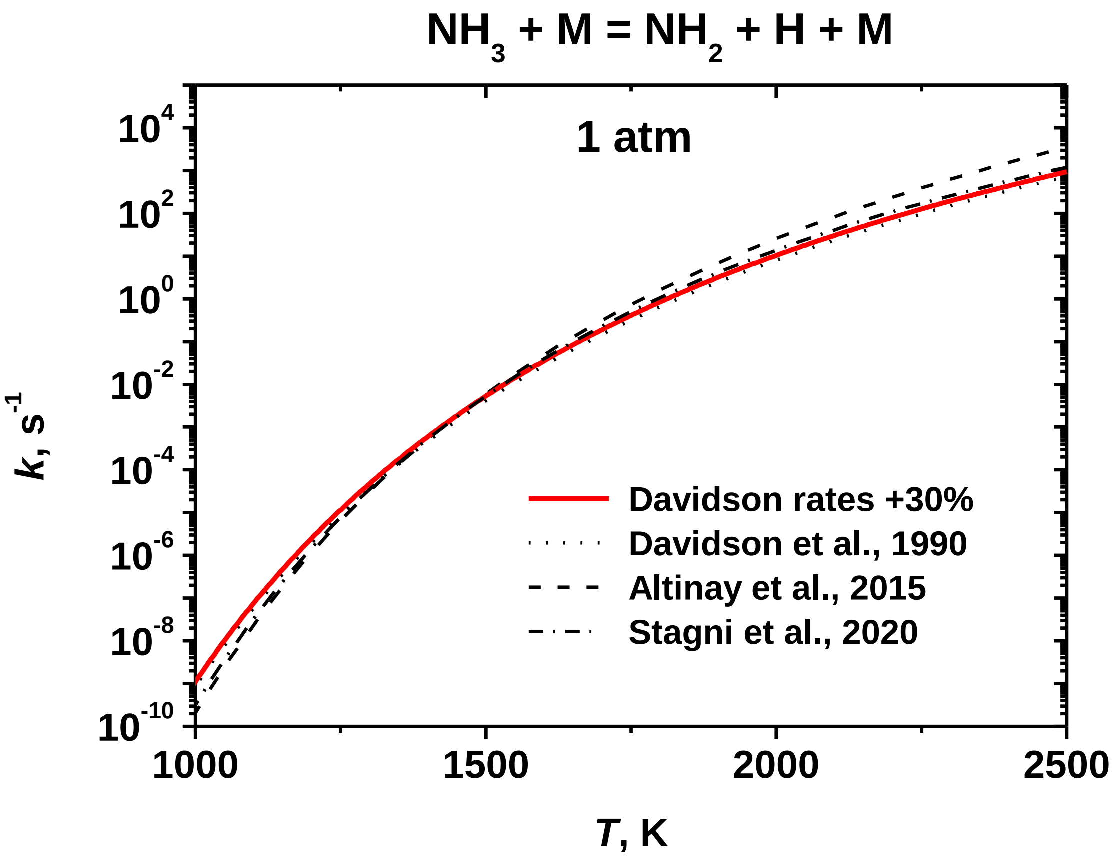


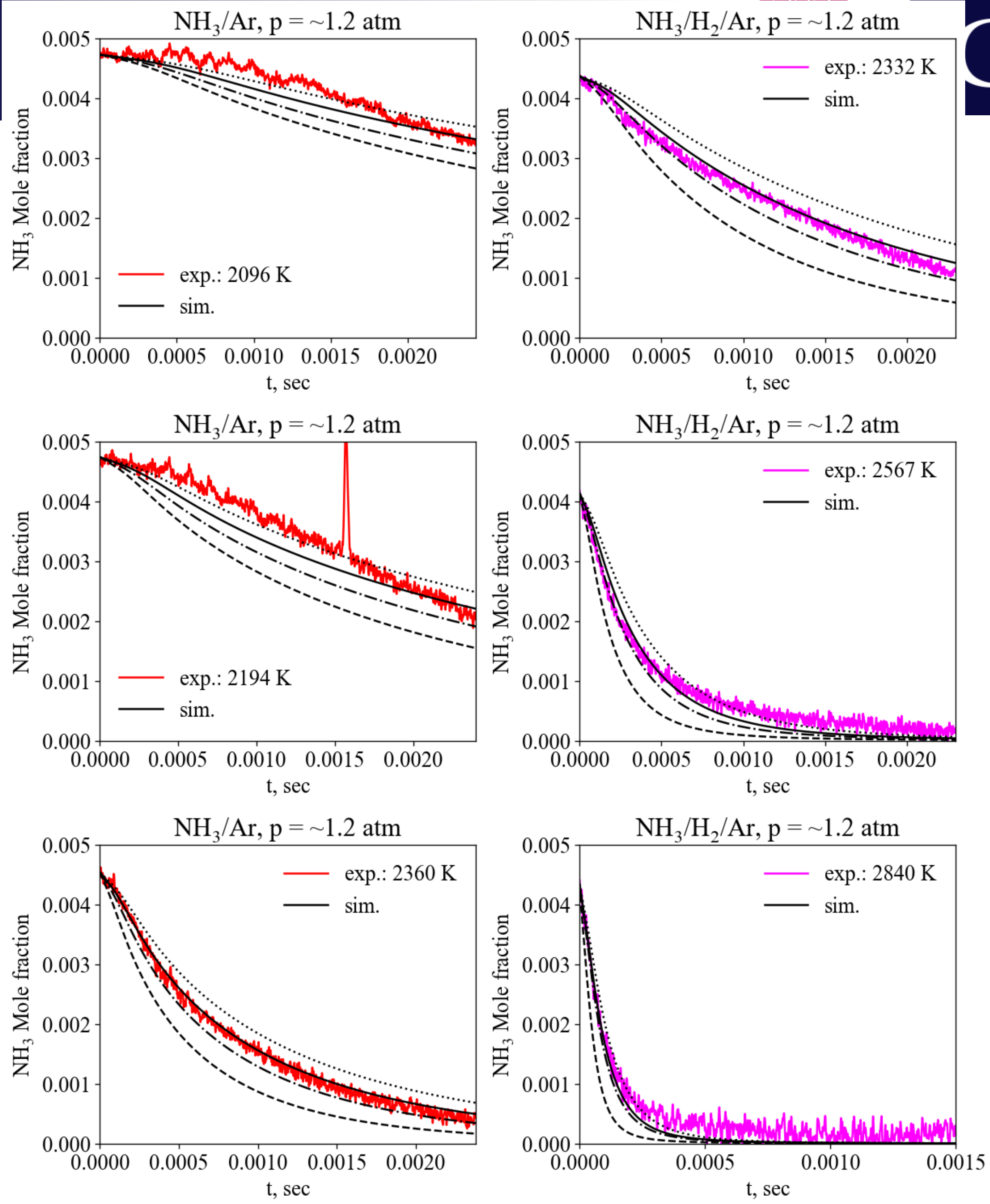
Experiment:

Alturaifi, S. A., Mathieu, O., & Petersen, E. L. (2022). An experimental and modeling study of ammonia pyrolysis. Combustion and Flame, 235, 111694.

NH_3 unimolecular decomposition

- Rate constants





Altinay, G., & Macdonald, R. G. (2015). The Journal of Physical Chemistry A, 119(28), 7593-7610.

Davidson, D. F., Kohse-Höinghaus, K., Chang, A. Y., & Hanson, R. K. (1990). International journal of chemical kinetics, 22(5), 513-535.

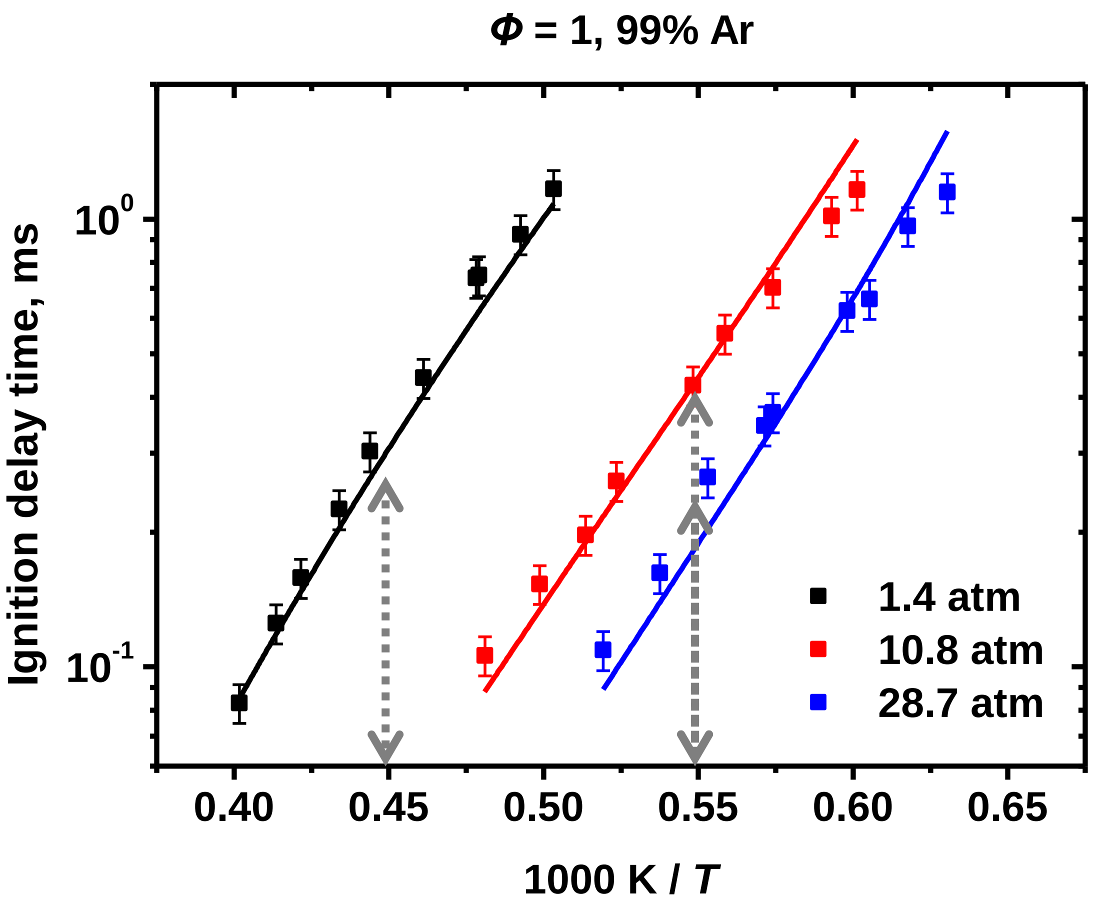
Stagni, A., Cavallotti, C., Arunthanayothin, S., Song, Y., Herbinet, O., Battin-Leclerc, F., & Faravelli, T. (2020). Reaction Chemistry & Engineering, 5(4), 696-711.

High-T reaction classes highlighted

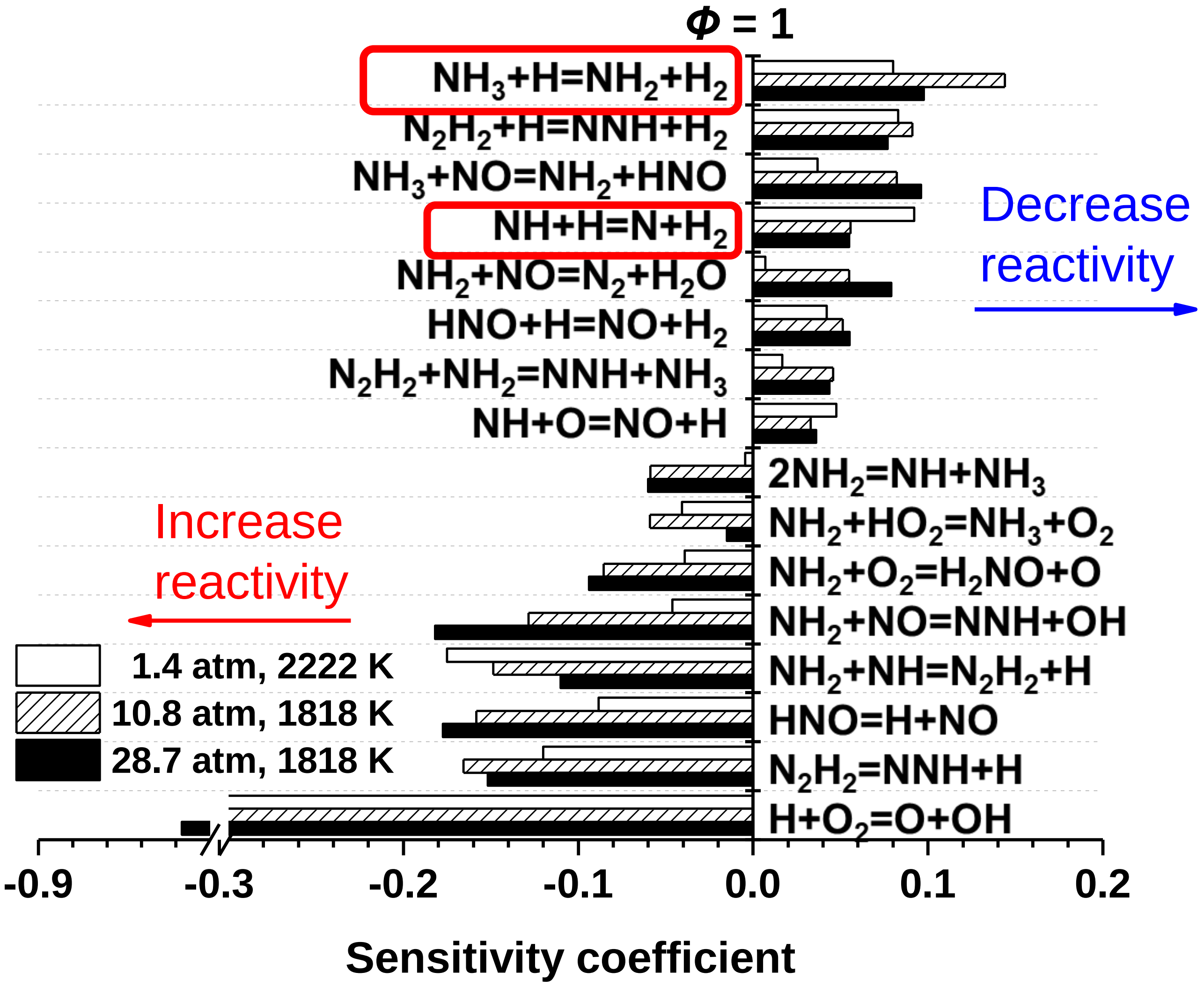
- $NH_3 + M = \dot{N}H_2 + \dot{H} + M$
- $NH_3 + \dot{R} = \dot{N}H_2 + RH = NH + RH = N + RH$
- $\dot{N}H_2 + NO = NNH + \dot{O}H$ / $N_2 + H_2O$
- $\dot{N}H_2 + NH = N_2H_2 + \dot{H}$
- $N_2H_2 (+M) = NNH + \dot{H} (+M)$; $N_2H_2 + \dot{R} = NNH + RH$
- $\dot{N}H_2 + \ddot{O} = HNO + \dot{H}$
- $HNO (+M) = NO + \dot{H} (+M)$; $HNO + \dot{R} = NO + RH$
- $\dot{N}H_2 + O_2 = H_2NO + \ddot{O}$ / $HNO + \dot{O}H$
- $H_2NO + \dot{R} = HNO + RH$

High-temperature chemistry

➢ NH_3 IDT sensitivity analyses

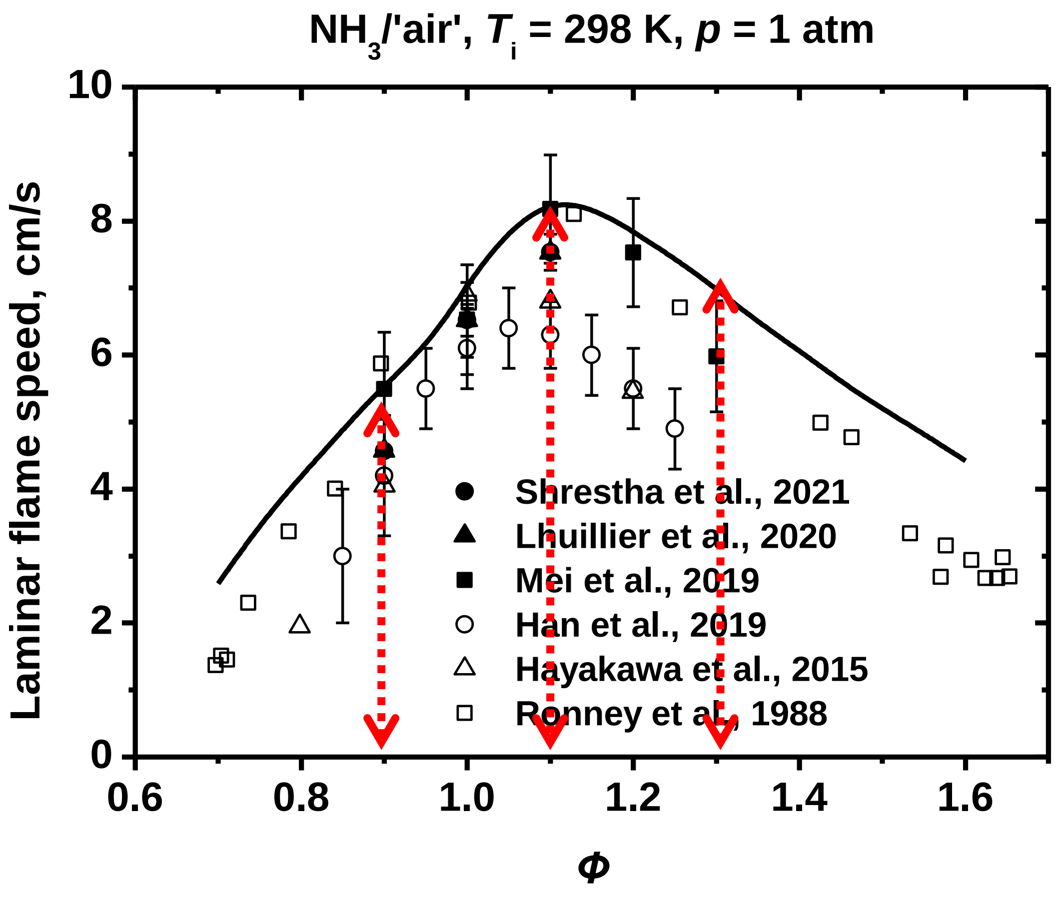


Shock tube ignition delay times
(Expt.: Mathieu 2015, CNF)

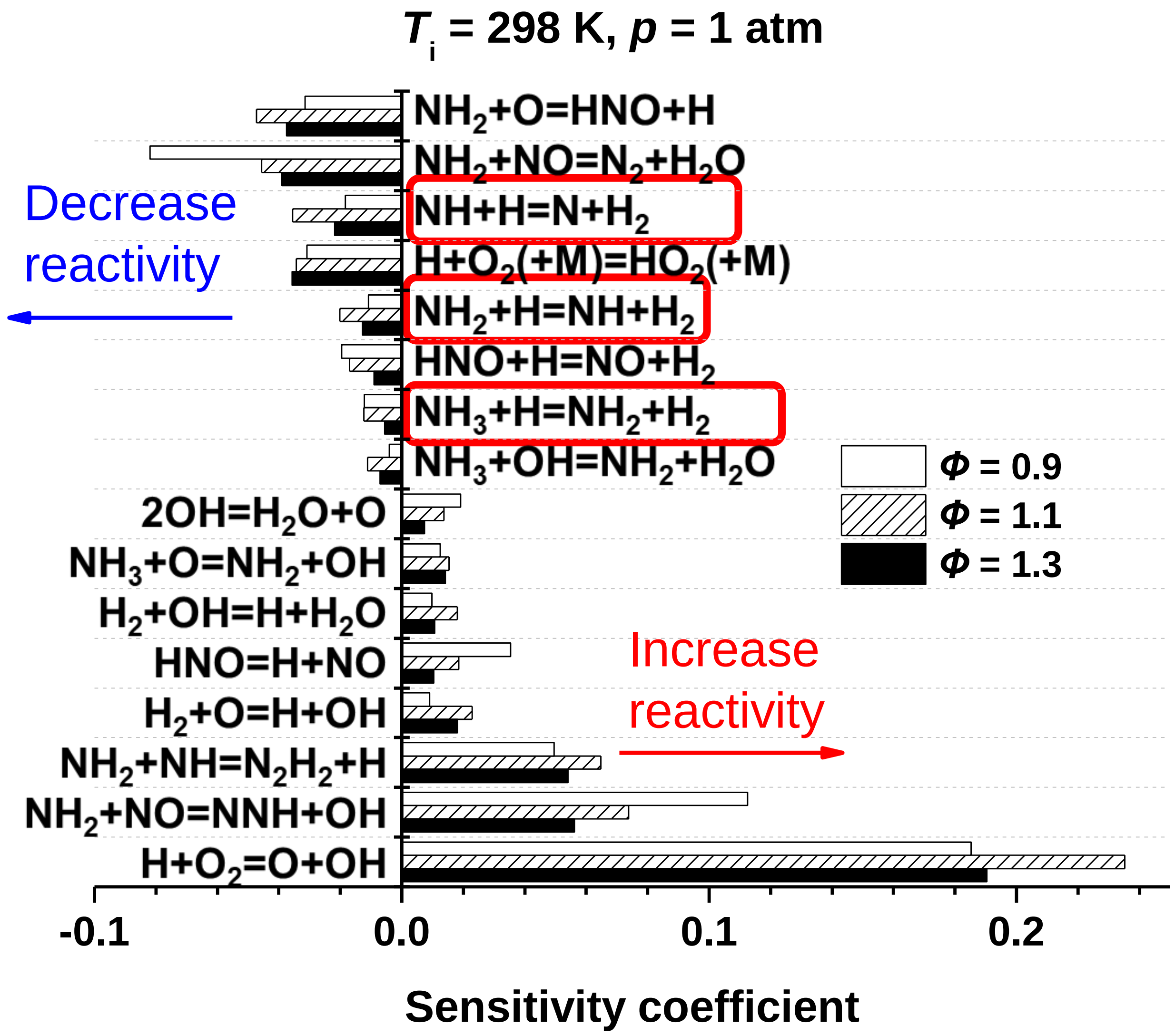


High-temperature chemistry

➢ NH_3 flame speed sensitivity analyses



(Expt.: cf. legend)

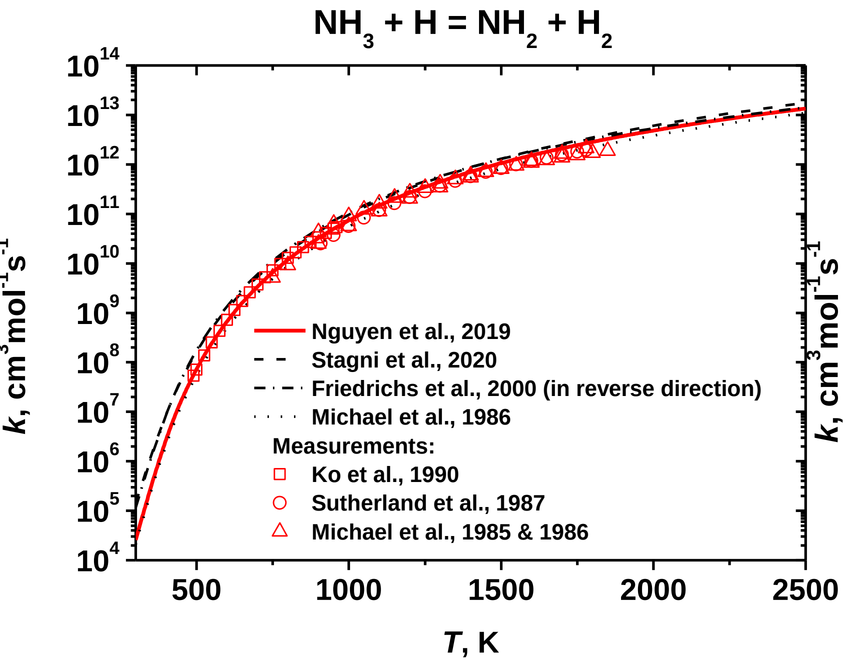


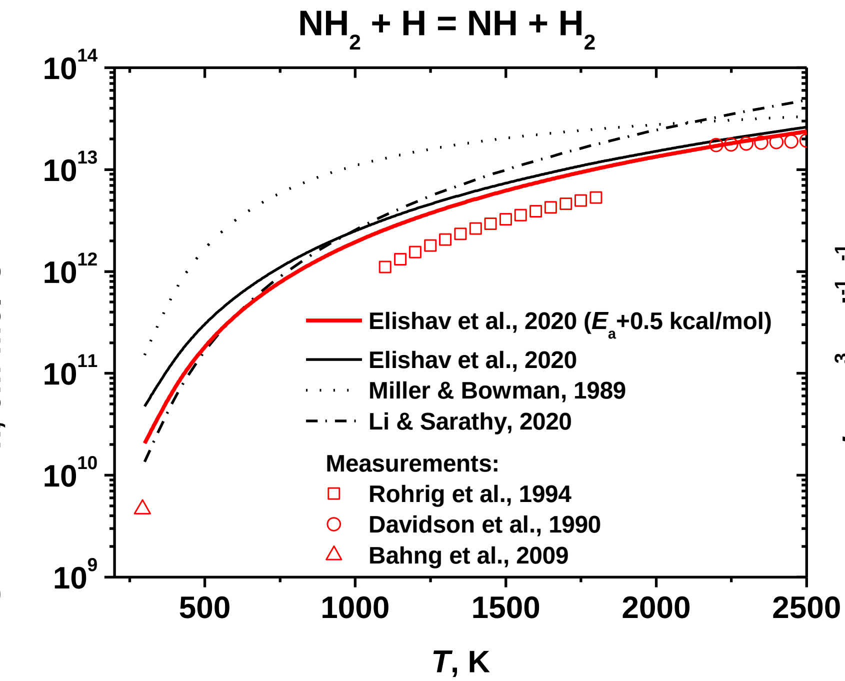
Decrease reactivity

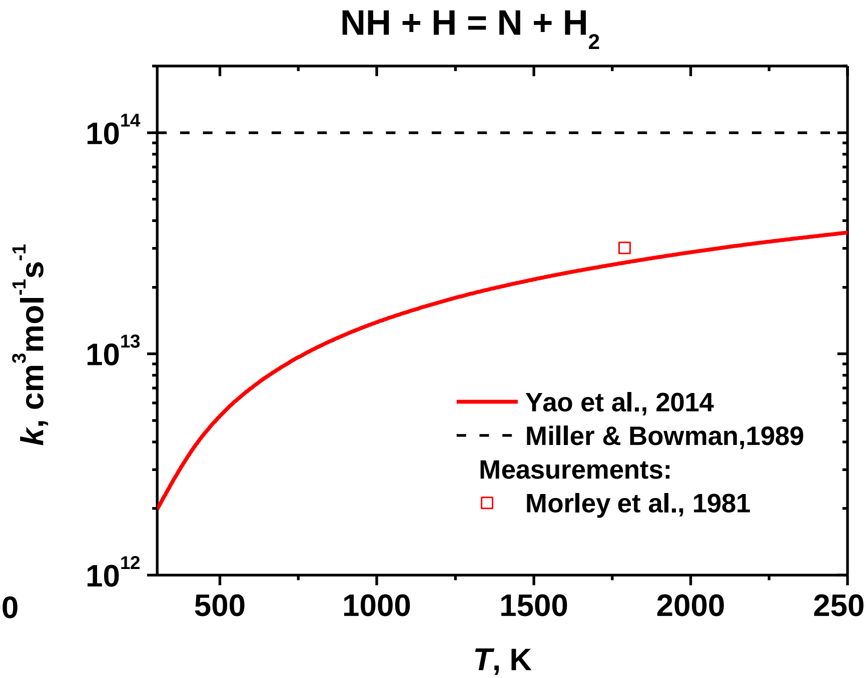
Increase reactivity

$NH_x + \dot{H} = NH_{x-1} + H_2$

➢ Rate constants







Stagni, A., et al. (2020). Reaction Chemistry & Engineering, 5(4), 696-711.

Friedrichs, G., & Wagner, H. G. (2000). Direct Measurements of the Reaction NH2+ H2→ NH3+ H at Temperatures from 1360 to 2130 K.

Nguyen, T. L., & Stanton, J. F. (2019). International Journal of Chemical Kinetics, 51(5), 321-328.

Michael, J. V., et al. (1986). The Journal of Physical Chemistry, 90(3), 497-500.

Miller, J. A., & Bowman, C. T. (1989). Progress in energy and combustion science, 15(4), 287-338.

Li, Y., & Sarathy, S. M. (2020). International Journal of Hydrogen Energy, 45(43), 23624-23637.

Elishav, O., et al. (2020). Chemical reviews, 120(12), 5352-5436.

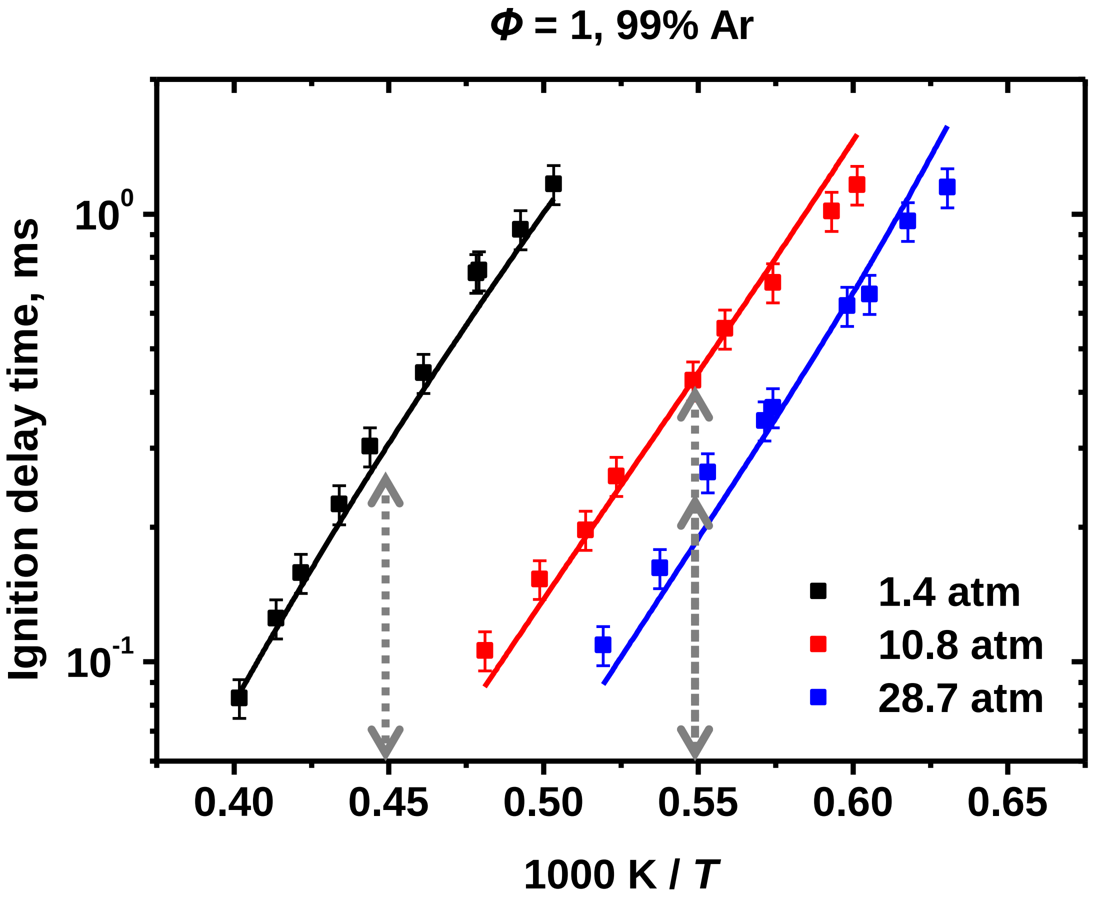
Yao, C. X., et al. (2014). Theoretical Chemistry Accounts, 133(6), 1-8.

High-T reaction classes highlighted

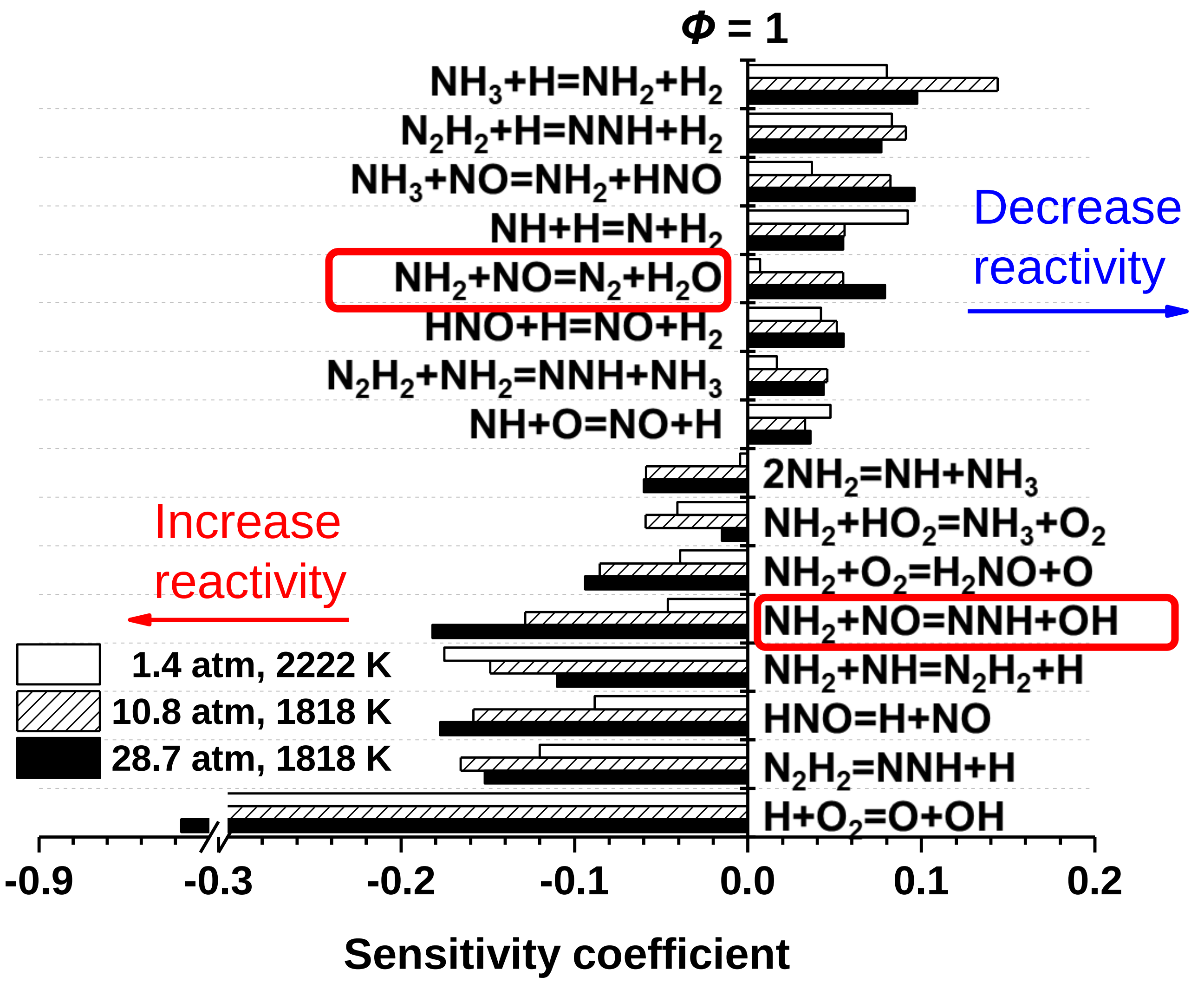
- $NH_3 + M = \dot{N}H_2 + \dot{H} + M$
- $NH_3 + \dot{R} = \dot{N}H_2 + RH = NH + RH = N + RH$
- $\dot{N}H_2 + NO = NNH + \dot{O}H / N_2 + H_2O$
- $\dot{N}H_2 + NH = N_2H_2 + \dot{H}$
- $N_2H_2\ (+M) = NNH + \dot{H}\ (+M);\ N_2H_2 + \dot{R} = NNH + RH$
- $\dot{N}H_2 + \ddot{O} = HNO + \dot{H}$
- $HNO\ (+M) = NO + \dot{H}\ (+M);\ HNO + \dot{R} = NO + RH$
- $\dot{N}H_2 + O_2 = H_2NO + \ddot{O} / HNO + \dot{O}H$
- $H_2NO + \dot{R} = HNO + RH$

High-temperature chemistry

➢ NH_3 IDT sensitivity analyses

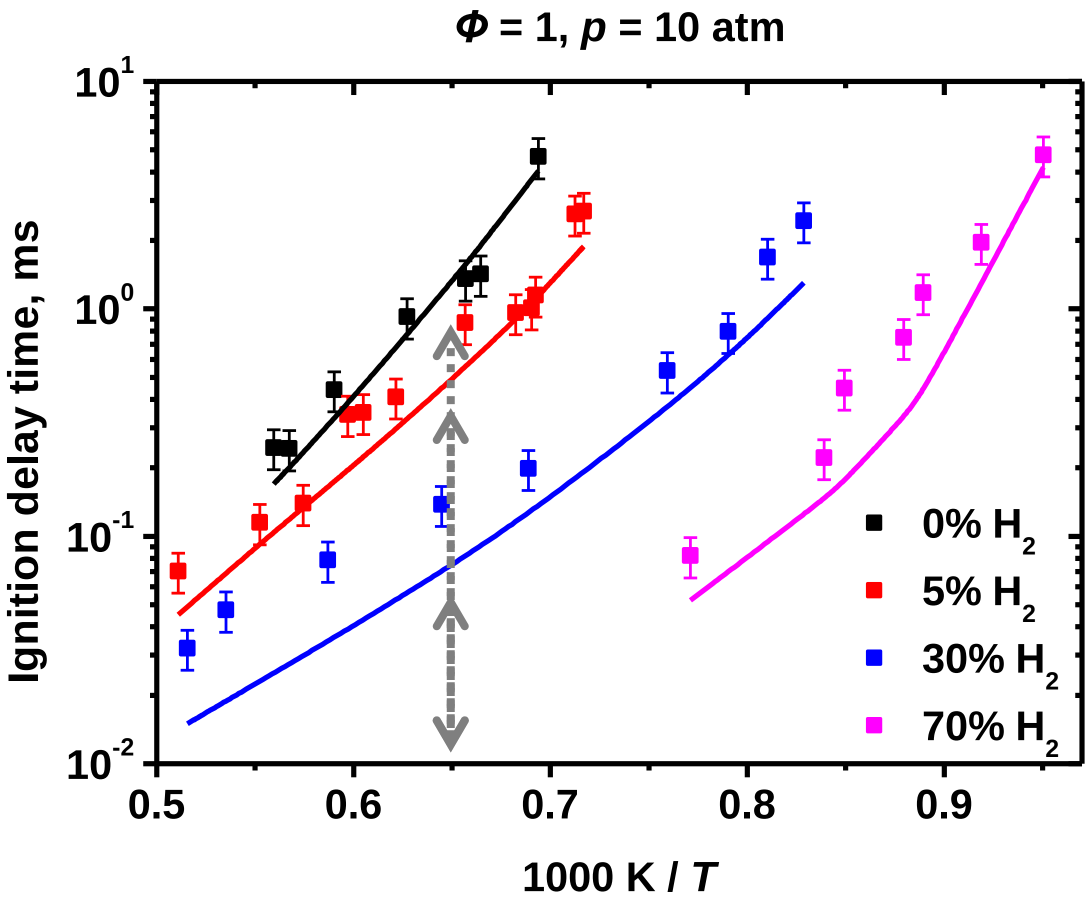


Shock tube ignition delay times
(Expt.: Mathieu 2015, CNF)

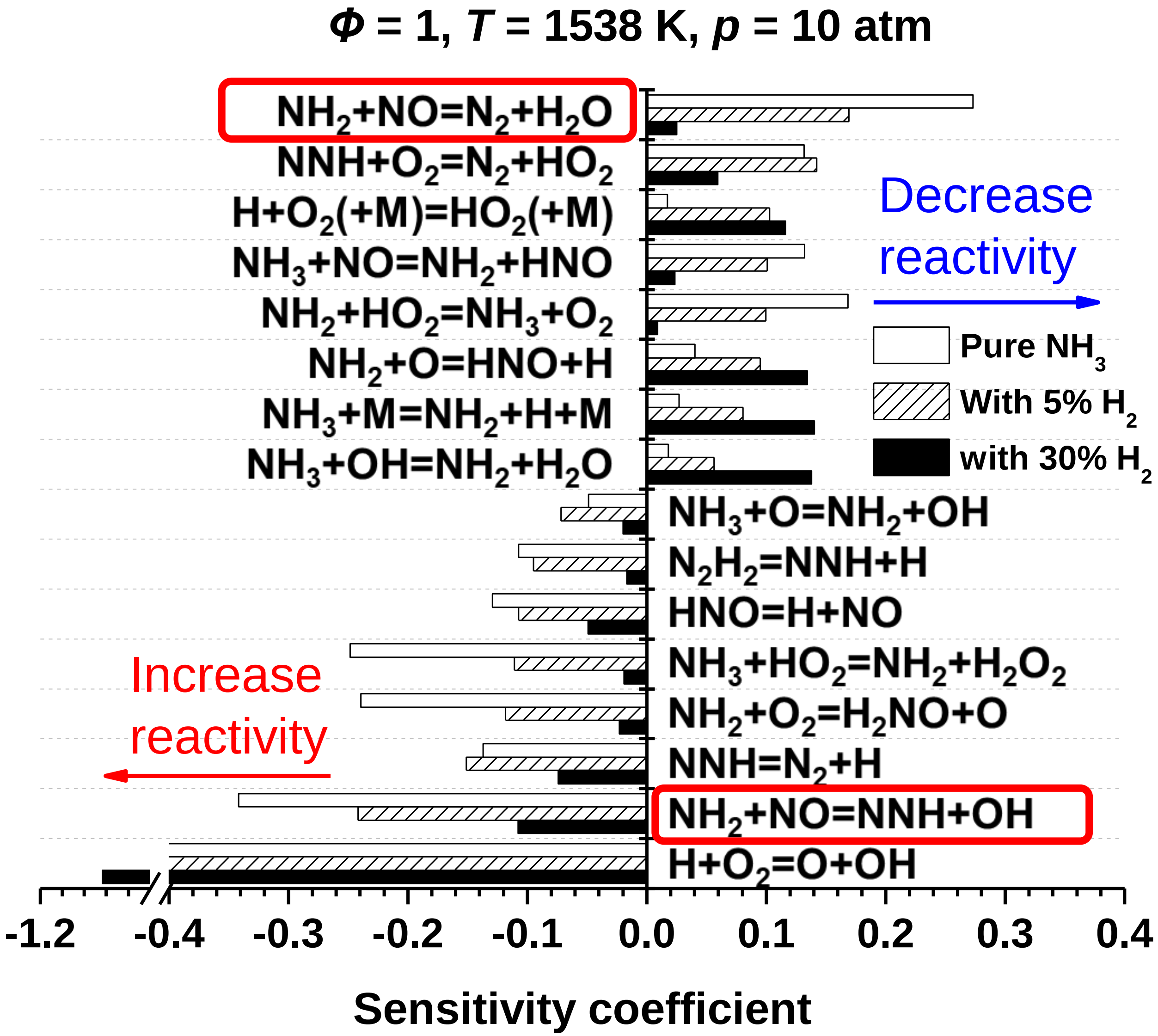


High-temperature chemistry

➢ NH_3/H_2 IDT sensitivity analyses

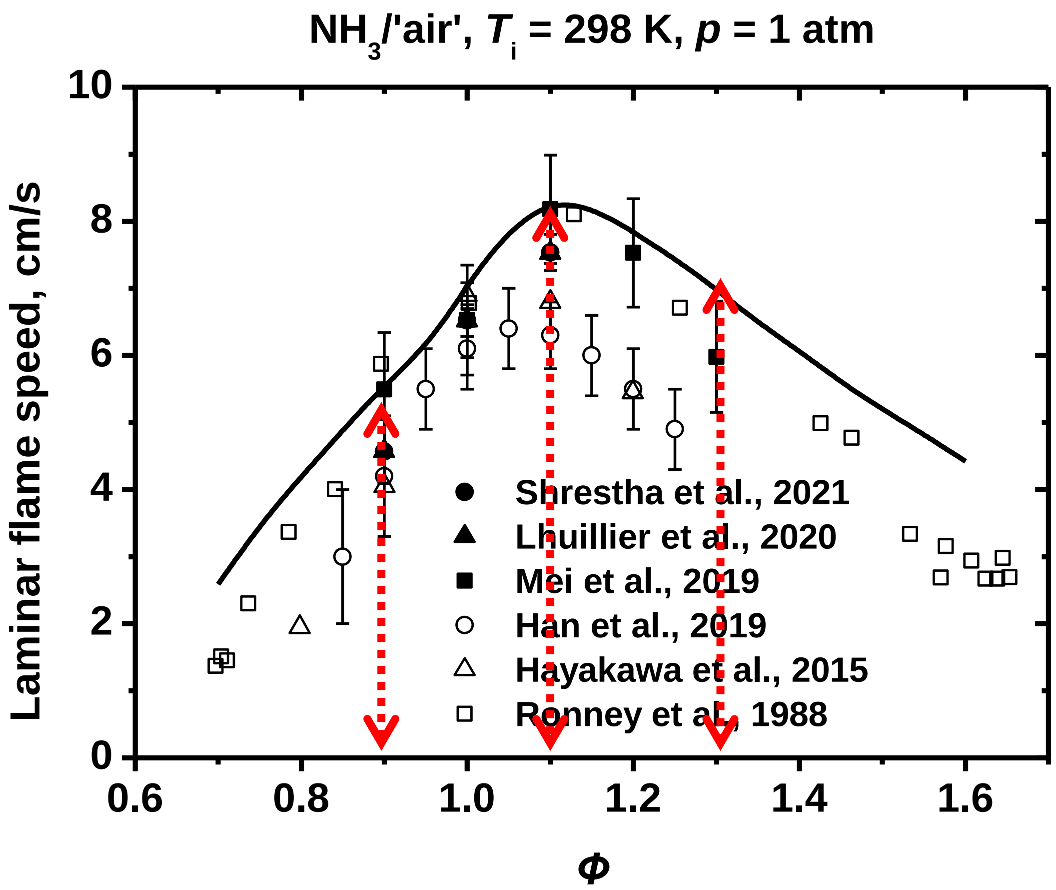


Shock tube ignition delay times
(Expt.: Chen 2021, Fuel)

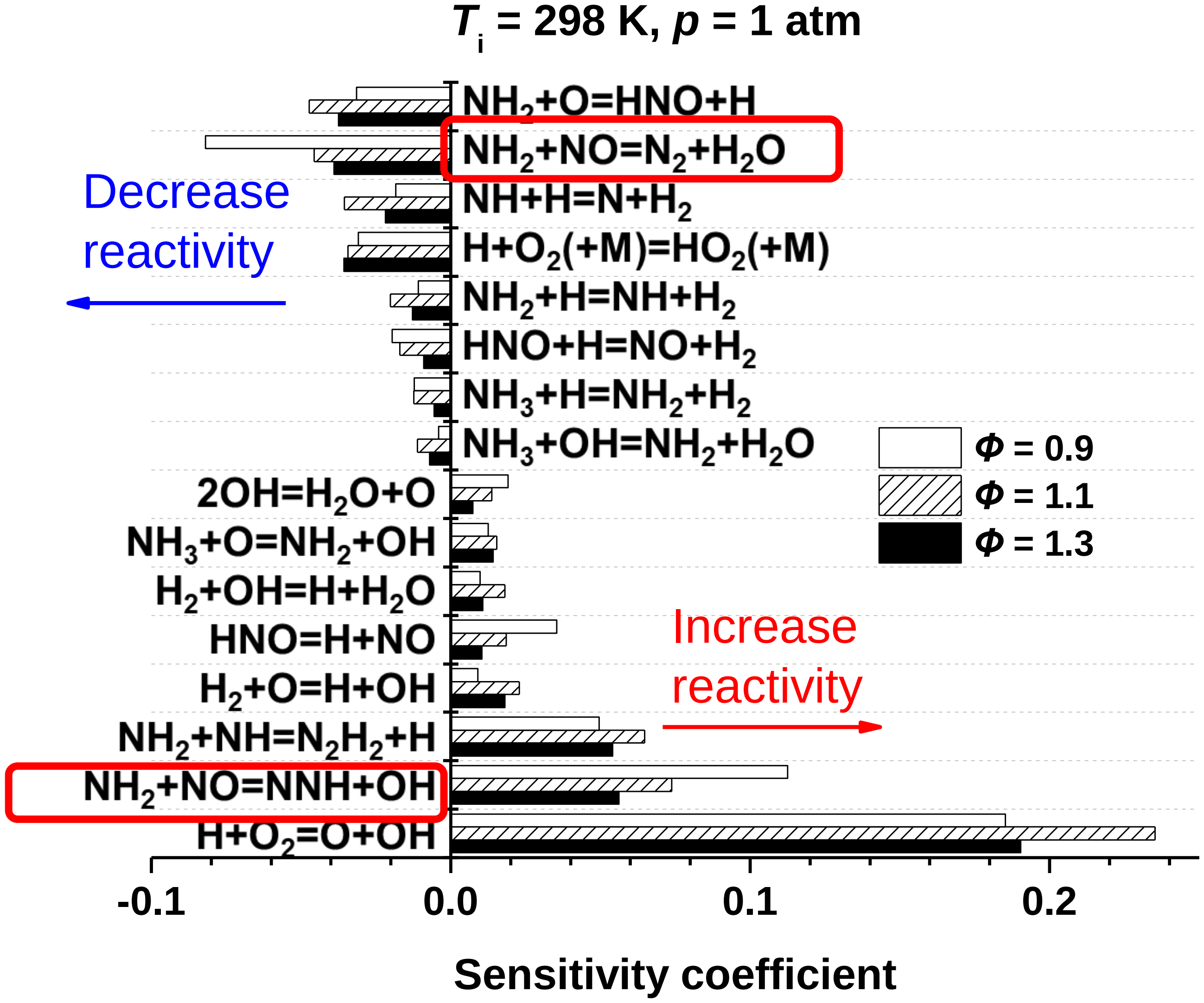


High-temperature chemistry

➢ NH_3 flame speed sensitivity analyses

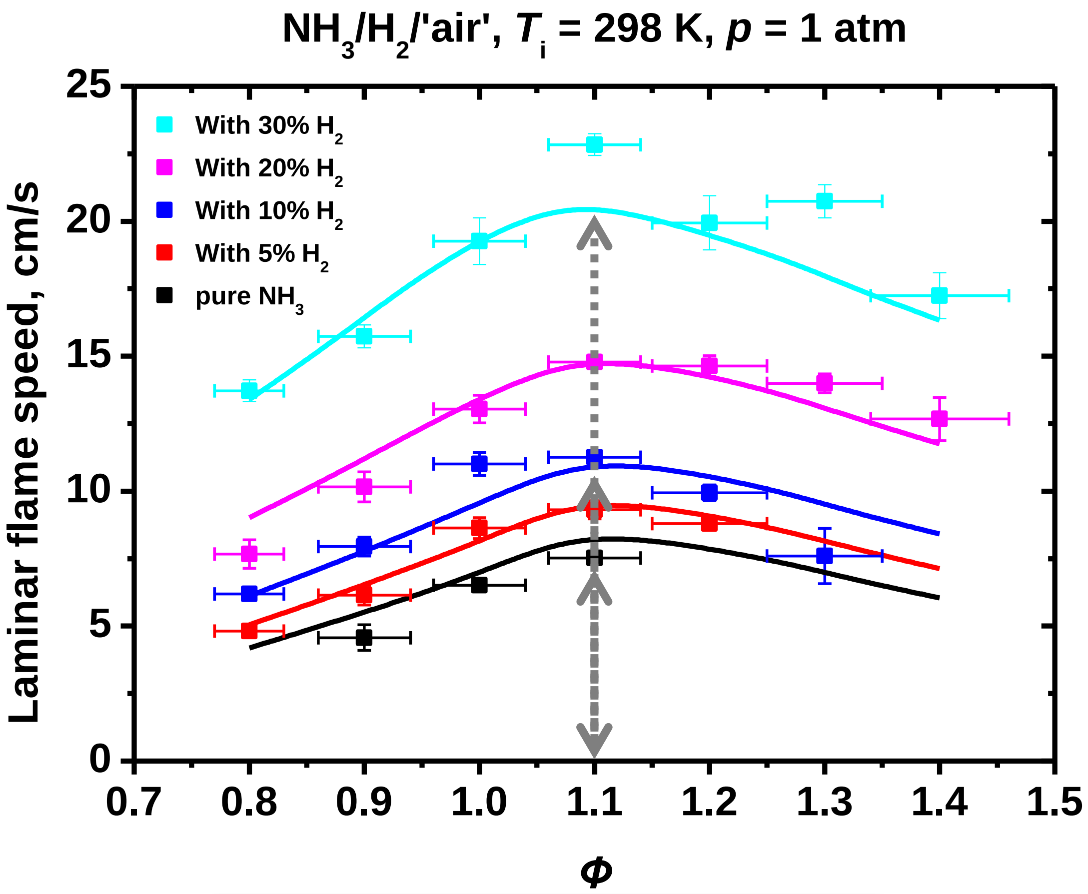


(Expt.: cf. legend)



