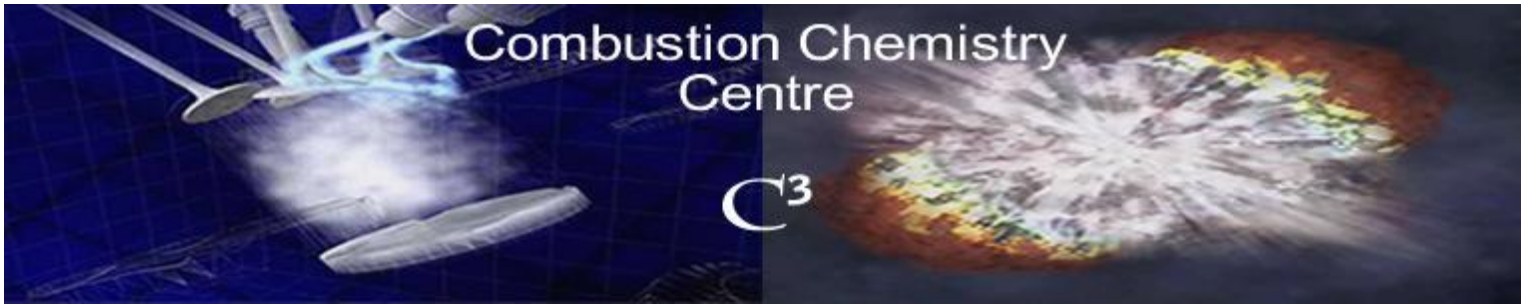

Kinetic Mechanism Development for Hydrocarbons and Oxygenated Fuels

Dr. Henry Curran and Dr. Philippe Dagaut

Combustion Chemistry Centre, NUI Galway, Ireland

CNRS Orleans, France