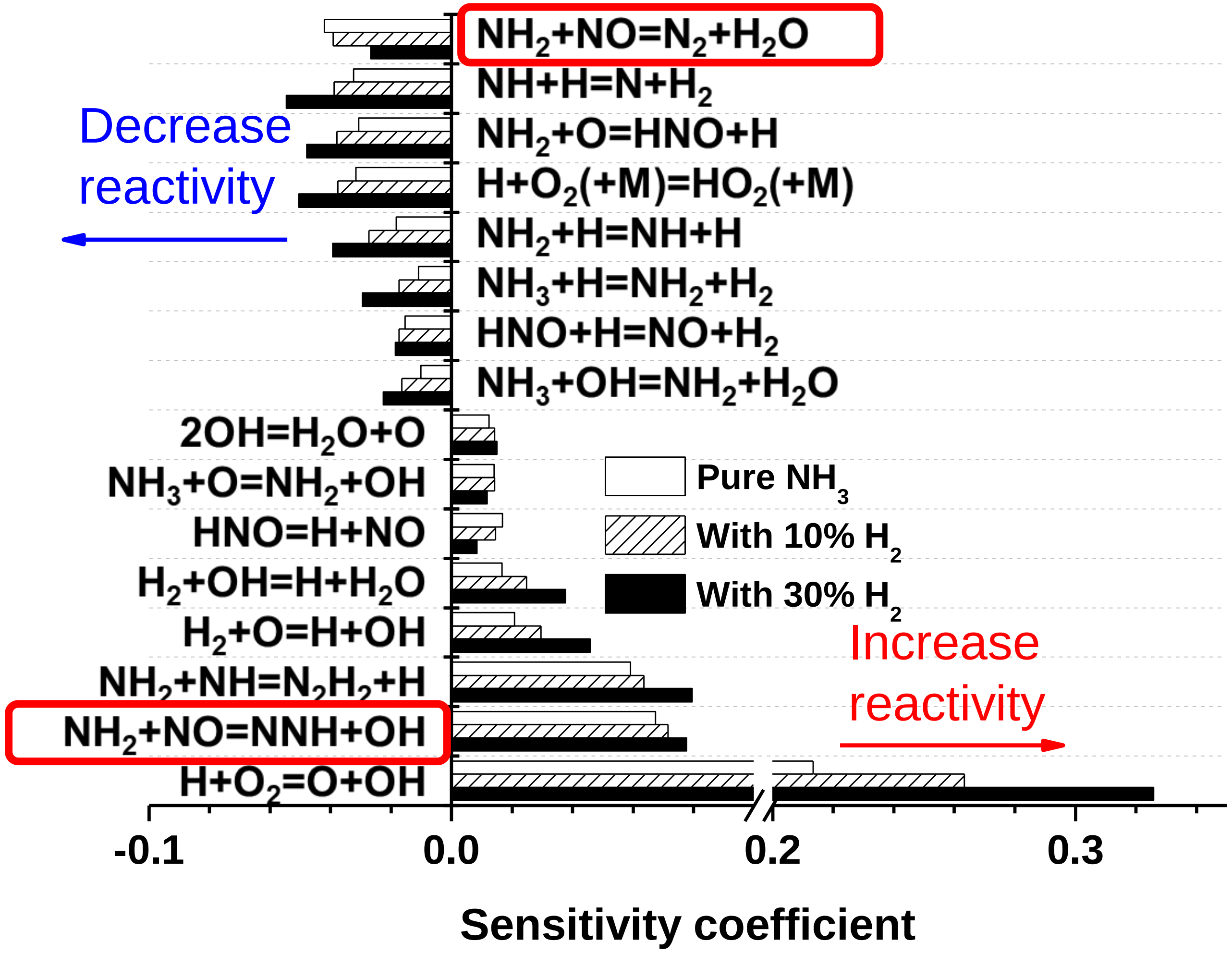
High-temperature chemistry

➢ NH_3/H_2 flame speed sensitivity analyses



(Expt.: Lhuillier 2020, Fuel)

Φ = 1.1, T_i = 298 K, p = 1 atm



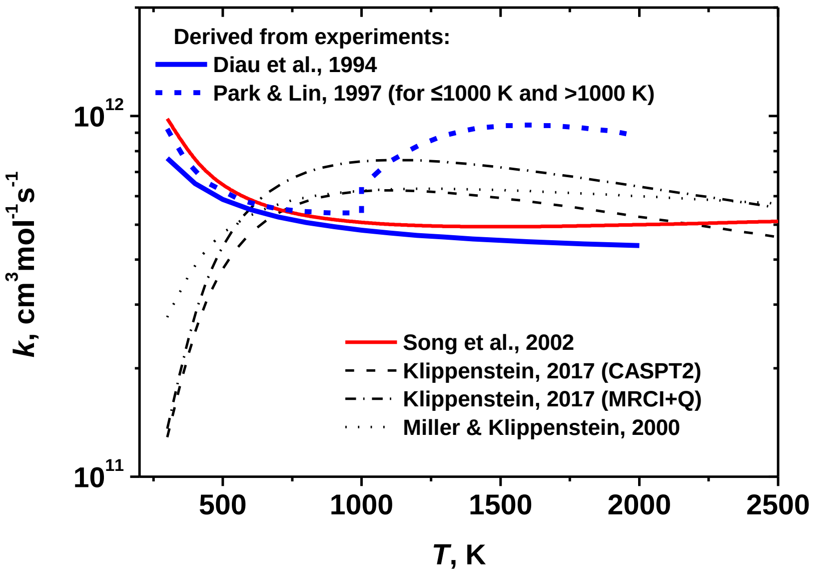
Decrease reactivity

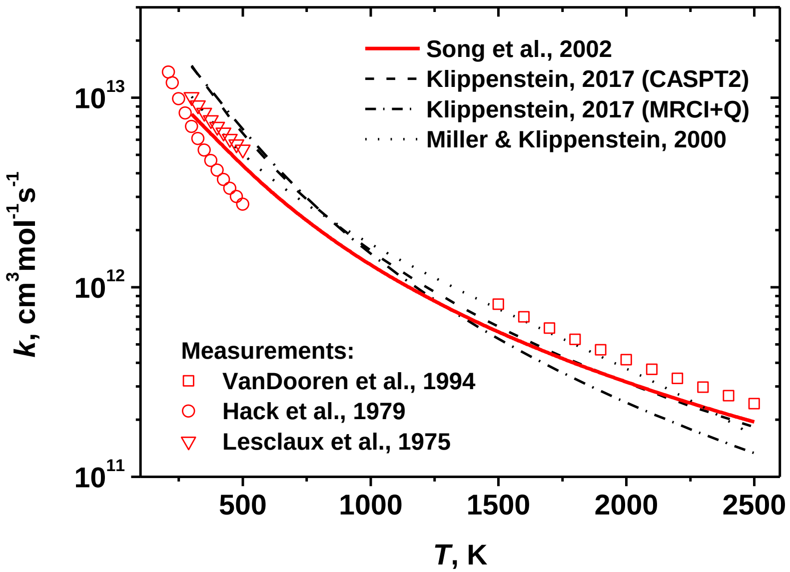
Increase reactivity

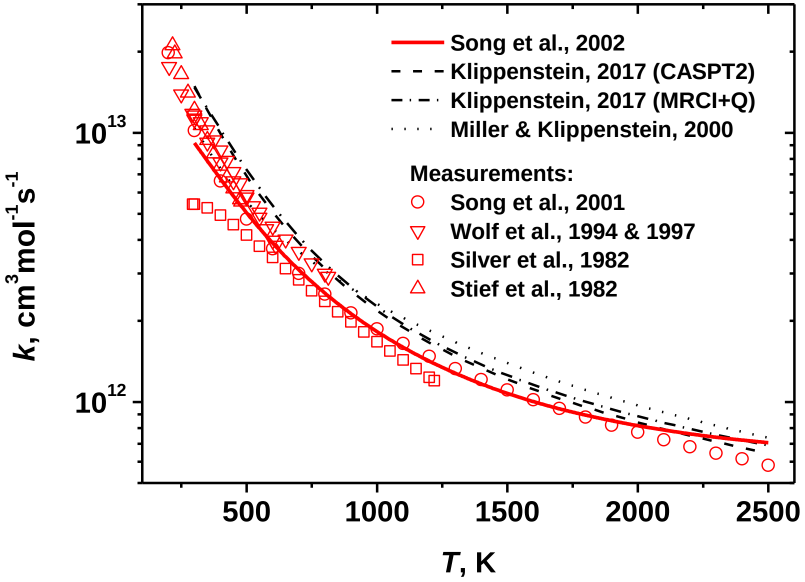
$\dot{N}H_2$ + NO reaction system

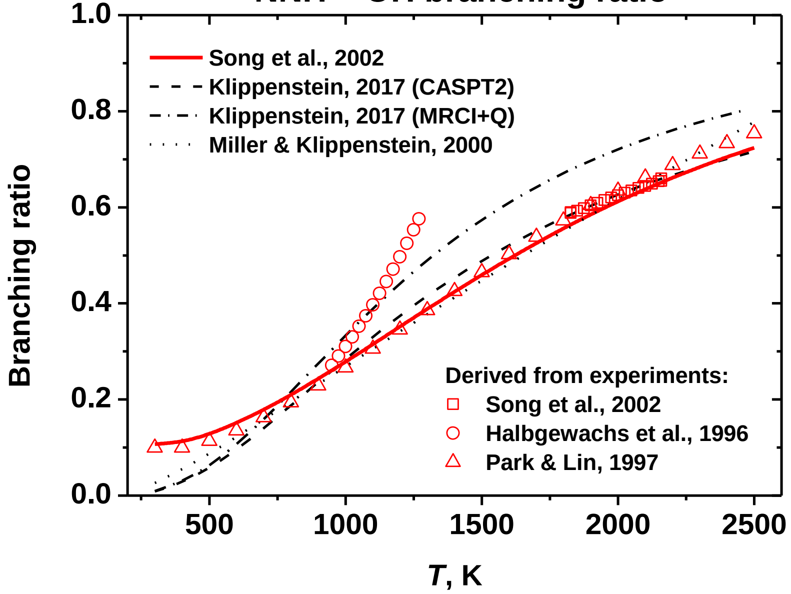
Rate constants

- = NNH + $\dot{O}H$
- = N_2 + H_2O


NH_2 + NO = NNH + OH


NH_2 + NO = N_2 + H_2O


Total rate constants


NNH + OH branching ratio

Klippenstein, S. J. (2017). Proceedings of the Combustion Institute, 36(1), 77-111.

Song, S., Hanson, R. K., Bowman, C. T., & Golden, D. M. (2002). The Journal of Physical Chemistry A, 106(40), 9233-9235.

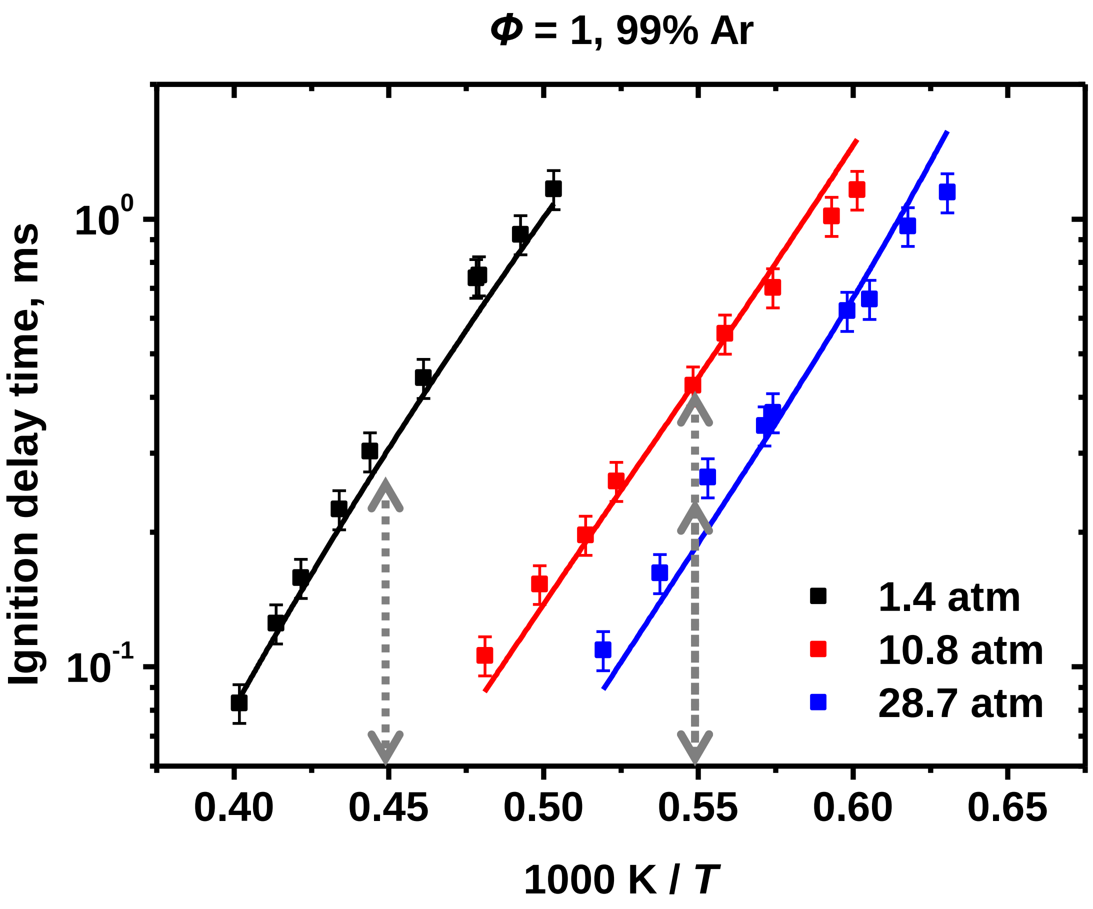
Miller, J. A., & Klippenstein, S. J. (2000). The Journal of Physical Chemistry A, 104(10), 2061-2069.

High-T reaction classes highlighted

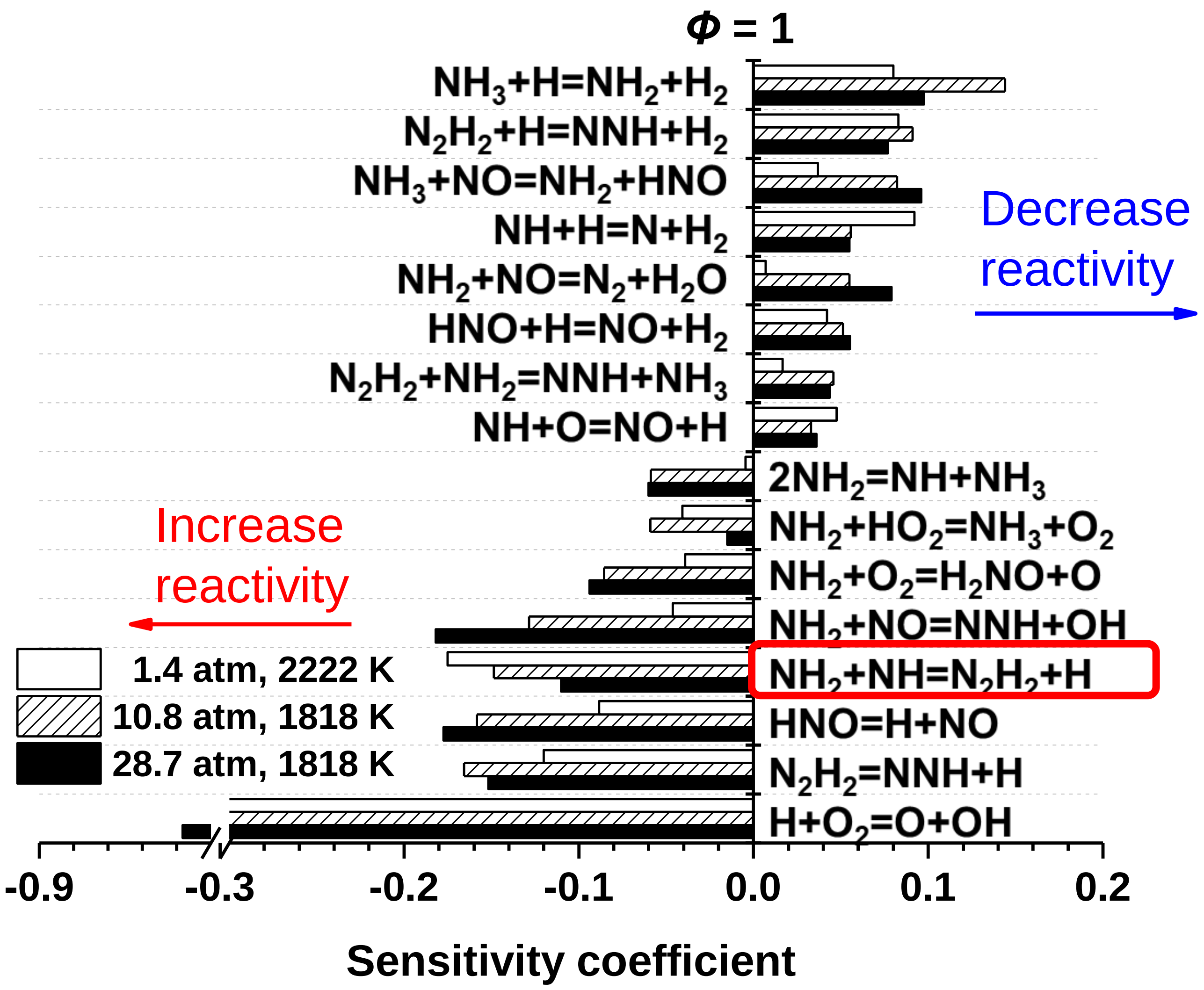
- $NH_3 + M = \dot{N}H_2 + \dot{H} + M$
- $NH_3 + \dot{R} = \dot{N}H_2 + RH = NH + RH = N + RH$
- $\dot{N}H_2 + NO = NNH + \dot{O}H$ / $N_2 + H_2O$
- $\dot{N}H_2 + NH = N_2H_2 + \dot{H}$
- $N_2H_2 (+M) = NNH + \dot{H} (+M)$; $N_2H_2 + \dot{R} = NNH + RH$
- $\dot{N}H_2 + \ddot{O} = HNO + \dot{H}$
- $HNO (+M) = NO + \dot{H} (+M)$; $HNO + \dot{R} = NO + RH$
- $\dot{N}H_2 + O_2 = H_2NO + \ddot{O}$ / $HNO + \dot{O}H$
- $H_2NO + \dot{R} = HNO + RH$

High-temperature chemistry

➢ NH_3 IDT sensitivity analyses

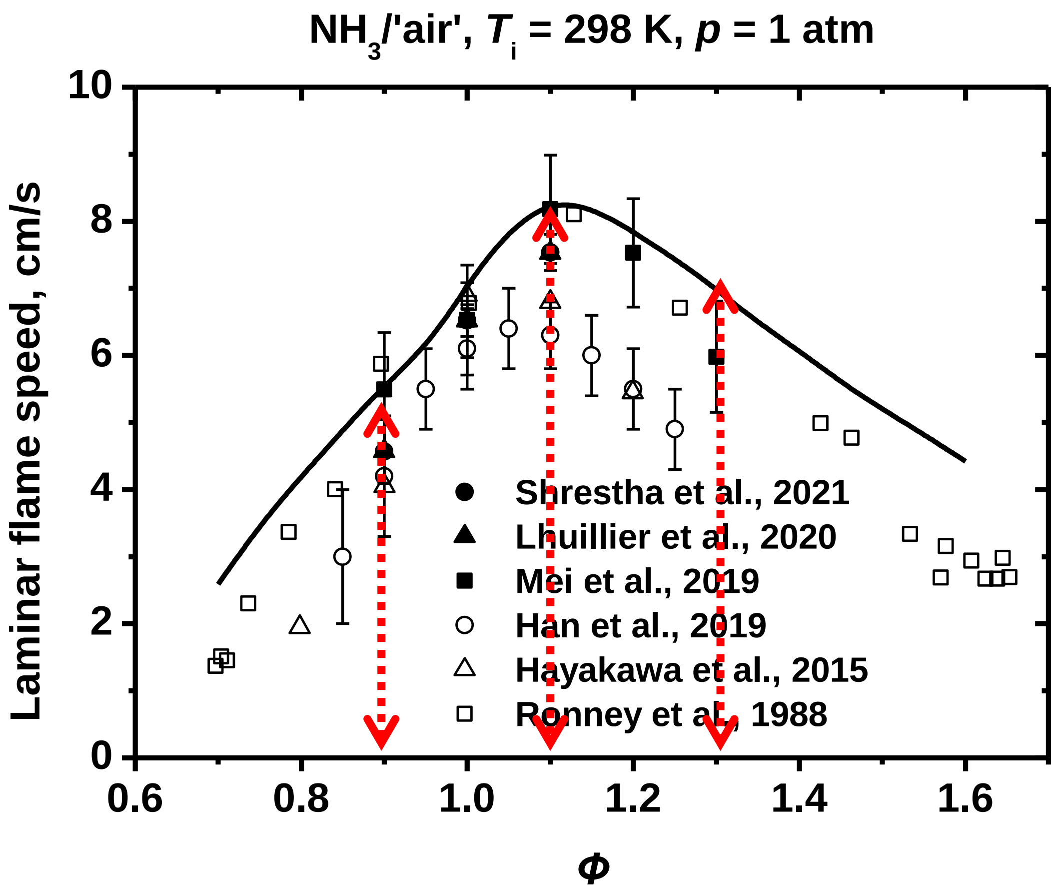


Shock tube ignition delay times
(Expt.: Mathieu 2015, CNF)

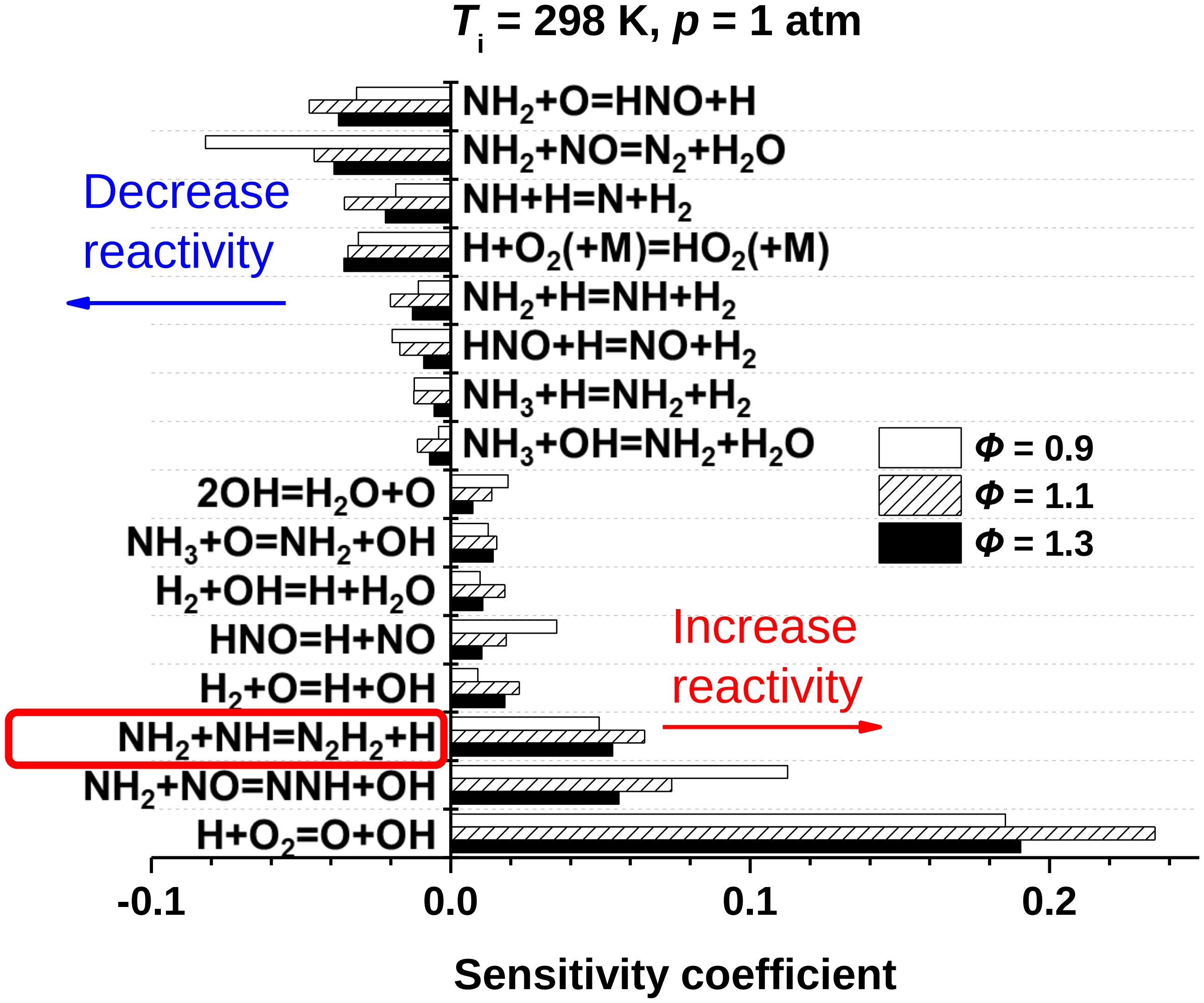


High-temperature chemistry

➢ NH_3 flame speed sensitivity analyses



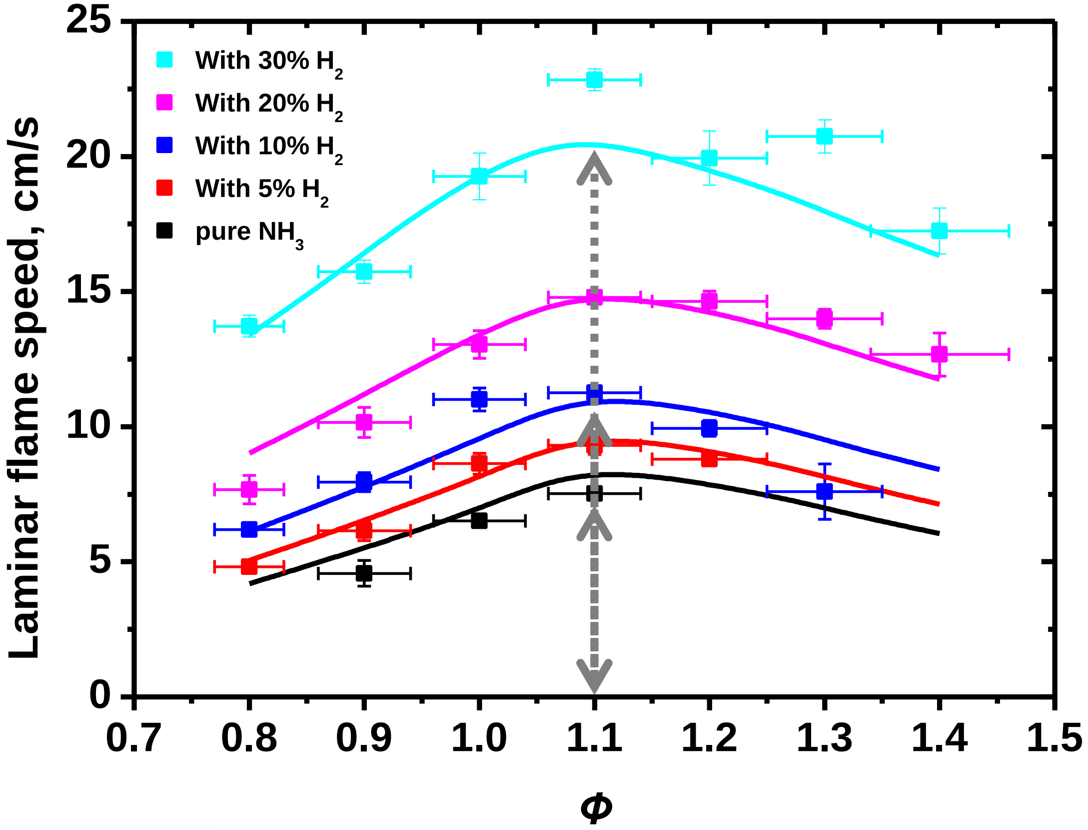
(Expt.: cf. legend)



High-temperature chemistry

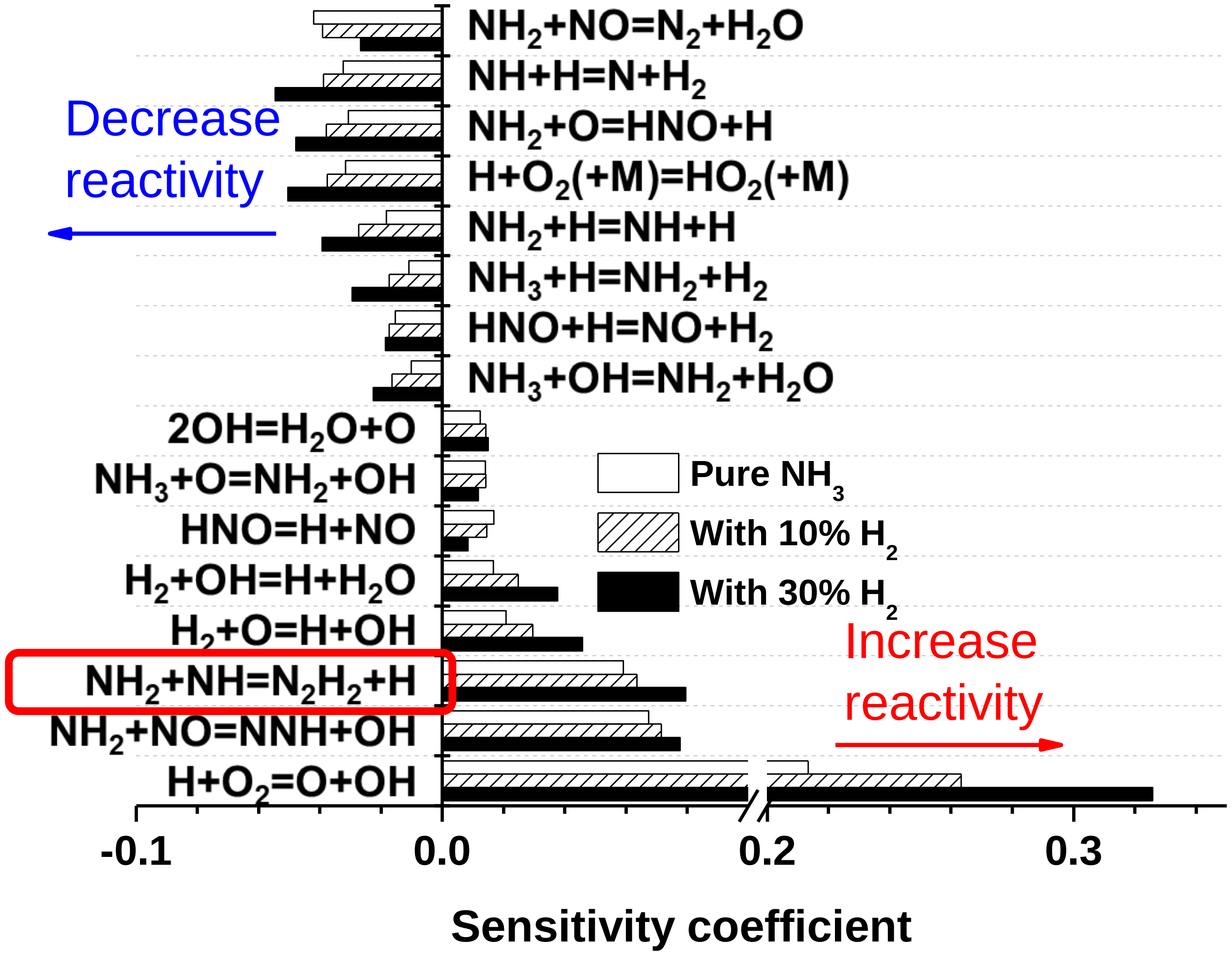
➢ NH_3/H_2 flame speed sensitivity analyses

$NH_3/H_2/'air'$, T_i = 298 K, p = 1 atm



(Expt.: Lhuillier 2020, Fuel)

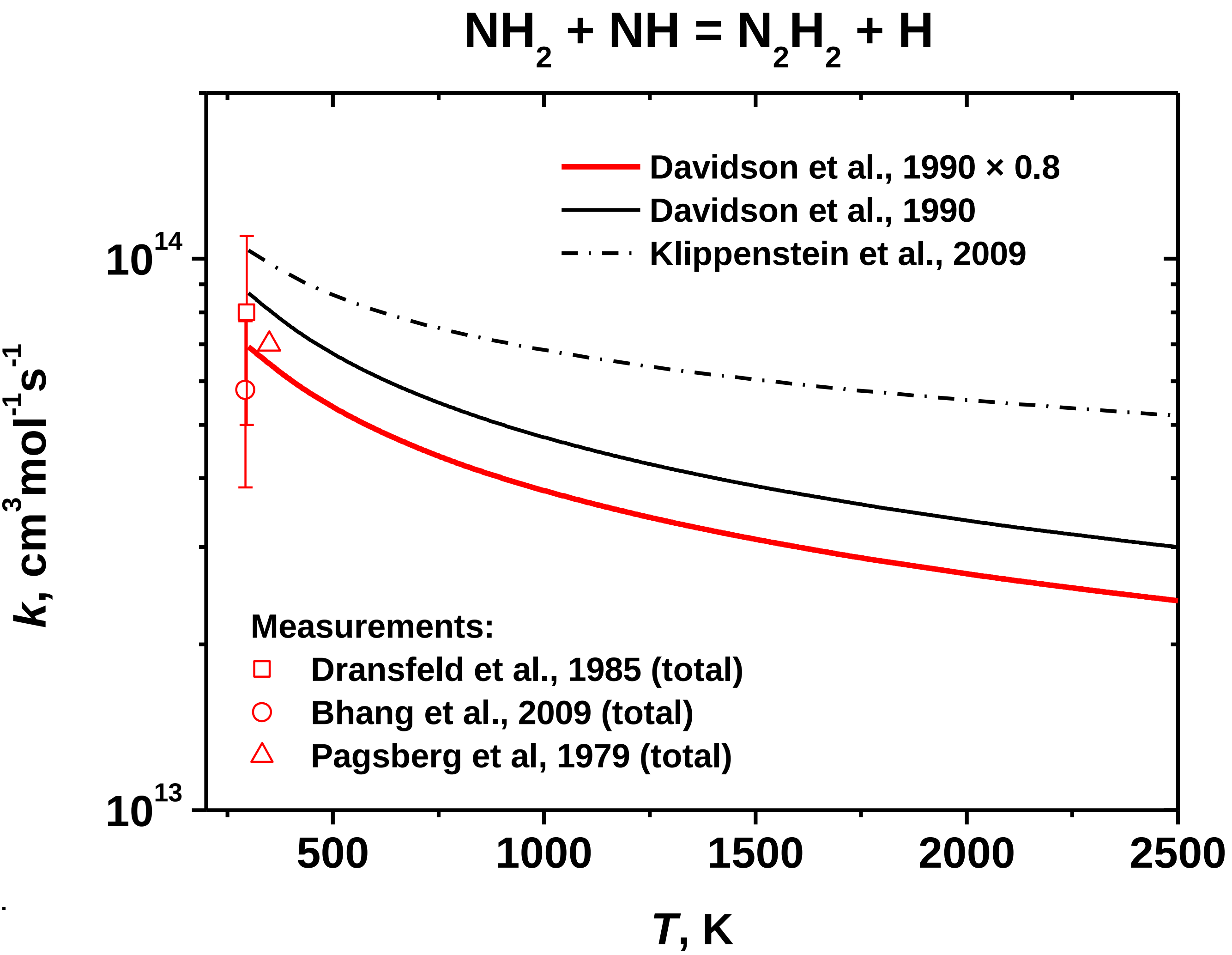
Φ = 1.1, T_i = 298 K, p = 1 atm



$\dot{N}H_2 + NH = N_2H_2 + \dot{H}$

➢ Rate constants

- $= N_2H_2 + \dot{H}$
- Minor products:
- $= N + NH_3$
- $= \dot{N}_2H_3$

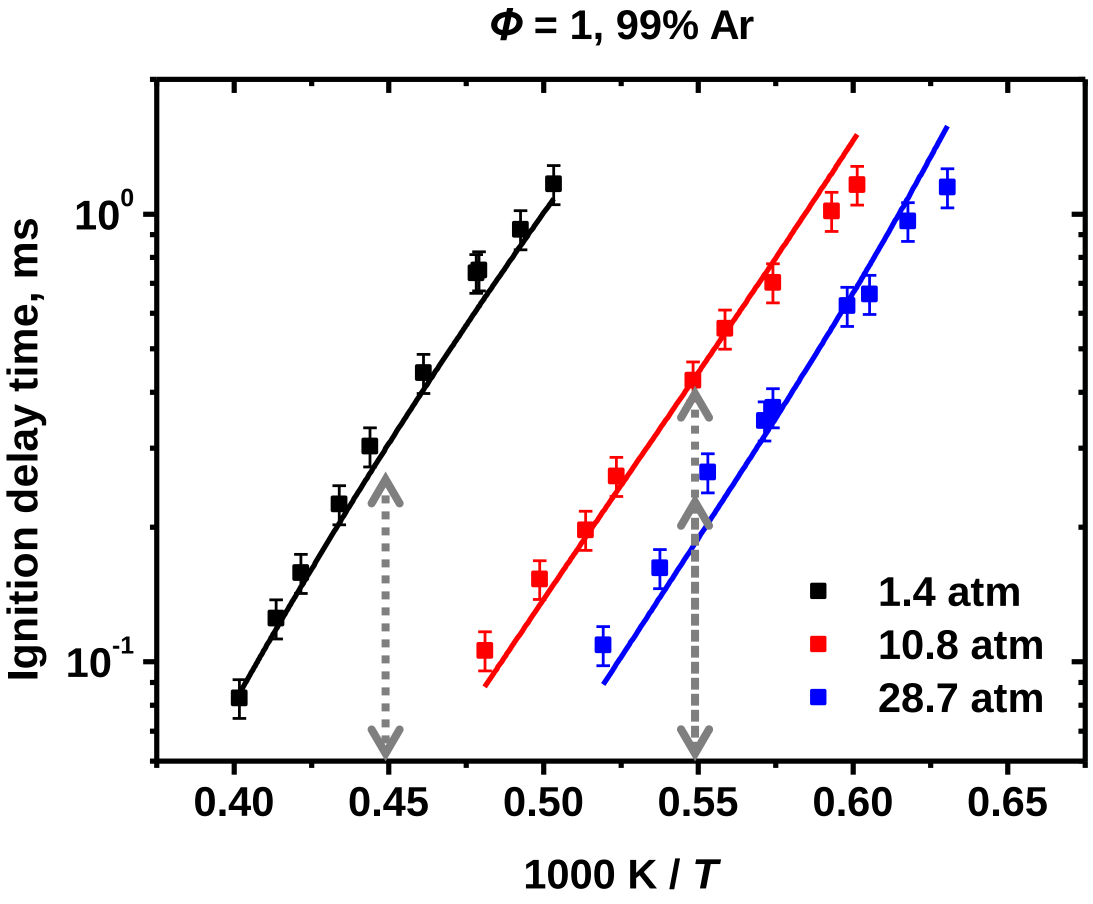


Davidson, D. F., Kohse-Höinghaus, K., Chang, A. Y., & Hanson, R. K. (1990). International journal of chemical kinetics, 22(5), 513-535.

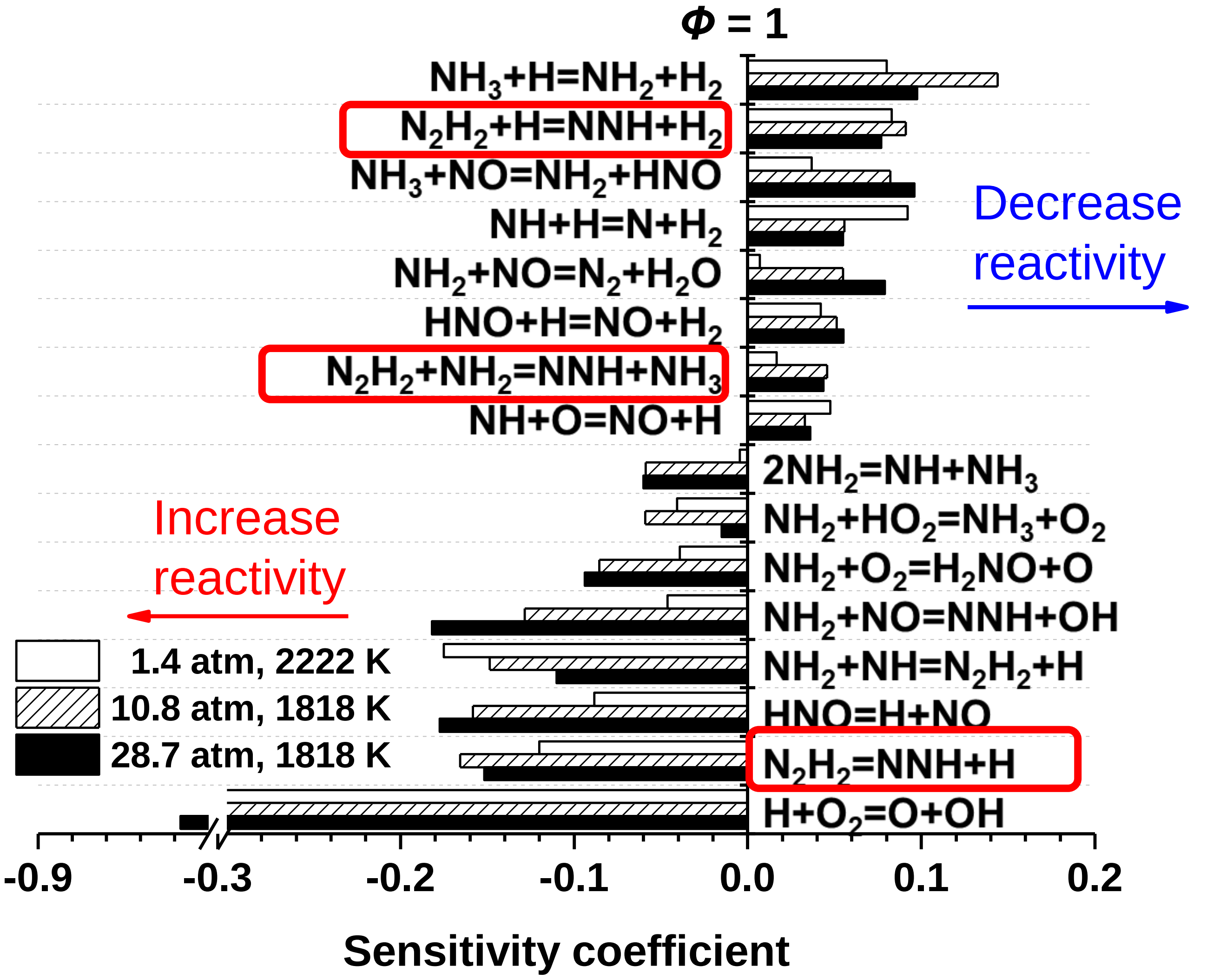
Klippenstein, S. J., et al. (2009). The Journal of Physical Chemistry A, 113(38), 10241-10259.

High-temperature chemistry

➢ NH_3 IDT sensitivity analyses

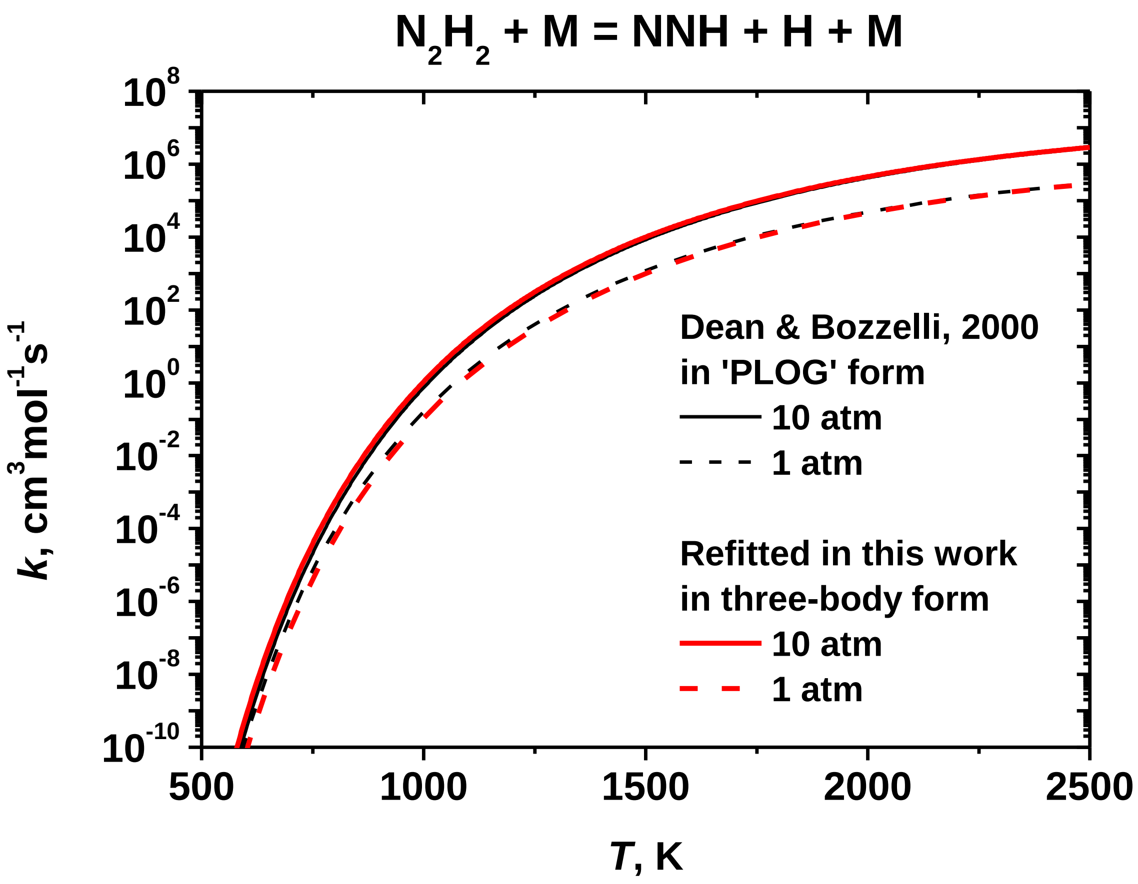


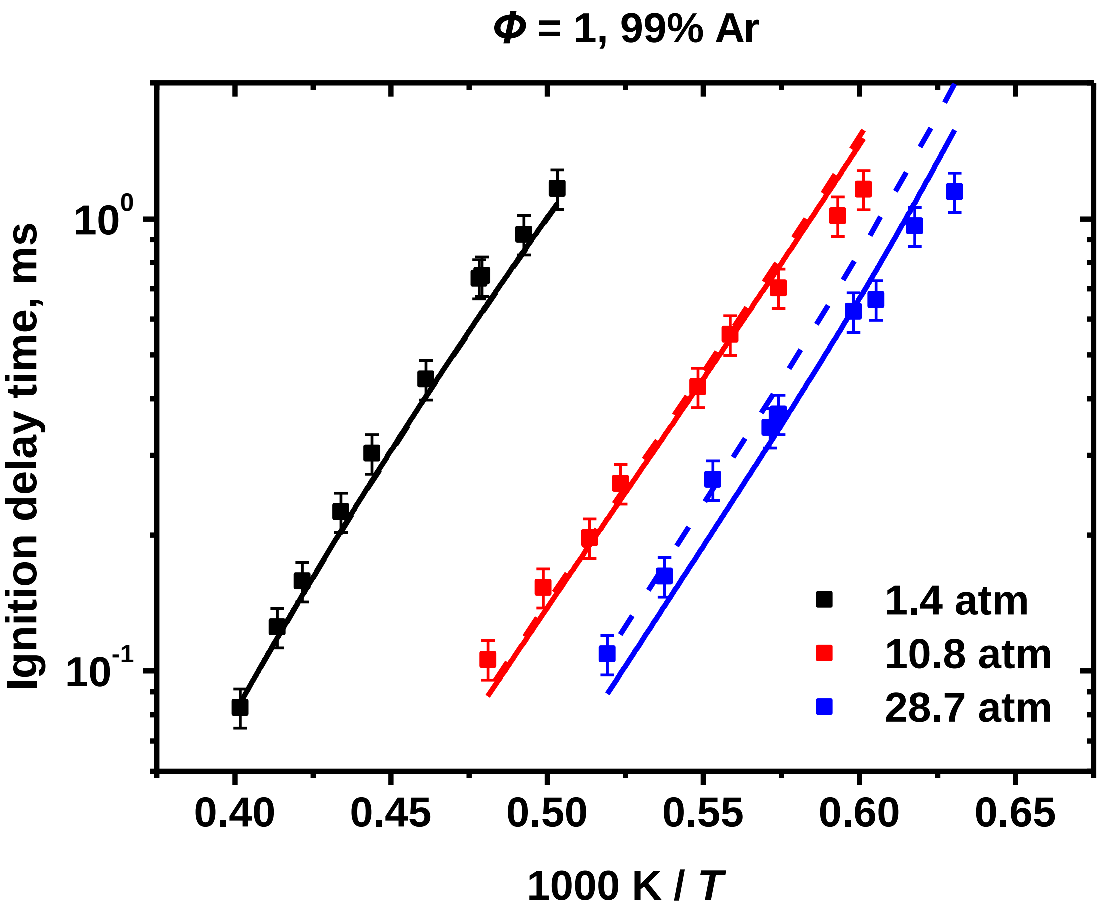
Shock tube ignition delay times
(Expt.: Mathieu 2015, CNF)



$N_2H_2 + M = NNH + \dot{H}$

➢ Rate constants





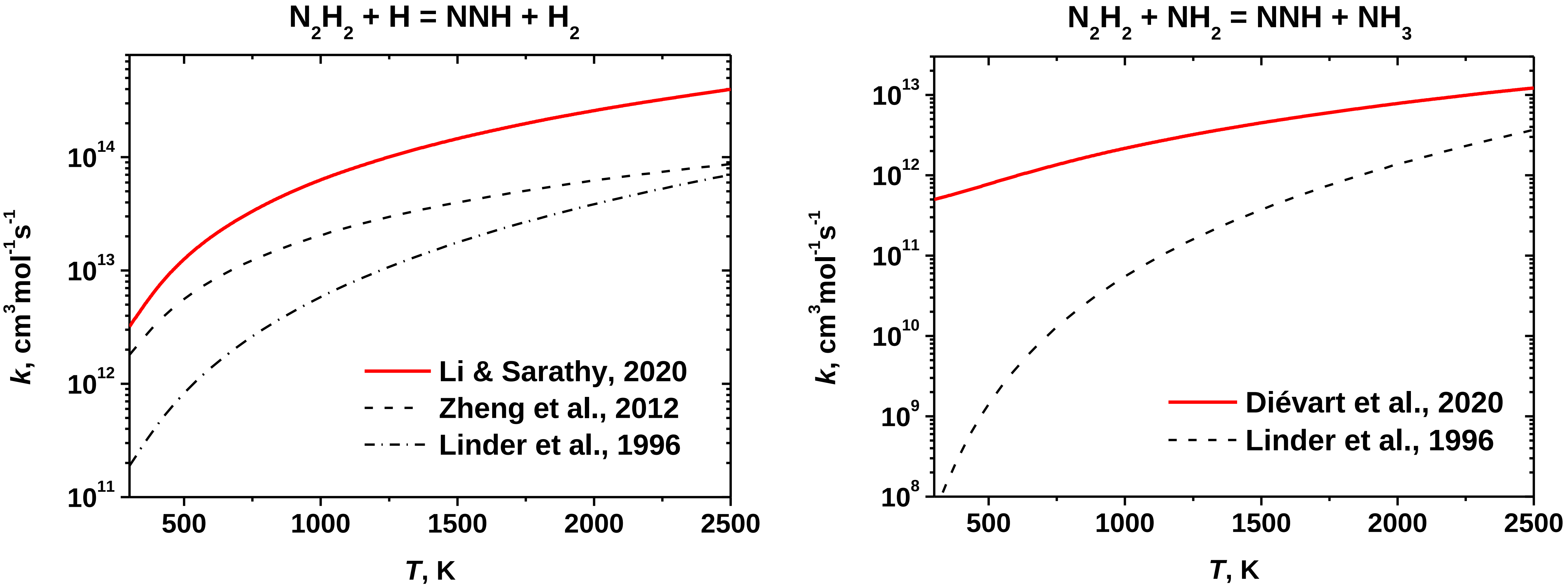
—— : Three-body rates allowed for pressures above 10 atm

– – – : PLOG rates defined up to 10 atm

Dean, A. M., & Bozzelli, J. W. (2000). Combustion chemistry of nitrogen. In Gas-phase combustion chemistry (pp. 125-341). Springer, New York, NY.

$N_2H_2 + \dot{R} = NNH + RH$

➢ Rate constants



Li, Y., & Sarathy, S. M. (2020). International Journal of Hydrogen Energy, 45(43), 23624-23637.

Zheng, J., et al. (2012). The Journal of Chemical Physics, 136(18), 184310.

Diévart, P., & Catoire, L. (2020). The Journal of Physical Chemistry A, 124(30), 6214-6236.

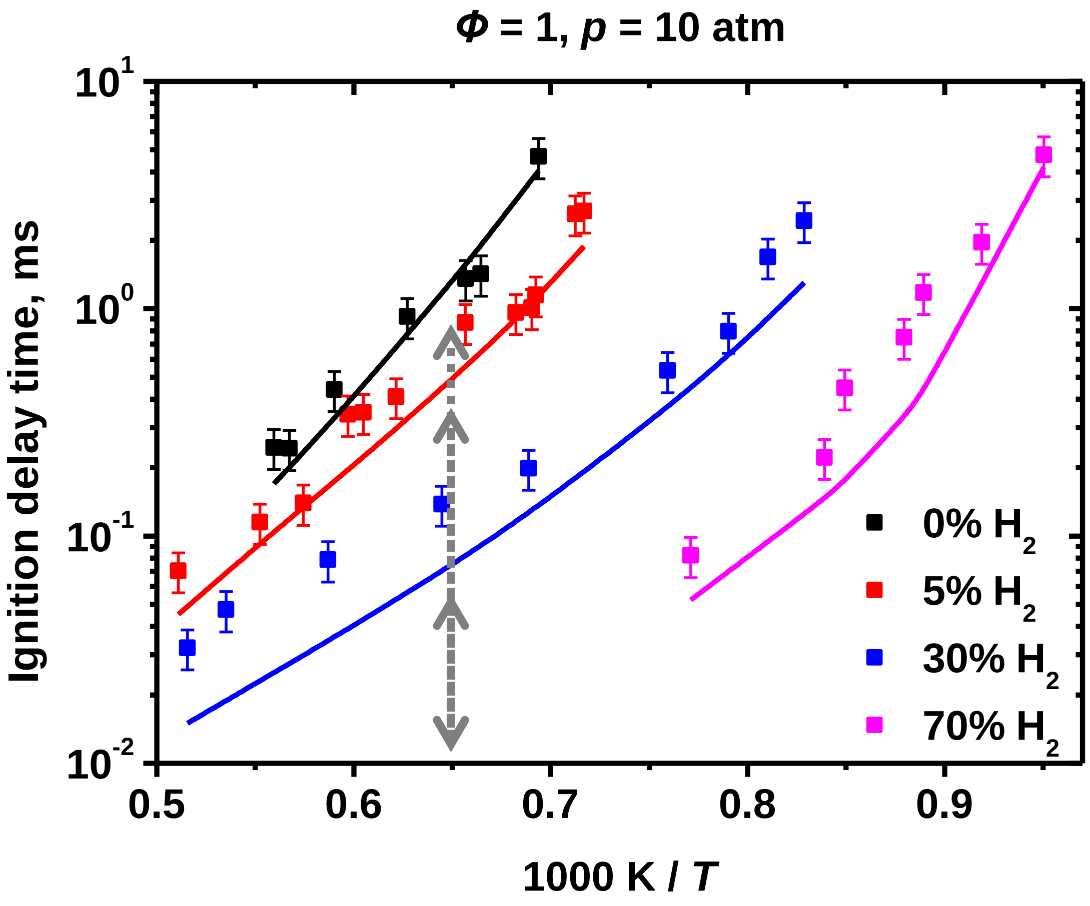
Linder, D. P., Duan, X., & Page, M. (1996). The Journal of chemical physics, 104(16), 6298-6307.

High-T reaction classes highlighted

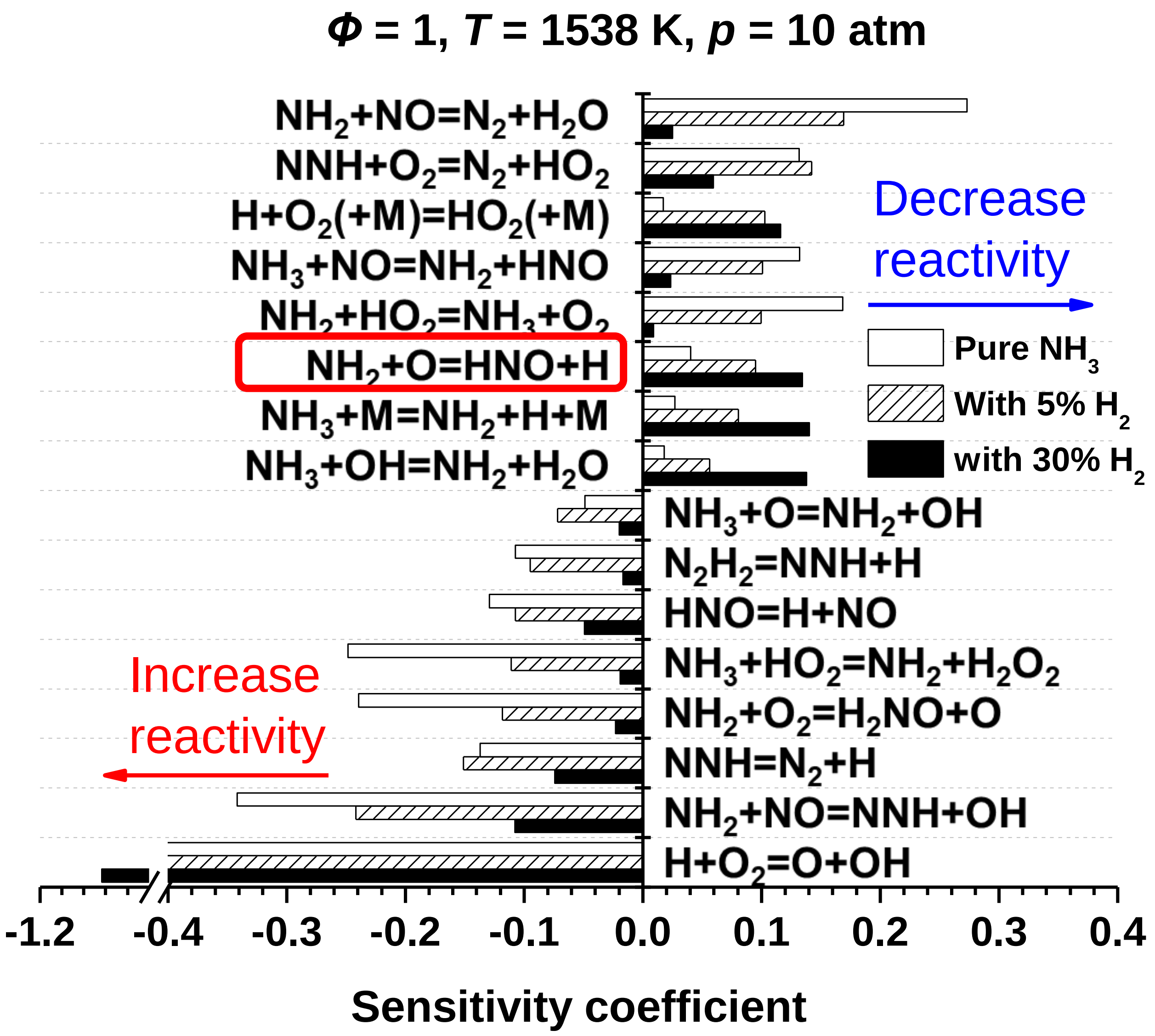
- $NH_3 + M = \dot{N}H_2 + \dot{H} + M$
- $NH_3 + \dot{R} = \dot{N}H_2 + RH = NH + RH = N + RH$
- $\dot{N}H_2 + NO = NNH + \dot{O}H\ /\ N_2 + H_2O$
- $\dot{N}H_2 + NH = N_2H_2 + \dot{H}$
- $N_2H_2\ (+M) = NNH + \dot{H}\ (+M);\ N_2H_2 + \dot{R} = NNH + RH$
- $\dot{N}H_2 + \ddot{O} = HNO + \dot{H}$
- $HNO\ (+M) = NO + \dot{H}\ (+M);\ HNO + \dot{R} = NO + RH$
- $\dot{N}H_2 + O_2 = H_2NO + \ddot{O}\ /\ HNO + \dot{O}H$
- $H_2NO + \dot{R} = HNO + RH$

High-temperature chemistry

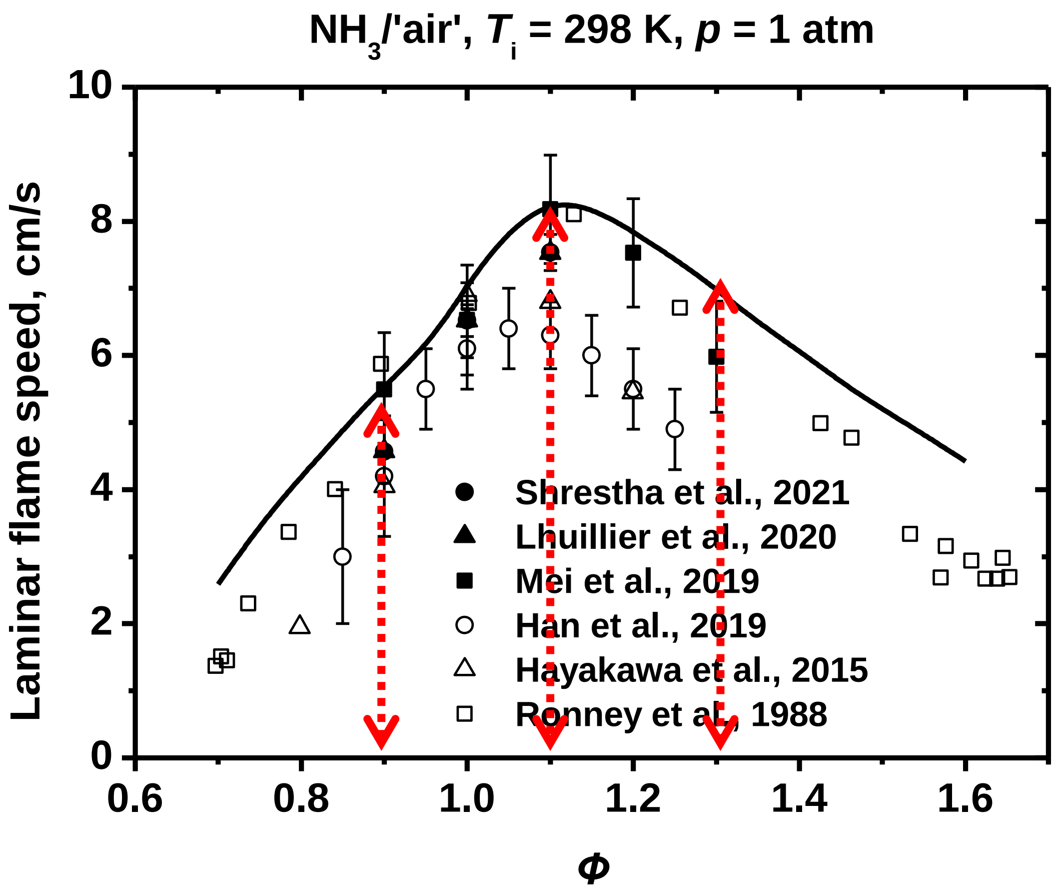
➢ NH_3/H_2 IDT sensitivity analyses



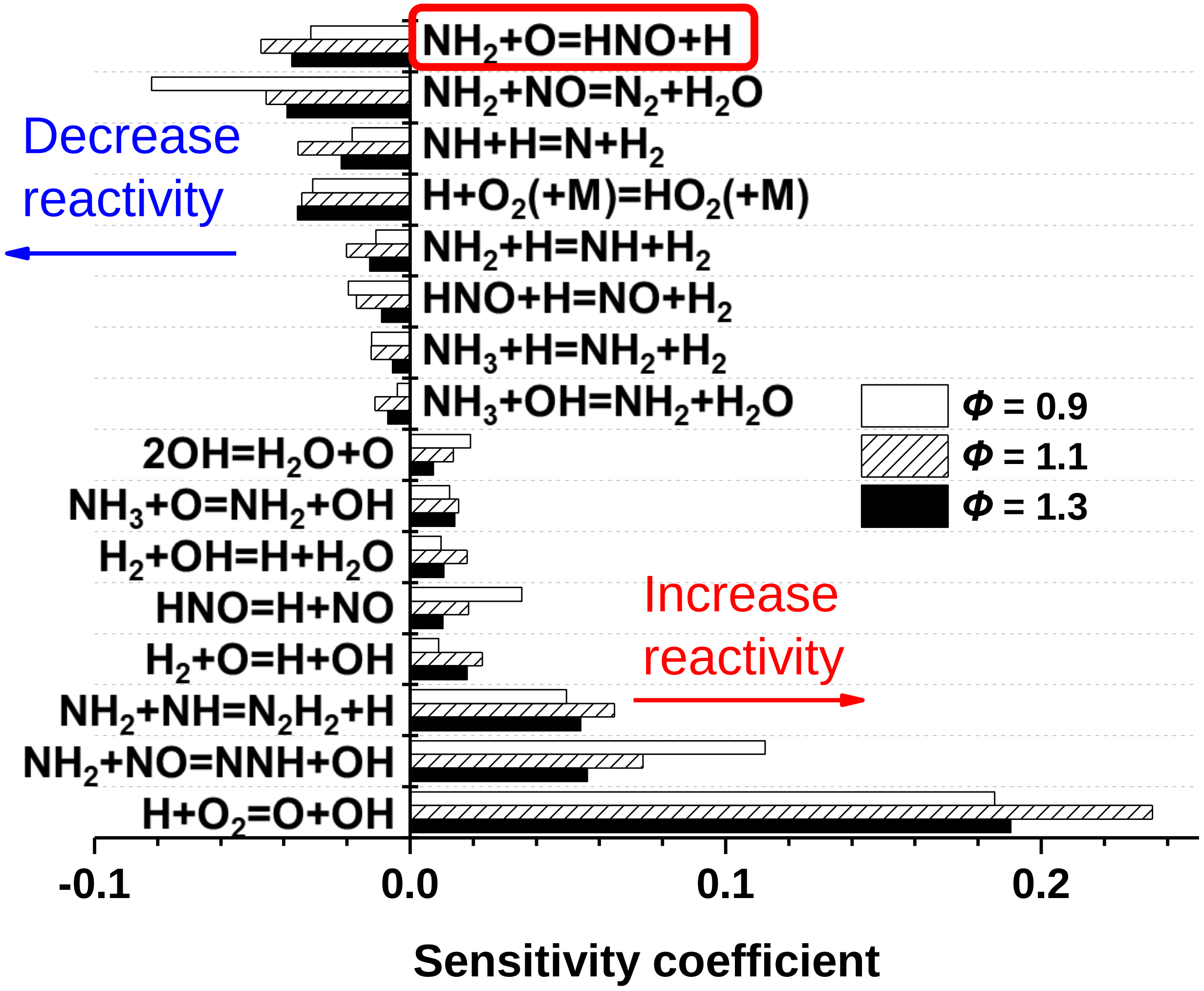
Shock tube ignition delay times
(Expt.: Chen 2021, Fuel)



➢ NH_3 flame speed sensitivity analyses

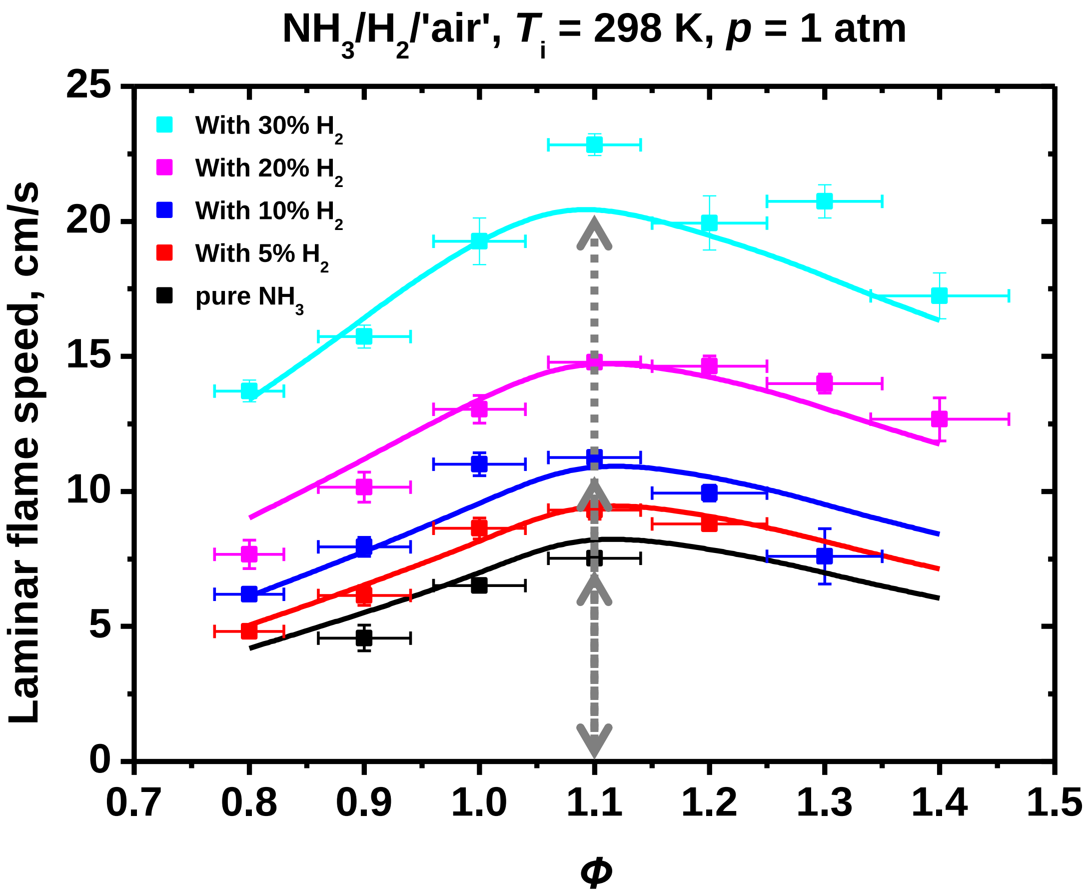

NH_3/'air', T_i = 298 K, p = 1 atm

(Expt.: cf. legend)

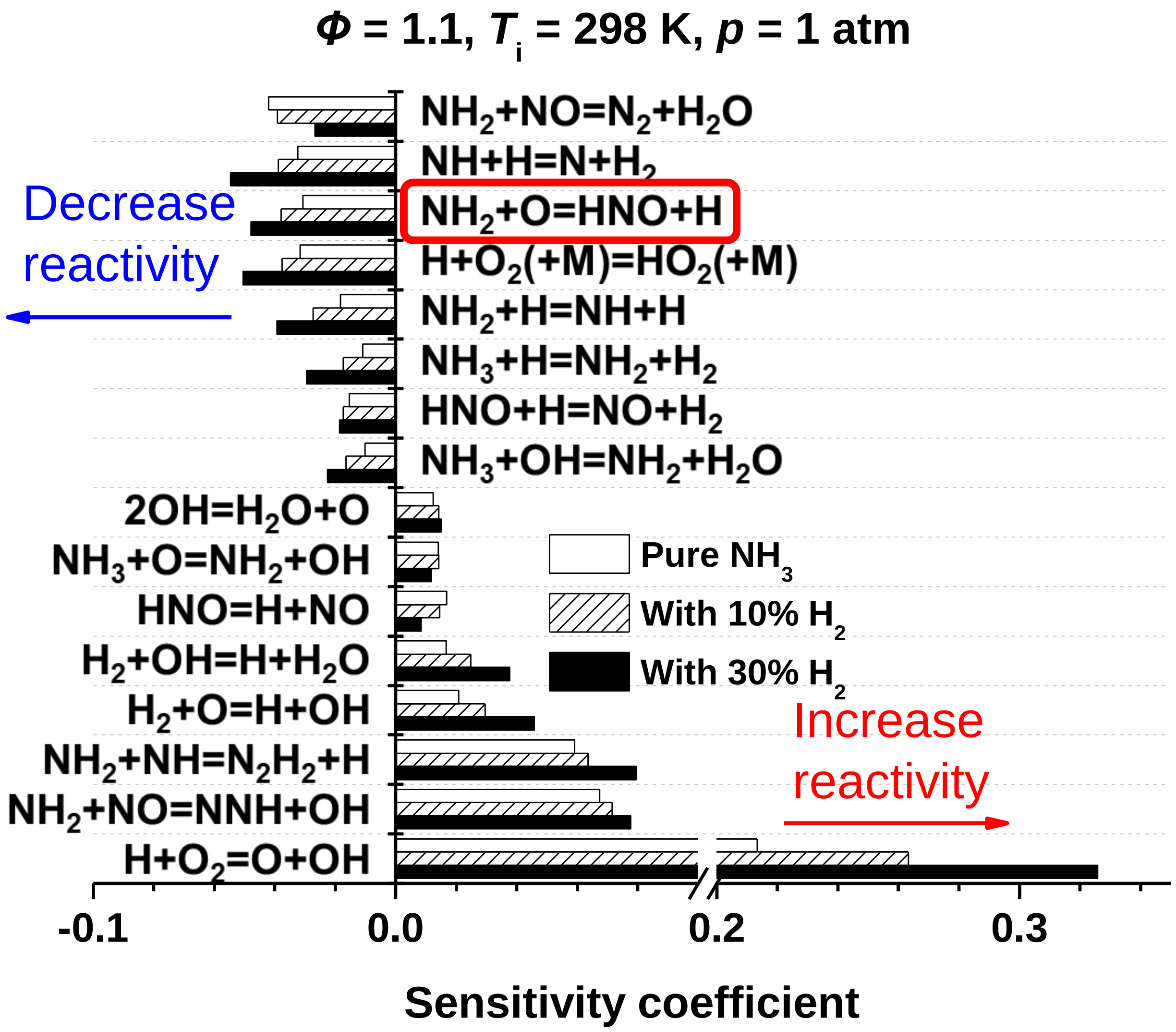

T_i = 298 K, p = 1 atm

High-temperature chemistry

➢ NH_3/H_2 flame speed sensitivity analyses



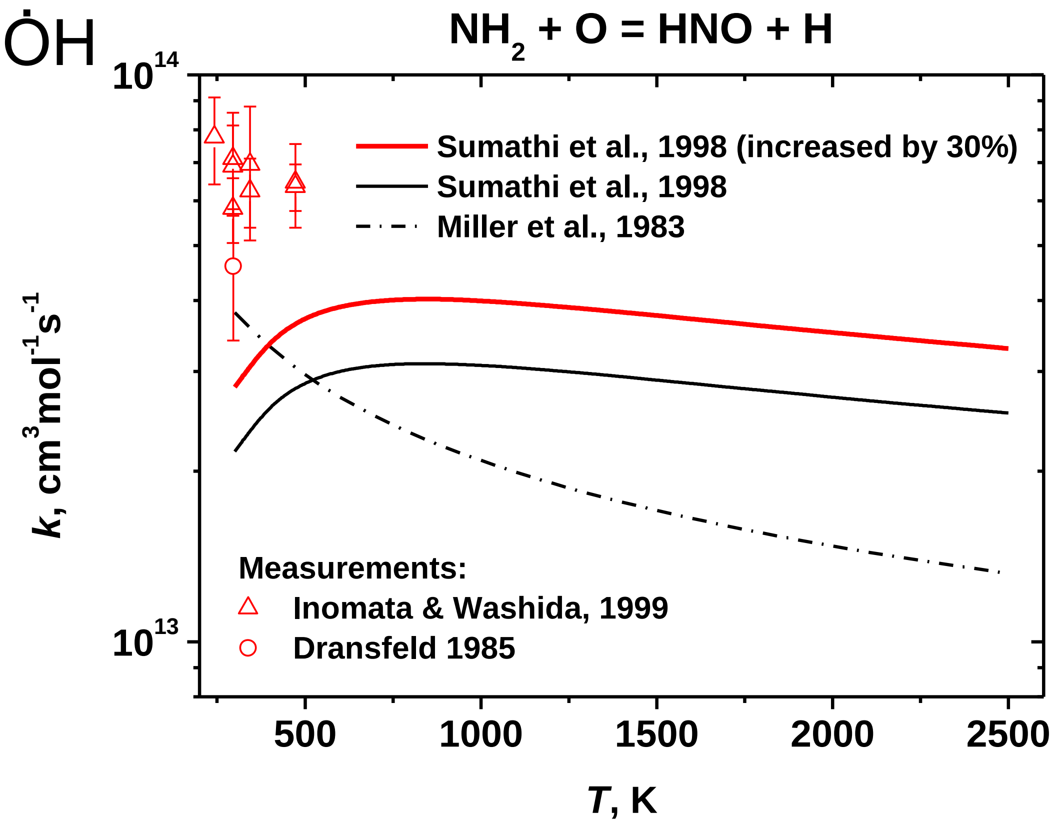
(Expt.: Lhuillier 2020, Fuel)

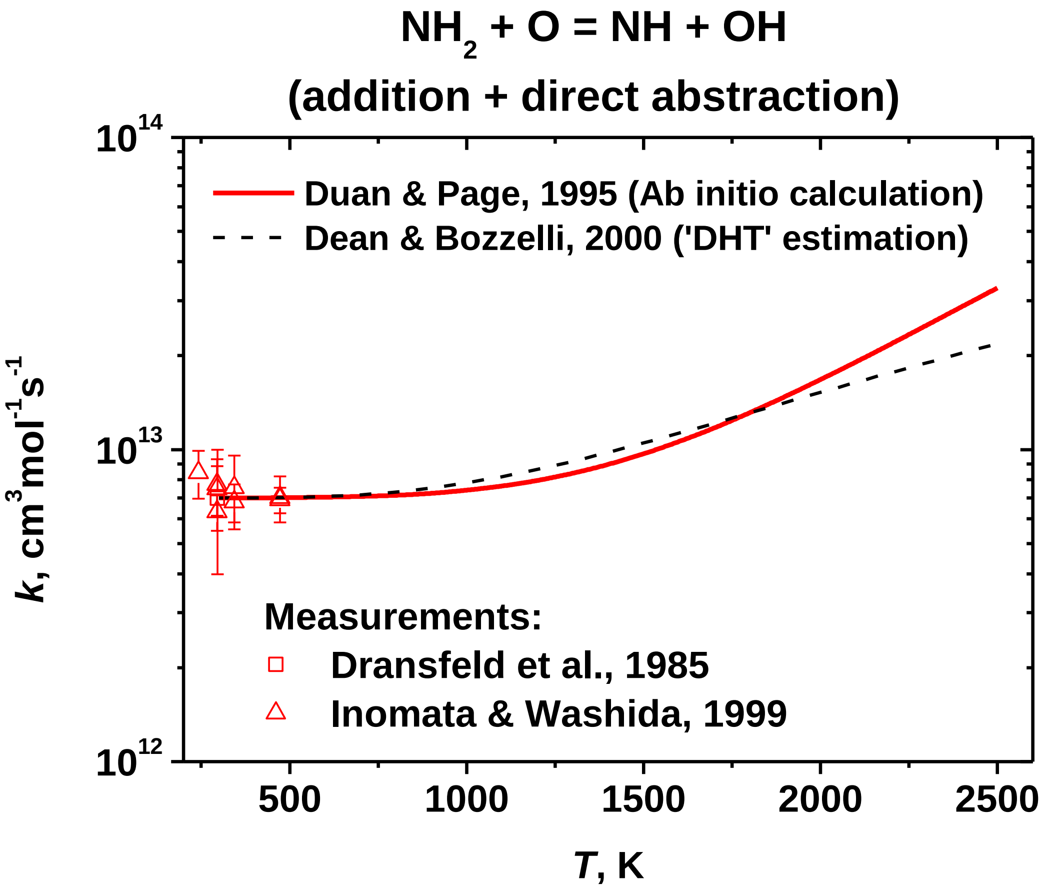


$\dot{N}H_2 + \ddot{O}$ reaction system

➢ Rate constants

- = HNO + $\dot{H}$
- = NH + $\dot{O}H$


$NH_2 + O = HNO + H$


$NH_2 + O = NH + OH$

(addition + direct abstraction)

Duan, X., & Page, M. (1995). The Journal of chemical physics, 102(15), 6121-6127.

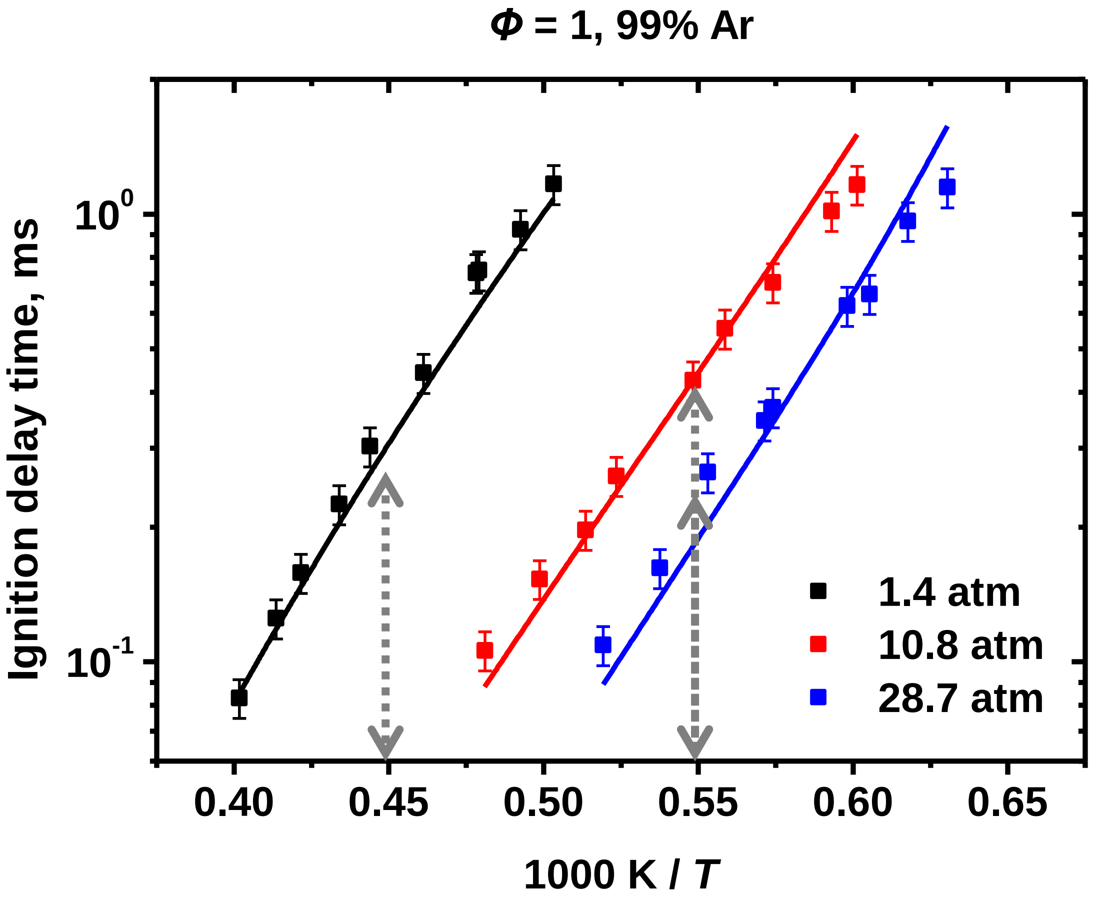
Dean, A. M., & Bozzelli, J. W. (2000). Combustion chemistry of nitrogen. In Gas-phase combustion chemistry (pp. 125-341). Springer, New York, NY.

Sumathi, R., Sengupta, D., & Nguyen, M. T. (1998). The Journal of Physical Chemistry A, 102(18), 3175-3183.

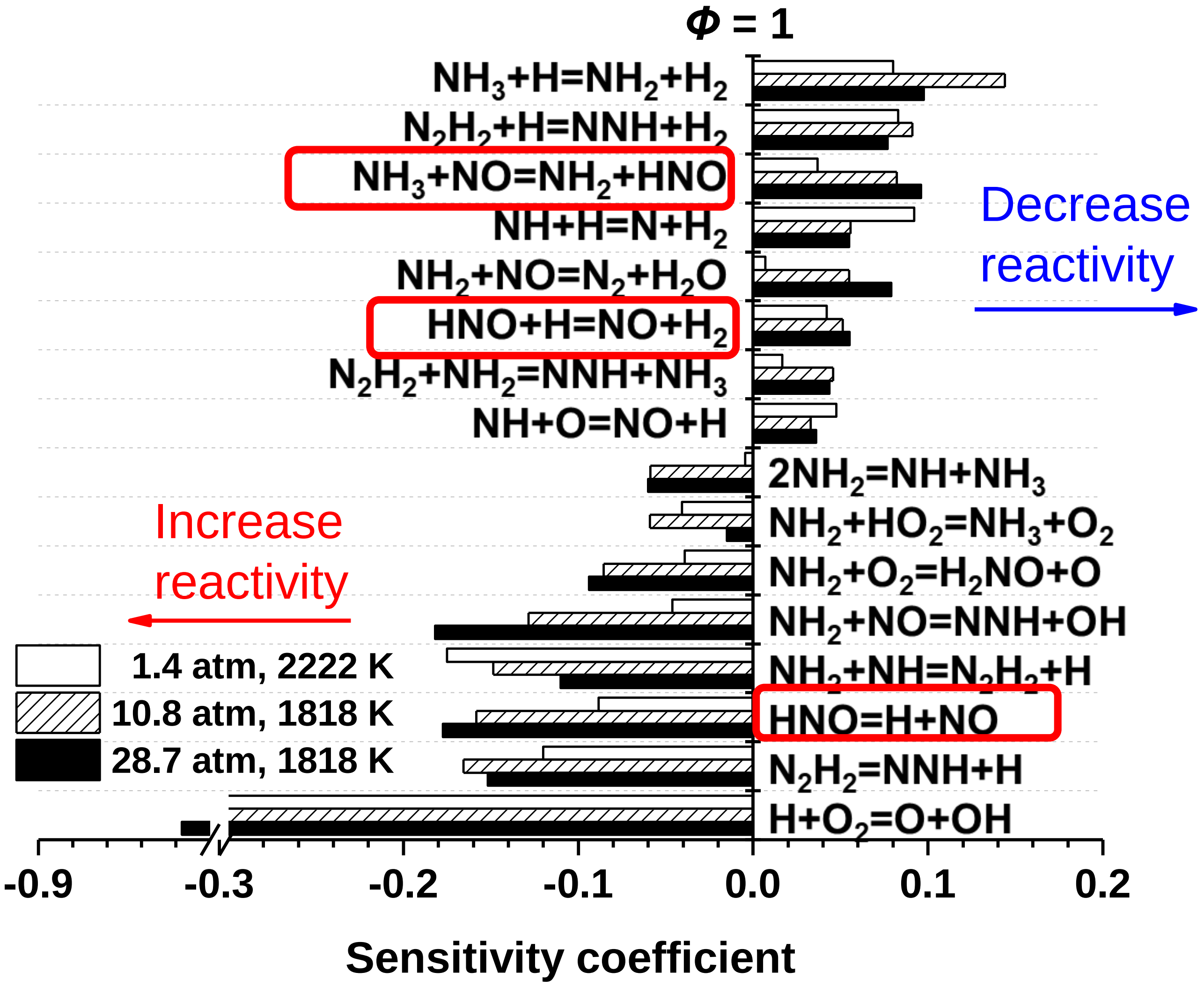
Miller, J. A., Smooke, M. D., Green, R. M., & Kee, R. J. (1983). Combustion Science and Technology, 34(1-6), 149-176.

High-temperature chemistry

- NH_3 IDT sensitivity analyses

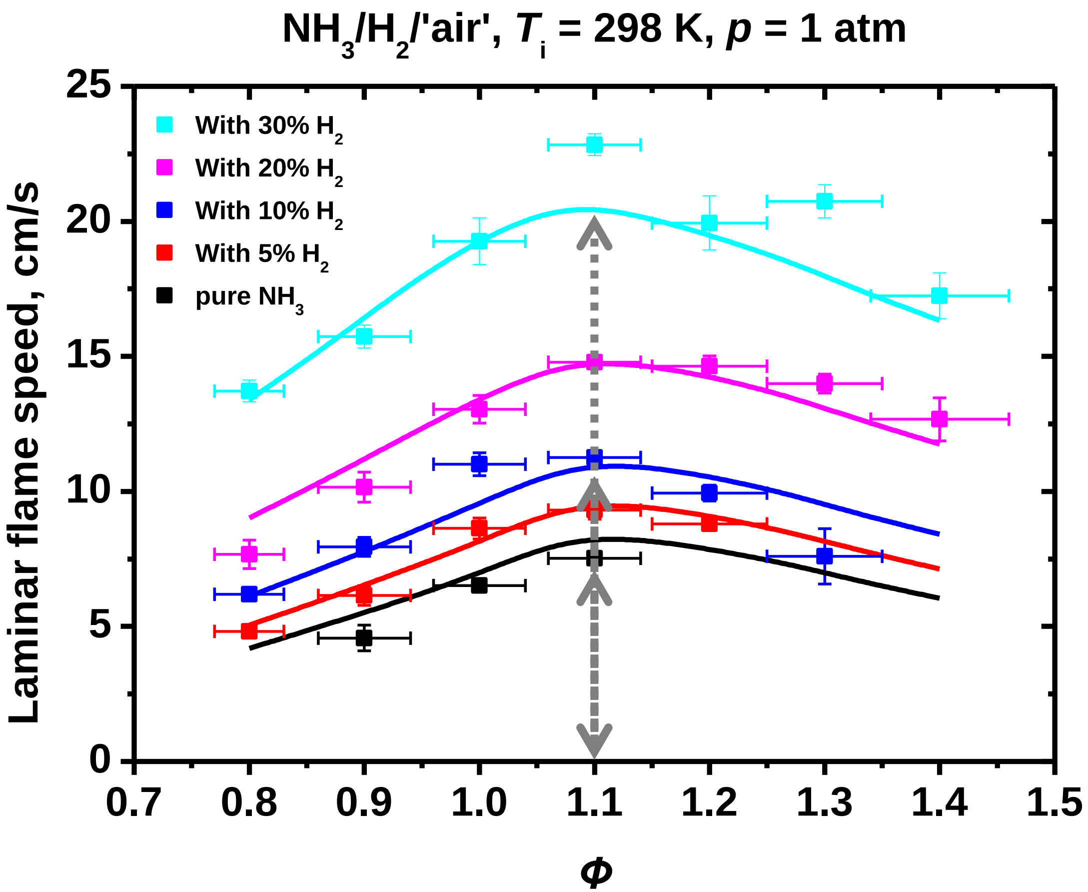


Shock tube ignition delay times
(Expt.: Mathieu 2015, CNF)

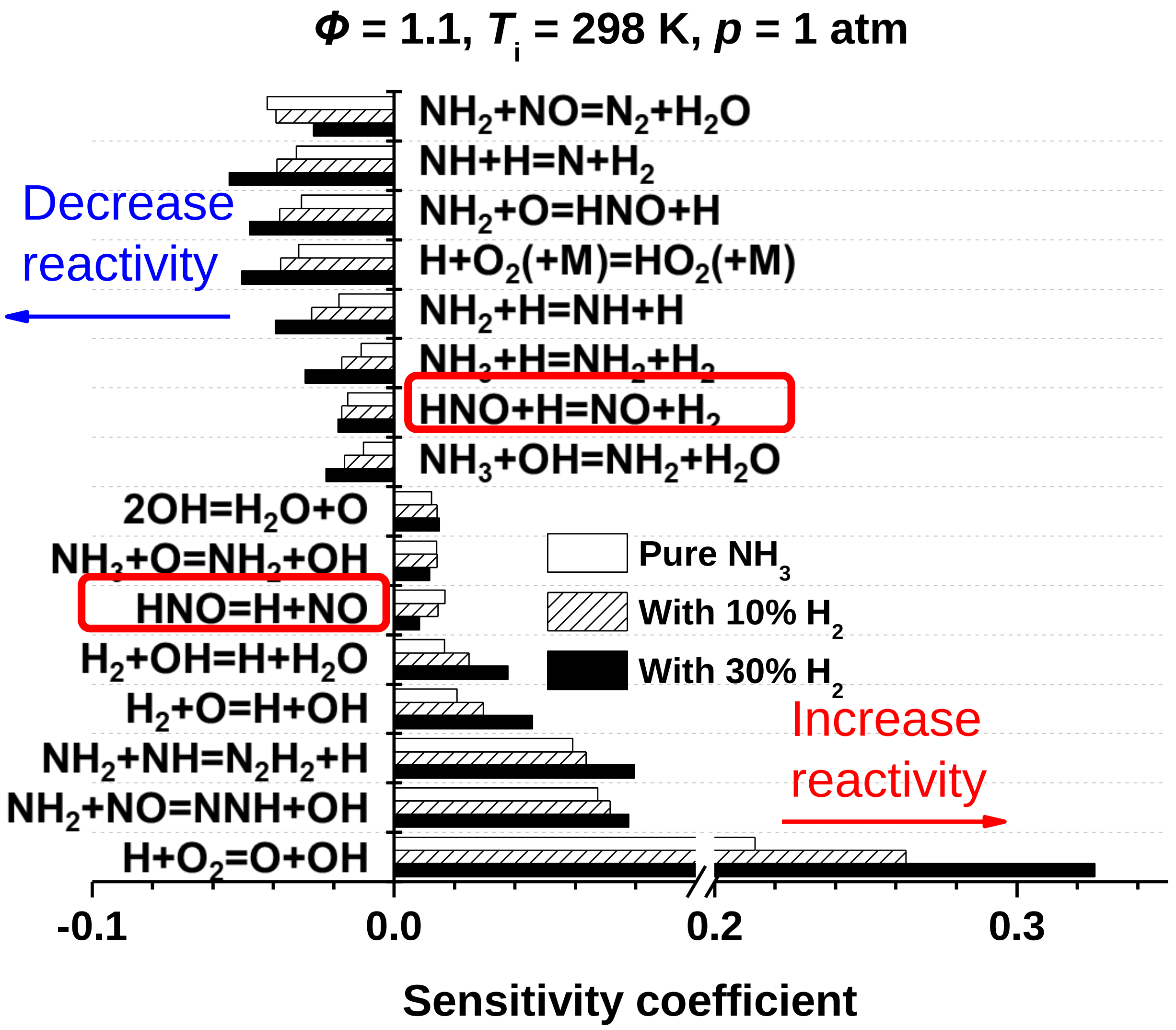


High-temperature chemistry

➢ NH_3/H_2 flame speed sensitivity analyses

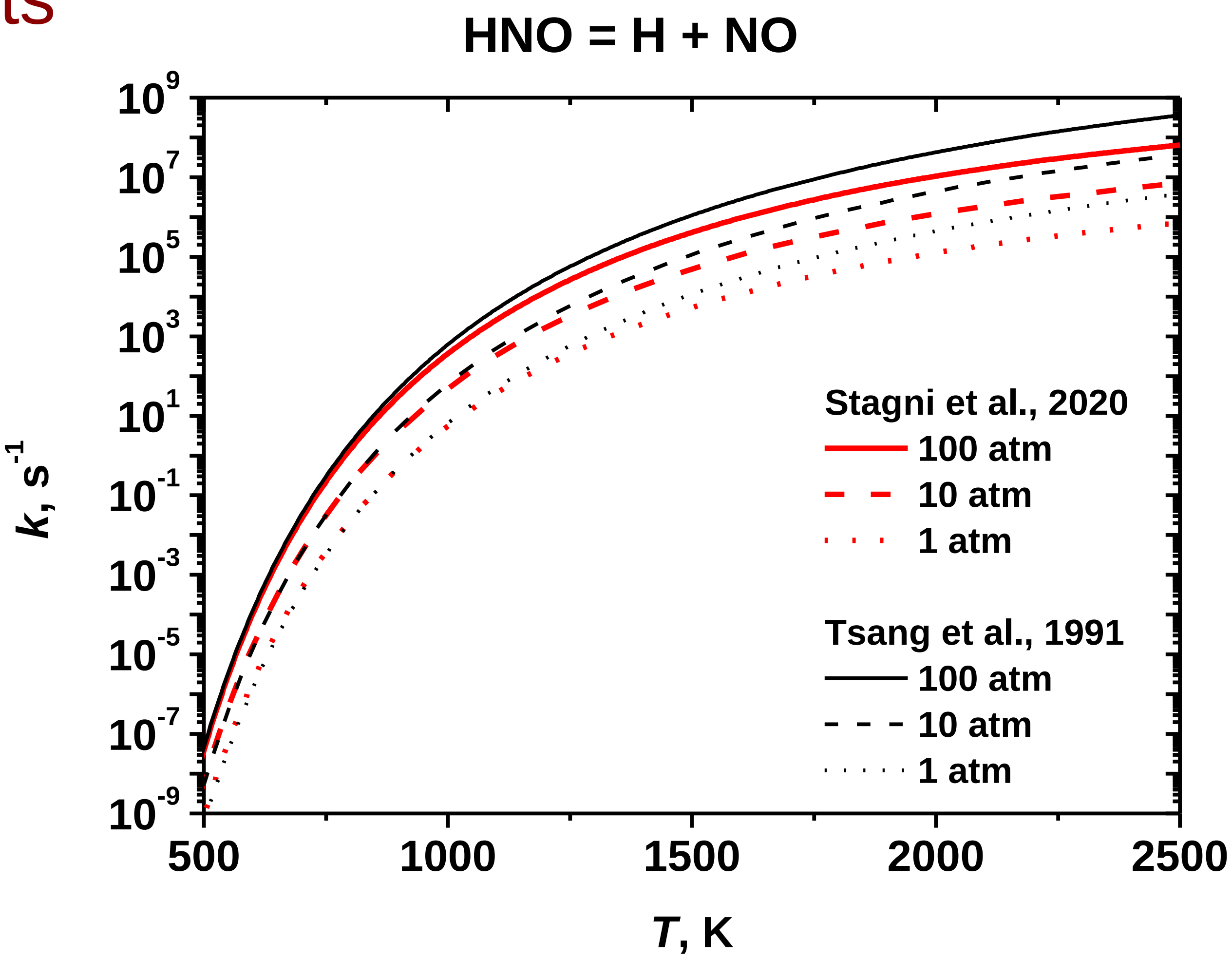


(Expt.: Lhuillier 2020, Fuel)



HNO = Ḣ + NO

- Rate constants



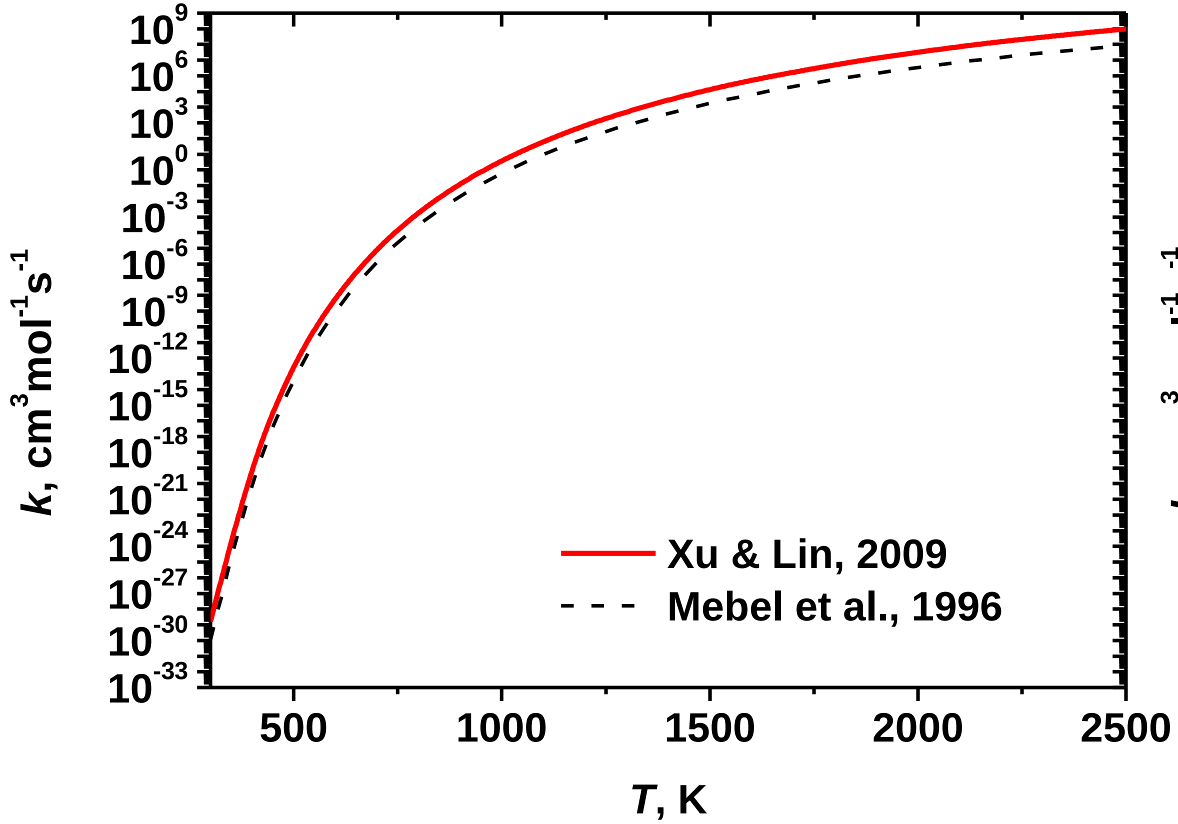
Stagni, A., et al. (2020). Reaction Chemistry & Engineering, 5(4), 696-711.