Lecture

1st Workshop on Flame Chemistry

July 28th, 2012

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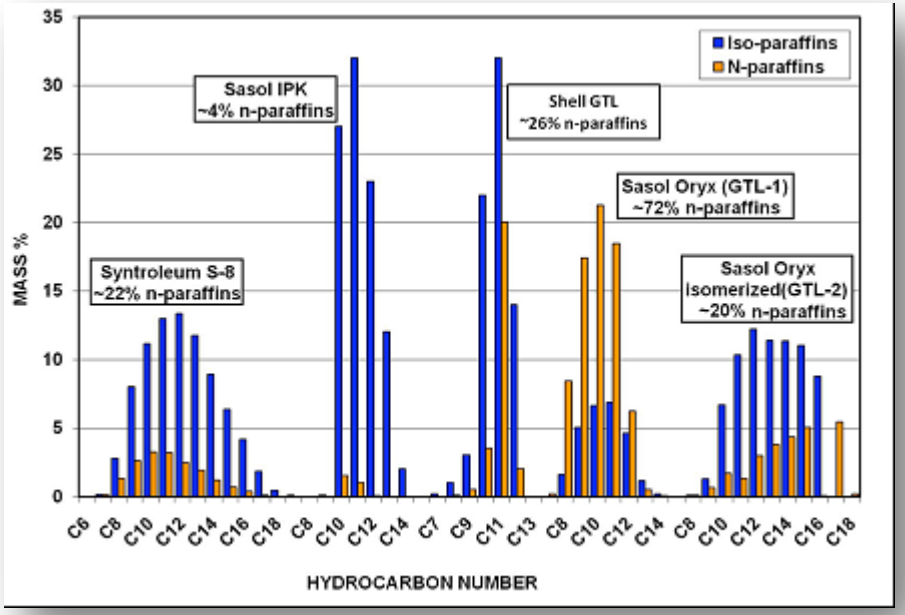
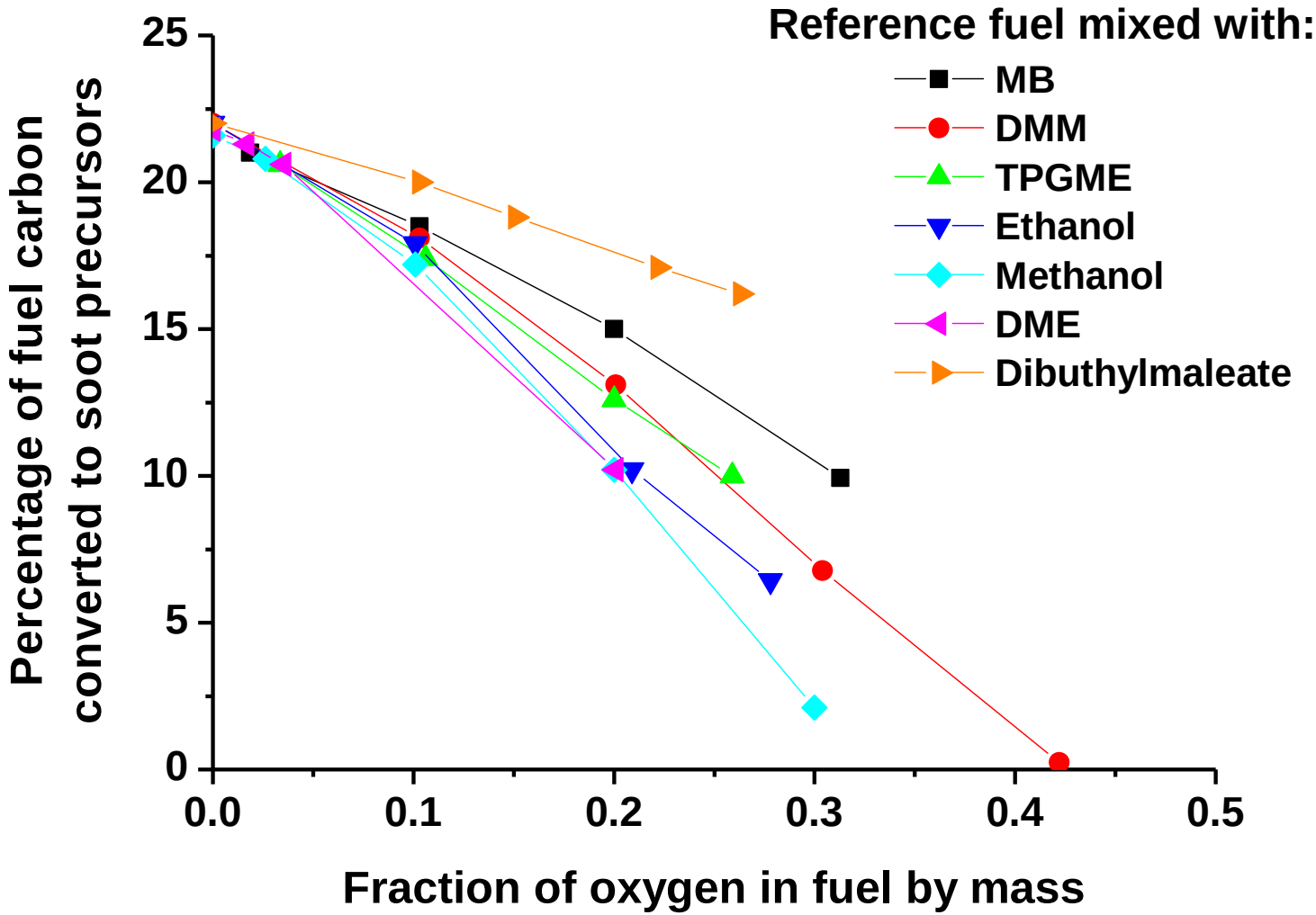
Future HC fuels - many sources