Tsang, W. (1991). Journal of Physical and Chemical Reference Data, 20(2), 221-273.

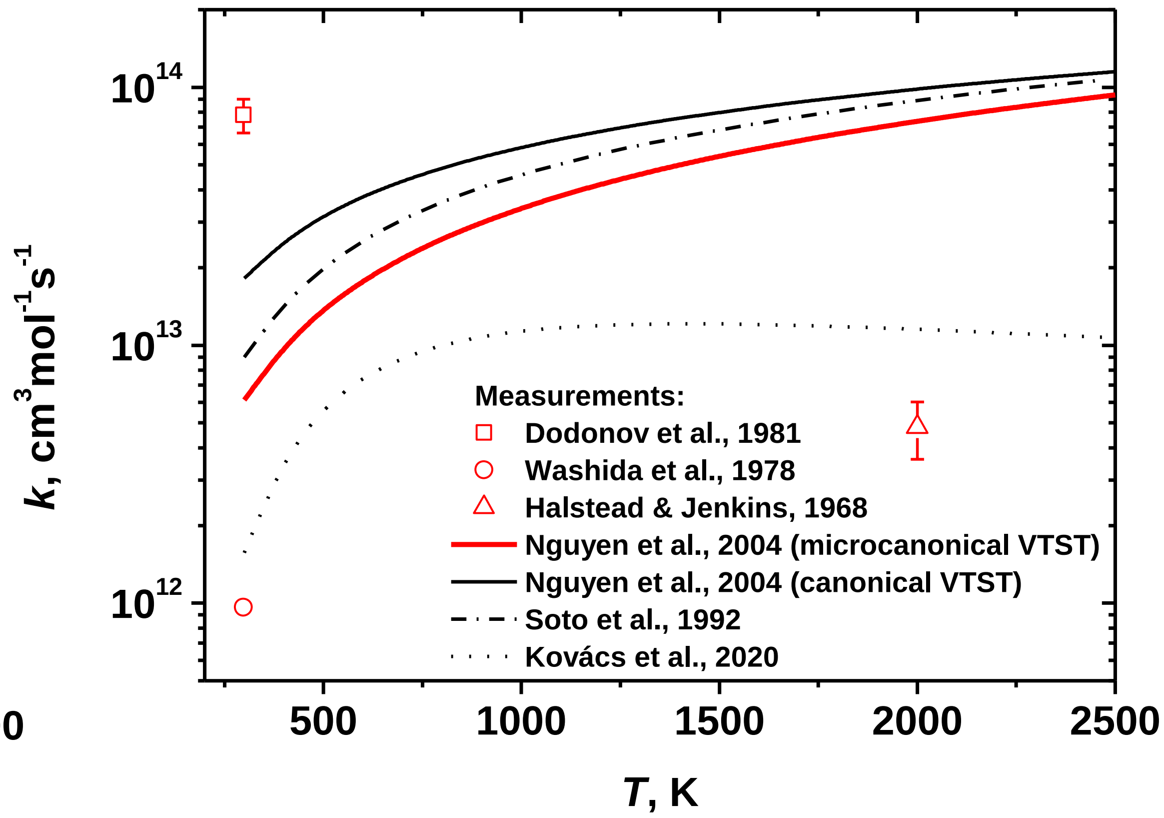
Riley, P. S., Cosic, B., & Fontijn, A. (2003). International journal of chemical kinetics, 35(8), 374-380.

HNO + Ṙ = NO + RH

Rate constants



$NH_3 + NO = HNO + NH_2$



$HNO + H = NO + H_2$

Xu, S., & Lin, M. C. (2009). International Journal of Chemical Kinetics, 41(11), 667-677.

Mebel, A. M., Diau, E. W. G., Lin, M. C., & Morokuma, K. (1996). The Journal of Physical Chemistry, 100(18), 7517-7525.

Nguyen, H. M. T., et al. (2004). Chemical physics letters, 388(1-3), 94-99.

Soto, M. R., & Page, M. (1992). The Journal of chemical physics, 97(10), 7287-7296.

Kovács, M., Papp, M., Zsély, I. G., & Turányi, T. (2020). Fuel, 264, 116720.

High-T reaction classes highlighted

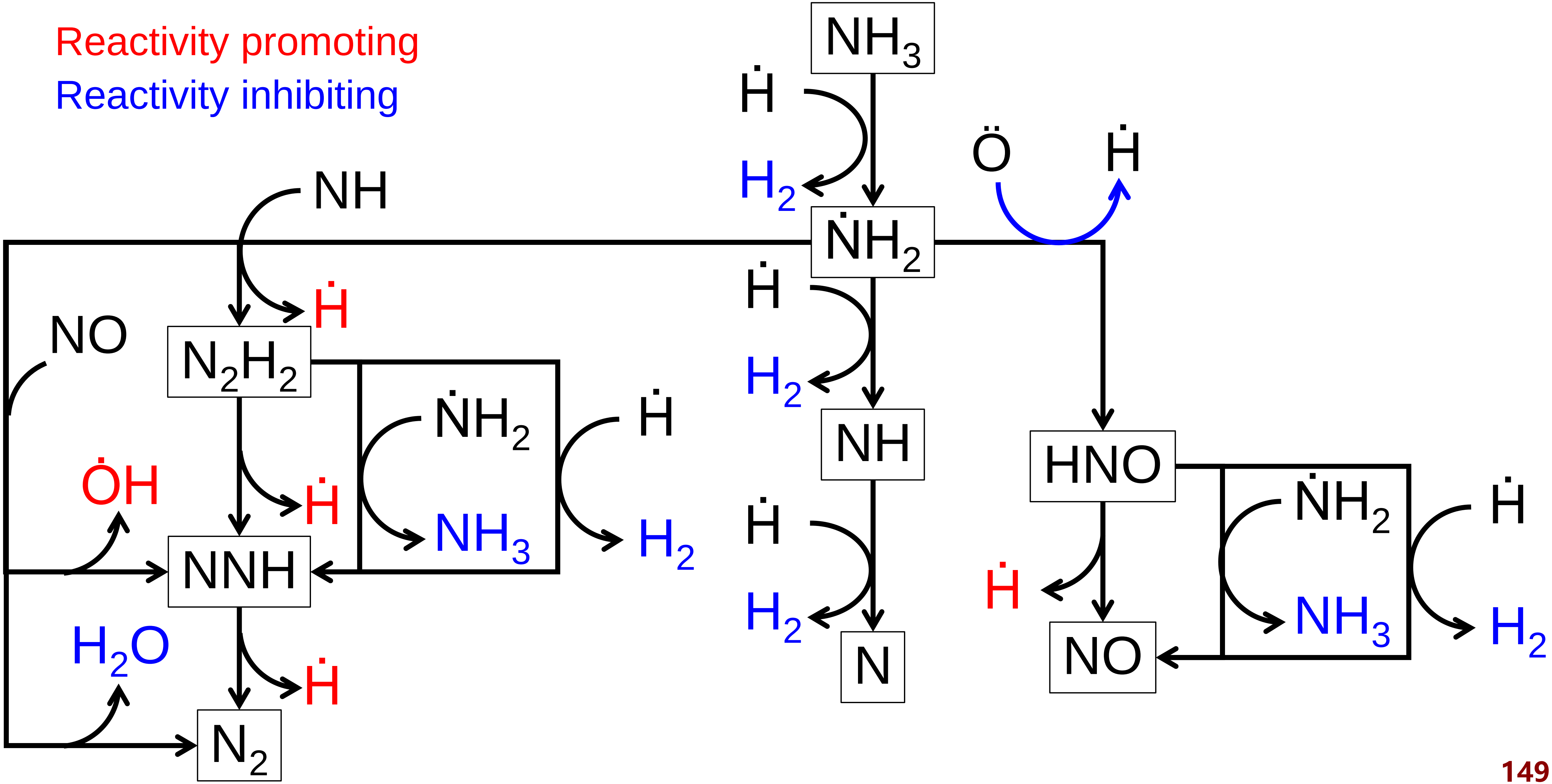
- $NH_3 + M = \dot{N}H_2 + \dot{H} + M$
- $NH_3 + \dot{R} = \dot{N}H_2 + RH = NH + RH = N + RH$
- $\dot{N}H_2 + NO = NNH + \dot{O}H$ / $N_2 + H_2O$
- $\dot{N}H_2 + NH = N_2H_2 + \dot{H}$
- $N_2H_2 (+M) = NNH + \dot{H} (+M)$; $N_2H_2 + \dot{R} = NNH + RH$
- $\dot{N}H_2 + \ddot{O} = HNO + \dot{H}$
- $HNO (+M) = NO + \dot{H} (+M)$; $HNO + \dot{R} = NO + RH$
- $\dot{N}H_2 + O_2 = H_2NO + \ddot{O}$ / $HNO + \dot{O}H$
- $H_2NO + \dot{R} = HNO + RH$

Also and more important at low temperatures, will be discussed later

Summary of important high-T reactions

Reactivity promoting

Reactivity inhibiting

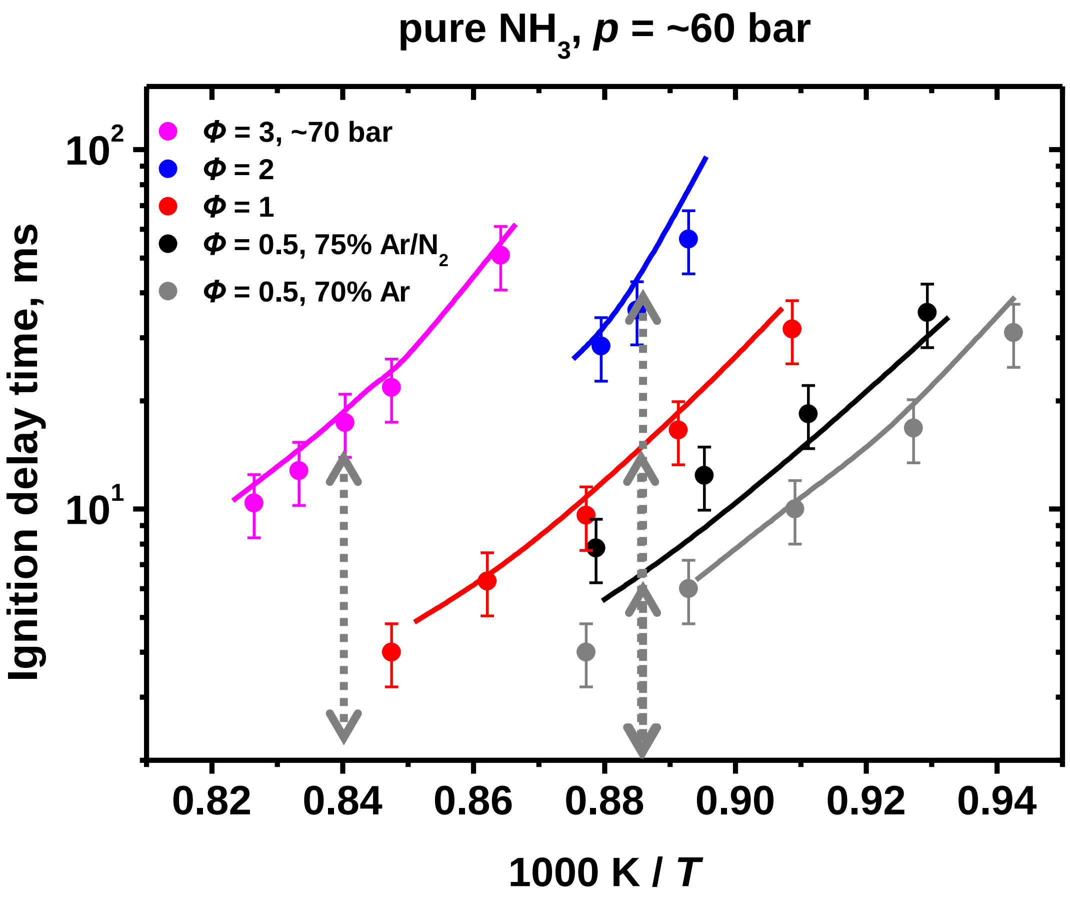


Low-T reaction classes highlighted

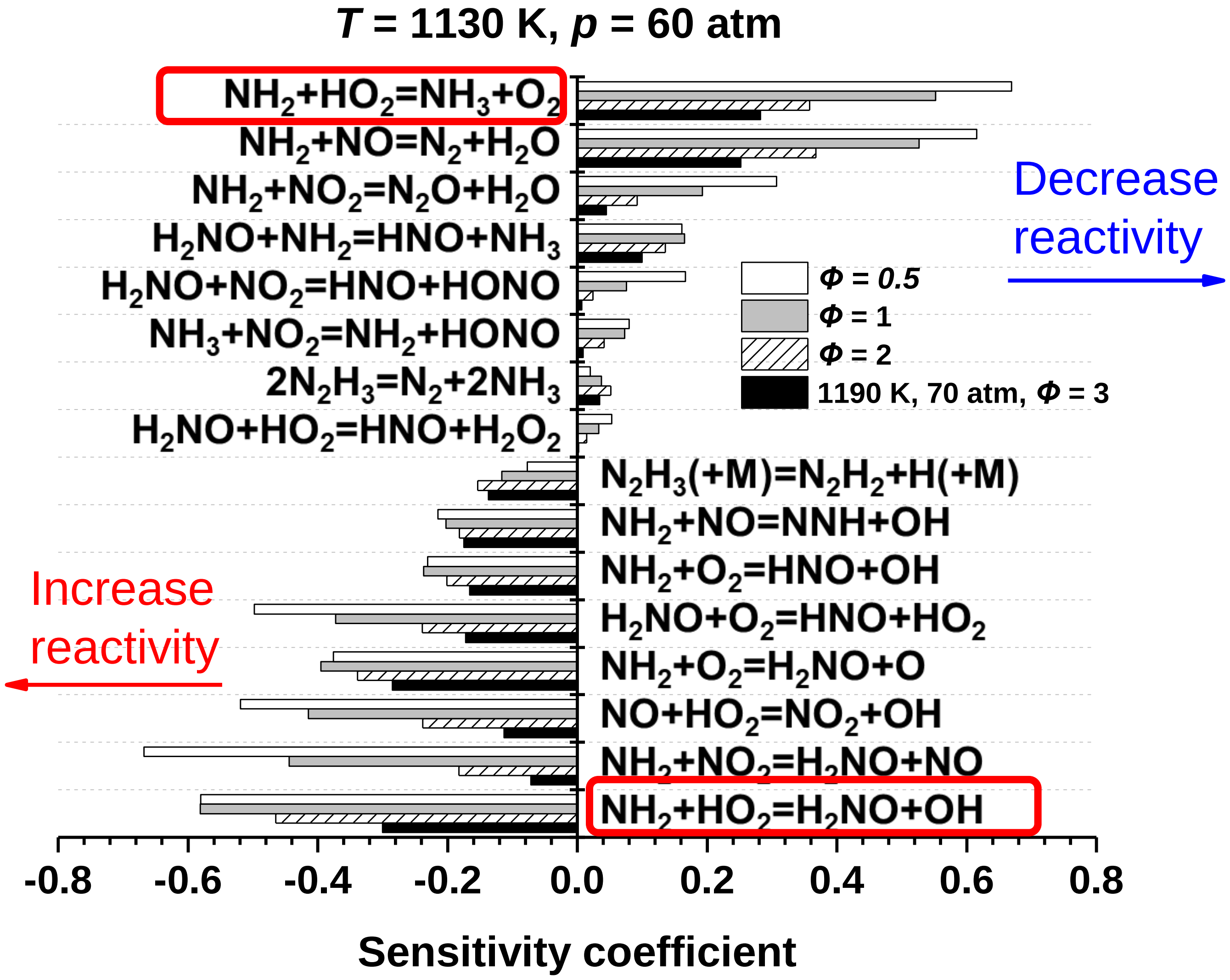
- $NH_3 + \dot{R} = \dot{N}H_2 + RH$ ($\dot{R} = \dot{O}H, H\dot{O}_2, NO_2$)
- $\dot{N}H_2 + H\dot{O}_2 = H_2NO + \dot{O}H$ / $NH_3 + O_2$
- $\dot{N}H_2 + NO_2 = H_2NO + NO$ / $N_2O + H_2O$
- $NO + H\dot{O}_2 = NO_2 + \dot{O}H$
- $\dot{N}H_2 + NO = NNH + \dot{O}H$ / $N_2 + H_2O$
- $\dot{N}H_2 + O_2 = H_2NO + \ddot{O}$ / $HNO + \dot{O}H$
- $H_2NO + \dot{R} = HNO + RH$ ($\dot{R} = O_2, H\dot{O}_2, \dot{N}H_2, NO_2$)

Low-temperature chemistry

➢ NH_3 IDT sensitivity analyses


pure NH_3, p = ~60 bar

RCM ignition delay times
(Expt.: Dai 2020, CNF)

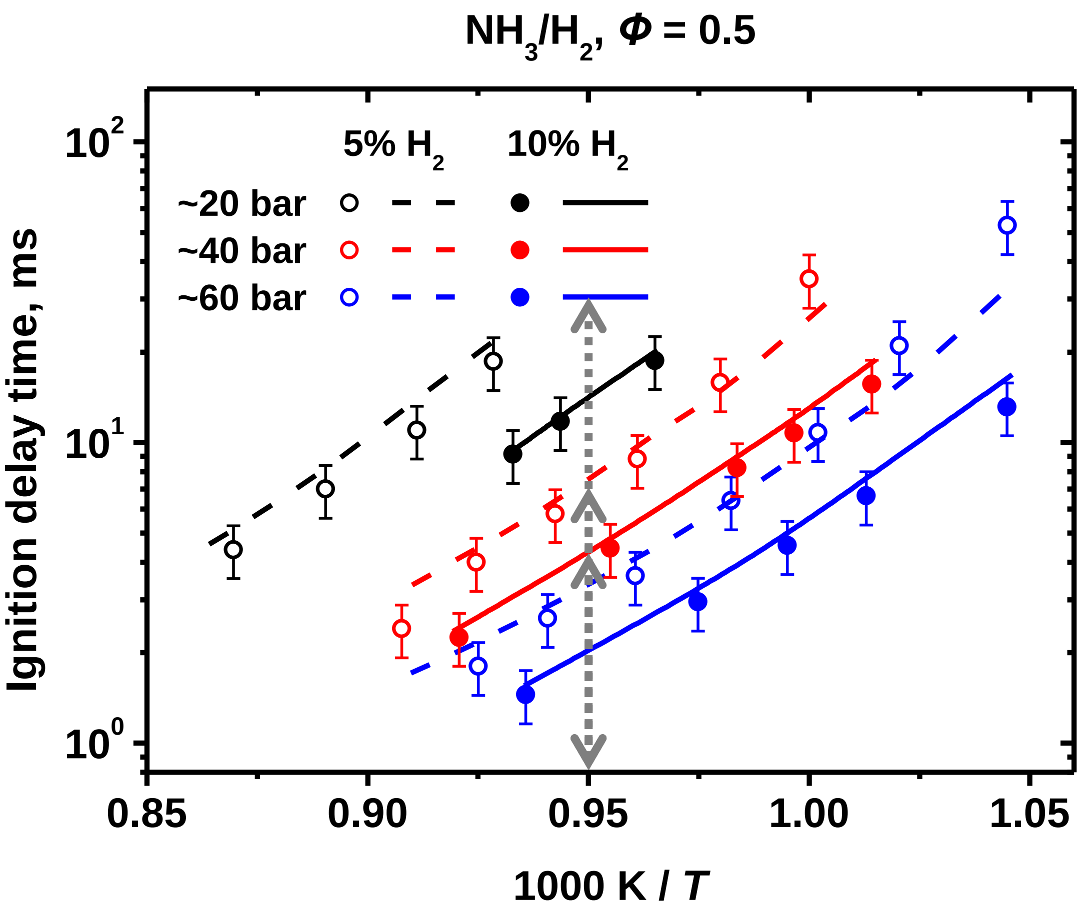

T = 1130 K, p = 60 atm

Decrease reactivity

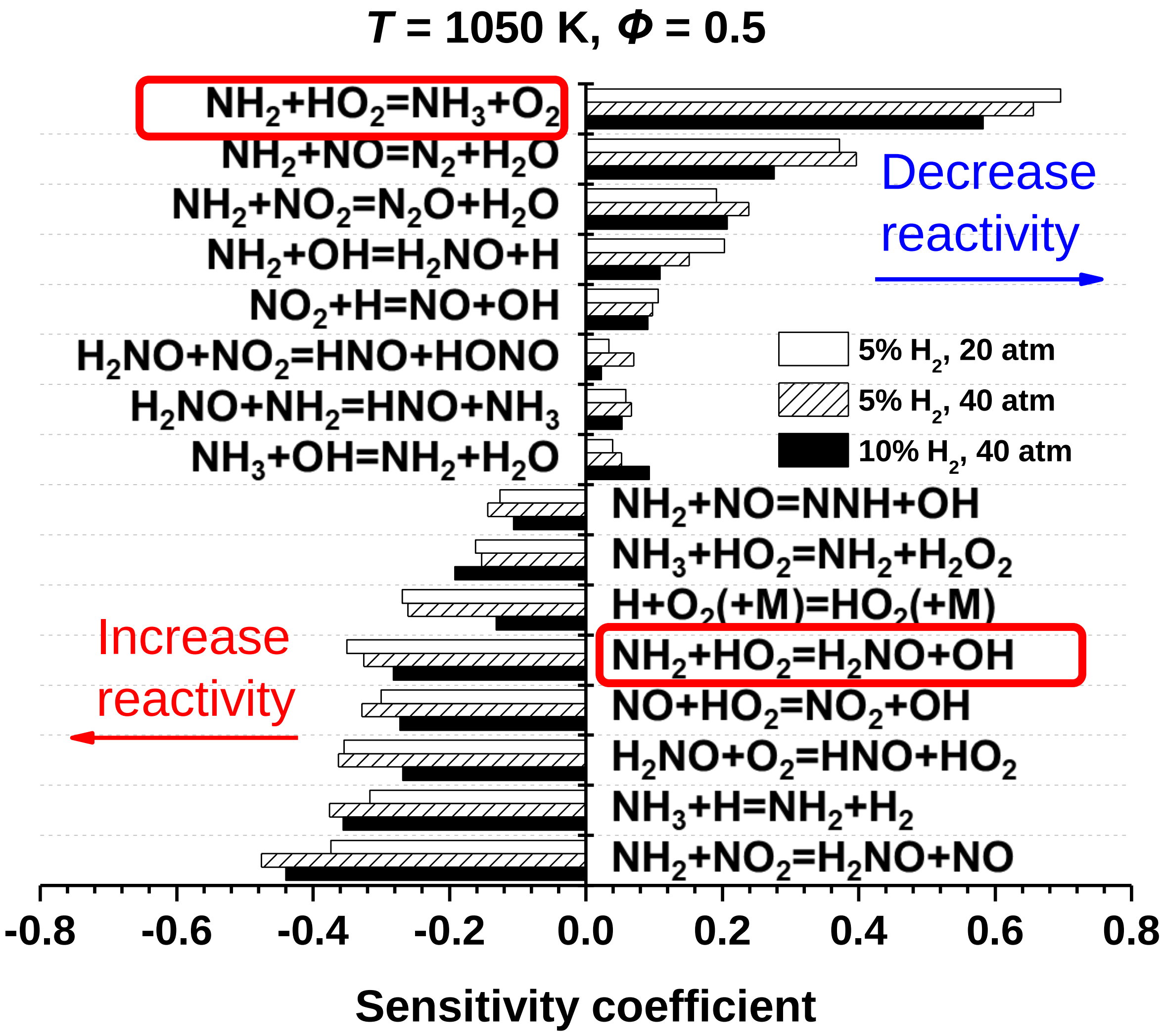
Increase reactivity

Low-temperature chemistry

➢ NH_3/H_2 IDT sensitivity analyses



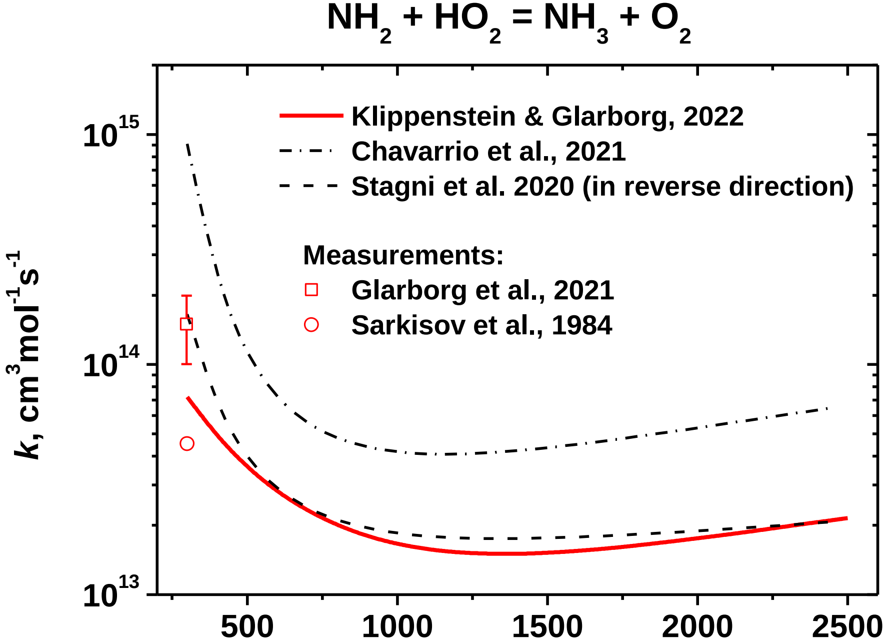
RCM ignition delay times
(Expt.: Dai 2020, CNF)

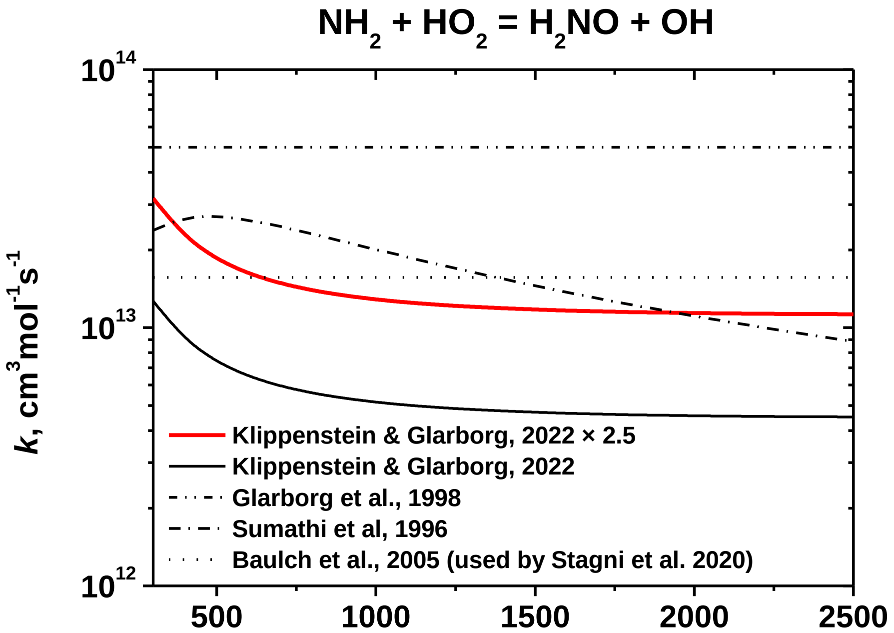


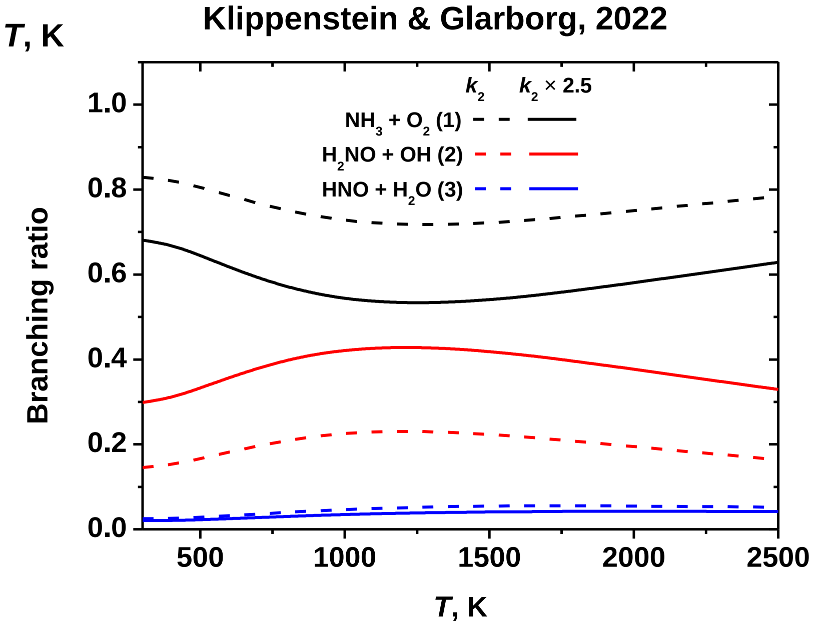
$\dot{N}H_2 + H\dot{O}_2$ reaction system

➢ Rate constants

- = $NH_3 + O_2$
- = $H_2NO + \dot{O}H$
- = $HNO + H_2O$







Klippenstein, S. J., & Glarborg, P. (2022). Combustion and Flame, 236, 111787.

Stagni, A., et al. (2020). Reaction Chemistry & Engineering, 5(4), 696-711.

Chavarrio Cañas, J. E., et al. (2021). Combustion and Flame, 235, 111708.

Baulch, D. L., et al. (2005). Journal of physical and chemical reference data, 34(3), 757-1397.

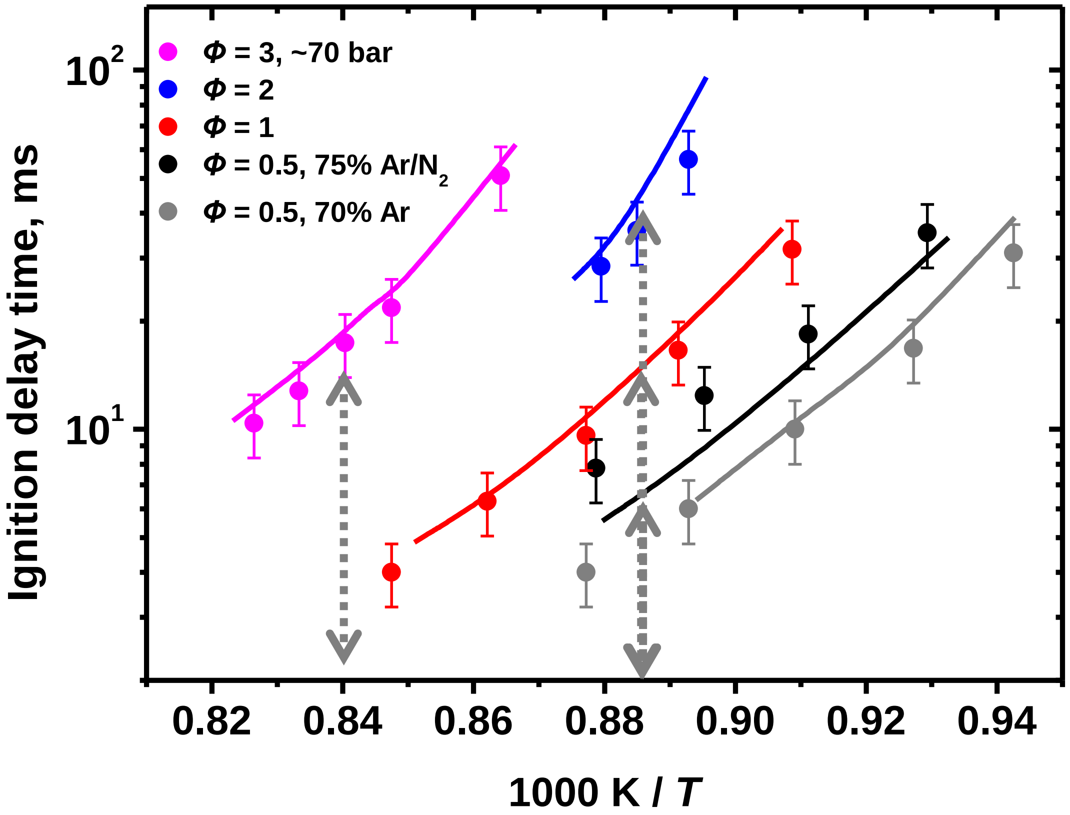
Sumathi, R., & Peyerimhoff, S. D. (1996). Chemical physics letters, 263(6), 742-748.

Low-T reaction classes highlighted

- $NH_3 + \dot{R} = \dot{N}H_2 + RH$ ($\dot{R} = \dot{O}H, H\dot{O}_2, NO_2$)
- $\dot{N}H_2 + H\dot{O}_2 = H_2NO + \dot{O}H$ / $NH_3 + O_2$
- $\dot{N}H_2 + NO_2 = H_2NO + NO$ / $N_2O + H_2O$
- $NO + H\dot{O}_2 = NO_2 + \dot{O}H$
- $\dot{N}H_2 + NO = NNH + \dot{O}H$ / $N_2 + H_2O$
- $\dot{N}H_2 + O_2 = H_2NO + \ddot{O}$ / $HNO + \dot{O}H$
- $H_2NO + \dot{R} = HNO + RH$ ($\dot{R} = O_2, H\dot{O}_2, \dot{N}H_2, NO_2$)

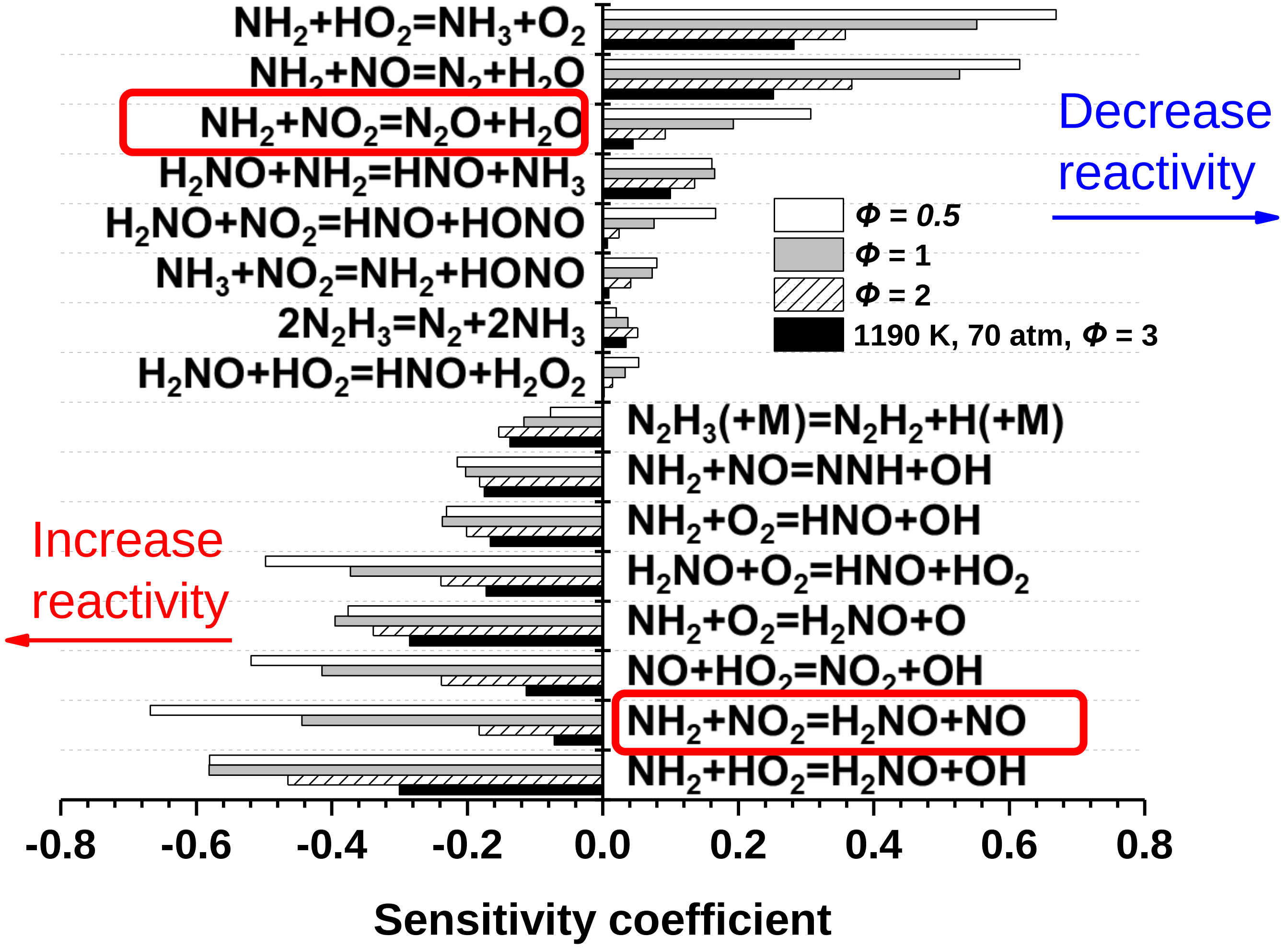
Low-temperature chemistry

➢ NH_3 IDT sensitivity analyses



pure NH_3, p = ~60 bar

RCM ignition delay times
(Expt.: Dai 2020, CNF)



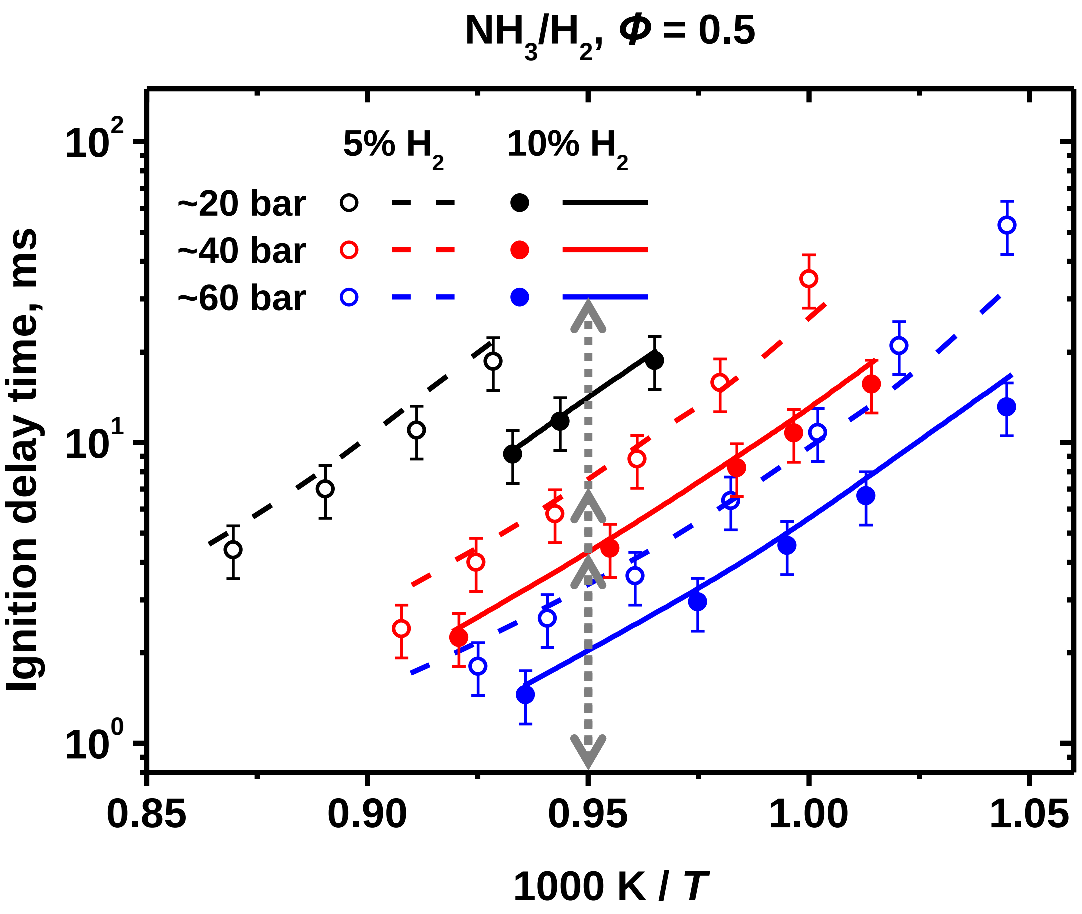
T = 1130 K, p = 60 atm

Decrease reactivity

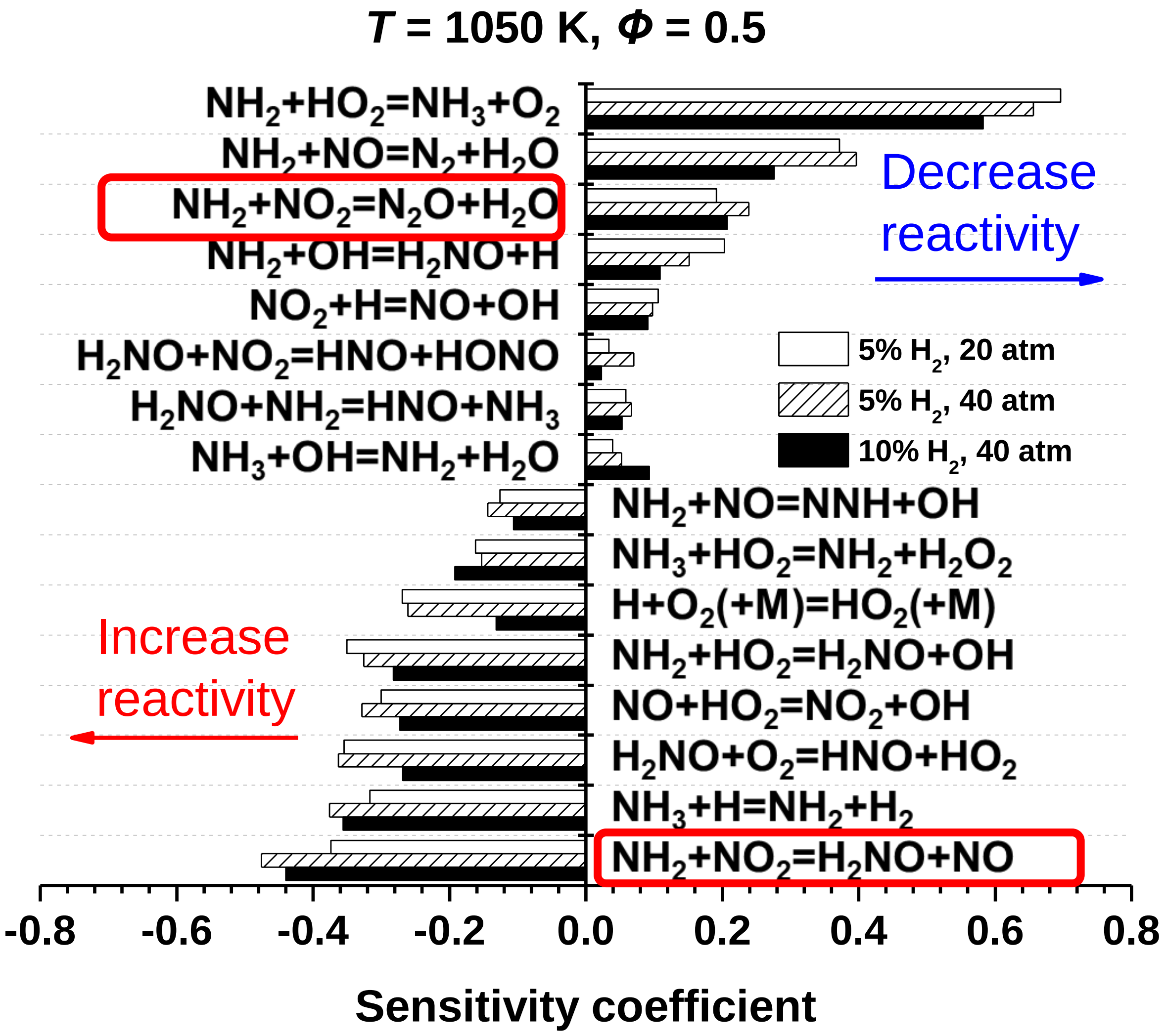
Increase reactivity

Low-temperature chemistry

➢ NH_3/H_2 IDT sensitivity analyses


NH_3/H_2, $\Phi = 0.5$

RCM ignition delay times
(Expt.: Dai 2020, CNF)

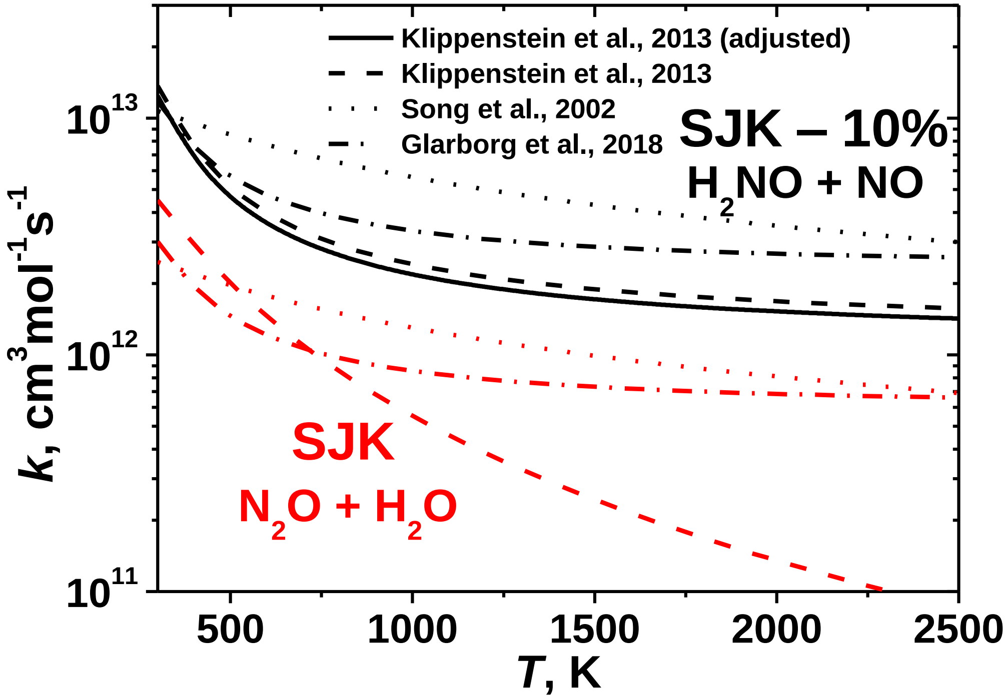

$T = 1050$ K, $\Phi = 0.5$

$\dot{N}H_2 + NO_2$ reaction system

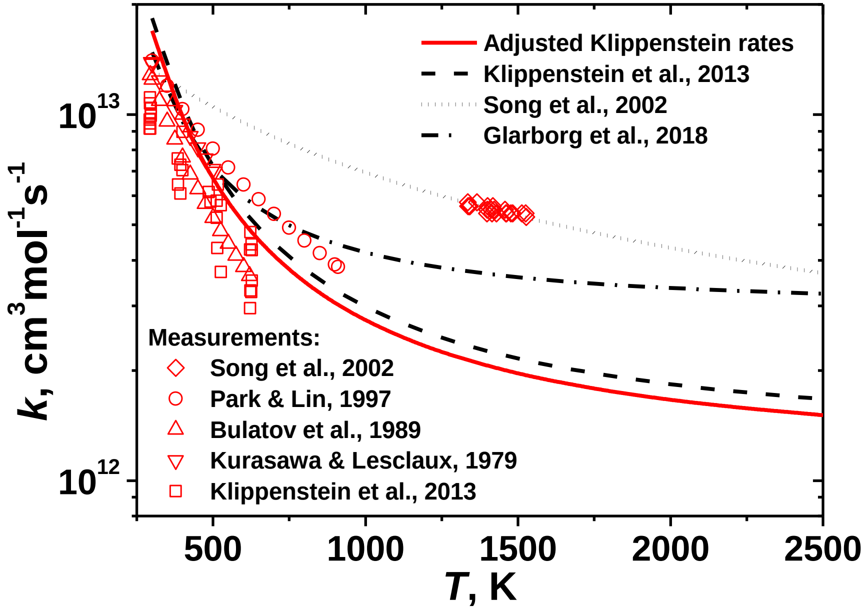
➢ Rate constants

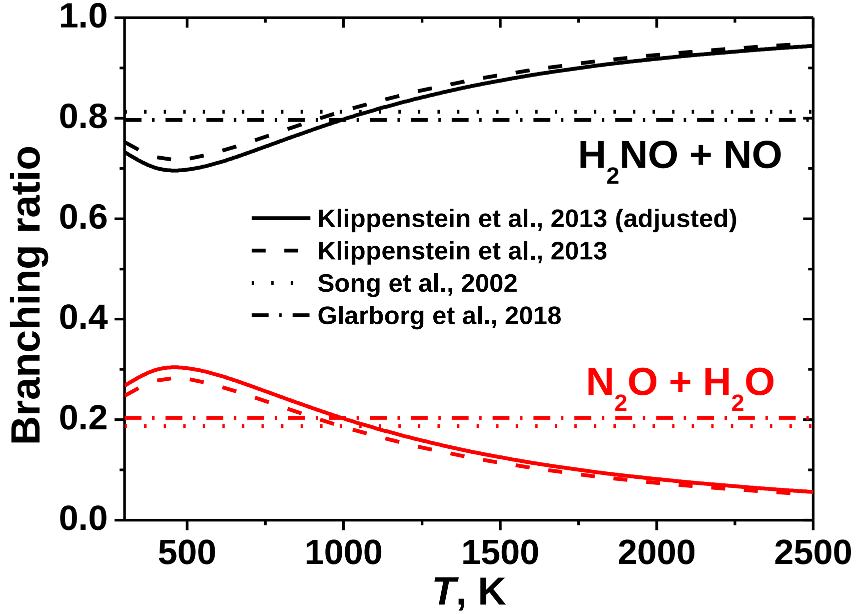
- = $H_2NO + NO$
- = $N_2O + H_2O$

Individual rate constants



Total rate constants





Klippenstein, S. J., et al. (2013). The Journal of Physical Chemistry A, 117(37), 9011-9022.

Glarborg, P., Miller, J. A., Ruscic, B., & Klippenstein, S. J. (2018). Progress in Energy and Combustion Science, 67, 31-68.

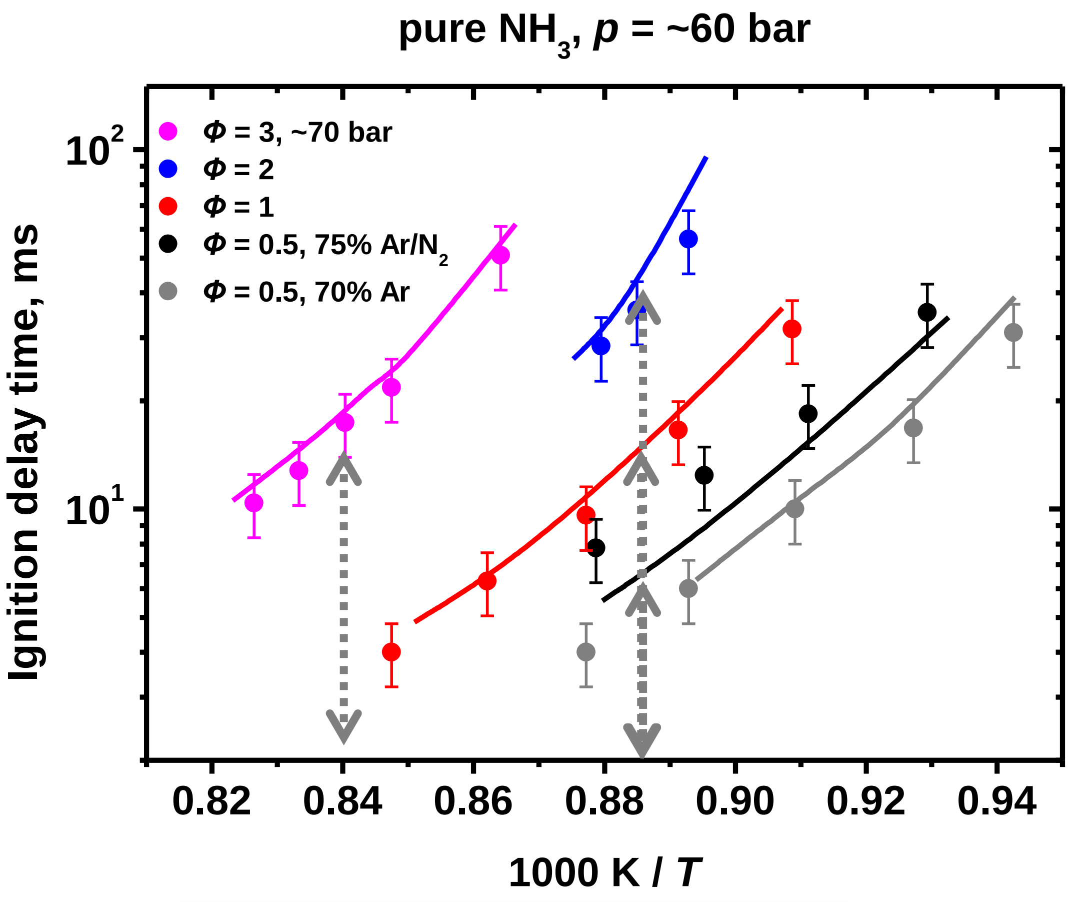
Song, S., Golden, D. M., Hanson, R. K., & Bowman, C. T. (2002). Proceedings of the Combustion Institute, 29(2), 2163-2170.

Low-T reaction classes highlighted

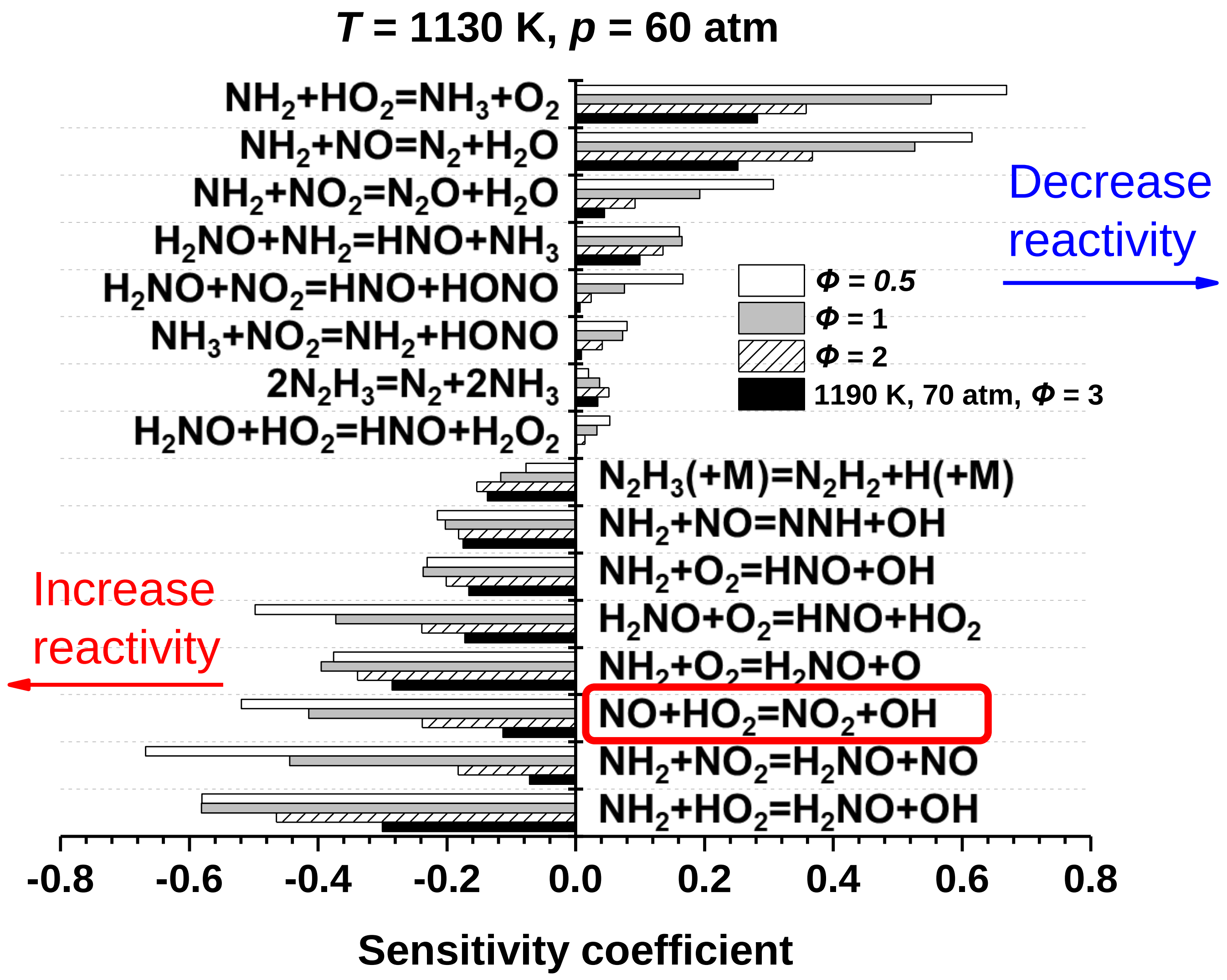
- $NH_3 + \dot{R} = \dot{N}H_2 + RH$ ($\dot{R} = \dot{O}H, H\dot{O}_2, NO_2$)
- $\dot{N}H_2 + H\dot{O}_2 = H_2NO + \dot{O}H$ / $NH_3 + O_2$
- $\dot{N}H_2 + NO_2 = H_2NO + NO$ / $N_2O + H_2O$
- $NO + H\dot{O}_2 = NO_2 + \dot{O}H$
- $\dot{N}H_2 + NO = NNH + \dot{O}H$ / $N_2 + H_2O$
- $\dot{N}H_2 + O_2 = H_2NO + \ddot{O}$ / $HNO + \dot{O}H$
- $H_2NO + \dot{R} = HNO + RH$ ($\dot{R} = O_2, H\dot{O}_2, \dot{N}H_2, NO_2$)

Low-temperature chemistry

➢ NH_3 IDT sensitivity analyses

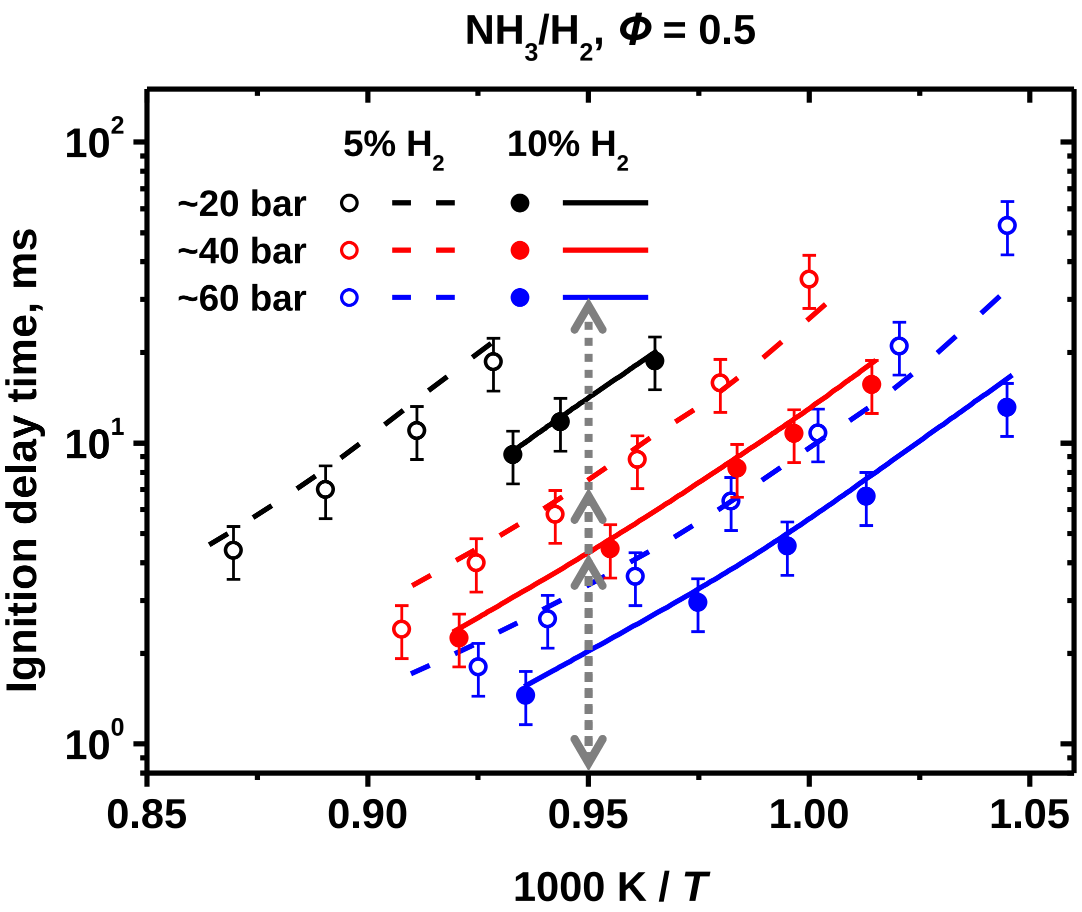


RCM ignition delay times
(Expt.: Dai 2020, CNF)

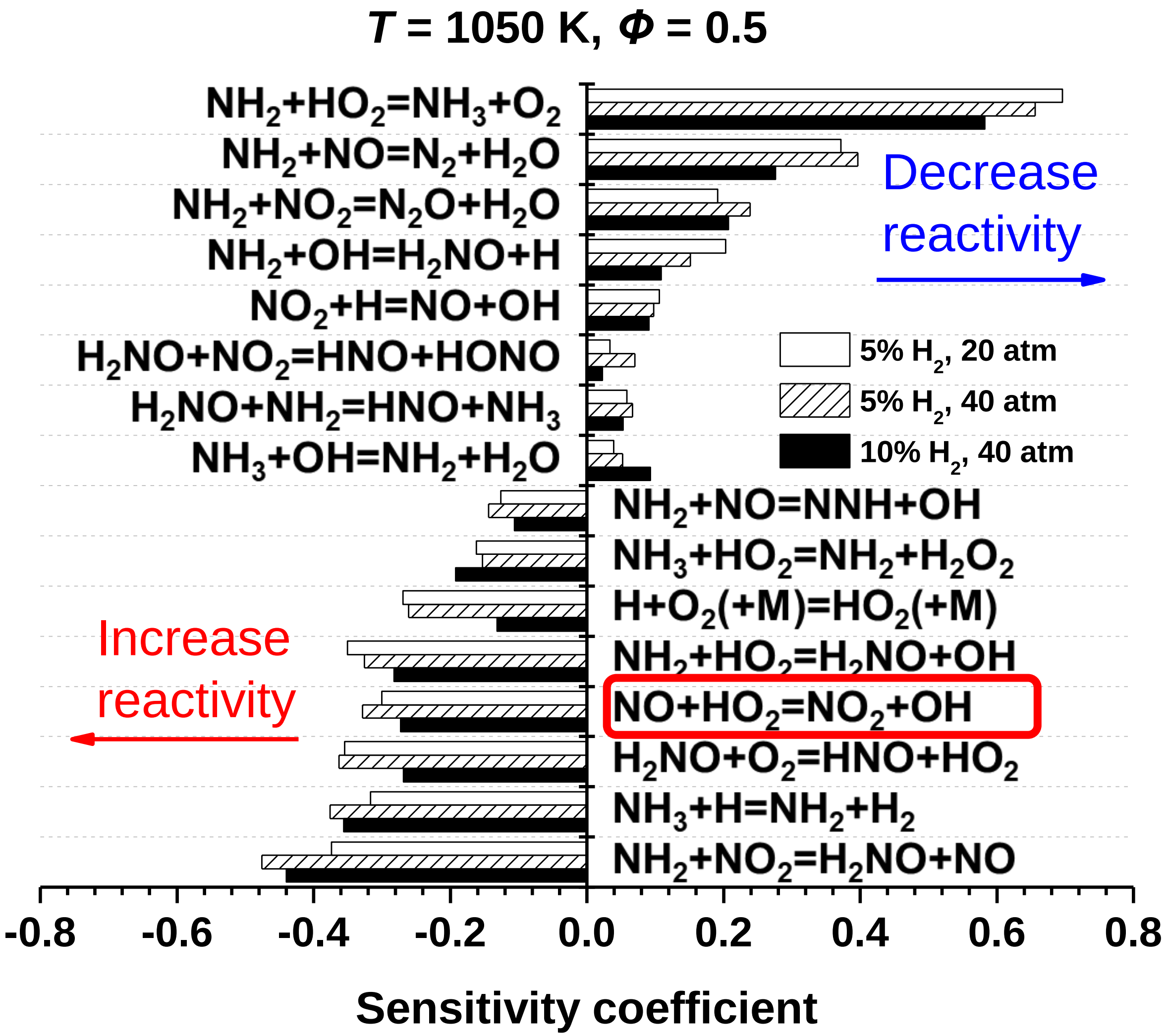


Low-temperature chemistry

➢ NH_3/H_2 IDT sensitivity analyses

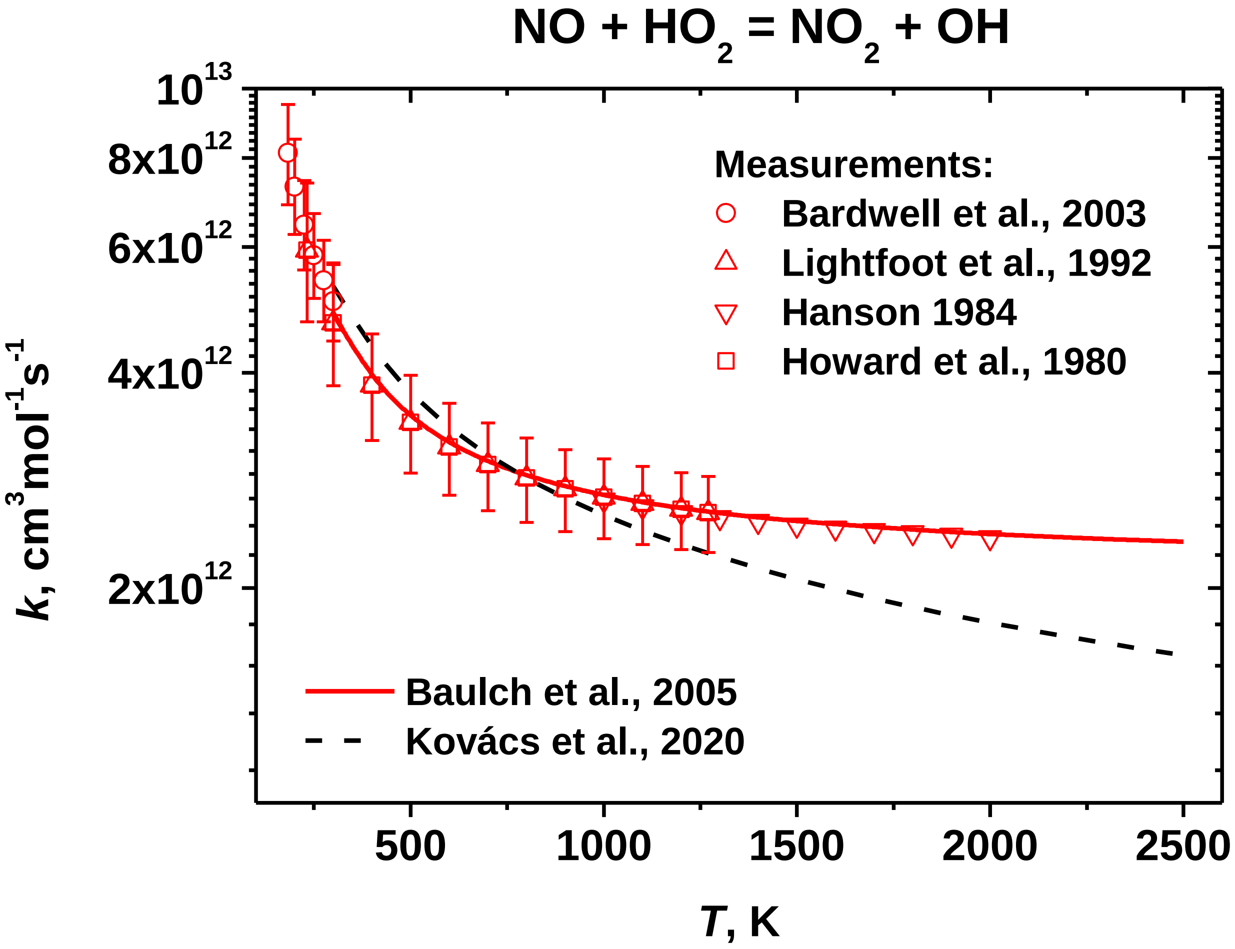


RCM ignition delay times
(Expt.: Dai 2020, CNF)



NO + HȮ$_2$ = NO$_2$ + ȮH

- Rate constants



Baulch, D. L., et al. (2005). Journal of physical and chemical reference data, 34(3), 757-1397.

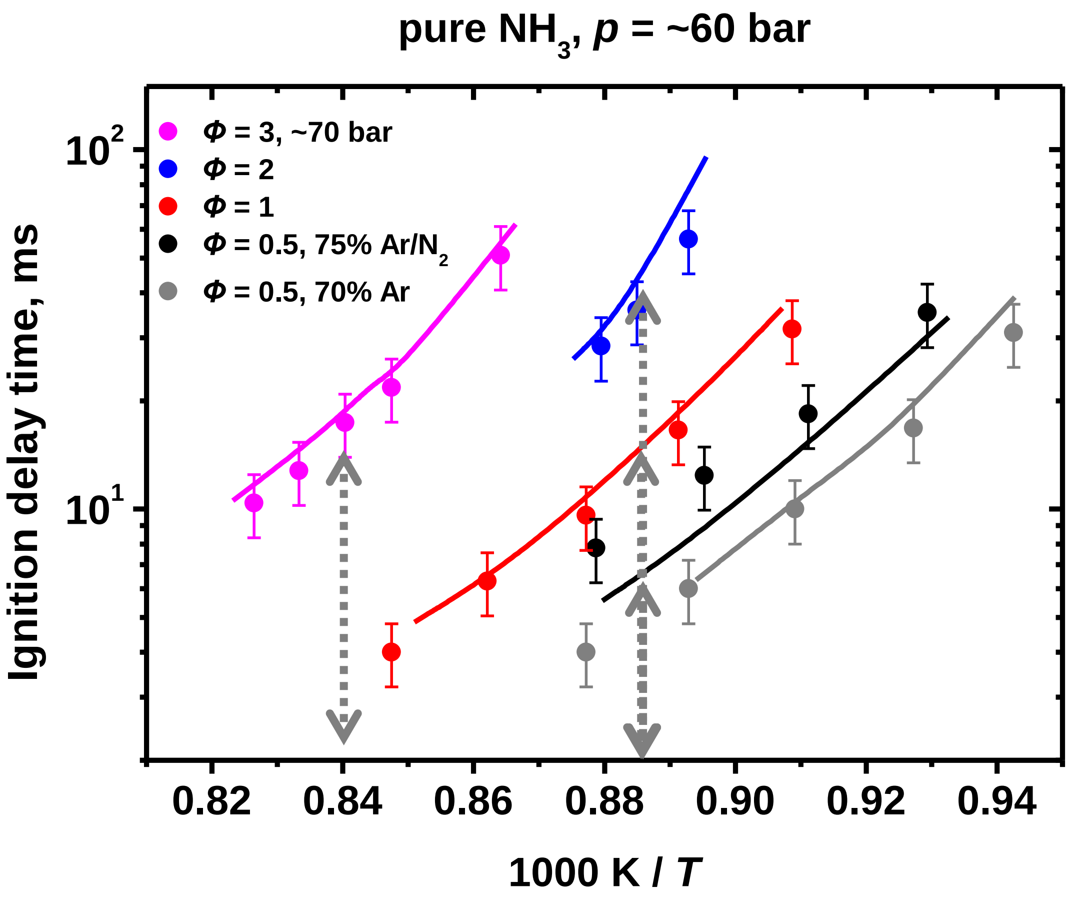
Kovács, M., Papp, M., Zsély, I. G., & Turányi, T. (2020). Fuel, 264, 116720.

Low-T reaction classes highlighted

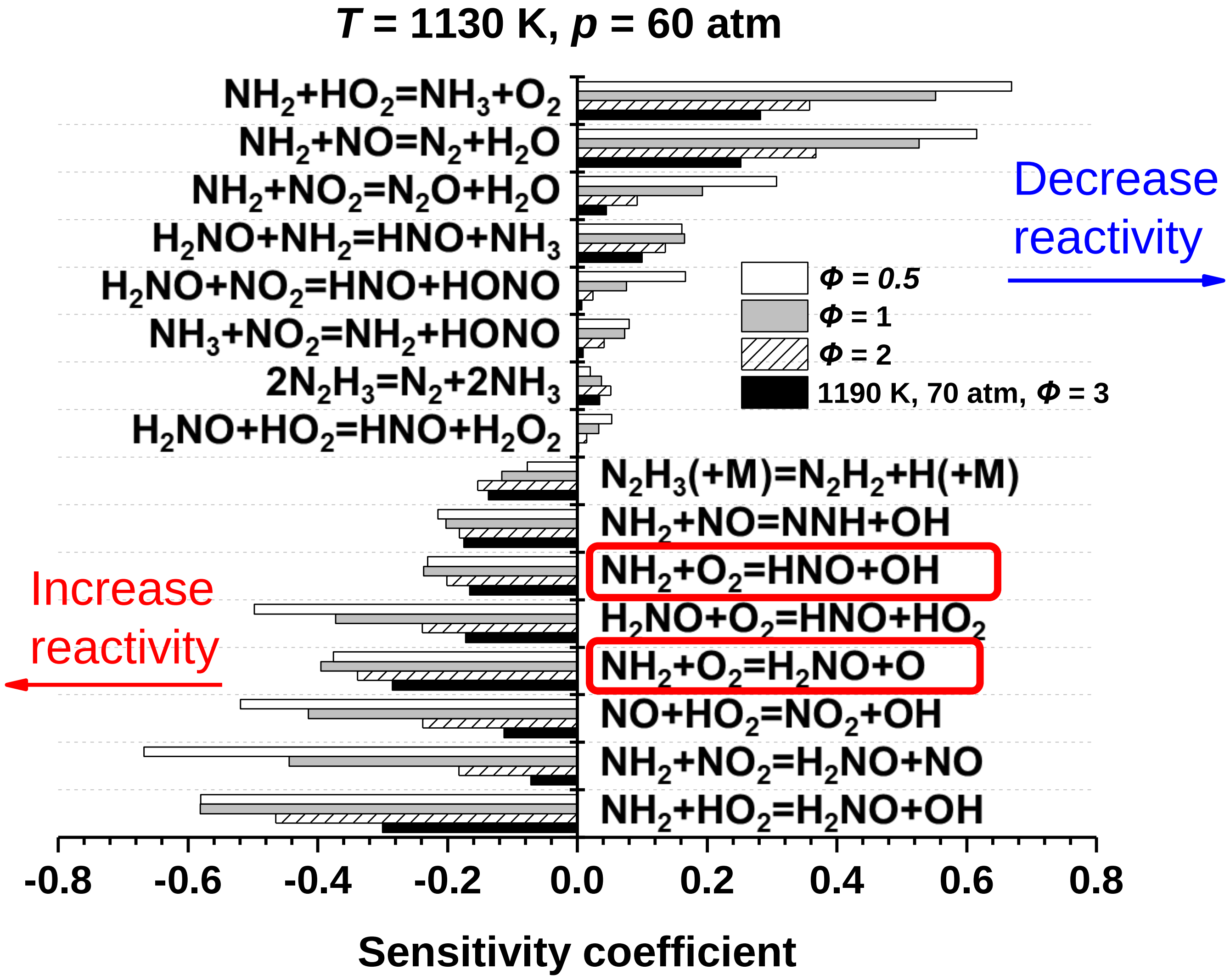
- $NH_3 + \dot{R} = \dot{N}H_2 + RH$ ($\dot{R} = \dot{O}H, H\dot{O}_2, NO_2$)
- $\dot{N}H_2 + H\dot{O}_2 = H_2NO + \dot{O}H$ / $NH_3 + O_2$
- $\dot{N}H_2 + NO_2 = H_2NO + NO$ / $N_2O + H_2O$
- $NO + H\dot{O}_2 = NO_2 + \dot{O}H$
- $\dot{N}H_2 + NO = NNH + \dot{O}H$ / $N_2 + H_2O$
- $\dot{N}H_2 + O_2 = H_2NO + \ddot{O}$ / $HNO + \dot{O}H$
- $H_2NO + \dot{R} = HNO + RH$ ($\dot{R} = O_2, H\dot{O}_2, \dot{N}H_2, NO_2$)

Low-temperature chemistry

➢ NH_3 IDT sensitivity analyses



RCM ignition delay times
(Expt.: Dai 2020, CNF)



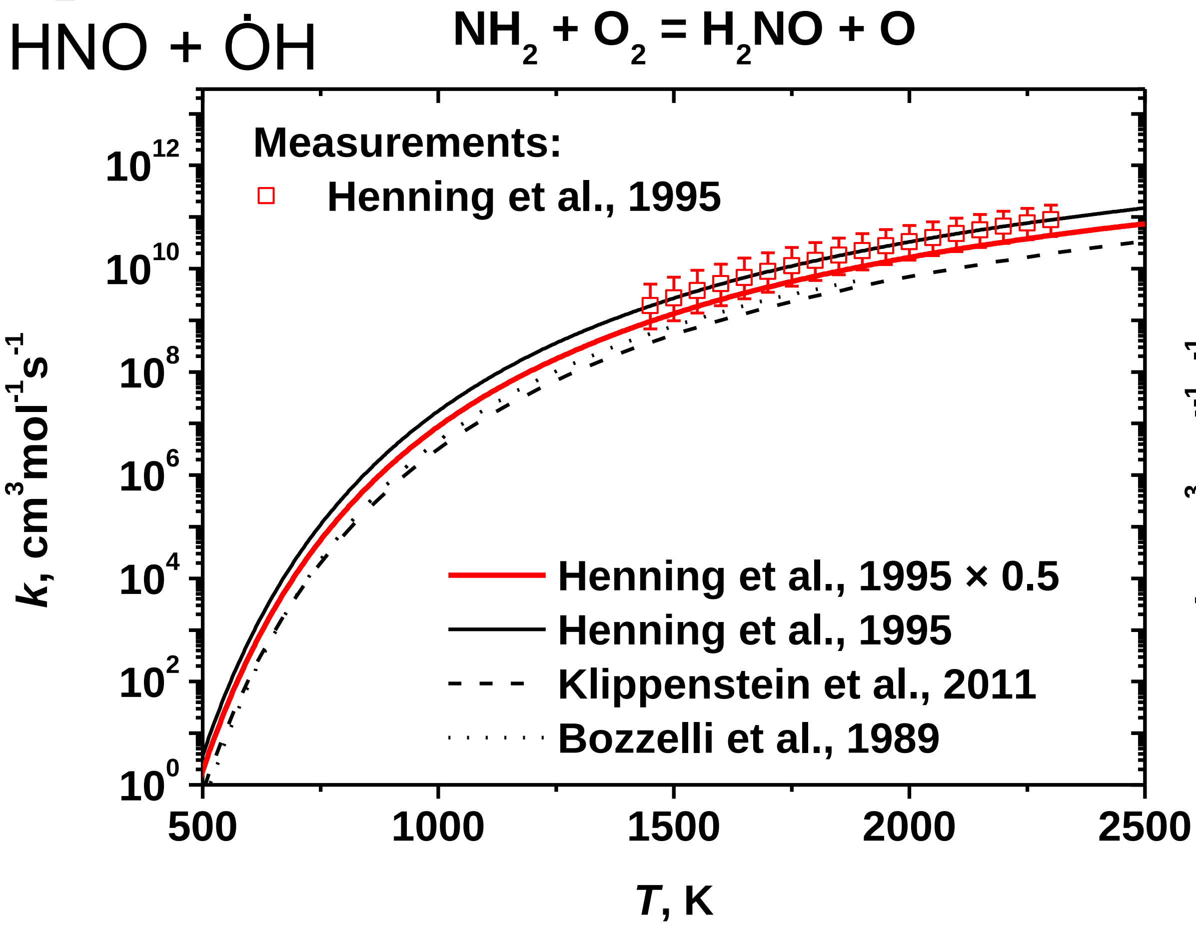
Decrease reactivity

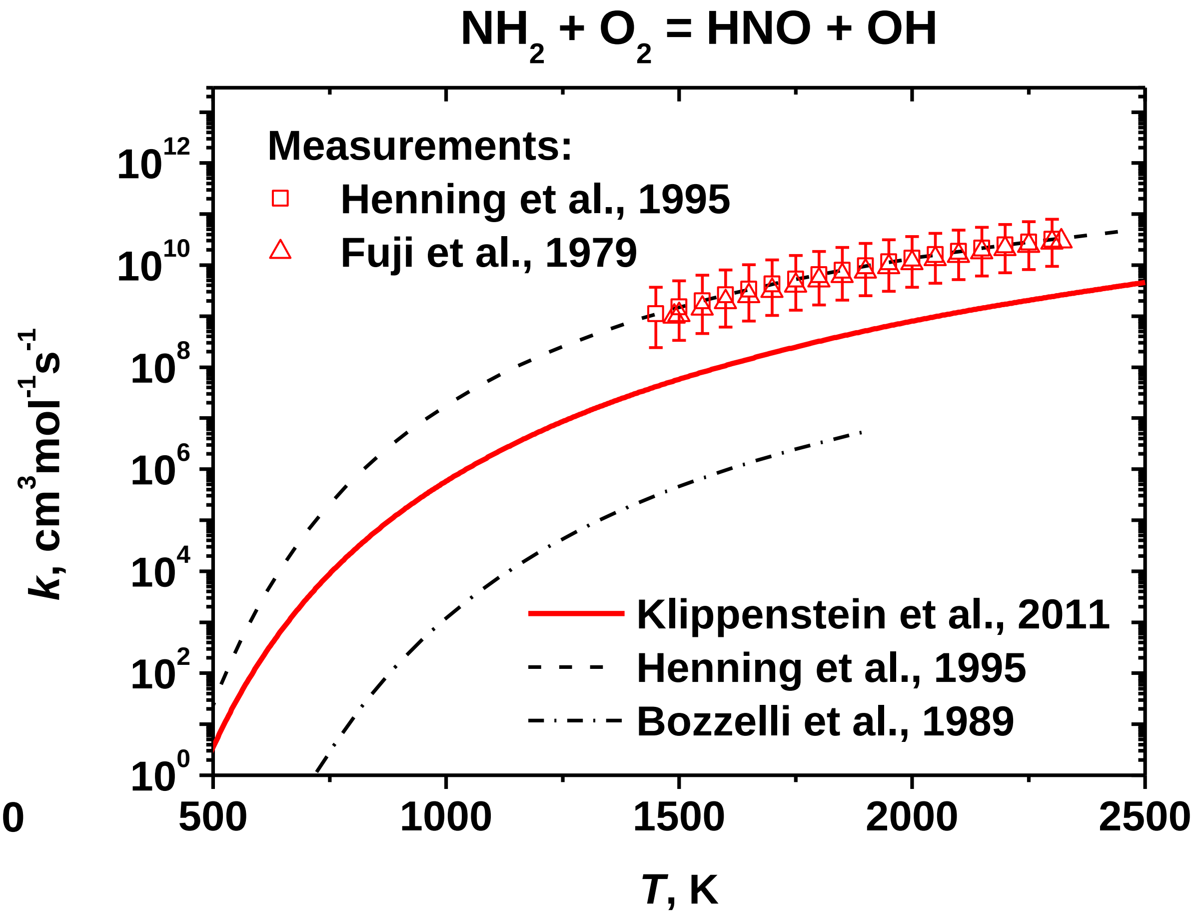
Increase reactivity

$\dot{N}H_2 + O_2$ reaction system

➢ Rate constants

- = $H_2NO + \ddot{O}$
- = $HNO + \dot{O}H$





Hennig, G., Klatt, M., Spindler, B., & Wagner, H. G. G. (1995). Berichte der Bunsengesellschaft für physikalische Chemie, 99(4), 651-657.

Klippenstein, S. J., Harding, L. B., Glarborg, P., & Miller, J. A. (2011). Combustion and Flame, 158(4), 774-789.

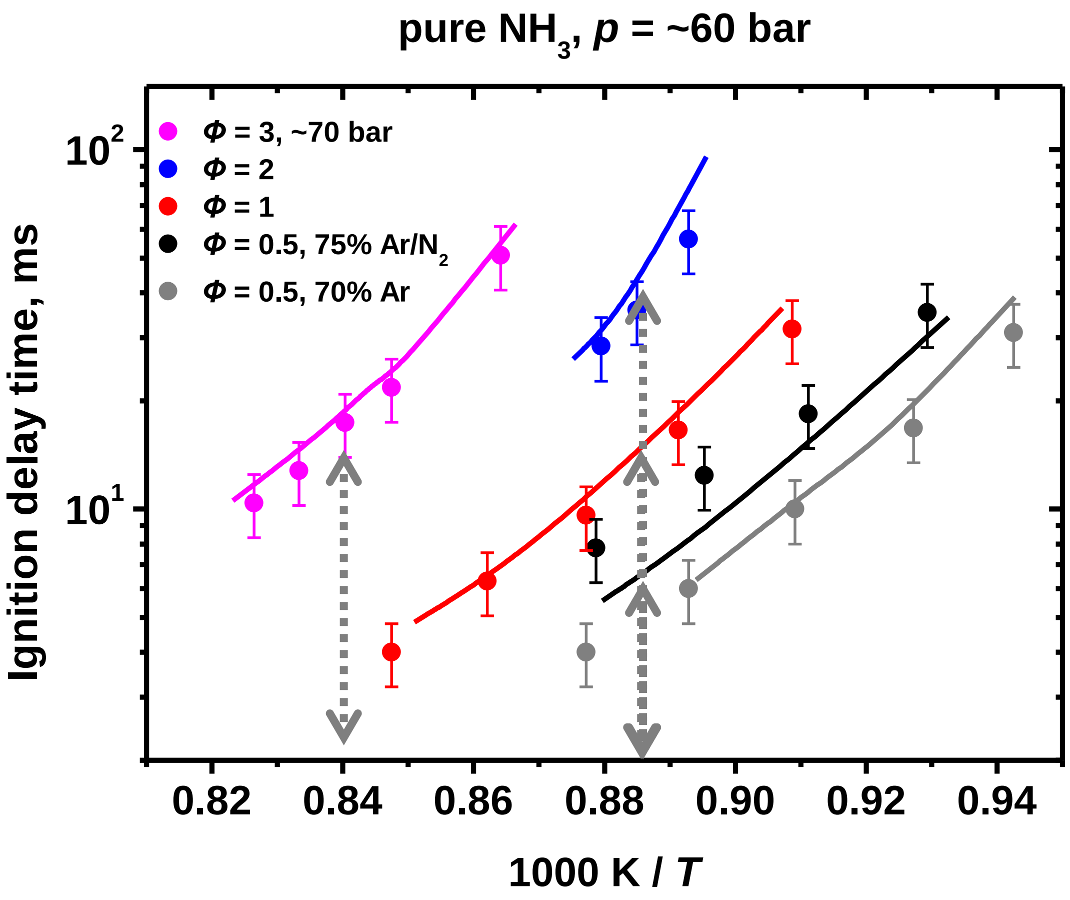
Bozzelli, J. W., & Dean, A. M. (1989). The Journal of Physical Chemistry, 93(3), 1058-1065.