- 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

How well an oxygenated fuel works depends on its molecular structure

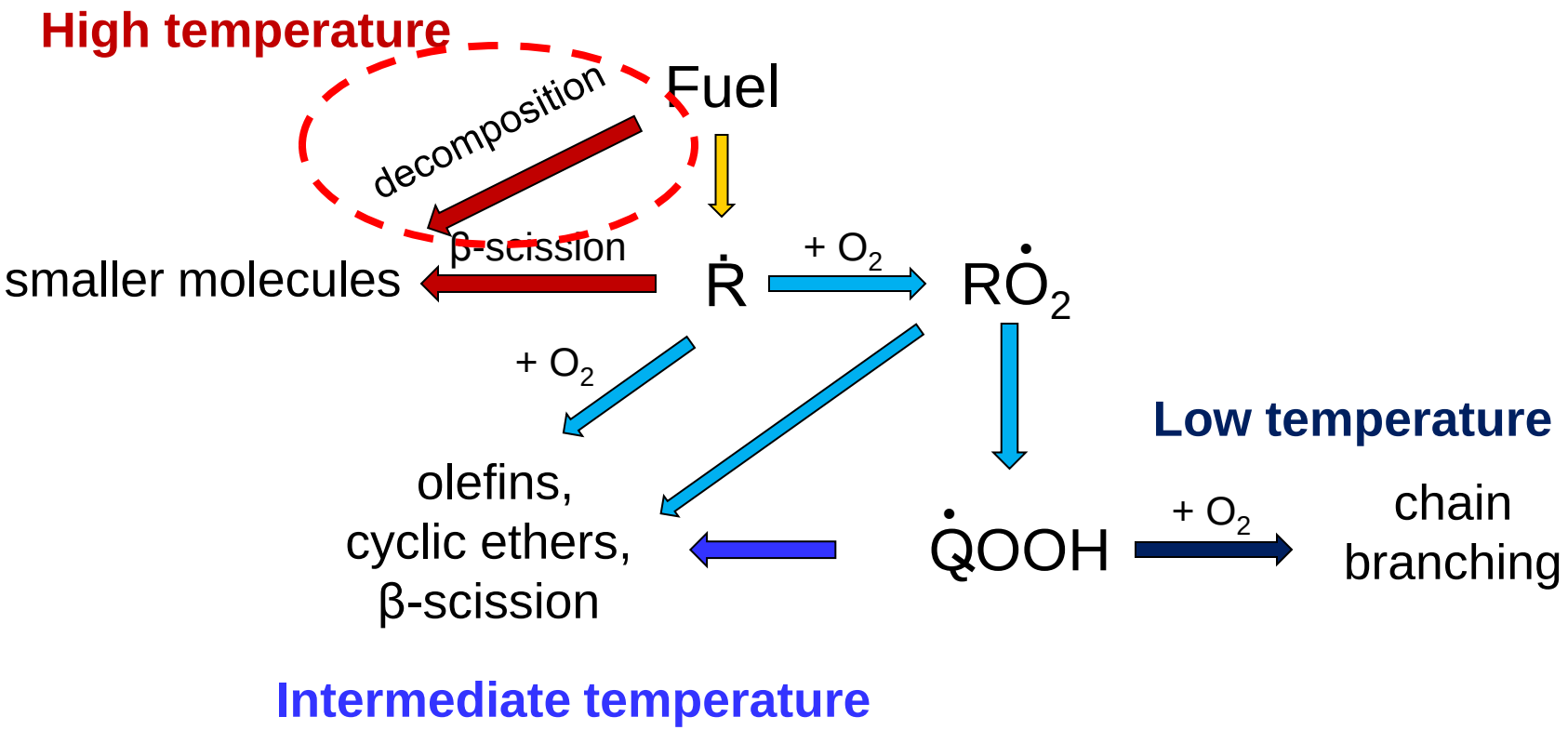


Miyamoto *et al.* Paper No. SAE 980506 (1998).
Westbrook *et al.* J. Phys. Chem. A (2006) *110:* 6912–6922.