Low-T reaction classes highlighted

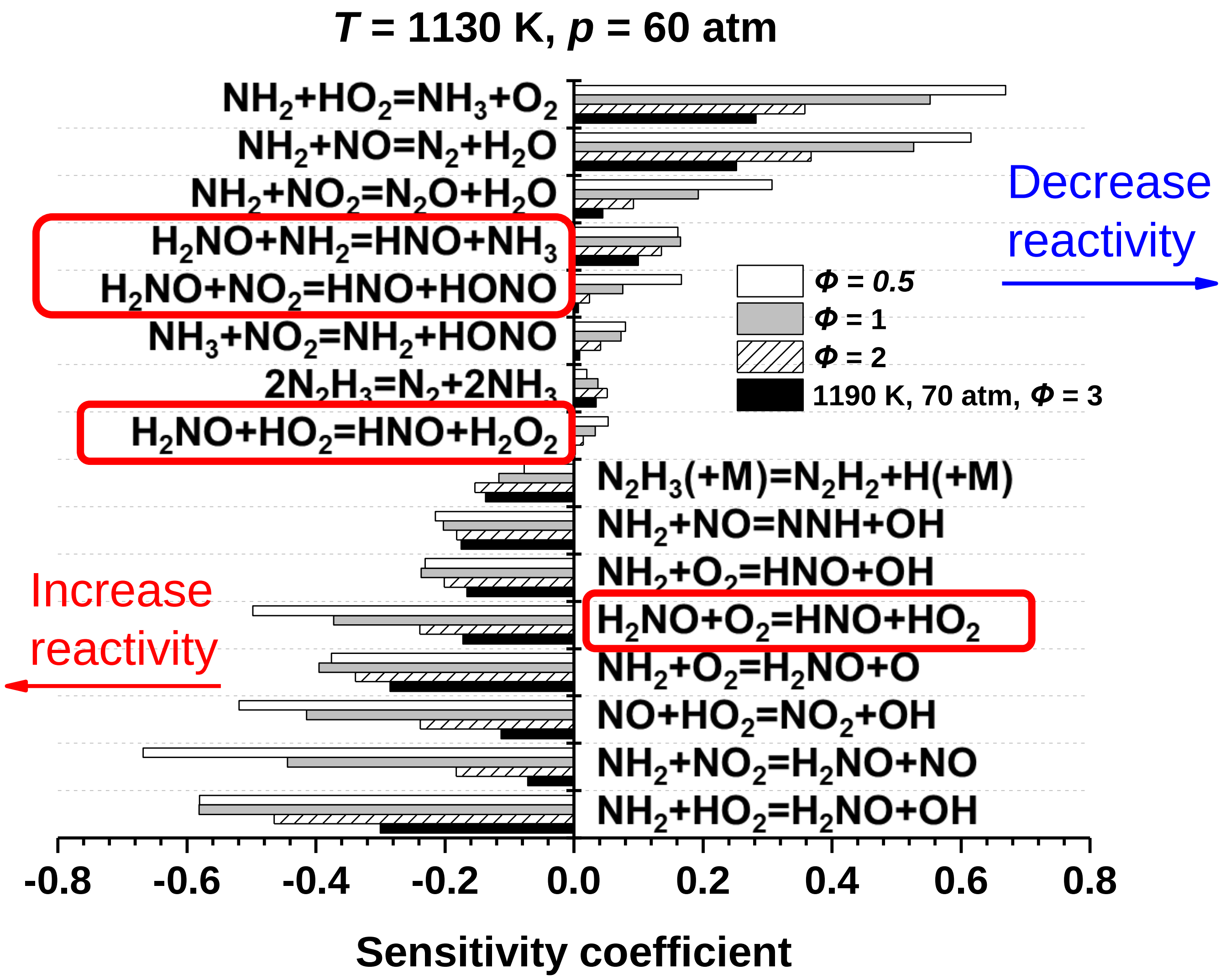
- $NH_3 + \dot{R} = \dot{N}H_2 + RH$ ($\dot{R} = \dot{O}H, H\dot{O}_2, NO_2$)
- $\dot{N}H_2 + H\dot{O}_2 = H_2NO + \dot{O}H$ / $NH_3 + O_2$
- $\dot{N}H_2 + NO_2 = H_2NO + NO$ / $N_2O + H_2O$
- $NO + H\dot{O}_2 = NO_2 + \dot{O}H$
- $\dot{N}H_2 + NO = NNH + \dot{O}H$ / $N_2 + H_2O$
- $\dot{N}H_2 + O_2 = H_2NO + \ddot{O}$ / $HNO + \dot{O}H$
- $H_2NO + \dot{R} = HNO + RH$ ($\dot{R} = O_2, H\dot{O}_2, \dot{N}H_2, NO_2$)

Low-temperature chemistry

➢ NH_3 IDT sensitivity analyses

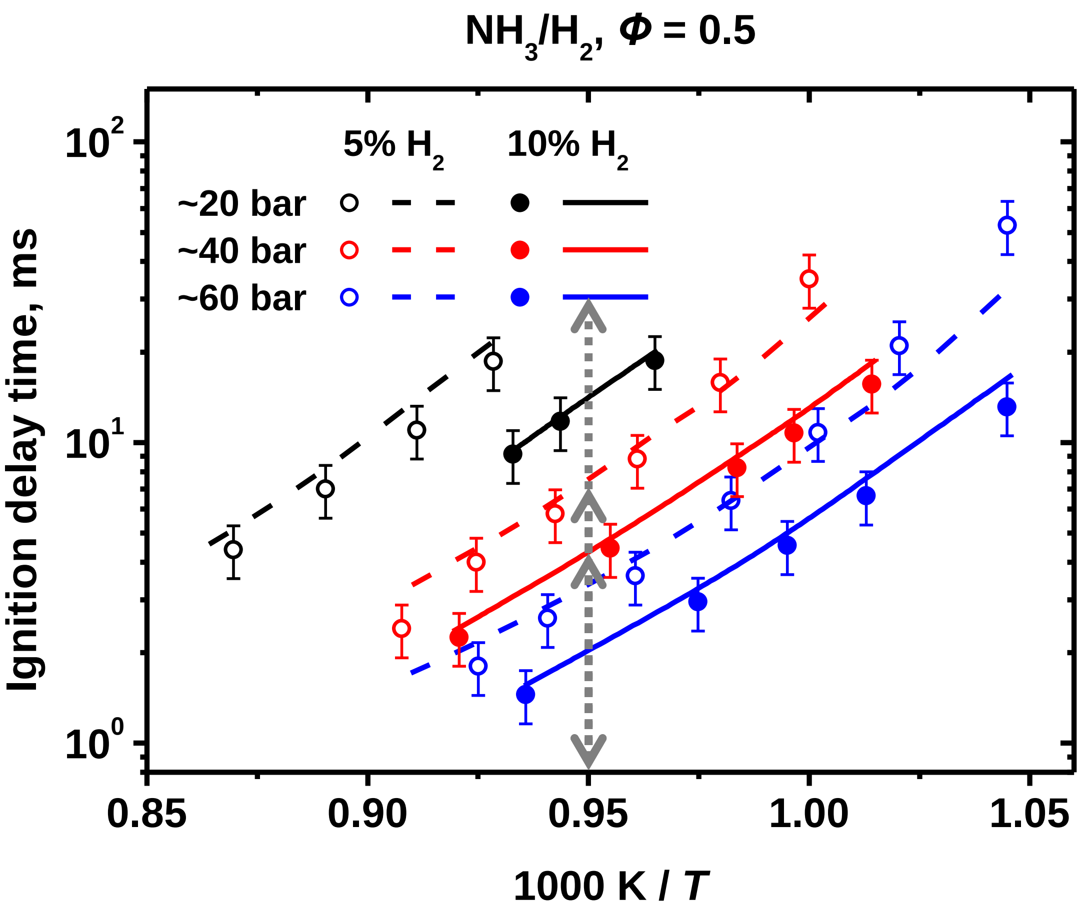


RCM ignition delay times
(Expt.: Dai 2020, CNF)

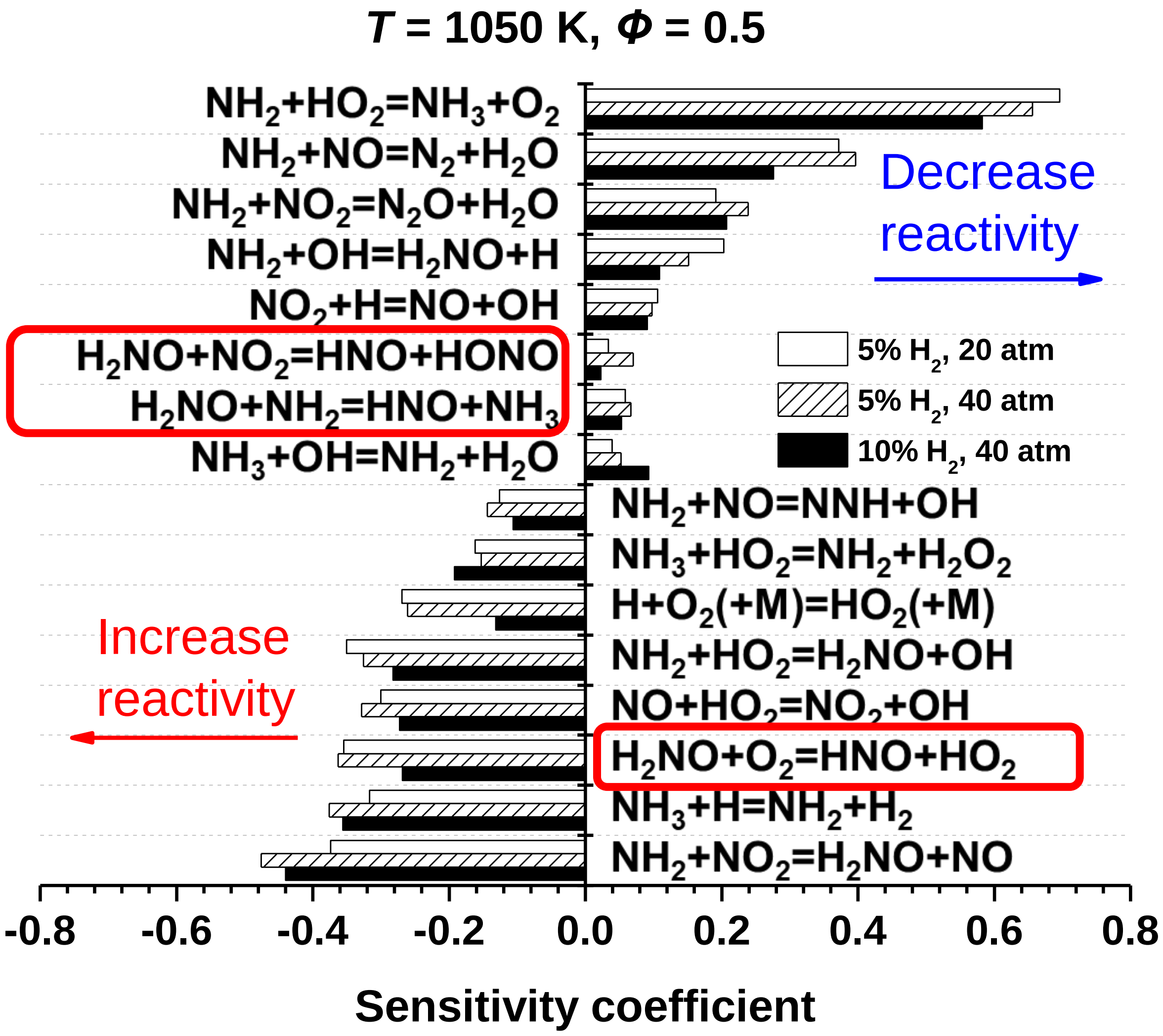


Low-temperature chemistry

➢ NH_3/H_2 IDT sensitivity analyses



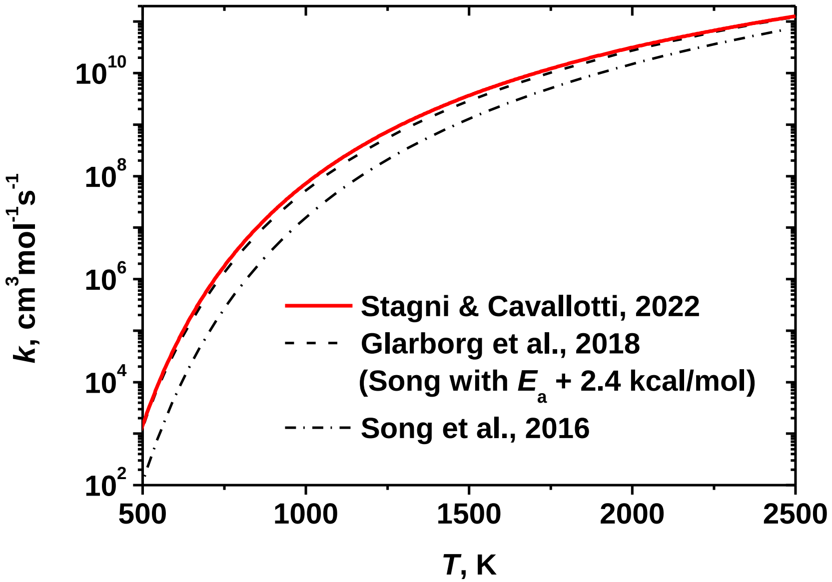
RCM ignition delay times
(Expt.: Dai 2020, CNF)



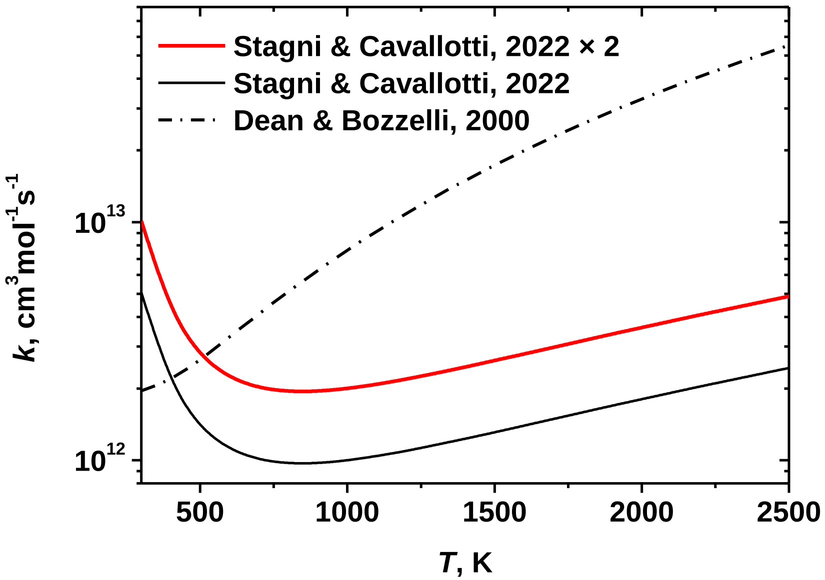
$H_2NO + \dot{R} = HNO + RH$

➢ Rate constants

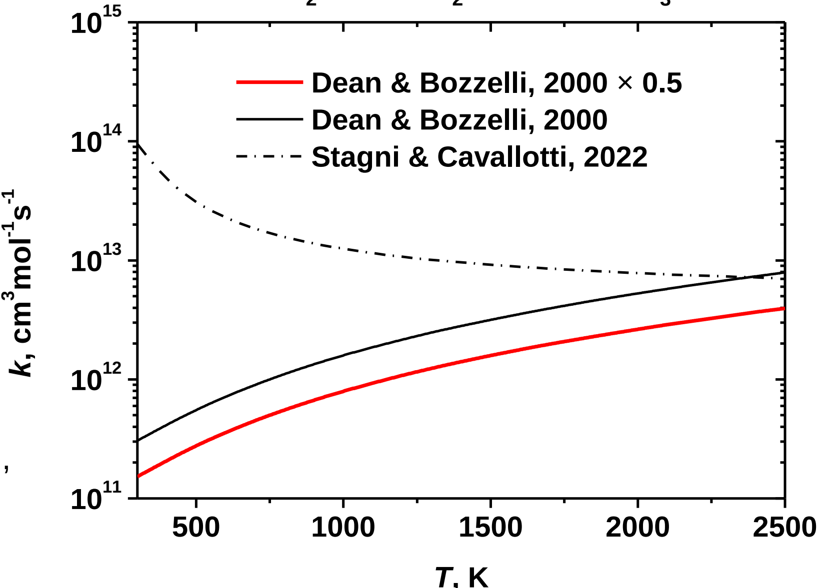
$H_2NO + O_2 = HNO + HO_2$



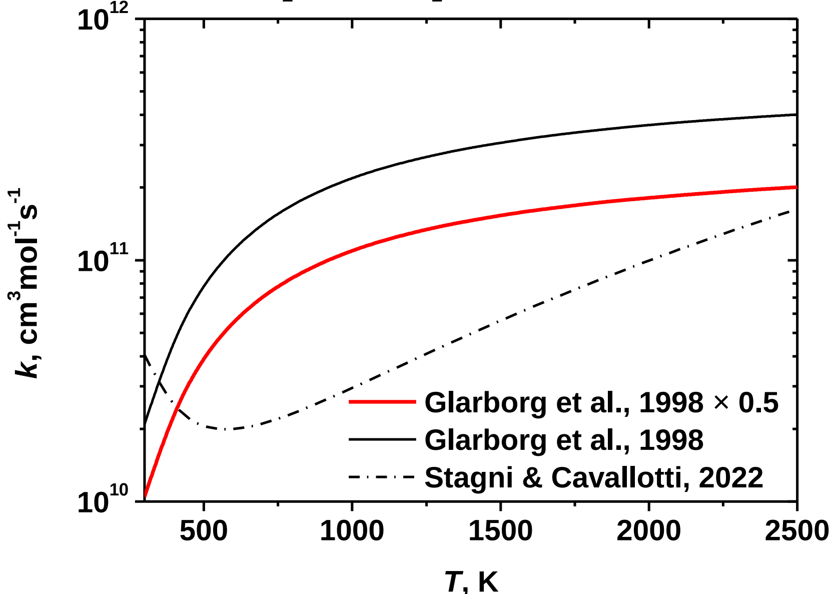
$H_2NO + HO_2 = HNO + H_2O_2$



$H_2NO + NH_2 = HNO + NH_3$



$H_2NO + NO_2 = HNO + HONO$



Stagni, A., & Cavallotti, C. (2022). Proceedings of the Combustion Institute.

Glarborg, P., et al. (2018). Progress in energy and combustion science, 67, 31-68.

Song, Y., et al. (2016). Fuel, 181, 358-365.

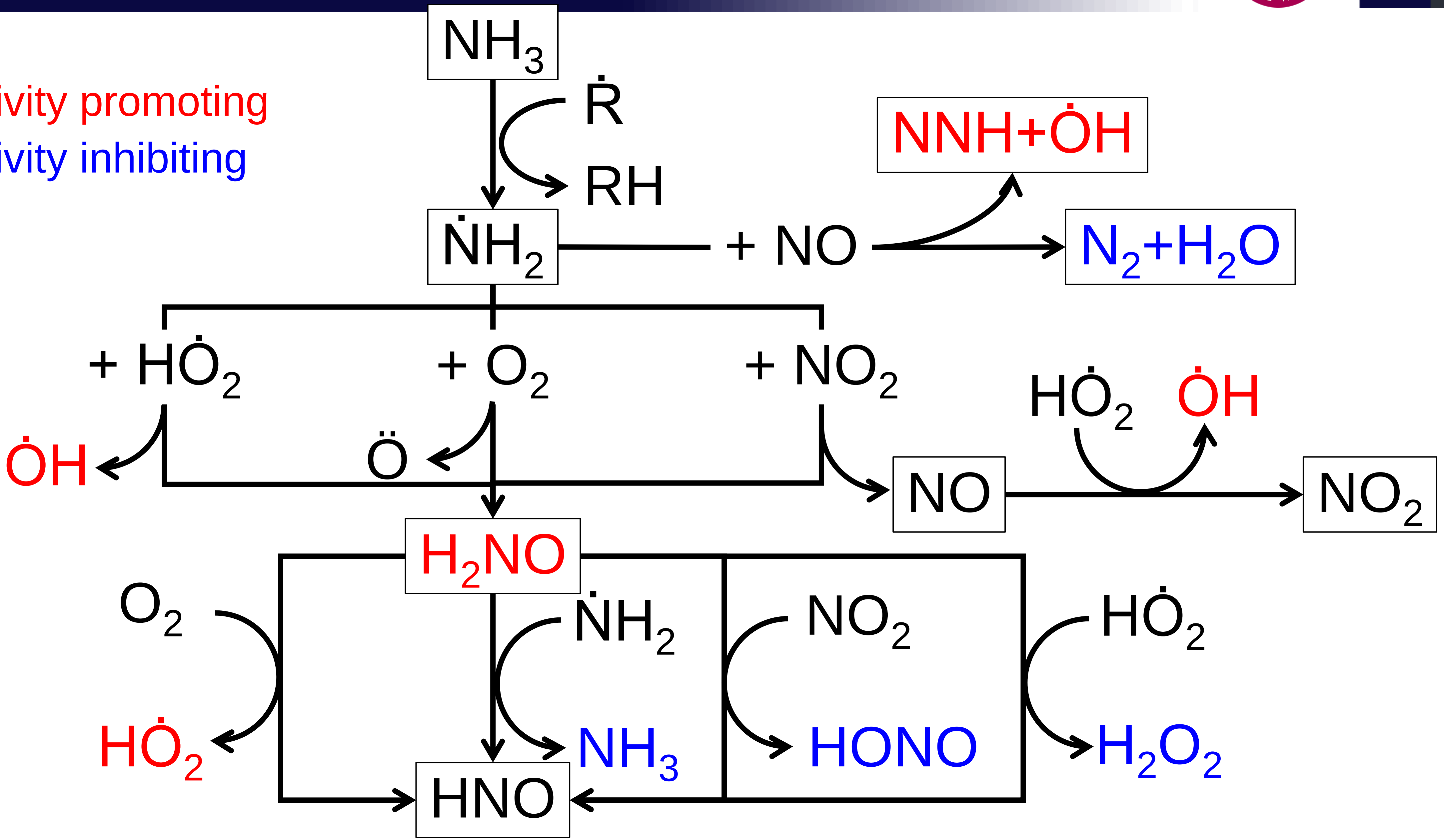
Dean, A. M., & Bozzelli, J. W. (2000). Combustion chemistry of nitrogen. In Gas-phase combustion chemistry (pp. 125-341). Springer, New York, NY.3

Glarborg, P., Alzueta, M. U., Dam-Johansen, K., & Miller, J. A. (1998). Combustion and flame, 115(1-2), 1-27.

Summary of important low-T reactions

Reactivity promoting

Reactivity inhibiting



Developing detailed chemical kinetic mechanisms for ammonia combustion

Henry J. Curran

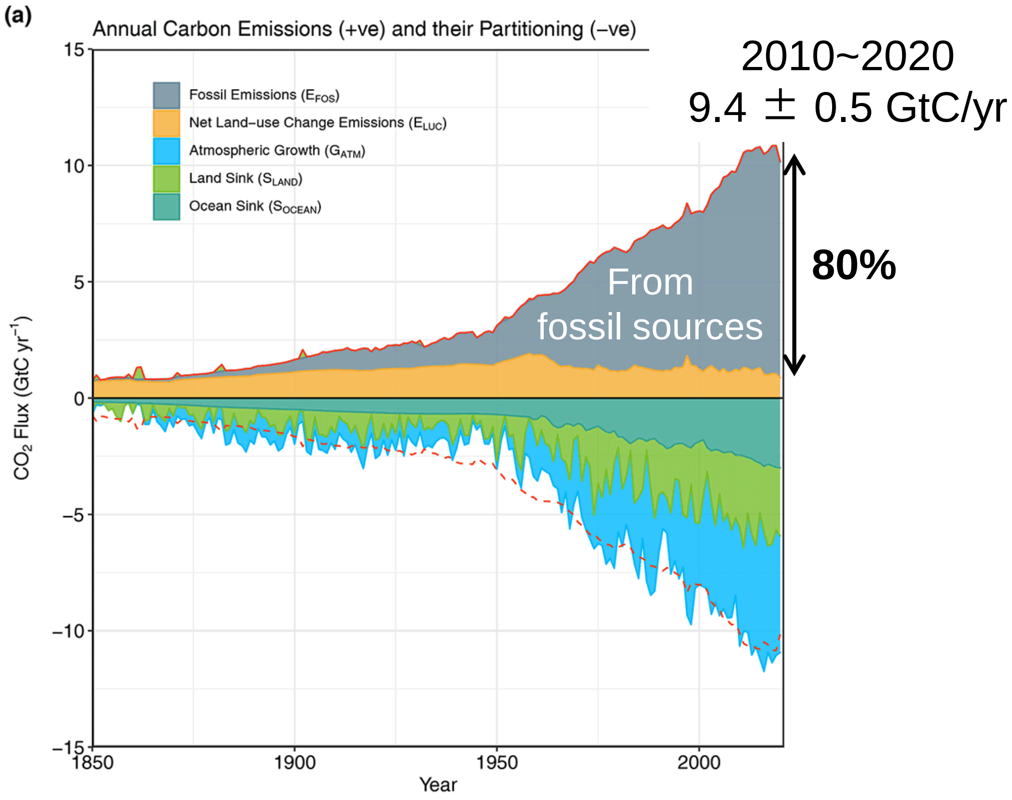
Combustion Chemistry Centre, School of Biological and Chemical Sciences, Ryan Institute, University of Galway, Galway, Ireland

Outline

1. Research motivation
2. Model development
3. Interaction chemistry for NH_3/H_2
4. Interaction chemistry for $NH_3/n\text{-}C_7H_{16}$
5. Influence of NO_x addition on propane ignitions
6. Conclusions

Background & motivation

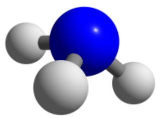
- There is an urgent need for decreasing CO_2 emission from combustion



Partitioning of the annual global CO_2 emissions from 1850 to 2020

[Friedlingstein, et al., "Global carbon budget 2021", Earth System Science Data. 14: 1917-2005 (2022).]

- Ammonia (NH_3) as a zero-carbon alternative fuel



- The 2nd most commercialized chemical in the world, massive production annually
- Prospective in fueling gas turbines and heavy-duty internal combustion engines for cleaner power, via e.g.

General Electric ™

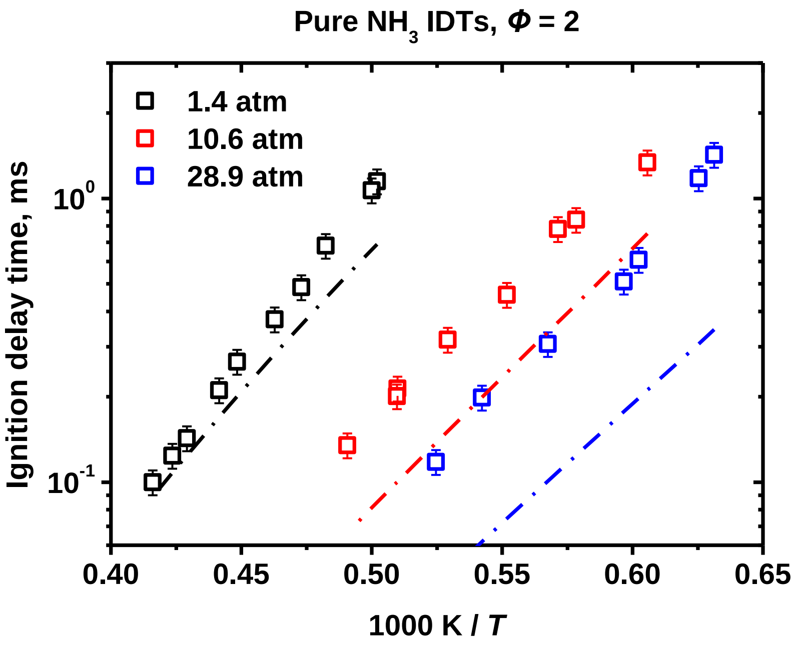
MAN Energy Solutions ™

Research background & motivations

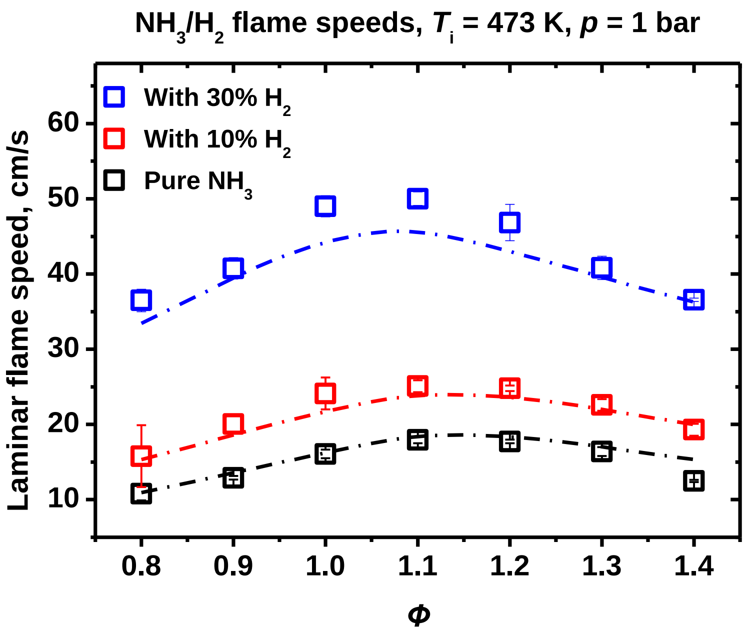
➢ Ammonia is relatively unreactive

- Blended with hydrogen to increase reactivity (75/25% NH_3/H_2 optimal)
- Understand the chemistry to develop combustors with higher efficiency & lower NO_x

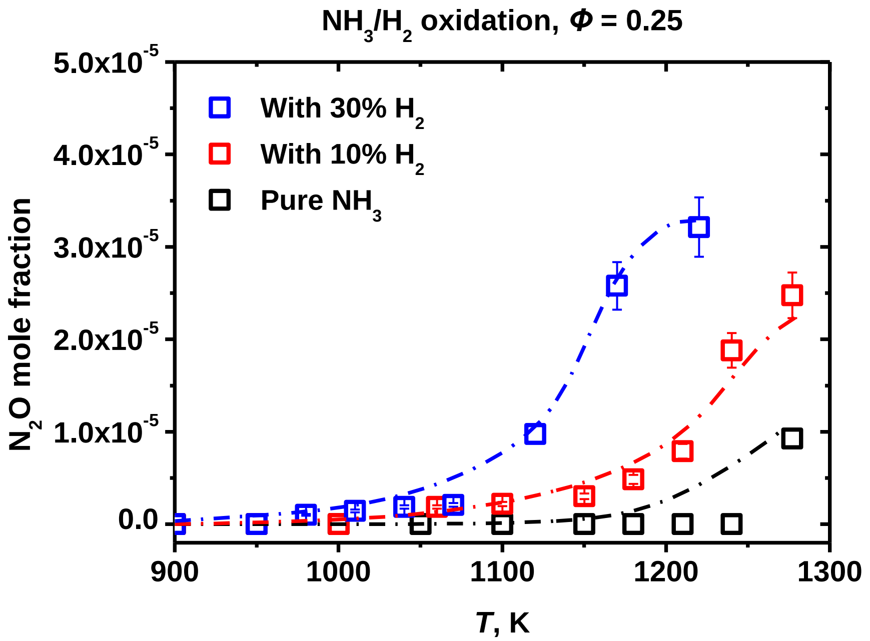
– · – : Zhang 2021 (KAUST)
- - - - : Otomo 2018 (Utokyo)
– – – : Stagni 2020 (POLIMI)
· · · · · : Glarborg 2018 (DTU)


Pure NH_3 IDTs, Φ = 2

Shock tube ignition delay times (IDT)
(Expt.: Mathieu 2015, CNF)


NH_3/H_2 flame speeds, T_i = 473 K, p = 1 bar

Laminar flame speeds
(Expt.: Shrestha 2021, PCI)


NH_3/H_2 oxidation, Φ = 0.25

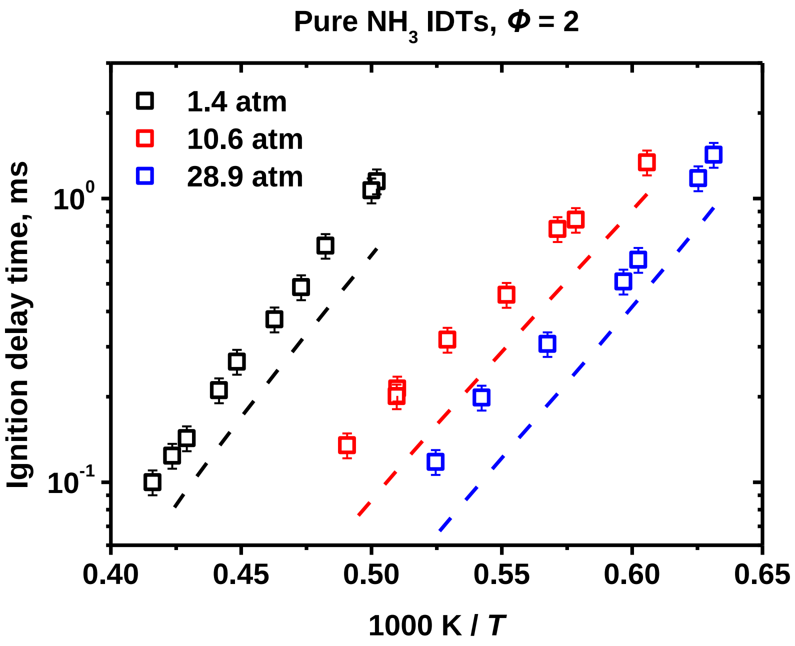
N_2O concentration profiles in jet-stirred reactor
(Expt.: Zhang 2021, CNF)

Research background & motivations

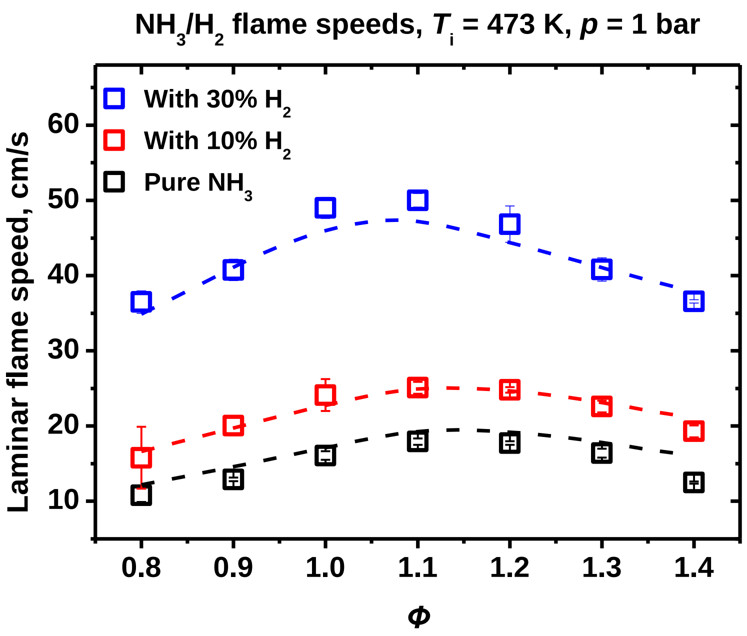
➢ Ammonia is relatively unreactive

- Blended with hydrogen to increase reactivity (75/25% NH_3/H_2 optimal)
- Understand the chemistry to develop combustors with higher efficiency & lower NO_x

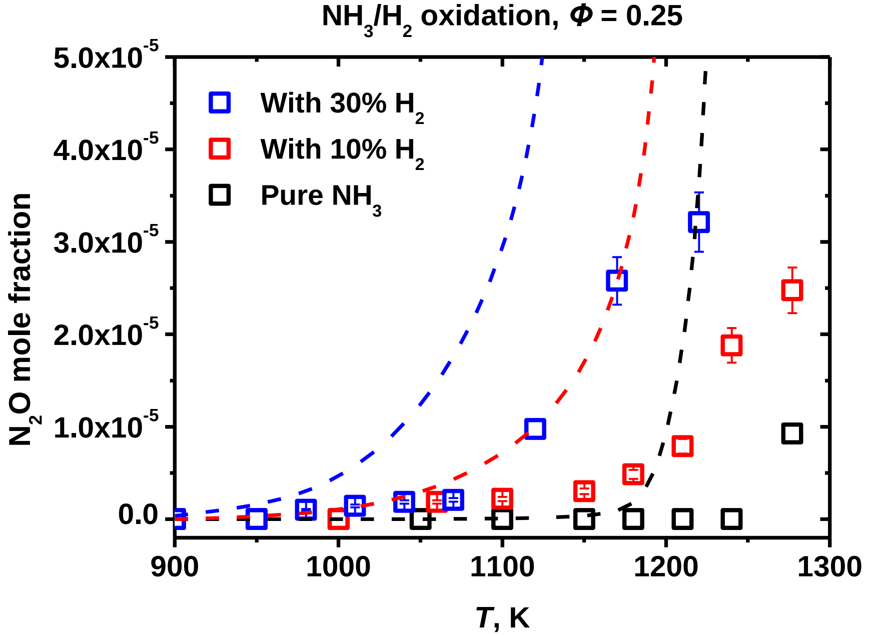
– · – : Zhang 2021 (KAUST) **- - - - : Otomo 2018 (Utokyo)**
– – – : Stagni 2020 (POLIMI) **· · · · · : Glarborg 2018 (DTU)**



Shock tube ignition delay times (IDT)
(Expt.: Mathieu 2015, CNF)



Laminar flame speeds
(Expt.: Shrestha 2021, PCI)



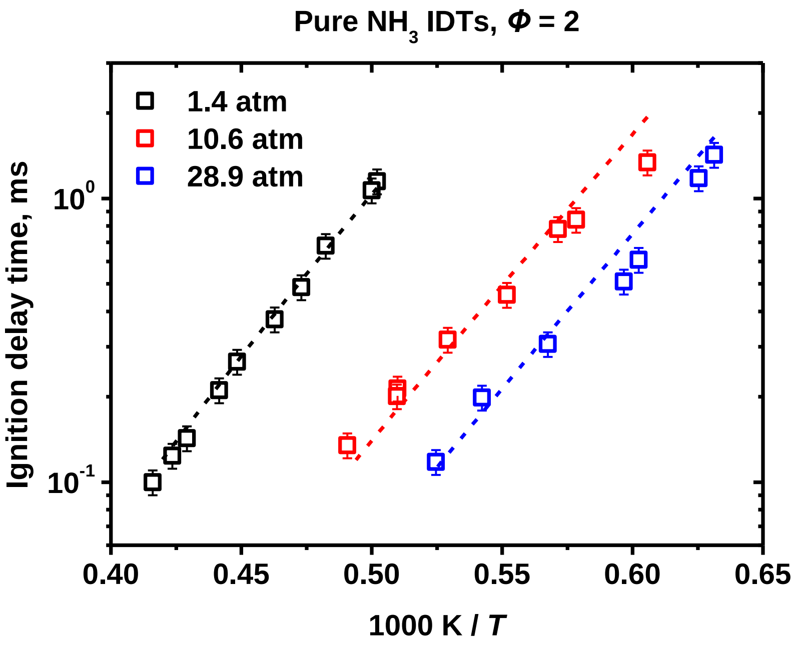
N_2O concentration profiles in jet-stirred reactor
(Expt.: Zhang 2021, CNF)

Research background & motivations

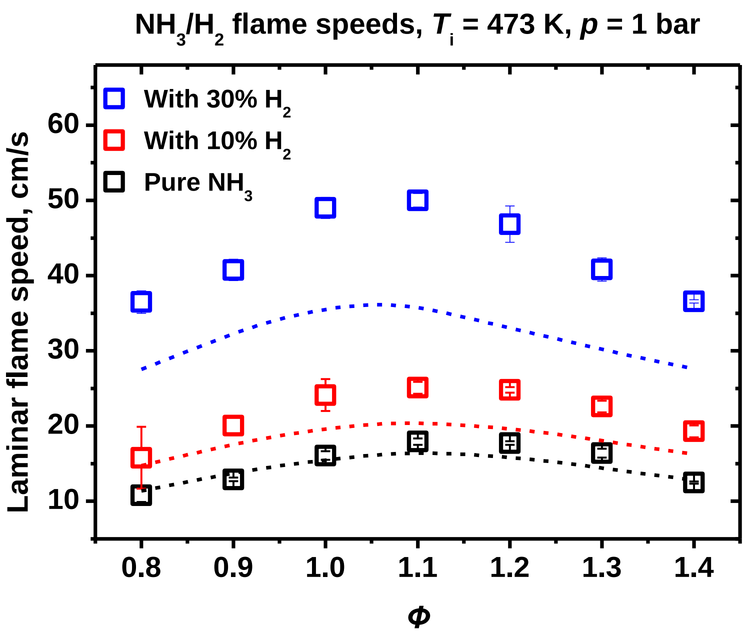
➢ Ammonia is relatively unreactive

- Blended with hydrogen to increase reactivity (75/25% NH_3/H_2 optimal)
- Understand the chemistry to develop combustors with higher efficiency & lower NO_x

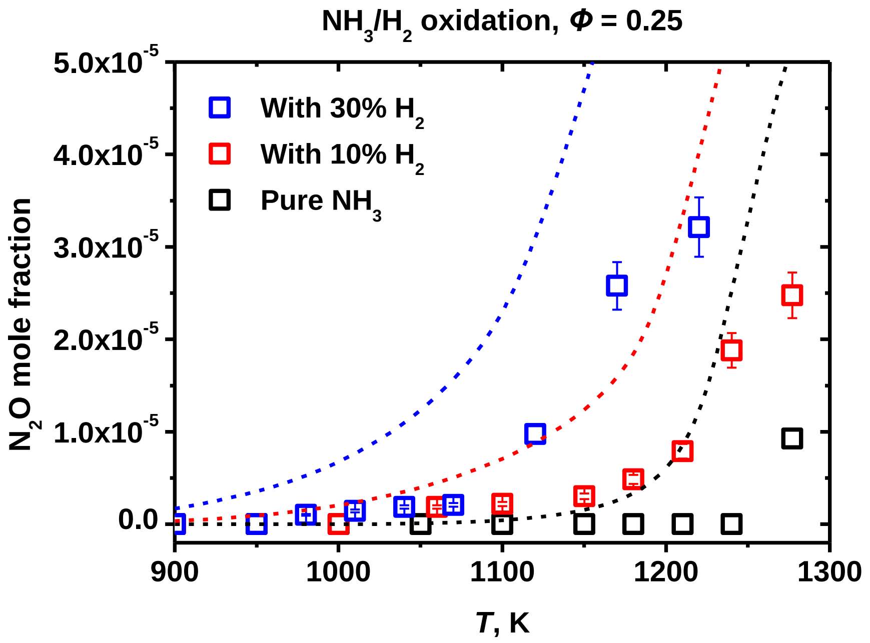
– · – : Zhang 2021 (KAUST)
– – – : Stagni 2020 (POLIMI)
- - - - : Otomo 2018 (Utokyo)
· · · · · : Glarborg 2018 (DTU)



Shock tube ignition delay times (IDT)
(Expt.: Mathieu 2015, CNF)



Laminar flame speeds
(Expt.: Shrestha 2021, PCI)



N_2O concentration profiles in jet-stirred reactor
(Expt.: Zhang 2021, CNF)

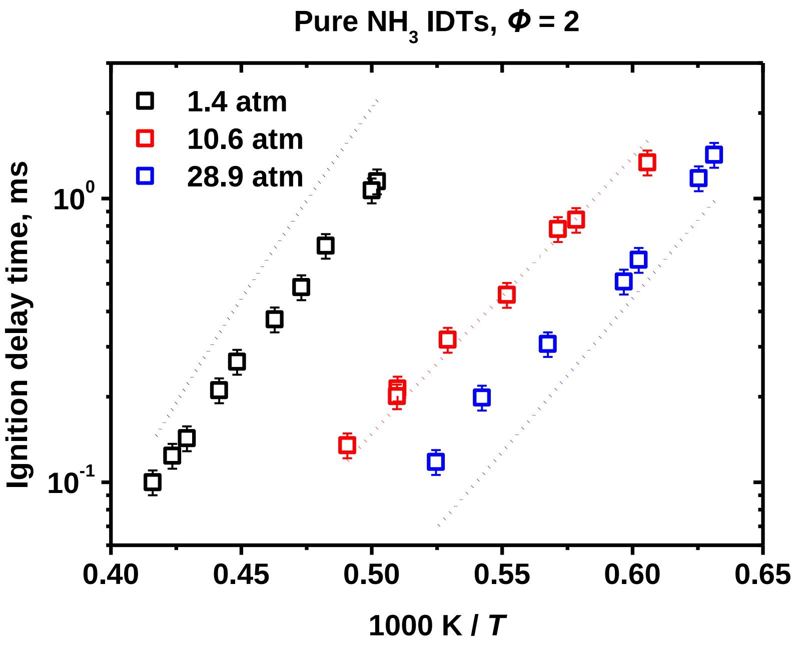
Research background & motivations

➢ Ammonia is relatively unreactive

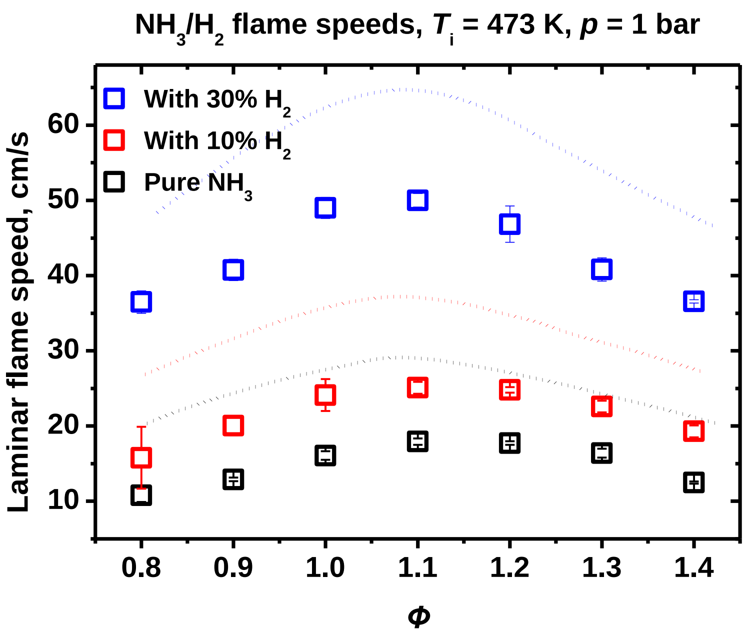
- Blended with hydrogen to increase reactivity (75/25% NH_3/H_2 optimal)
- Understand the chemistry to develop combustors with higher efficiency & lower NO_x

– · – : Zhang 2021 (KAUST) **- - - - : Otomo 2018 (Utokyo)**

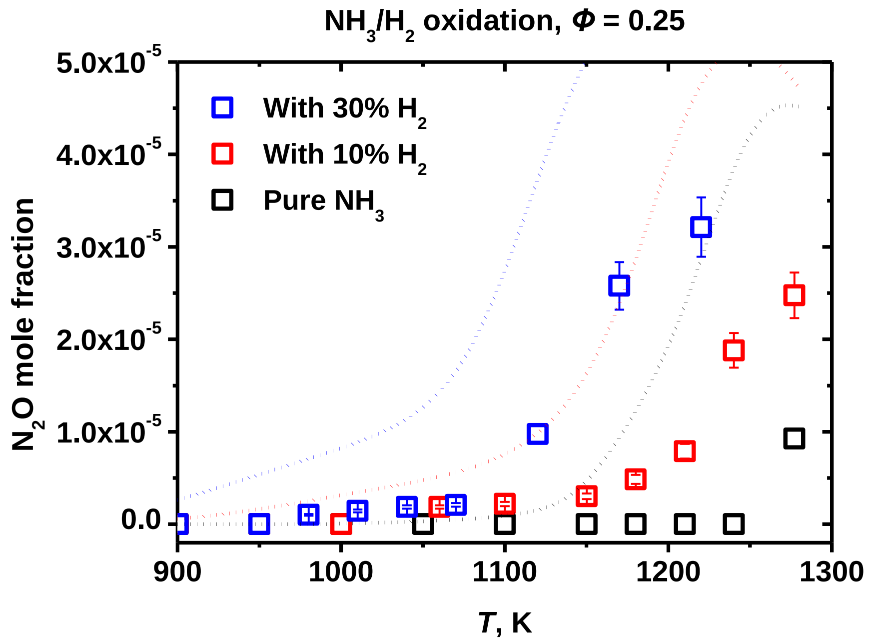
– – – : Stagni 2020 (POLIMI) **· · · · · : Glarborg 2018 (DTU)**



Shock tube ignition delay times (IDT)
(Expt.: Mathieu 2015, CNF)



Laminar flame speeds
(Expt.: Shrestha 2021, PCI)



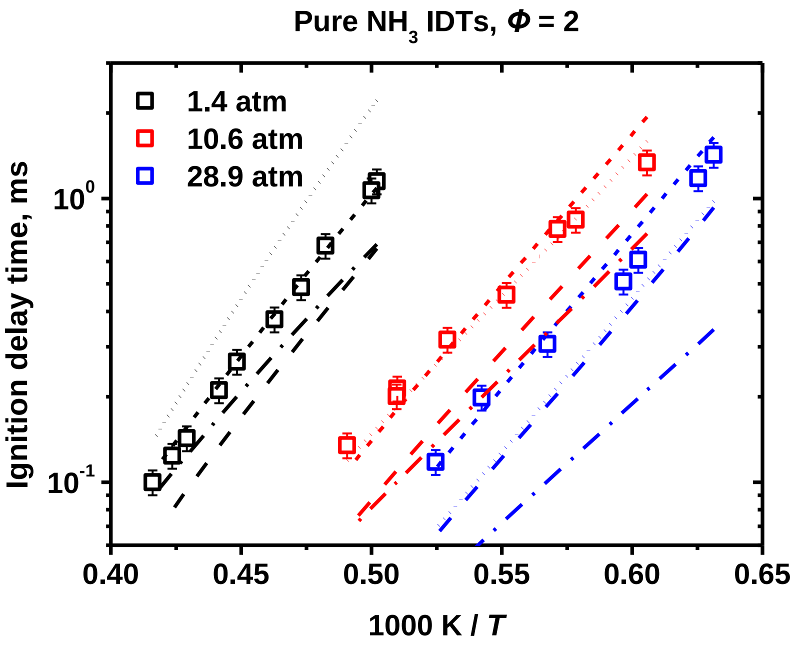
N_2O concentration profiles in jet-stirred reactor
(Expt.: Zhang 2021, CNF)

Research background & motivations

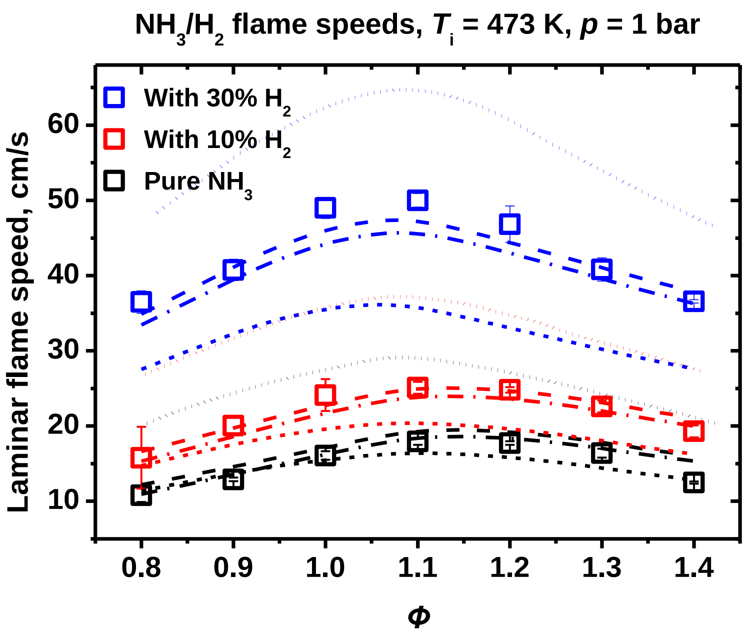
➢ Ammonia is relatively unreactive

- Blended with hydrogen to increase reactivity (75/25% NH_3/H_2 optimal)
- Understand the chemistry to develop combustors with higher efficiency & lower NO_x

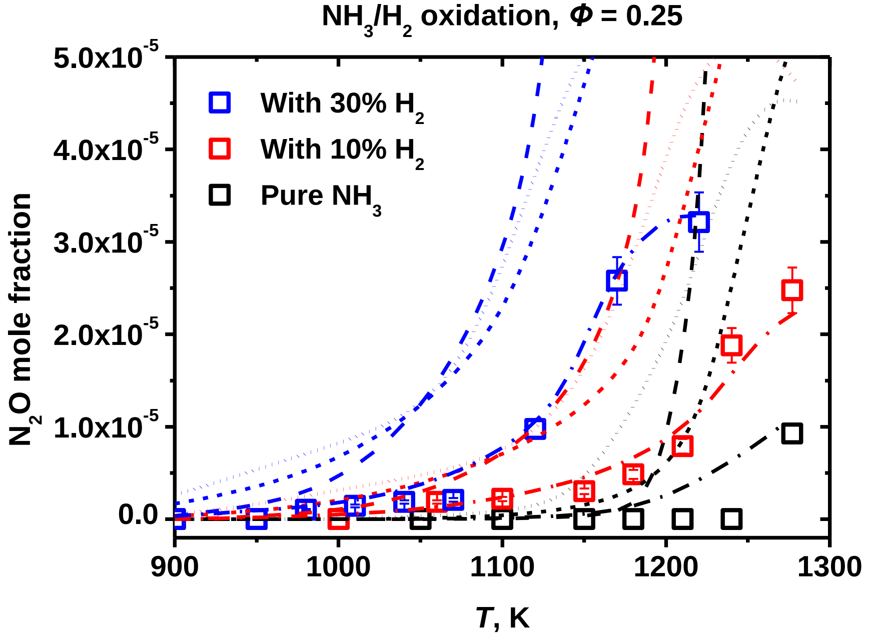
– · – : Zhang 2021 (KAUST)
- - - - : Otomo 2018 (Utokyo)
– – – : Stagni 2020 (POLIMI)
· · · · · : Glarborg 2018 (DTU)


Pure NH_3 IDTs, Φ = 2

Shock tube ignition delay times (IDT)
(Expt.: Mathieu 2015, CNF)


NH_3/H_2 flame speeds, T_i = 473 K, p = 1 bar

Laminar flame speeds
(Expt.: Shrestha 2021, PCI)


NH_3/H_2 oxidation, Φ = 0.25

N_2O concentration profiles in jet-stirred reactor
(Expt.: Zhang 2021, CNF)

Background literature_IDT

Mixture	φ	*T* / K	Pressure	Facilities	Ref.
$NH_3/O_2/Ar$	0.5, 1.0, and 2.0	1560 – 2455	1.4, 11, 30 atm	Shock tube	O. Mathieu, E.L. Petersen, Combust. Flame. 162 (2015) 554–570.
$NH_3/O_2/Ar$	0.5, 1.0, and 2.0	1100 – 1600	20, 40 atm	Shock tube	B. Shu et al. Proc. Combust. Inst. 37(1) (2019) 205–211.
$NH_3/H_2/O_2/N_2/Ar$	0.5, 1.0, 2.0	900 – 1200	20 – 70 bar	Rapid Compression Machine	L. Dai, et al., Combust. Flame. 215 (2020) 134–144.
$NH_3/H_2/O_2/N_2/Ar$	0.2, 0.35, 0.5,	1000 – 1100	43, 65 bar	Rapid Compression Machine	M. Pochet, et al., Proc. Combust. Inst. 37 (2019) 621–629.
NH_3/H_2/air	0.5, 1.0, 2.0	960 – 1130	20 – 60 atm	Rapid Compression Machine	X He et al. Combustion and Flame, 206 (2019) 189-200.
NH_3/H_2/air	1.0	1020 – 1945	1.2, 10 atm	Shock tube	J. Chen et al., Fuel, 287 (2021) 119563.
NH_3/H_2 (50% & 100%)	1.0	1438 – 1694	2.2 atm	Shock tube	J. Baker t al., JEGTP, (2022) .
NH_3/H_2(0, 10% & 25%) NH_3/N_2O(25% & 50%)	0.5, 1.0, 1.5	952 – 1408	30 bar	Rapid Compression Machine	Liao et al. Proc. Combust. Inst. 39 (2023) in press.
NH_3/Bio-syngas/O_2/Ar	0.5	990 – 1995	1.7, 12, 31 atm	Shock tube	O. Mathieu, et al., Proc. Combust. Inst. 34 (2013) 3211–3218.
NH_3/CH_4/air	0.5, 1.0, 2.0	1446 – 1776	2, 5, 10 atm	Shock tube	H. Xiao, et al., Int. J. Energy Res. 44 (2020) 6939–6949.
$NH_3/CH_4/O_2/Ar/N_2$	0.5, 1.0, 2.0	900 – 1100	20, 40 bar	Rapid Compression Machine	B. Shu, et al., Proc. Combust. Inst. 38 (2021) 261–268.
NH_3/DME/air	0.5, 1.0	650 – 950	20, 40 bar	Rapid Compression Machine	G. Issayev, et al., Renew. Energy. 181 (2022) 1353–1370.
NH_3/DME/O_2/Ar	0.5, 1.0, 2.0	610 – 1180	10 – 70 bar	Rapid Compression Machine	L. Dai, et al., Combust. Flame. 227 (2021) 120–134.
NH_3/nC_7H_{16}	1.0, 2.0	635 – 945	10, 15 atm	Rapid Compression Machine	L. Yu, et al., Combust. Flame. 217 (2020) 4–11.