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)

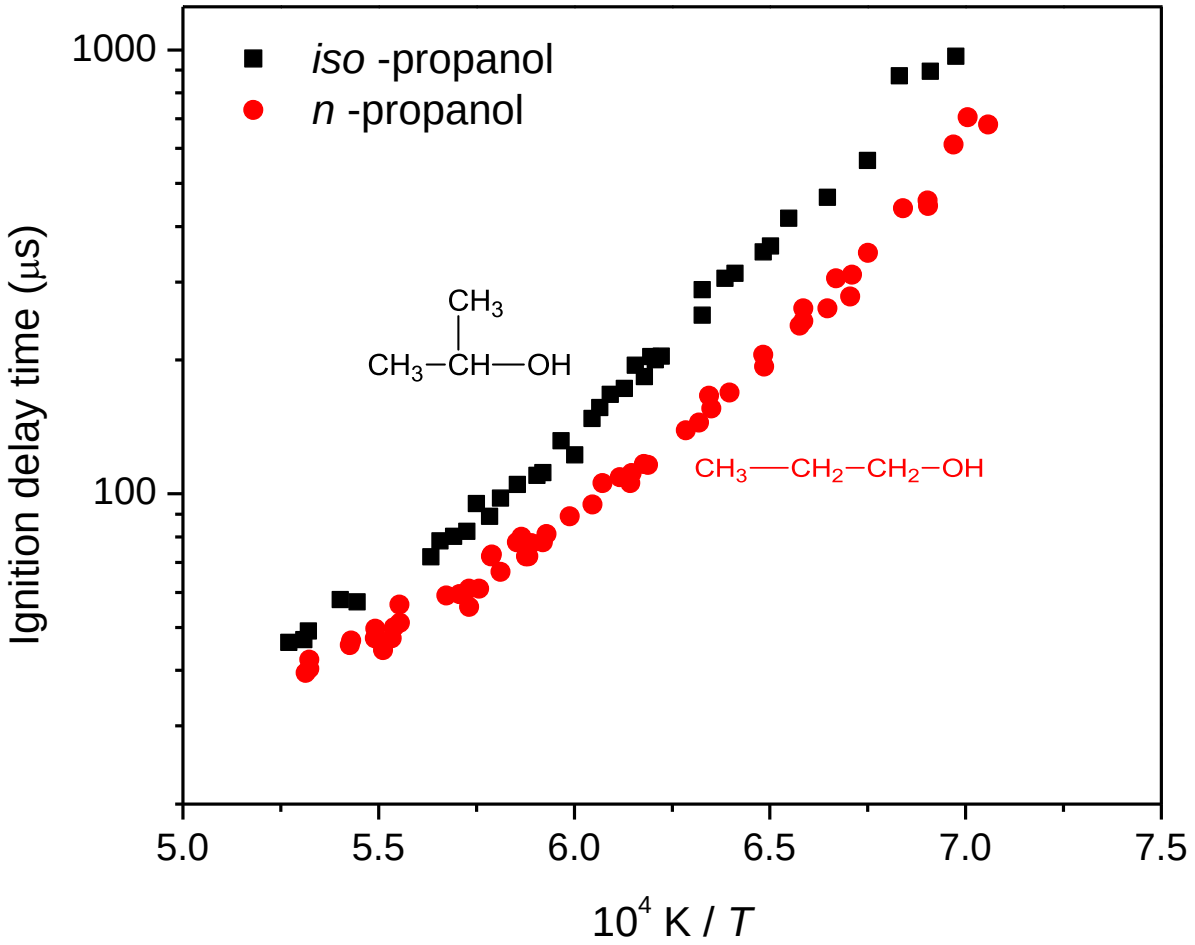
General reaction scheme



Fuel decomposition reactions

Propanol isomers: Comparison of reactivity

0.5% fuel, 2.25% O_2, ϕ = 1.0, P = 1 atm



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

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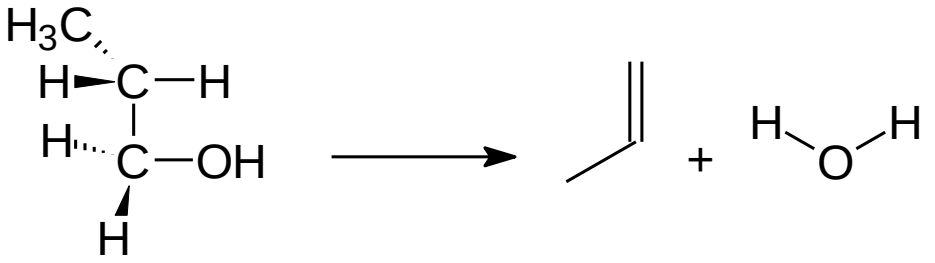
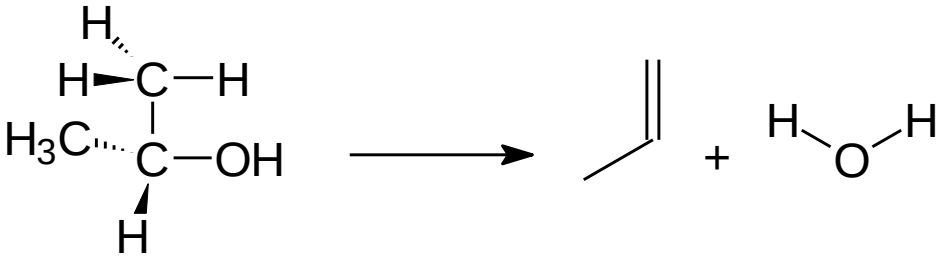
Alcohol molecular elimination



n-propanol propene + water

$k = 3.52 \times 10^{13}$ 0. 67300. s^{-1}