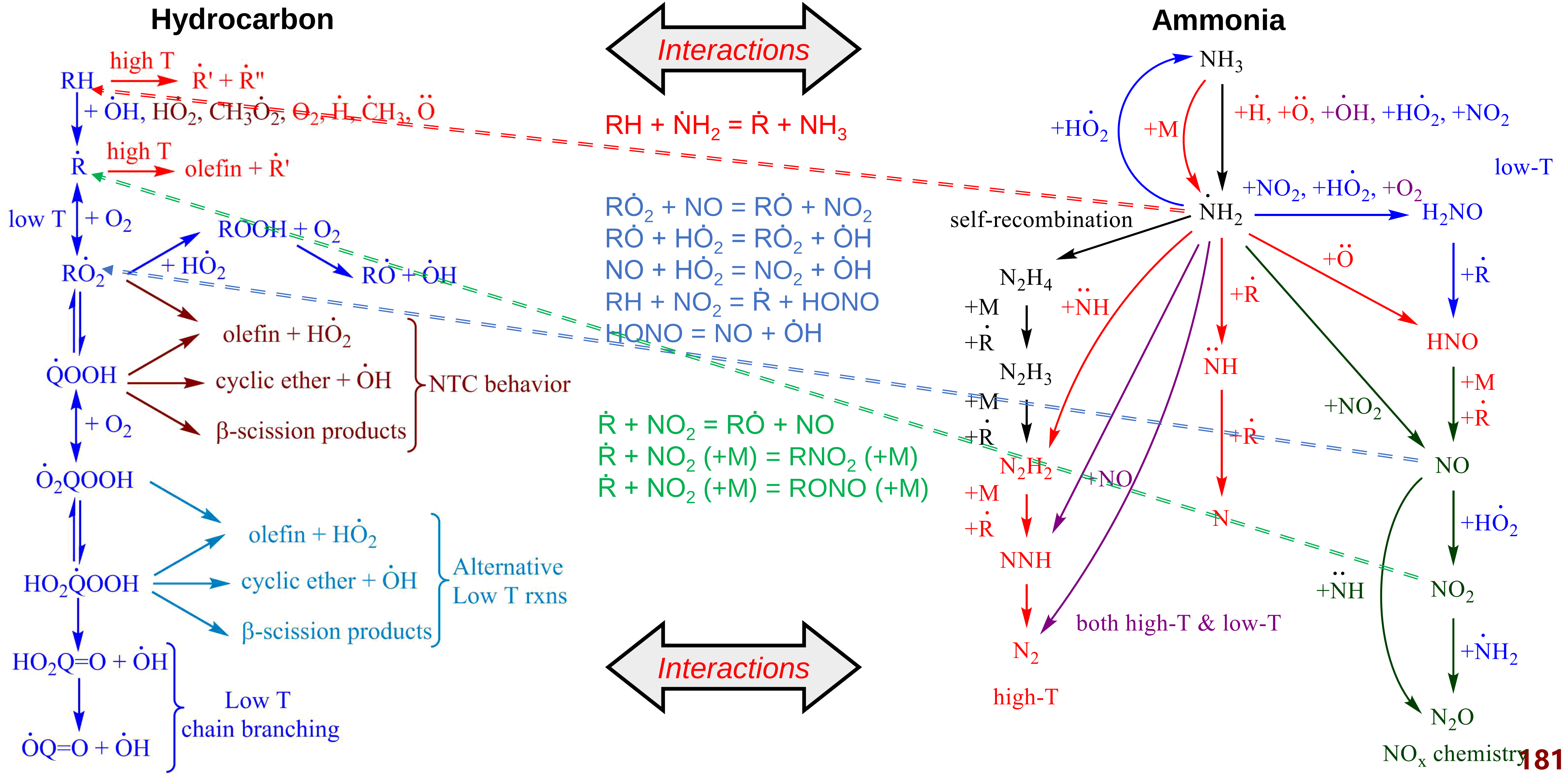
Background literature_LBV

Mixture	**φ**	**T / K**	**Pressure**	**Facility**	**Ref.**
NH_3/air mixtures	0.7 – 1.3	298	1, 3, 5 atm	Constant volume vessel	A. Hayakawa et al. Fuel 159 (2015) 98–106.
NH_3/air	0.6 – 1.8	413	1 atm	Heat flux burner	X. Han et al. Combust. Flame 206 (2019) 214–226.
NH_3/air mixtures	0.6 – 1.5	298	1 atm	Constant volume vessel	B. Mei et al. Combust. Flame 210 (2019) 236–246.
NH_3/O_2(30%)/N_2(70%); NH_3/O_2(30%)/He(70%)	1, 1.2, 1.4	298	1 – 7 atm	Constant volume vessel	B. Zhang et al. Energy & Fuels 36(15) (2022) 8528–8537.
NH_3/H_2 (X = 0 – 0.6)/air	0.8 – 1.4	298, 323, 373, 423, 473	1 atm	Constant volume vessel	C. Lhuillier et al. Fuel 263 (2020) 116653.
NH_3+H_2 (X=0.15,0.25,0.35,0.4)	0.7 – 1.6	298, 448	1atm	Heat flux burner	Z. Wang et al. Combust. Flame 229 (2021) 111392.
NH_3/H_2 (14.3–85.7%)	0.7 – 1.4	298	1, 2, 5, 10 atm	Constant volume vessel	B. Mei et al. Combust. Flame 231 (2021) 111472.
NH_3/H_2/air	0.8 – 1.8	298	1, 5 atm	Constant volume vessel	G.J. Gotama et al. Combust. Flame 236 (2022) 111753.
NH_3+H_2 (X=0.15,0.25,0.35,0.4)	0.7 – 1.6	298, 448	1 atm	Heat flux burner	Z. Wang, et al., Combust. Flame. 229 (2021) 111392.
NH_3/H_2(0–30%); NH_3/O_2(21–30%)/N_2 (or O_2/He)	0.8 – 1.4	298 – 473	1, 3, 5, 10 atm	Constant volume vessel	Shrestha et al. Proc. Combust. Inst. 38(2) (2021) 2163–2174.
NH_3/NO(50%)/N_2(50%)	1.1 – 1.9	298	1 atm	Constant volume vessel	B. Mei et al. Proc. Combust. Inst. 38(2) (2021) 2477–2485.
NH_3/CH_4/air	0.7 – 1.3	298	1, 3, 5 atm	Constant volume vessel	A. Hayakawa et al. Fuel 159 (2015) 98–106.
NH_3(X=0 – 0.3) /CH_4/air	0.8 – 1.3	298	1 atm	Constant volume vessel	E.C. Okafor et al. Combust. Flame 187 (2018) 185–198.
NH_3/CH_4	0.6– 1.4	300	1, 2, 5, 10, 20 atm	Counterflow flame	S. Liu et al. Energy 175 (2019) 250–258.
NH_3+CH_3OH / C_2H_5OH (X=0 – 1.0)	0.8 – 1.3	318 – 338	1 – 5 atm	Heat flux burner	M.B. Raida et al. Combust. Flame 230 (2021) 111435.
NH_3+syngas	0.7 – 1.5	298	1, 1.2, 5, 10 atm	Constant volume vessel	B. Mei, et al., Combust. Flame. 220 (2020) 368–377.
NH_3/DME/air	0.8 – 1.3	300	1, 3, 5 bar	Constant volume vessel	G. Issayev, et al., Renew. Energy. 181 (2022) 1353–1370.

Background literature_JSR/FR

Mixture	T, K	p, atm	φ	Dilution	t_{res}, s	Ref.
JSRs						
NH_3/NO (0–50%)	1100–1460	1.00 bar	0.1–2.0	99% N_2	0.1 & 0.2	2019, Dagaut
NH_3	500–1200	1.05	0.010 & 0.019	97% He	1.5	2020, Stagni et al.
NH_3/H_2 (0–70%)	800–1280	1.00	0.25 & 1.00	99% N_2	1.0	2021, Zhang et al.
NH_3	700–1200	1.00	0.1, 0.5 & 1.0	83–97% Ar	3.0	2022, Tang et al.
NH_3/H_2 (0 & 30%)	800–1300	1.00	0.6, 1.0 & 1.5	99% Ar	1.0	2022, Osipova et al.
Shock tubes						
NH_3	2000–3200	0.8–1.1	∞	99% Ar	/	1990, Davisdson et al.
NH_3/H_2 (0 & 83%)	2100–3000	~1.0	∞	99% Ar	/	2022, Alturaifi et al.
NH_3	1829–2198	~1.2	0.5, 1.0 & 1.8	97% Ar	/	2022, Alturaifi et al.
Flow reactors						
NH_3	700–1000	30 & 100 bar	0.200	96% N_2	T-dependent	2016, Song et al.
NH_3	1300–2000	1.25	0.375	99% He	~50 ms	2020, Stagni et al.
NH_3	875–1450	1.00	0.046–∞	99% N_2	T-dependent	2021, Abián et al.

Model development



Hydrocarbon

RH $\xrightarrow{\text{high T}}$ $\dot{R}' + \dot{R}''$

+ $\dot{O}H$, $H\dot{O}_2$, $CH_3\dot{O}_2$, O_2, $\dot{H}$, $\dot{C}H_3$, $\ddot{O}$

$\dot{R}$ $\xrightarrow{\text{high T}}$ olefin + $\dot{R}'$

low T + O_2

$R\dot{O}_2$ + $H\dot{O}_2$ → ROOH + O_2 → $R\dot{O} + \dot{O}H$

olefin + $H\dot{O}_2$

$\dot{Q}OOH$ → cyclic ether + $\dot{O}H$

β-scission products

NTC behavior

+ O_2

$\dot{O}_2QOOH$

olefin + $H\dot{O}_2$

$HO_2\dot{Q}OOH$ → cyclic ether + $\dot{O}H$

β-scission products

Alternative Low T rxns

$HO_2Q{=}O + \dot{O}H$

$\dot{O}Q{=}O + \dot{O}H$

Low T chain branching

Interactions

$RH + \dot{N}H_2 = \dot{R} + NH_3$

$R\dot{O}_2 + NO = R\dot{O} + NO_2$
$R\dot{O} + H\dot{O}_2 = R\dot{O}_2 + \dot{O}H$
$NO + H\dot{O}_2 = NO_2 + \dot{O}H$
$RH + NO_2 = \dot{R} + HONO$
$HONO = NO + \dot{O}H$

$\dot{R} + NO_2 = R\dot{O} + NO$
$\dot{R} + NO_2\ (+M) = RNO_2\ (+M)$
$\dot{R} + NO_2\ (+M) = RONO\ (+M)$

Interactions

Ammonia

NH_3

$+H\dot{O}_2$, +M, $+\dot{H}$, $+\ddot{O}$, $+\dot{O}H$, $+H\dot{O}_2$, $+NO_2$

$\dot{N}H_2$

$+NO_2$, $+H\dot{O}_2$, $+O_2$ → H_2NO low-T

$+\dot{R}$ → HNO

$+\ddot{O}$ → HNO

+M $+\dot{R}$ → NO

$+NO_2$ → NO

self-recombination → N_2H_4

+M $+\dot{R}$ → N_2H_3

+M $+\dot{R}$ → N_2H_2

$+\ddot{N}H$

+M $+\dot{R}$ → NNH → N_2

high-T

$+\dot{R}$ → $\ddot{N}H$ → $+\dot{R}$ → N

+NO

both high-T & low-T

NO → $+H\dot{O}_2$ → NO_2 → $+\dot{N}H_2$ → N_2O

$+\ddot{N}H$

NO_x chemistry

Model development

➢ Kinetics data

- H_2/O_2 subset: adopted from NUIGMech1.3
- NH_3 subset:
  1. Fuel molecule & radicals: NH_3 NH_2 NH N N_2
  2. From fuel radical recombination: N_2H_4 N_2H_3 N_2H_2 H_2NN NNH
  3. Nitrogen oxides: NO NO_2 N_2O NO_3
  4. Nitroxide species: H_2NO HNOH NH_2OH HNO HON HONO HNO_2 $HONO_2$ HNNO H_2NNO_2

➢ Thermochemistry data

- Mostly adopted from the work of Bugler et al. [J. Phys. Chem. A, 2016] for most nitrogen species, based on CBS-APNO, G3, and G4 averaged $\Delta H_{f,0K}$ and B3LYP/cc-pVTZ rotational-vibrational properties

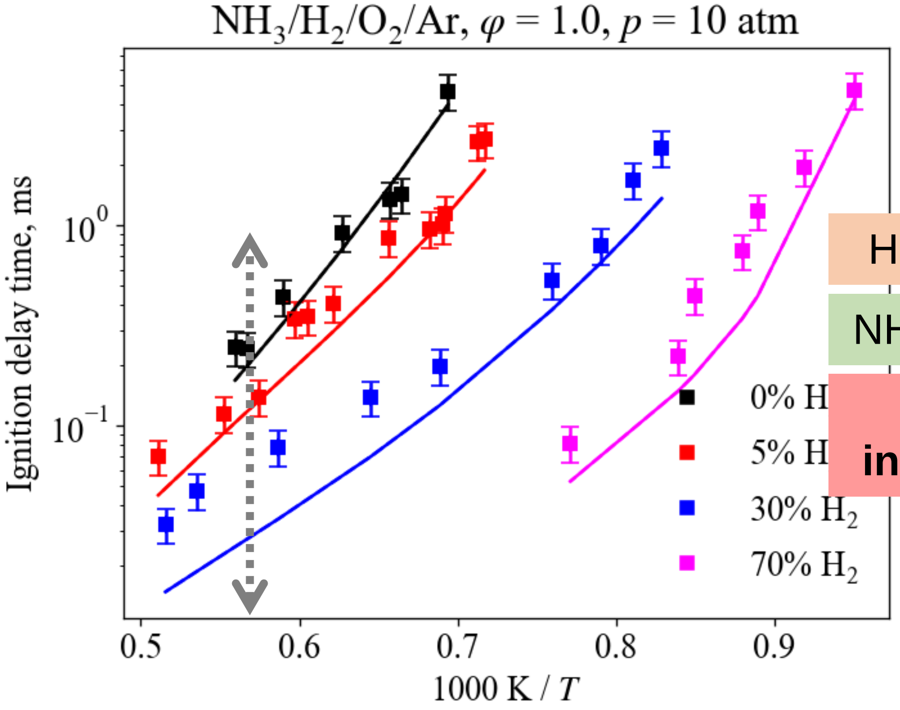
➢ Transport data

- Adopted from NUIGMech 1.3

✓ 39 species, 306 reactions

NH_3-H_2 interactions chemistry at high-*T*

➢ NH_3-H_2 ST IDT sensitivity analyses

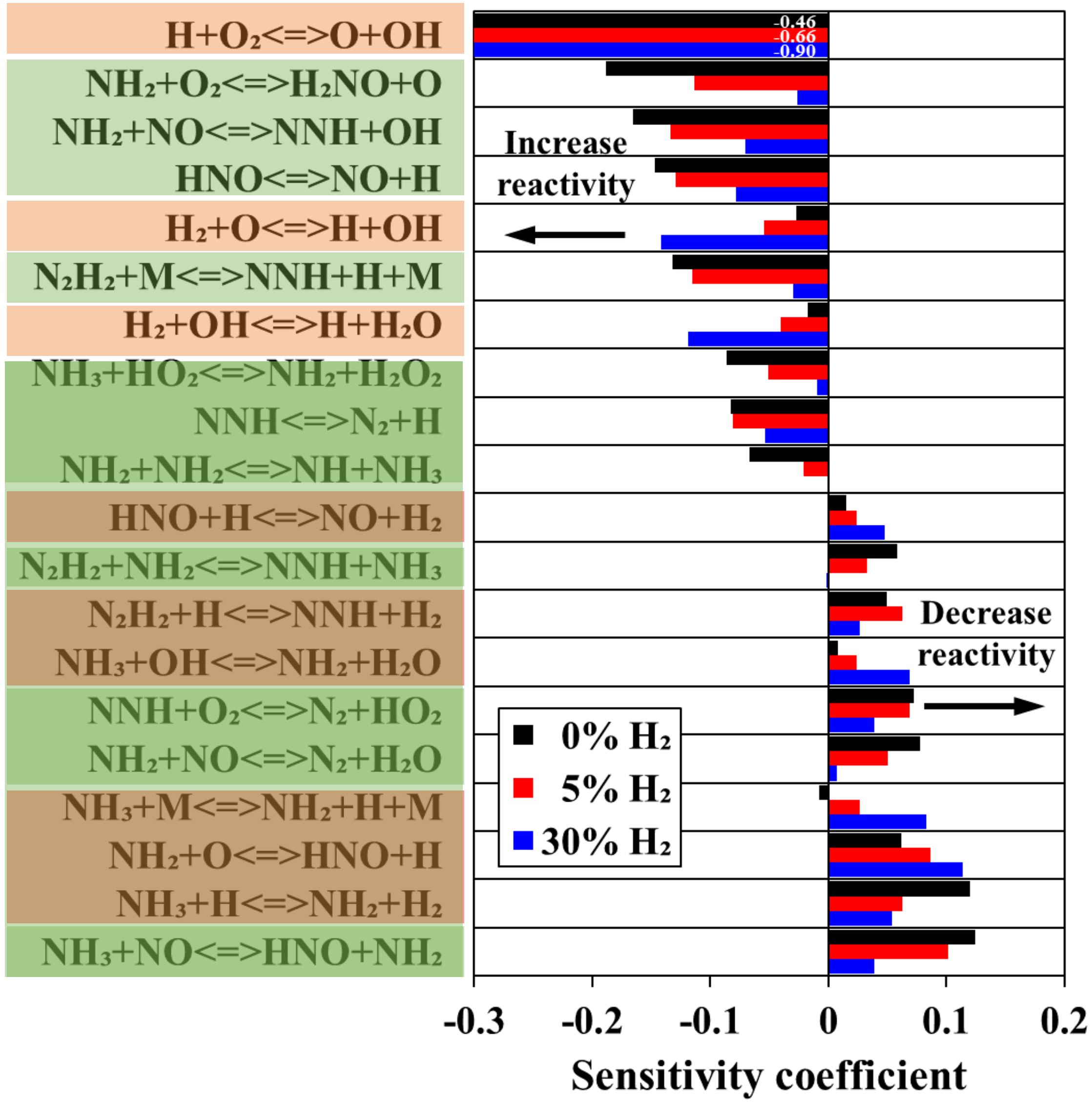


H_2 oxidation

NH_3 oxidation

NH_3-H_2 interactions

Experimental data:
Chen, J., Jiang, X., Qin, X., & Huang, Z. (2021). *Fuel*, *287*, 119563.



@ $\varphi = 1.0$, *T* = 1800 K, *p* = 10 atm

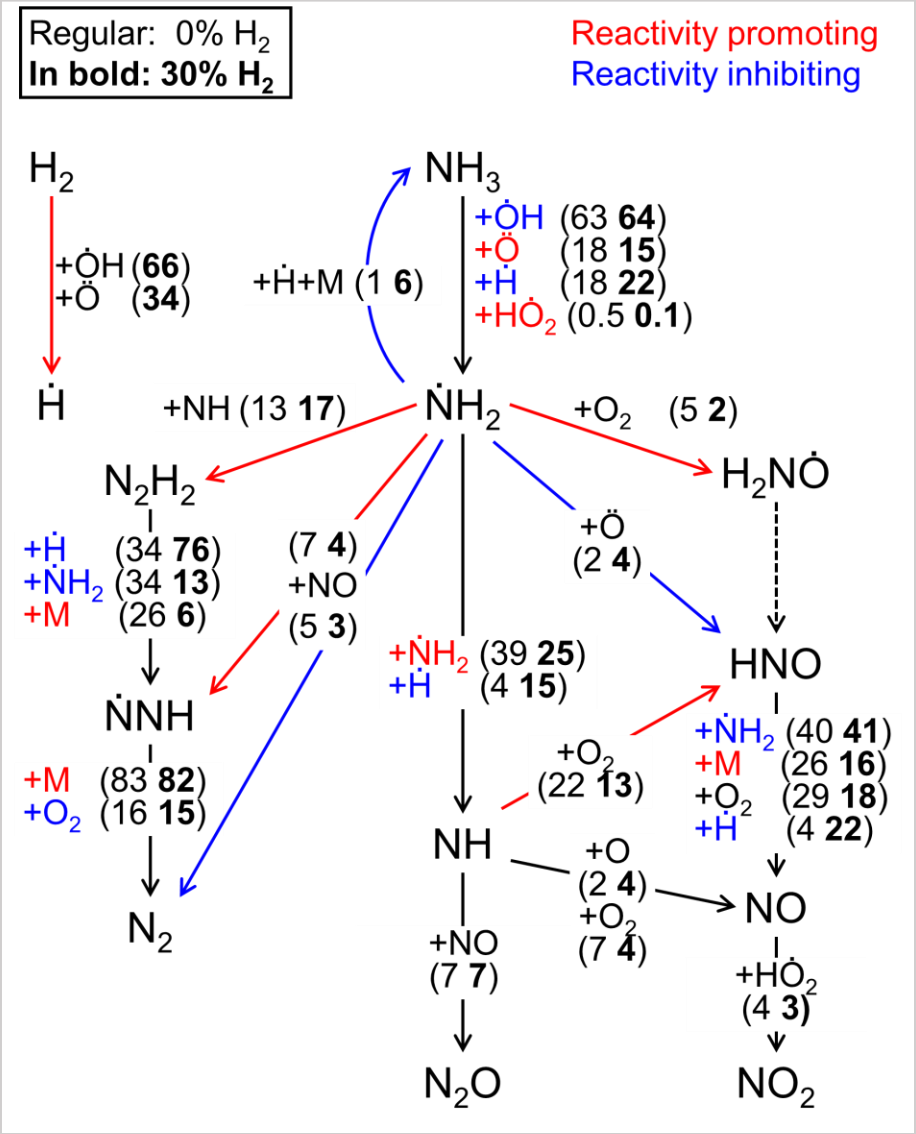
NH_3-H_2 interactions chemistry at high-*T*

➢ Flux analyses

H_2 oxidation

- $H_2 + \ddot{O} = \dot{H} + \dot{O}H$
- $H_2 + \dot{O}H = \dot{H} + H_2O$
- $\dot{H} + O_2 = \ddot{O} + \dot{O}H$

The H_2 in the fuel enhances $\dot{H} + O_2$ chain-branching, promoting reactivity



Fluxes (%) @ *T* = 1800 K, *p* = 10 atm, *φ* = 1.0 and 20% NH_3 consumption

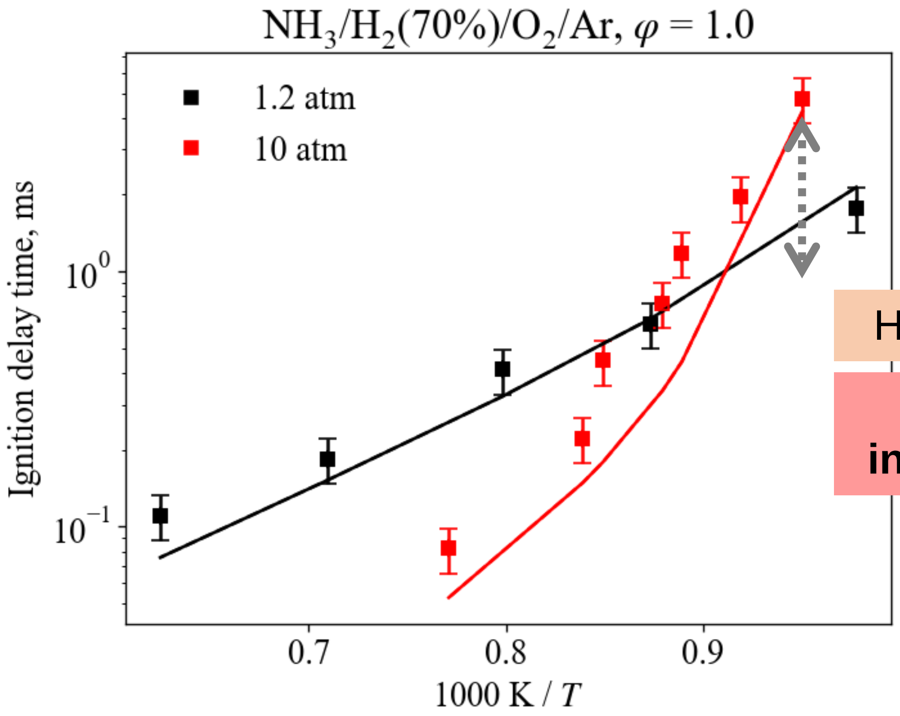
NH_3 oxidation

- $NH_3 + M \leftarrow \dot{N}H_2 + \dot{H} + M$
- $NH_3 + \dot{O}H = \dot{N}H_2 + H_2O$
- $NH_3 + \dot{H} = \dot{N}H_2 + H_2$
- $\dot{N}H_2 + \ddot{O} = HNO + \dot{H}$
- $HNO + \dot{H} = NO + H_2$
- $\dot{N}H_2 + \ddot{N}H = N_2H_2 + \dot{H}$
- $N_2H_2 + \dot{H} = \dot{N}NH + H_2$

NH_3 initiation reactions with $\dot{O}H$ and $\dot{H}$; $\dot{N}H_2$, HNO and N_2H_2 additions with $\dot{H}$ and $\ddot{O}$ compete with H_2 oxidation, inhibiting reactivity

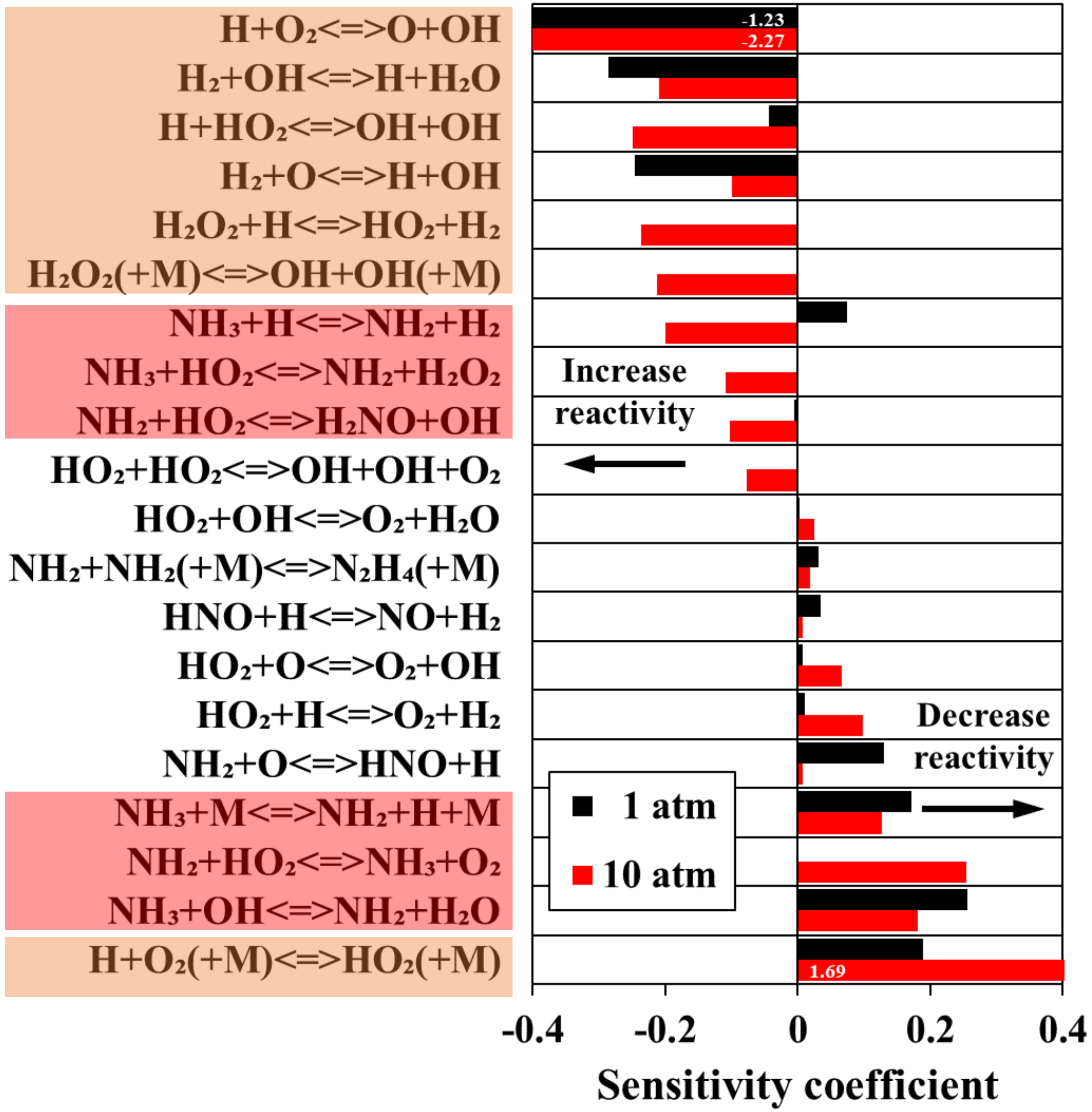
NH_3-H_2 interactions chemistry at high-*T*

➢ NH_3-H_2 ST IDT sensitivity analyses



H_2 oxidation

NH_3-H_2 interactions



@ $\varphi = 1.0$, $T = 1050$ K and 70% H_2

At $T < 1100$ K, NH_3/H_2 (70%) ignite slower when pressure increases

Experimental data:
Chen, J., Jiang, X., Qin, X., & Huang, Z. (2021). *Fuel*, *287*, 119563.

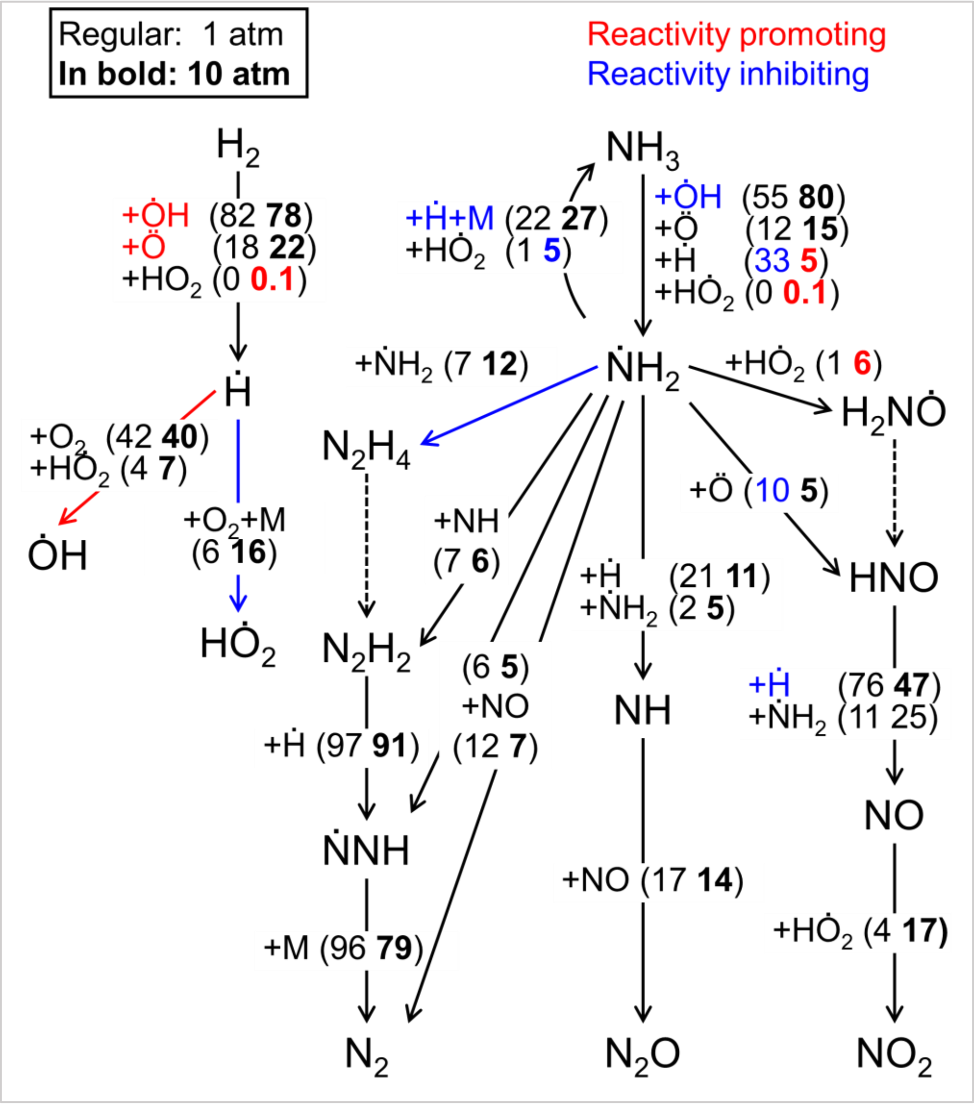
NH_3-H_2 interactions chemistry at high-*T*

➢ Flux analyses

H_2 oxidation

- $H_2 + \dot{O}H = \dot{H} + H_2O$
- $H_2 + \ddot{O} = \dot{H} + \dot{O}H$
- $H_2O_2 + \dot{H} \leftarrow H_2 + H\dot{O}_2$
- $\dot{H} + O_2 = \ddot{O} + \dot{O}H$
- $\dot{H} + O_2\ (+M) = H\dot{O}_2\ (+M)$
- $\dot{H} + H\dot{O}_2 = \dot{O}H + \dot{O}H$
- $H_2O_2\ (+M) = \dot{O}H + \dot{O}H\ (+M)$

As *p* increases, $\dot{H} + O_2\ (+M)$ becomes more important and produces more $H\dot{O}_2$; $H\dot{O}_2$ then abstract an H atom to form H_2O_2 which can decompose to two $\dot{O}H$



Regular: 1 atm
In bold: 10 atm

Reactivity promoting
Reactivity inhibiting

H_2
$+\dot{O}H$ (82 **78**)
$+\ddot{O}$ (18 **22**)
$+HO_2$ (0 **0.1**)
$\dot{H}$
$+O_2$ (42 **40**)
$+H\dot{O}_2$ (4 **7**)
$\dot{O}H$
$+O_2+M$ (6 **16**)
$H\dot{O}_2$

NH_3
$+\dot{O}H$ (55 **80**)
$+\ddot{O}$ (12 **15**)
$+\dot{H}$ (33 **5**)
$+H\dot{O}_2$ (0 **0.1**)
$\dot{N}H_2$
$+\dot{H}+M$ (22 **27**)
$+H\dot{O}_2$ (1 **5**)
$+\dot{N}H_2$ (7 **12**)
N_2H_4
N_2H_2
$+NH$ (7 **6**)
$+\dot{H}$ (97 **91**)
$\dot{N}NH$
$+M$ (96 **79**)
(6 **5**)
$+NO$ (12 **7**)
N_2
$+\dot{H}$ (21 **11**)
$+\dot{N}H_2$ (2 **5**)
NH
$+NO$ (17 **14**)
N_2O
$+H\dot{O}_2$ (1 **6**)
$H_2N\dot{O}$
$+\ddot{O}$ (10 **5**)
HNO
$+\dot{H}$ (76 **47**)
$+\dot{N}H_2$ (11 **25**)
NO
$+H\dot{O}_2$ (4 **17**)
NO_2

Fluxes (%) for NH_3/H_2(70%) @ T = 1050 K, φ = 1.0 and 20% NH_3 consumption

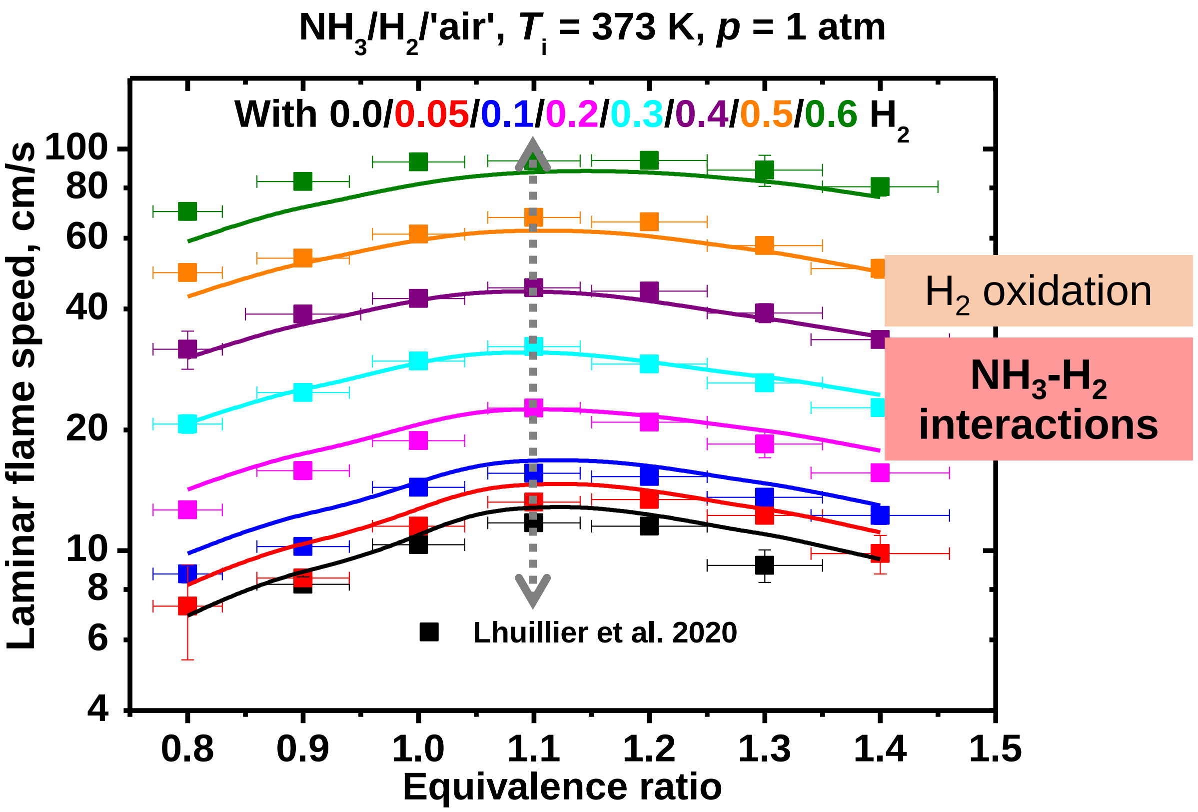
NH_3 oxidation

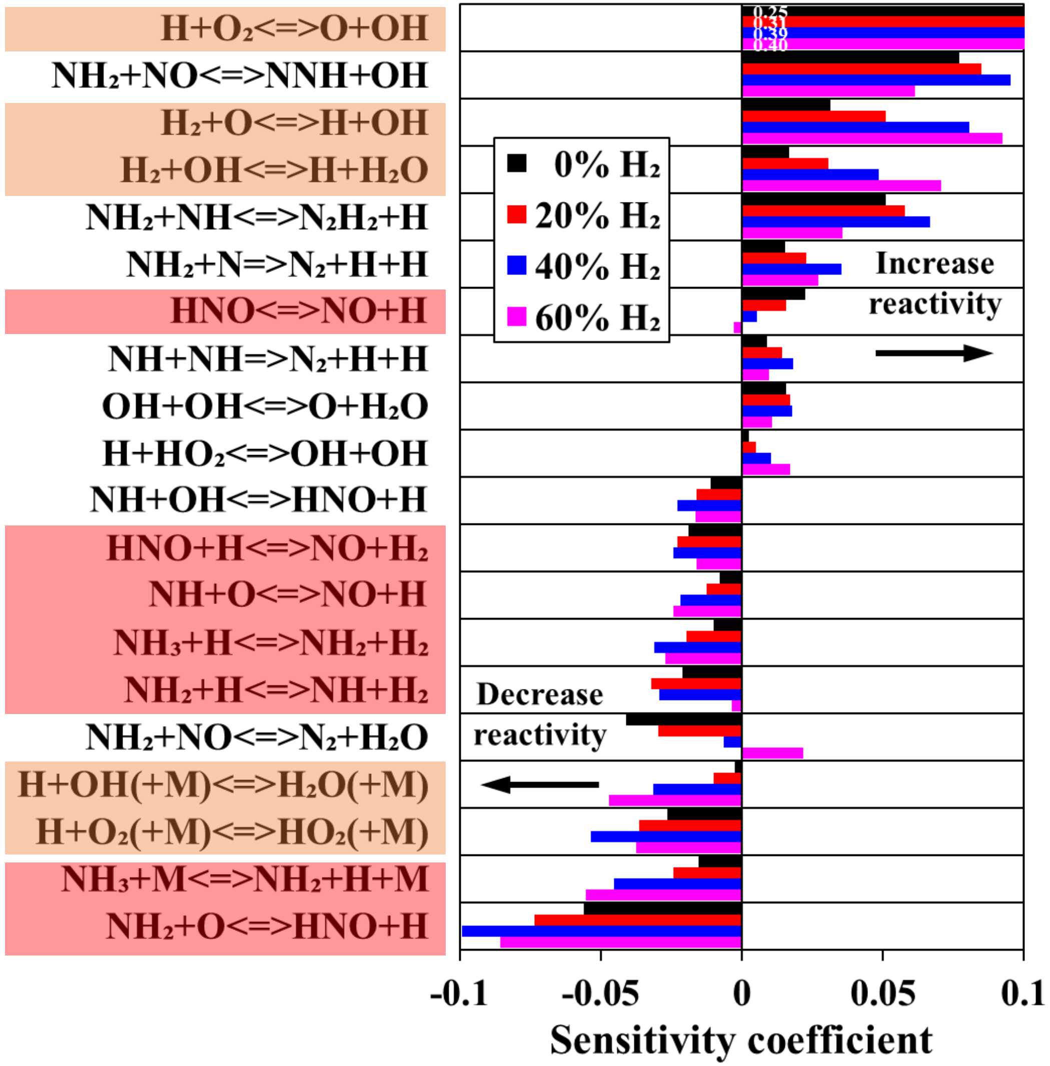
- $NH_3 + M \leftarrow \dot{N}H_2 + \dot{H} + M$
- $NH_3 + \dot{O}H = \dot{N}H_2 + H_2O$
- $NH_3 + \dot{H} = \dot{N}H_2 + H_2$
- $NH_3 + H\dot{O}_2 = \dot{N}H_2 + H_2O_2$
- $\dot{N}H_2 + H\dot{O}_2 = NH_3 + O_2$
  $= H_2N\dot{O} + \dot{O}H$

As *p* increases, chain-termination $\dot{N}H_2 + H\dot{O}_2$ & $\dot{N}H_2 + \dot{H} + M$ get more important, inhibiting fuel reactivity

NH_3-H_2 interactions chemistry at high-*T*

➤ NH_3-H_2 flame speed sensitivity analyses





Experimental data:
Lhuillier, C., Brequigny, P., Lamoureux, N., Contino, F., & Mounaïm-Rousselle, C. (2020). Fuel, 263, 116653.

@ T_i = 373 K, p = 1 atm and φ = 1.1

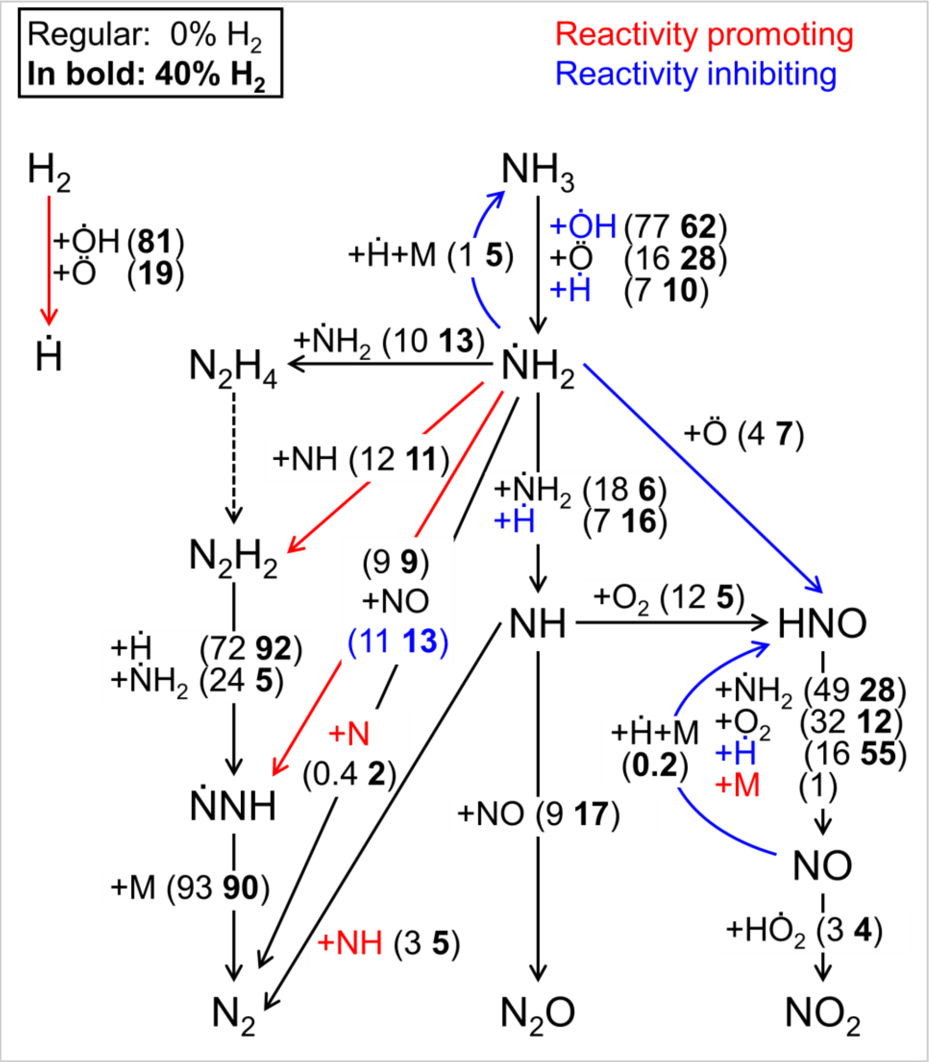
NH_3-H_2 interactions chemistry at high-*T*

➢ Flux analyses

H_2 oxidation

- $H_2 + \dot{O}H = \dot{H} + H_2O$
- $H_2 + \ddot{O} = \dot{H} + \dot{O}H$
- $\dot{H} + O_2 = \ddot{O} + \dot{O}H$
- $\dot{H} + O_2\ (+M) = H\dot{O}_2\ (+M)$
- $\dot{H} + \dot{O}H\ (+M) = H_2O\ (+M)$

The H_2 in the fuel enhances $\dot{H} + O_2$ chain-branching, promoting reactivity



Fluxes (%) for NH_3/H_2 @ 1 atm, $T_i = 373$ K, $\varphi = 1.1$ and the position of maximum $[NH_3]$ drop

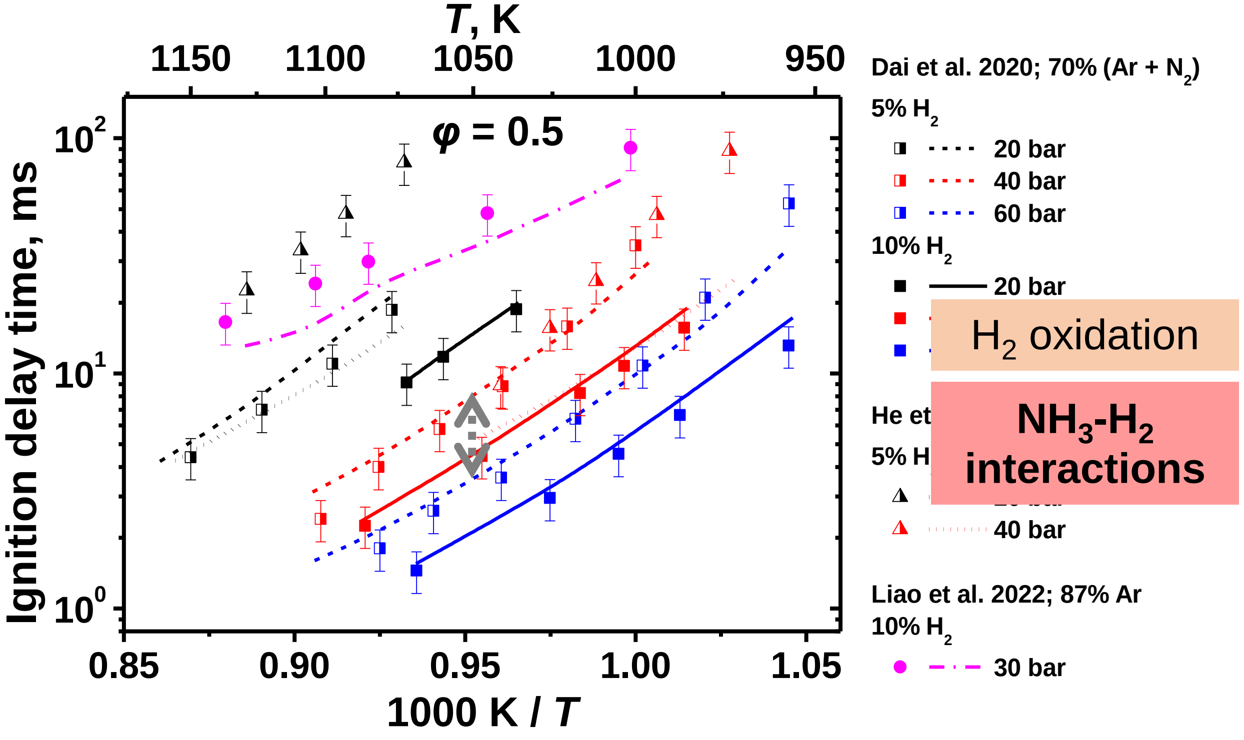
NH_3 oxidation

- $NH_3 + M \leftarrow \dot{N}H_2 + \dot{H} + M$
- $NH_3 + \dot{H} = \dot{N}H_2 + H_2$
- $\dot{N}H_2 + \dot{H} = \ddot{N}H + H_2$
- $\dot{N}H_2 + \ddot{O} = HNO + \dot{H}$
- $HNO = NO + \dot{H}$
- $HNO + \dot{H} = NO + H_2$
- $\dot{N}H_2 + \ddot{N}H = N_2H_2 + \dot{H}$

H-abstraction reactions by $\dot{H}$, and $\dot{N}H_2$ additions with $\dot{H}$ and $\ddot{O}$ compete with H_2 oxidation, inhibiting reactivity;
$\dot{N}H_2 + \ddot{N}H$ and HNO decomposition produce $\dot{H}$, promoting reactivity

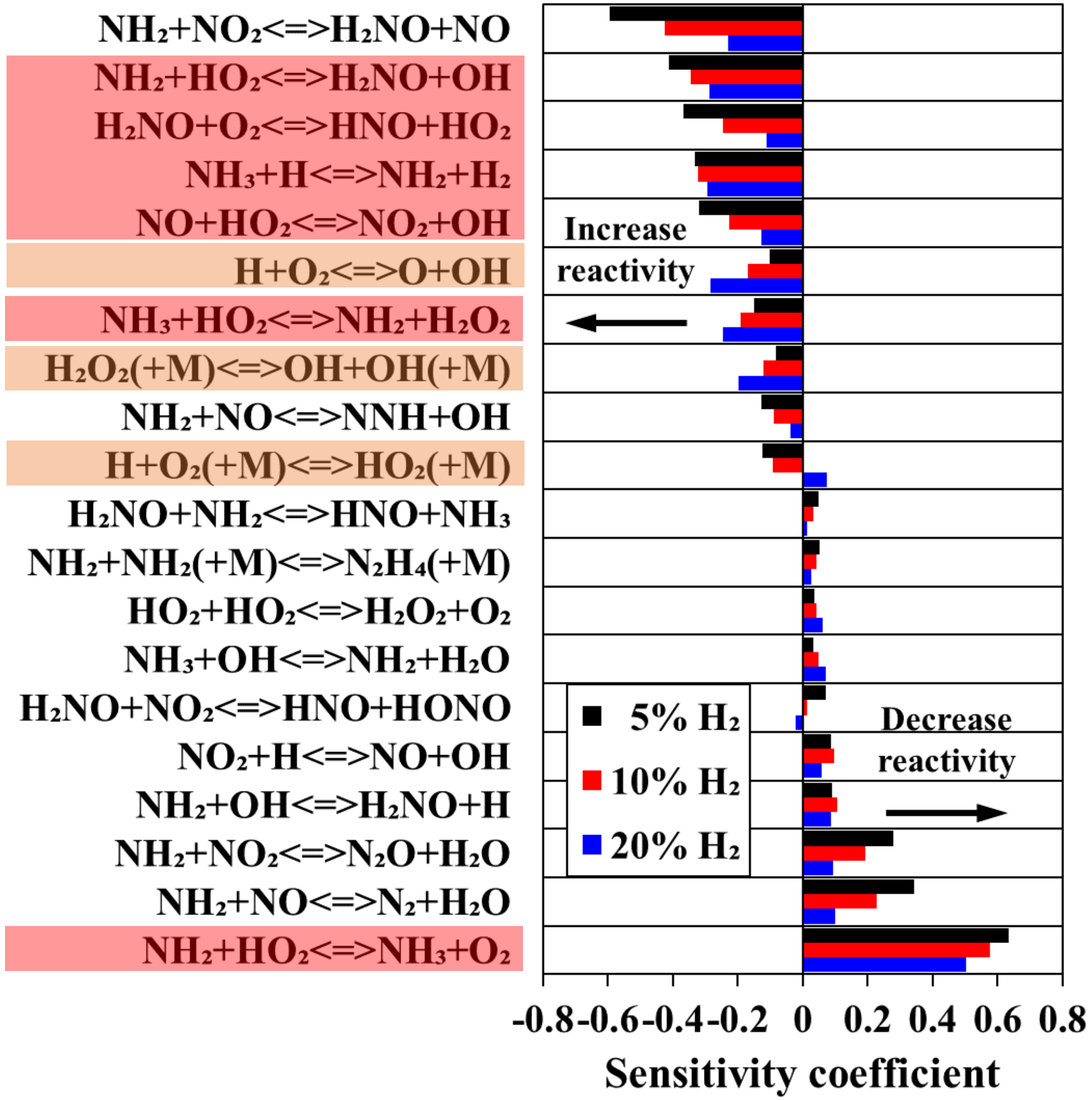
NH_3-H_2 interactions chemistry at low-*T*

➢ NH_3-H_2 RCM IDT sensitivity analyses



H_2 oxidation

NH_3-H_2 interactions



Experimental data:
Dai, L., Gersen, S., Glarborg, P., Levinsky, H., & Mokhov, A. (2020). *Combustion and flame*, *215*, 134-144.
He, X., Shu, B., Nascimento, D., Moshammer, K., Costa, M., & Fernandes, R. X. (2019). *Combustion and Flame*, *206*, 189-200.
Liao, W., Chu, Z., Wang, Y., Li, S., & Yang, B. (2023). *Proceedings of the Combustion Institute*, *39*(4), 4377-4385.

@ φ = 0.5, *T* = 1050 K, *p* = 40 atm

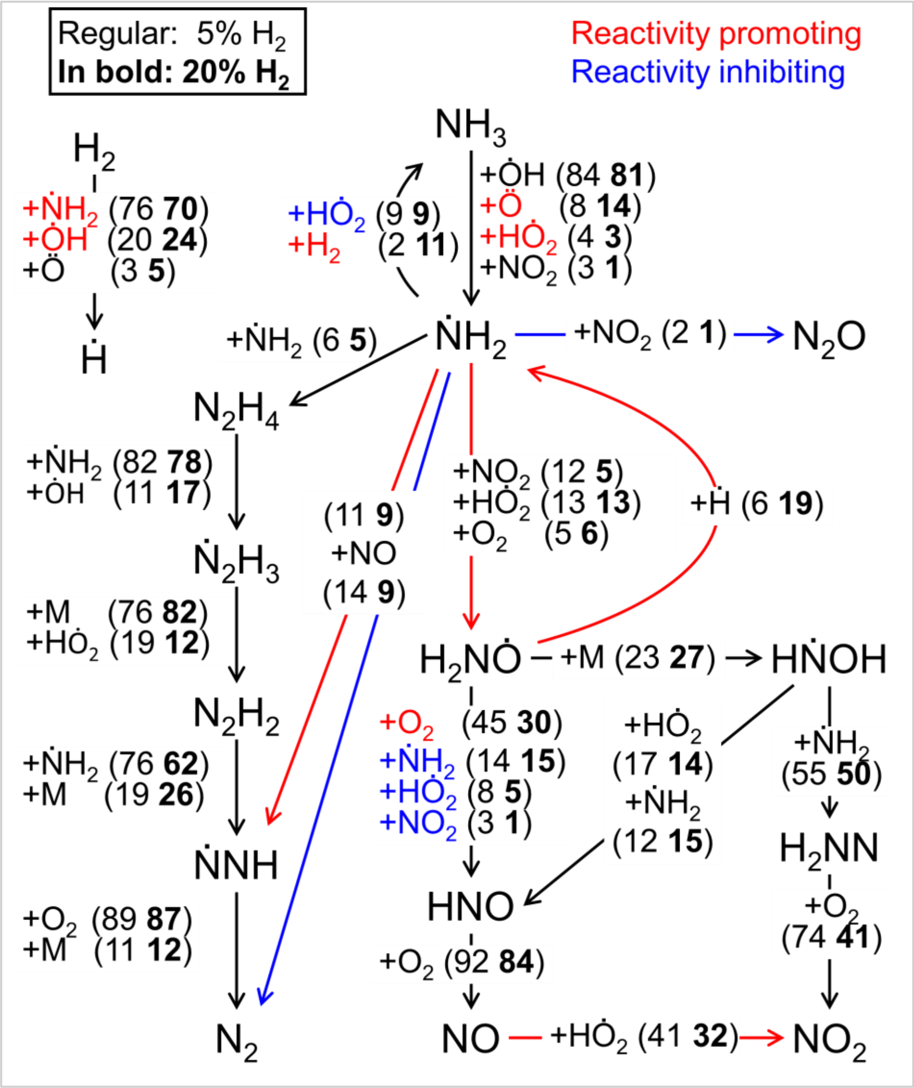
NH_3-H_2 interactions chemistry at low-T

➢ Flux analyses

H_2 oxidation

- $NH_3 + \dot{H} \leftarrow \dot{N}H_2 + H_2$
- $H_2 + \dot{O}H = \dot{H} + H_2O$
- $\dot{H} + O_2 = \ddot{O} + \dot{O}H$
- $\dot{H} + O_2\ (+M) = H\dot{O}_2\ (+M)$
- $NH_3 + H\dot{O}_2 = \dot{N}H_2 + H_2O_2$
- $H_2O_2\ (+M) = \dot{O}H + \dot{O}H\ (+M)$

The H_2 in the fuel converts $\dot{N}H_2$ into $\dot{H}$, and produces more $H\dot{O}_2$; $H\dot{O}_2$ then react with NH_3, $\dot{N}H_2$ and NO…



Fluxes (%) for NH_3/H_2 @ T = 1050 K, φ = 0.5, p = 40 atm and 20% NH_3 consumption

NH_3 oxidation

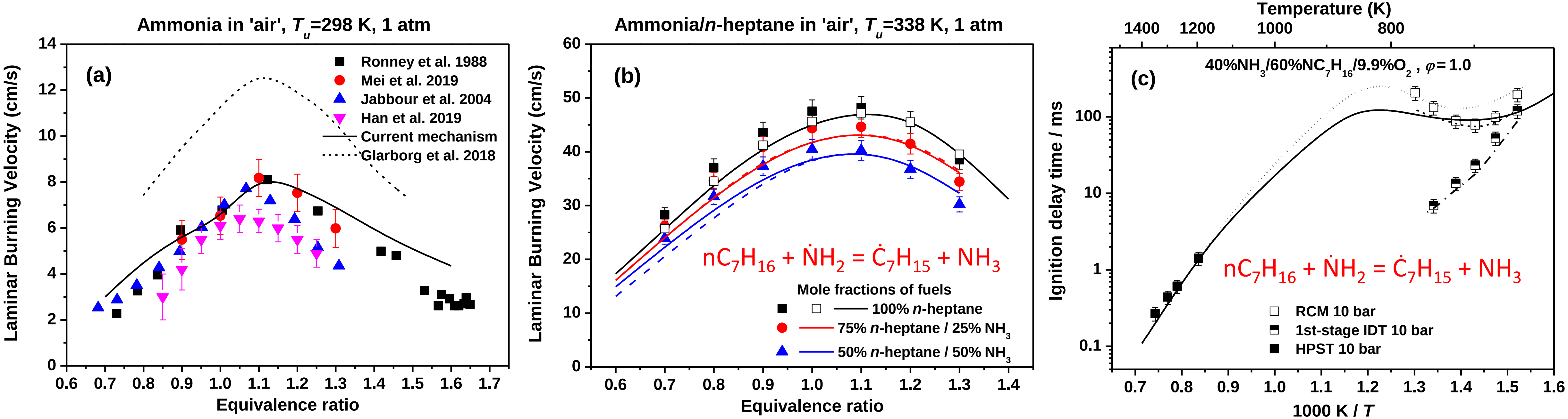
- $NH_3 + \dot{O}H = \dot{N}H_2 + H_2O$
- $NH_3 + \dot{H} \leftarrow \dot{N}H_2 + H_2$
- $NH_3 + H\dot{O}_2 = \dot{N}H_2 + H_2O_2$
- $\dot{N}H_2 + H\dot{O}_2 = NH_3 + O_2$
  $= H_2N\dot{O} + \dot{O}H$
- $H_2N\dot{O} + O_2 = HNO + H\dot{O}_2$
- $NO + H\dot{O}_2 = NO_2 + \dot{O}H$

$H\dot{O}_2$ reactions with NH_3, $\dot{N}H_2$ and NO either produce $\dot{O}H$ directly, or produce H_2O_2 which then decomposes to two $\dot{O}H$

Kinetic modeling of ammonia/*n*-heptane blends

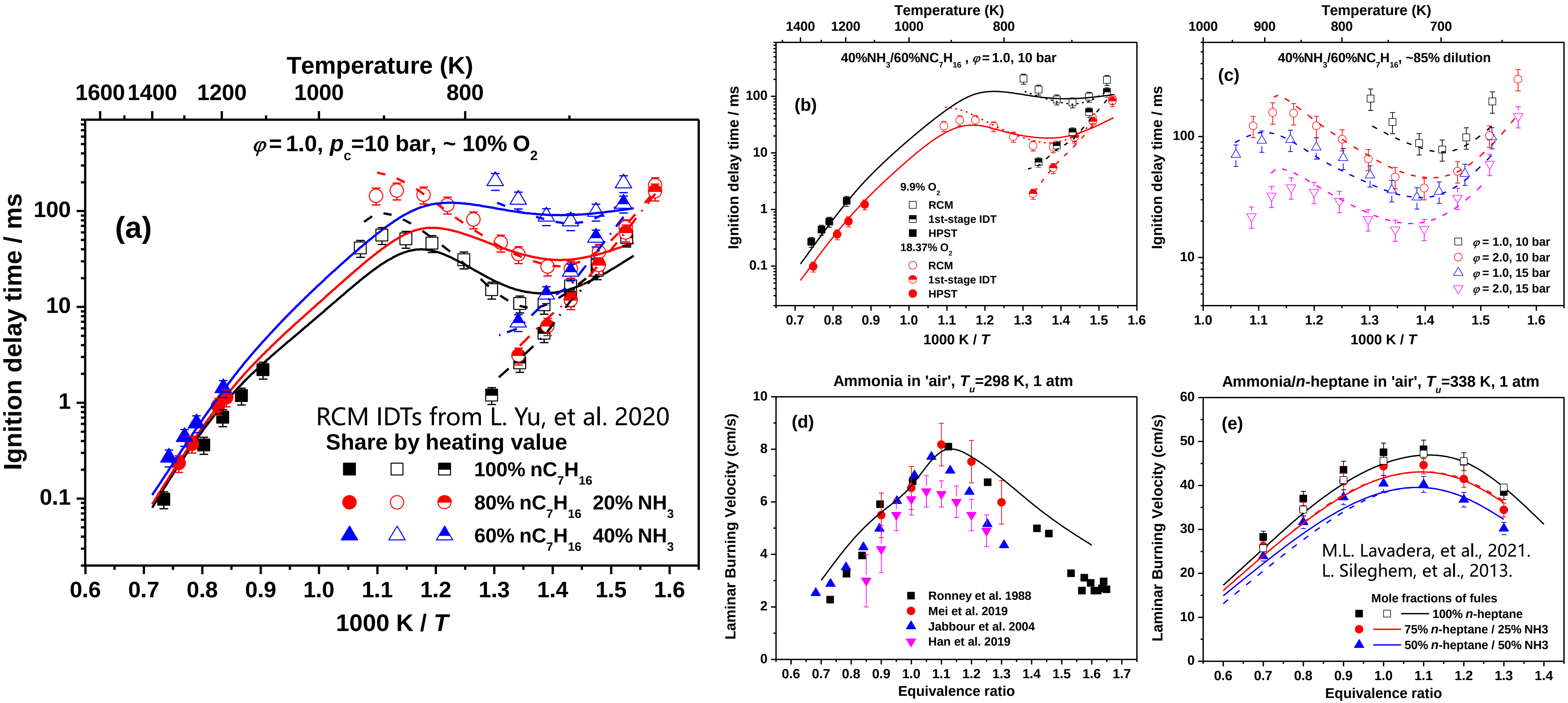
☐ NOx sub-chemistry (Glarborg et al. Prog. Energy Combust. Sci. 67 (2018) 31–68.)

- ➢ NH_3 pyrolysis chemistry (S.A. Alturaifi et al., Combust. Flame. (2021) 111694), improving ammonia LBV predictions.
- ➢ $nC_7H_{16}+\dot{N}H_2$ (S. Song et al., Int. J. Chem. Kinet. 35 (2003) 304–309.), most important interaction reactions between ammonia and *n*-heptane.



S. Dong, B. Wang, Z. Jiang, Y. Li, W. Gao, Z. Wang, X. Cheng, H.J. Curran, An experimental and kinetic modeling study of ammonia/n-heptane blends, Combust. Flame. 246 (2022) 112428.

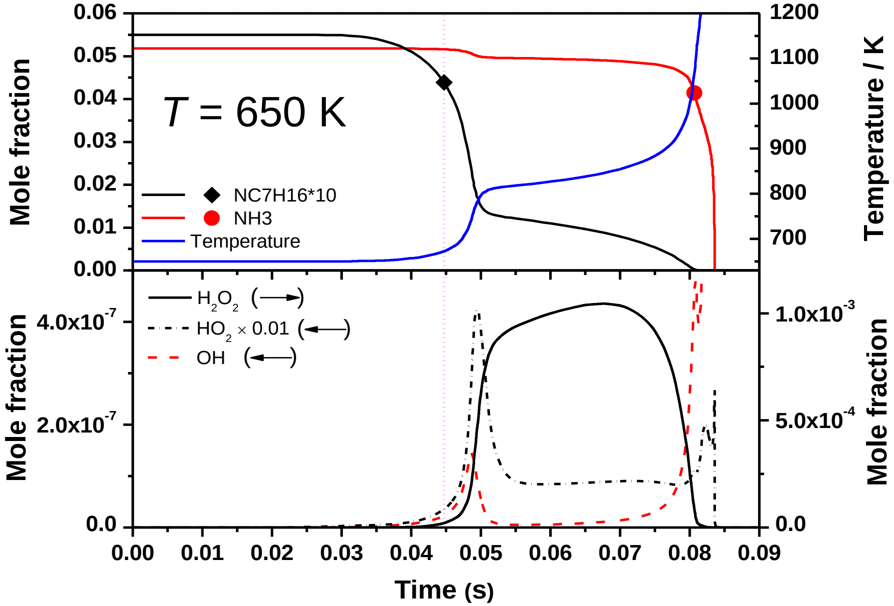
Kinetic modeling of ammonia/*n*-heptane blends



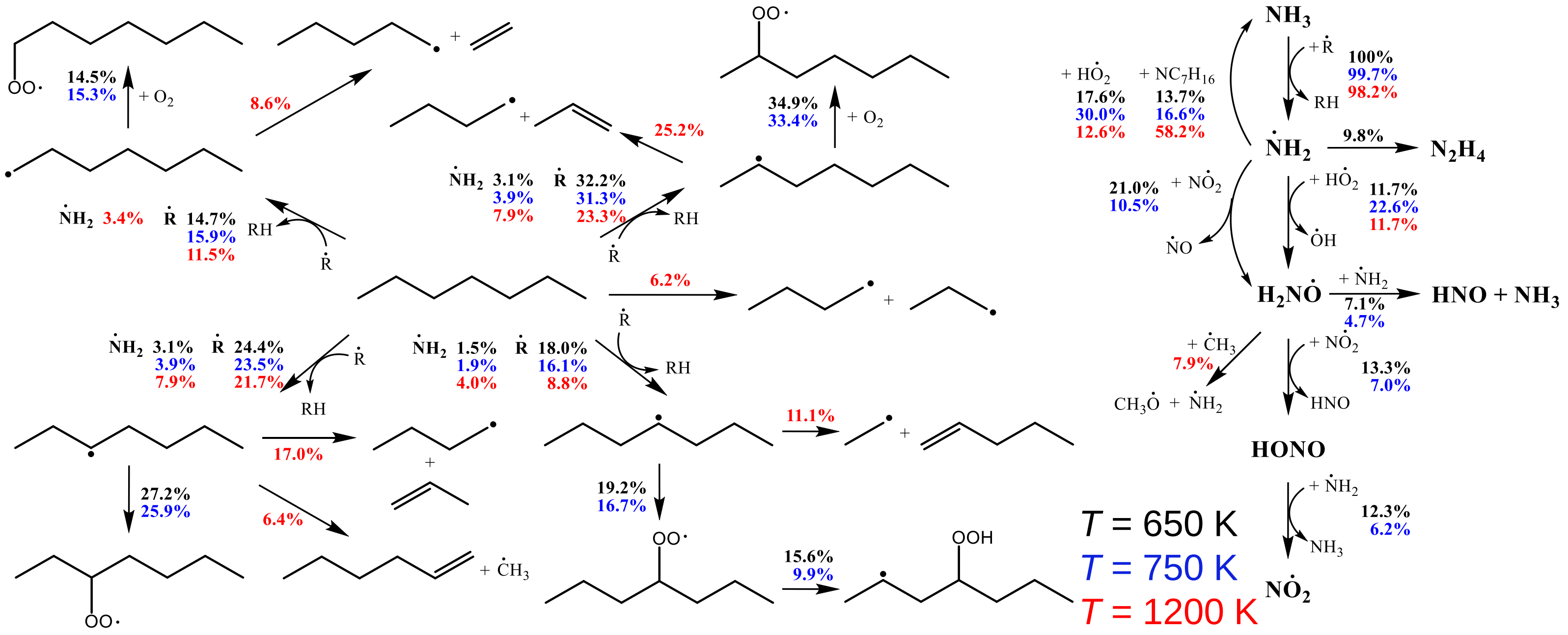
S. Dong, B. Wang, Z. Jiang, Y. Li, W. Gao, Z. Wang, X. Cheng, H.J. Curran, An experimental and kinetic modeling study of ammonia/n-heptane blends, Combust. Flame. 246 (2022) 112428.

Kinetic modeling of ammonia/*n*-heptane blends

40% ammonia/60% *n*-heptane (by energy) at $\varphi = 1.0$ and ~85% dilution (Mixture 4), $p = 10$ atm



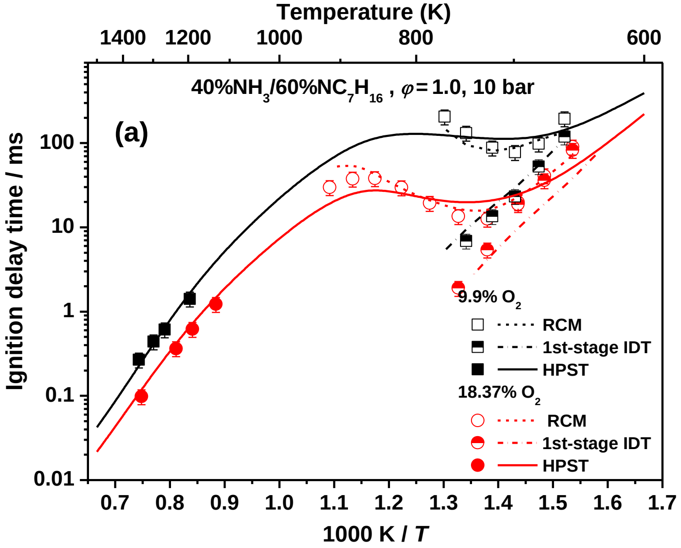
Species profiles during oxidation

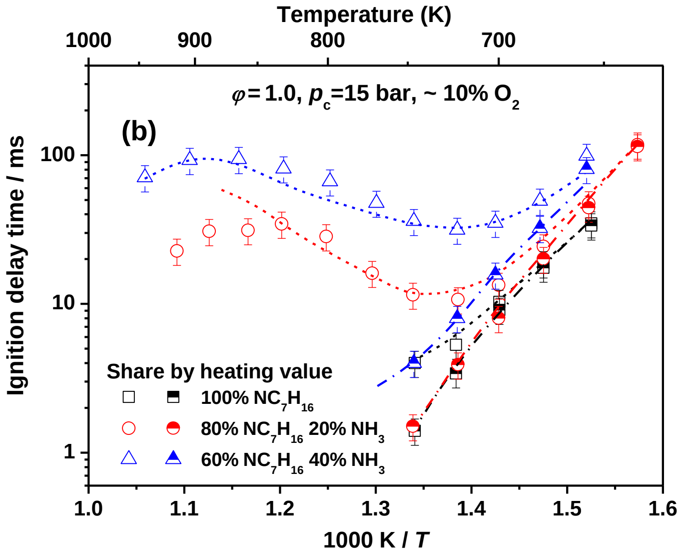


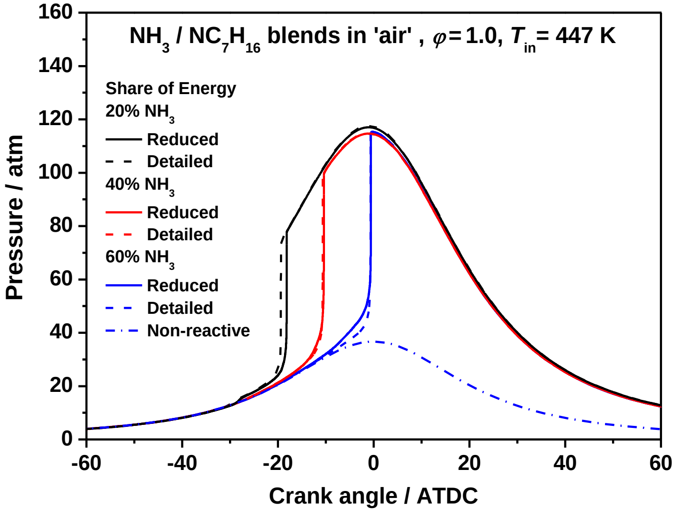
Flux analysis

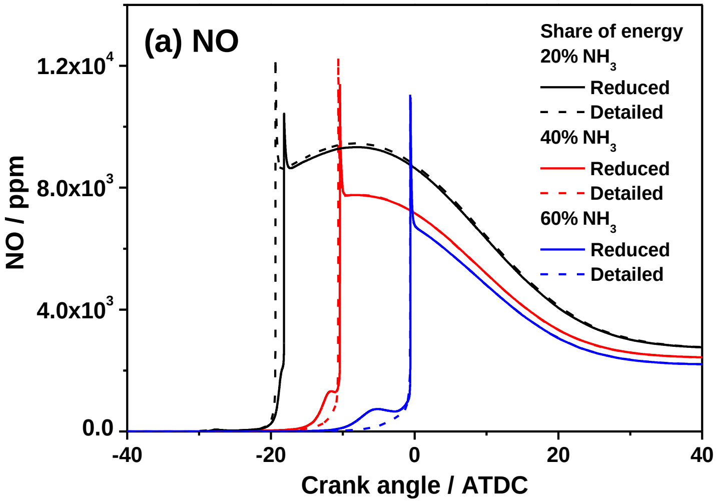
- ☐ The oxidation of *n*-heptane dominates the first-stage heat release. Ammonia mainly consumed during the second stage ignition.
- ☐ Terminating reactions of $\dot{N}H_2 + H\dot{O}_2$ significantly decrease fuel reactivity in NTC regions.

Ammonia/*n*-heptane mechanism reduction









Skeletal NH_3/nC_7H_{16} mechanism:

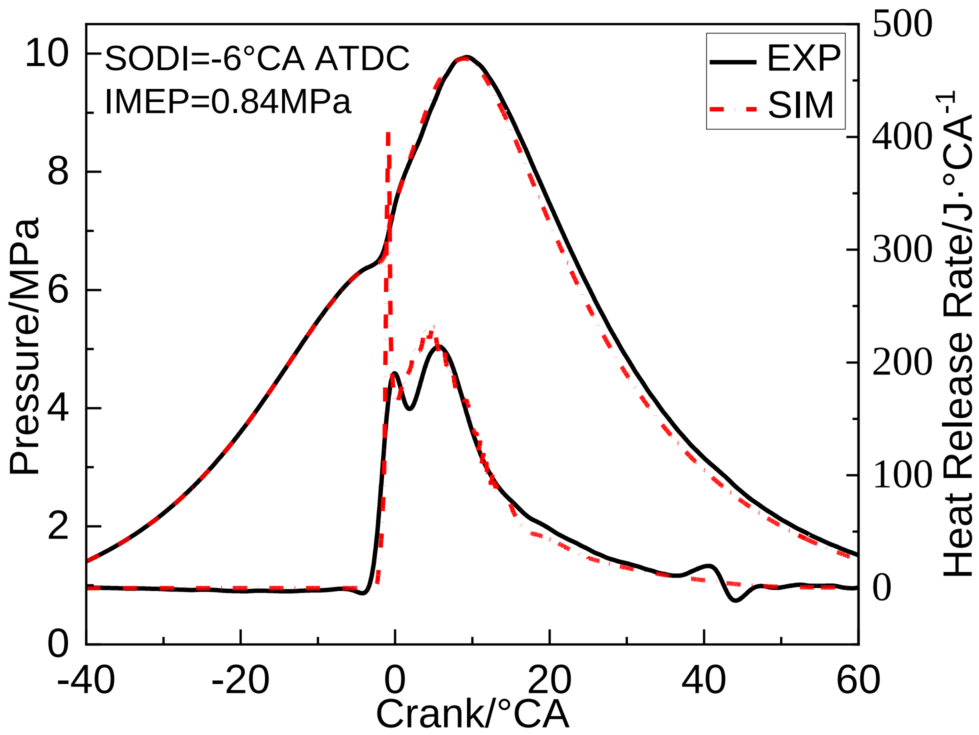
☐ 74 species and 495 reactions;

☐ Simulate well the IDTs of ammonia/*n*-heptane blends;

☐ HCCI engine simulation results of the detailed and skeletal mechanisms match well;

B. Wang, S. Dong, Z. Jiang, W. Gao, Z. Wang, J. Li, C. Yang, Z. Wang, X. Cheng, Development of a reduced chemical mechanism for ammonia/n-heptane blends, Fuel. 338 (2023) 127358.

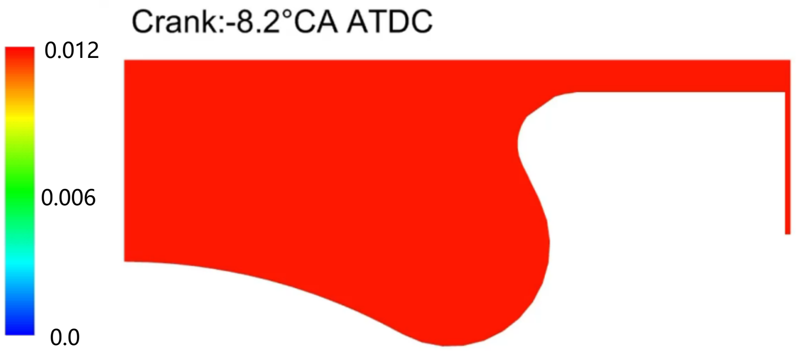
Ammonia/*n*-heptane mechanism reduction



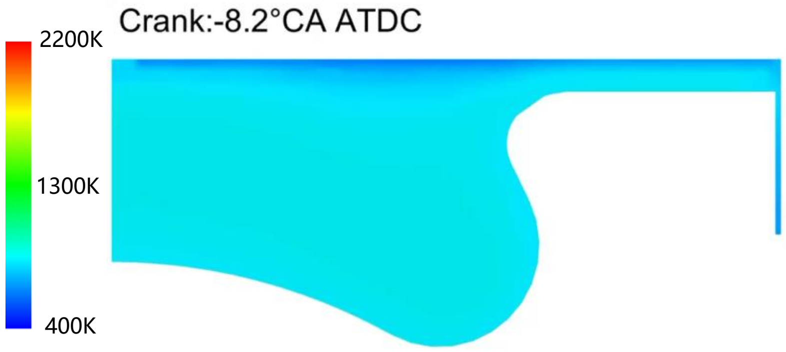
Engine conditions	Values
Engine speed	1200 r/min
Intake pressure	0.17 MPa
Intake temperature	40℃
Injection pressure	80 MPa
Injection timing	-6°CA ATDC
Ammonia ratio	20%

- Using Converge and the skeletal mechanism, the combustion process of ammonia/*n*-heptane dual-fuel engine is well simulated.
- 48 CPU cores @ 2.99GHz, maximum cell number 440,000, ~6 hours from IVC-EVO.

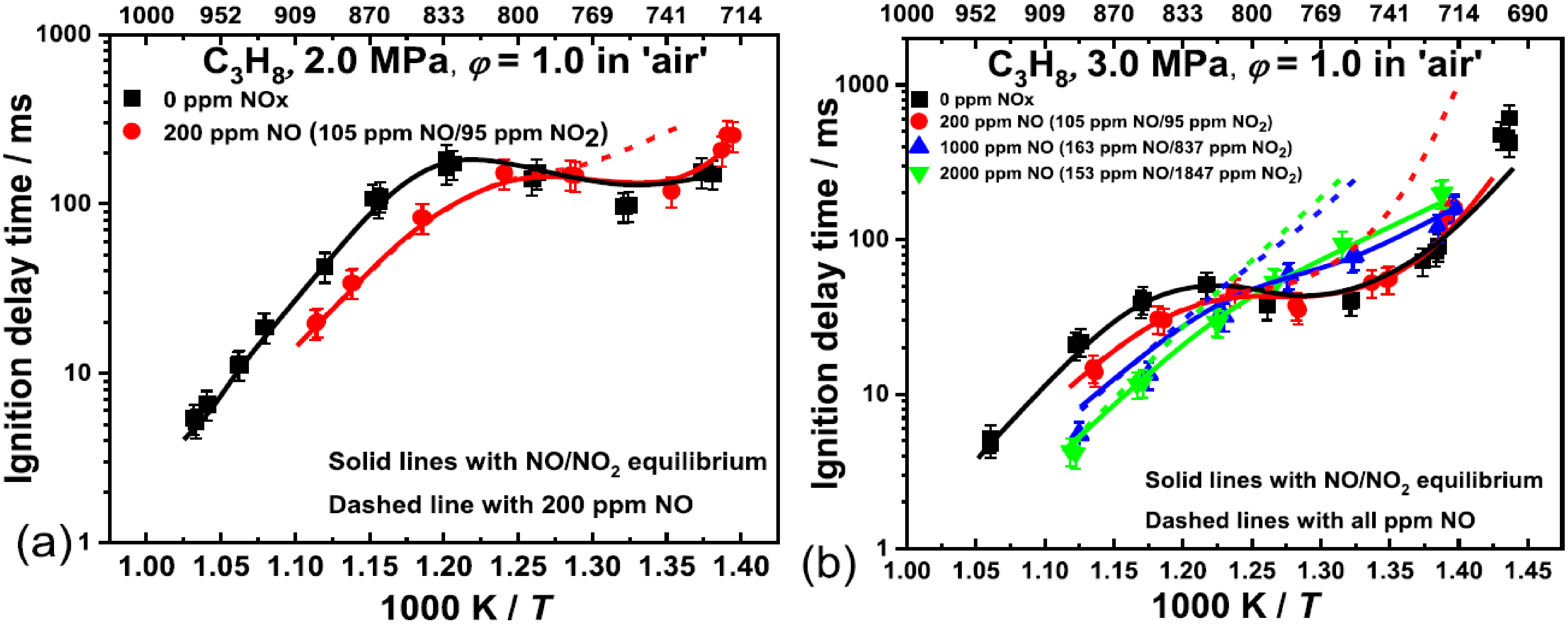
Ammonia mass fraction



Gas temperature

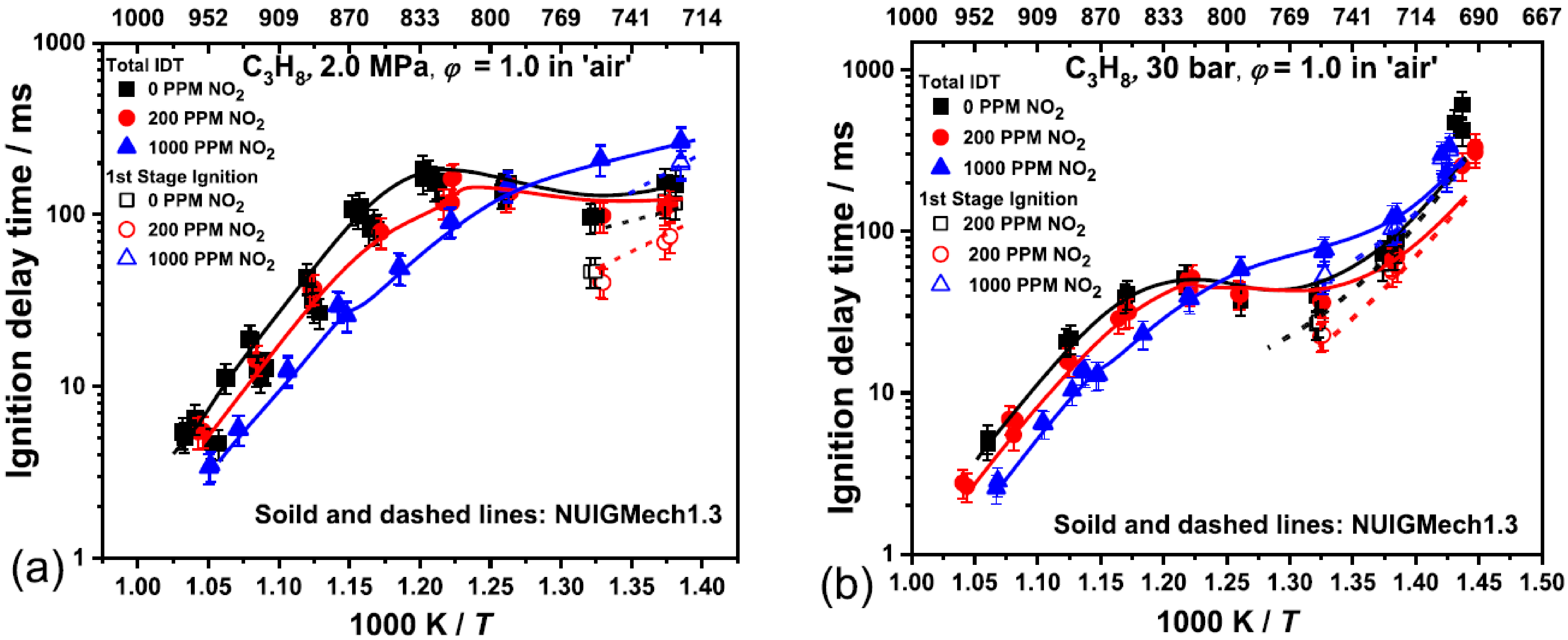


Effect of NO on Propane IDT



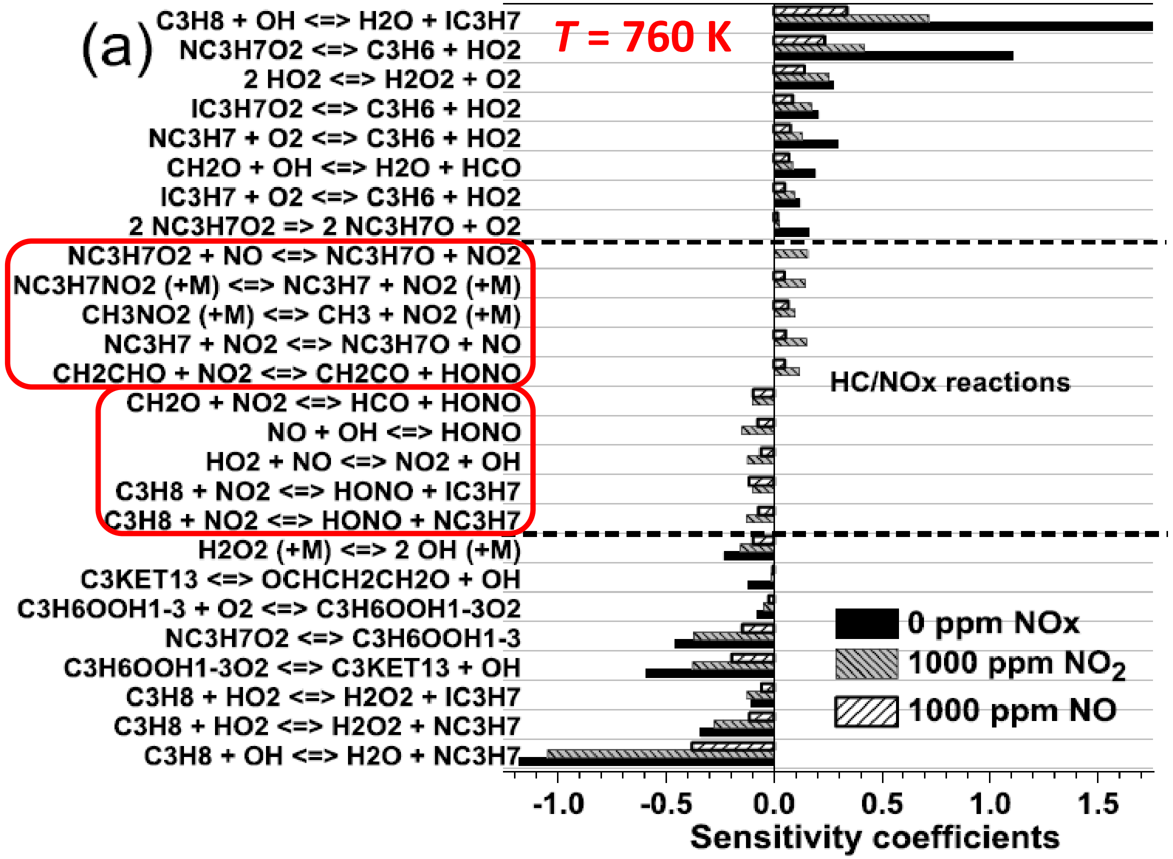
A. Mohamed et al. Combust. Flame 245 (2022) 112306.

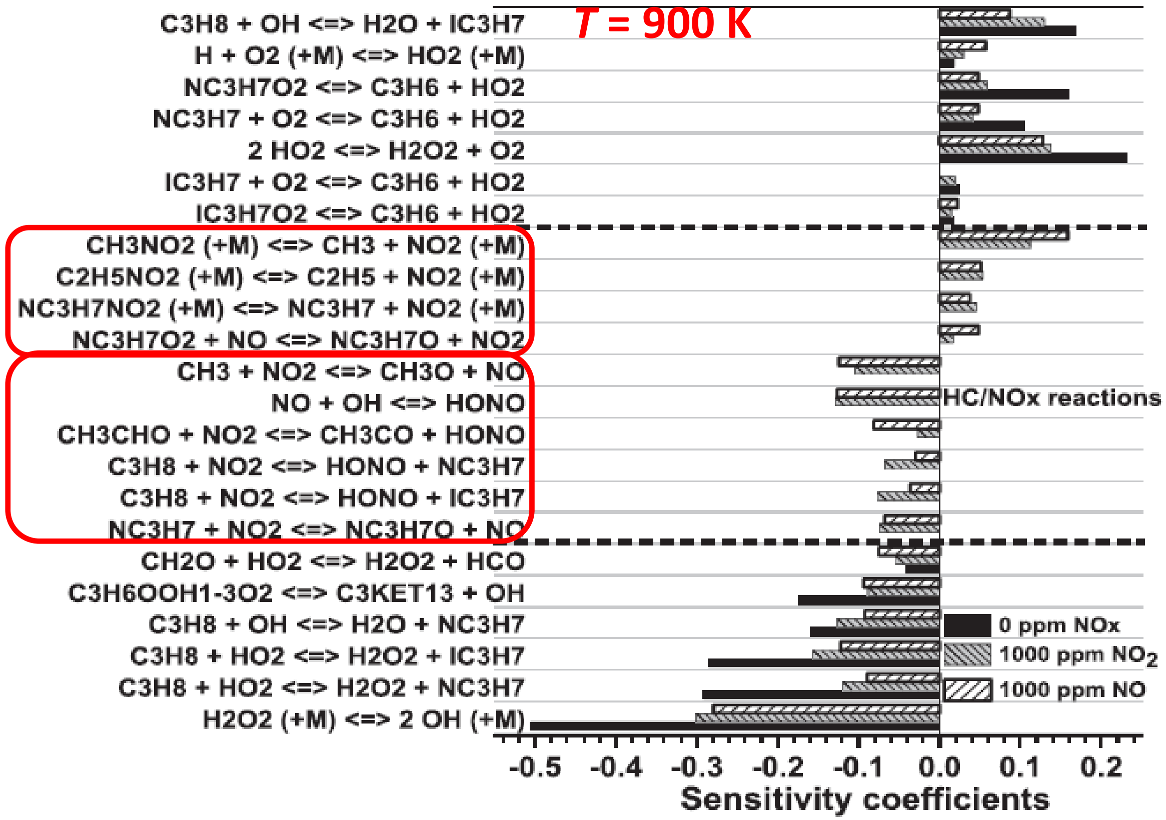
Effect of NO_2 on Propane IDT



A. Mohamed et al. Combust. Flame 245 (2022) 112306.

Effect of NO on Propane IDT, φ = 1.0, p = 30 atm





Low T

Inhibiting reactivity

$R\dot{O}_2 + NO = R\dot{O} + NO_2$

$\dot{R} + NO_2 = R\dot{O} + NO$

$\dot{R} + NO_2\ (+M) = RNO_2\ (+M)$

Enhancing reactivity

$H\dot{O}_2 + NO = NO_2 + \dot{O}H$

$RH + NO_2 = \dot{R} + HONO$

$HONO = NO + \dot{O}H$

High T

Inhibiting reactivity

$R\dot{O}_2 + NO = R\dot{O} + NO_2$

$\dot{R} + NO_2\ (+M) = RNO_2\ (+M)$

Enhancing reactivity

$H_2O_2\ (+M) = \dot{O}H + \dot{O}H\ (+M)$

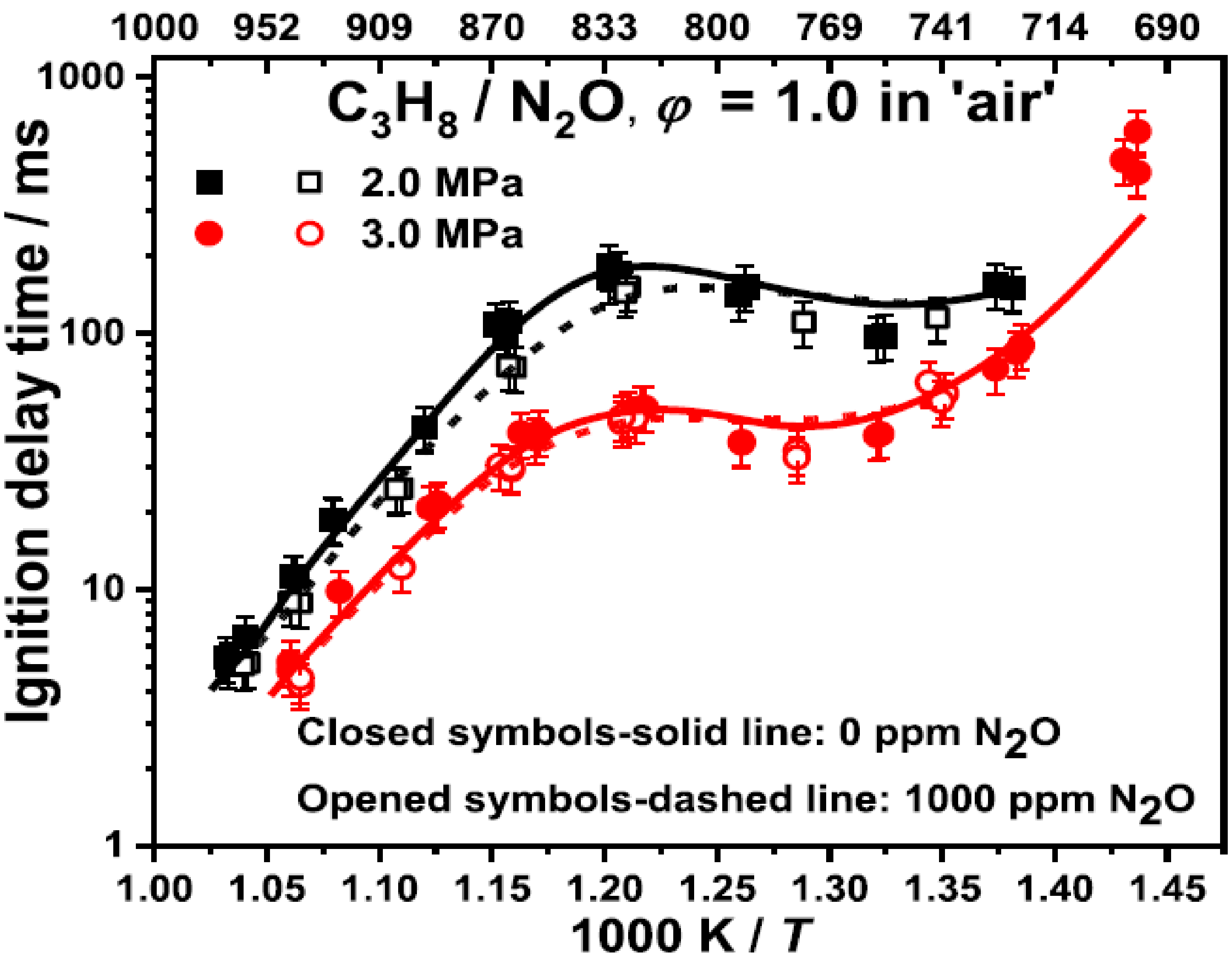
$\dot{R} + NO_2 = R\dot{O} + NO$

$HONO = NO + \dot{O}H$

A. Mohamed et al. Combust. Flame 245 (2022) 112306.

M. Hori et al. Proc. Combust. Inst. 27 (1998) 389-396.

Effect of N_2O on Propane IDT: little to no effect!



A. Mohamed et al. Combust. Flame 245 (2022) 112306.

Conclusions

1. Comprehensive chemical kinetic modeling studies of NH_3/H_2, NH_3/*n*-heptane and alkane/NO_x combustion have been carried out
2. The developed combustion kinetic model has reasonably good predictions at most experimental conditions that are available
3. The NH_3/H_2 model also forms a basis for future model development and improvement for NH_3 fuel blends with other hydrocarbons, or NO_x-fuel interactions in EGR
4. By employing appropriate model reduction method, reduced models can be obtained and incorporated into combustor CFD simulations

Conclusions

- Oxygenated fuels react differently compared to HC fuels at both low and high *T*
- Oxygenated fuels can show NTC behaviour
- Need for more thermochemistry studies of oxygenated fuels to better understand and refine chemistry
- Rate rules can/will be developed to generate chemistry models describing low *T* oxidation of alcohols, ethers, esters, aldehydes, ketones, furans, etc.