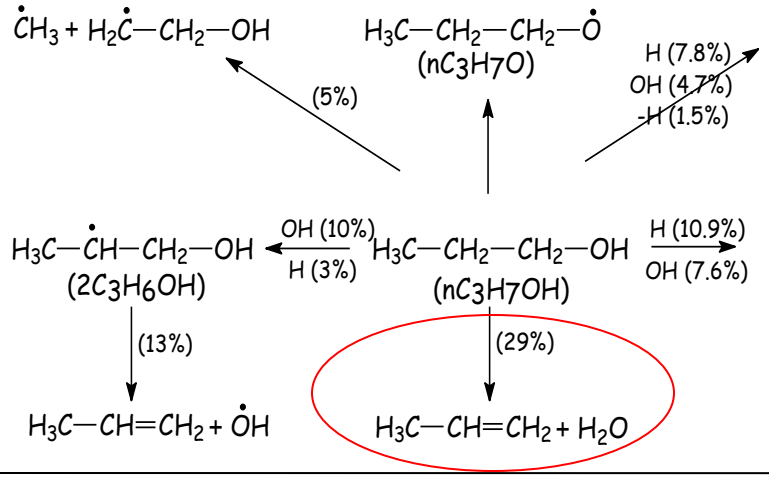


iso-propanol propene + water

$k = 2.11 \times 10^{14}$ 0. 67300. s^{-1}

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

Water elimination is much more important for iso-propanol



0.5% *n*-propanol

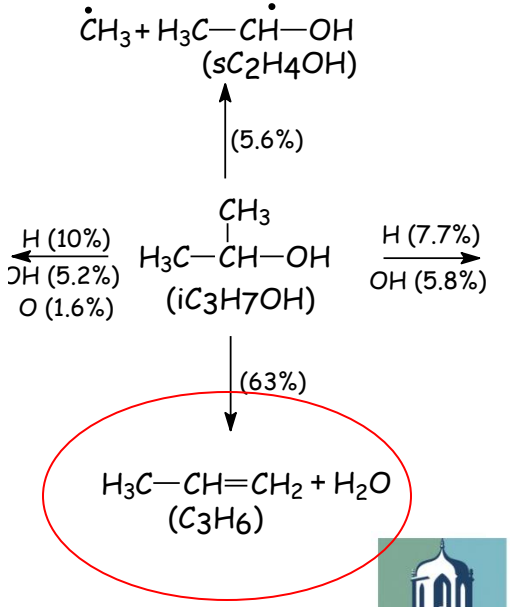
ϕ = 1.0, T = 1600 K

30% fuel consumed

0.5% *iso*-propanol

ϕ = 1.0, T = 1600 K

30% fuel consumed



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

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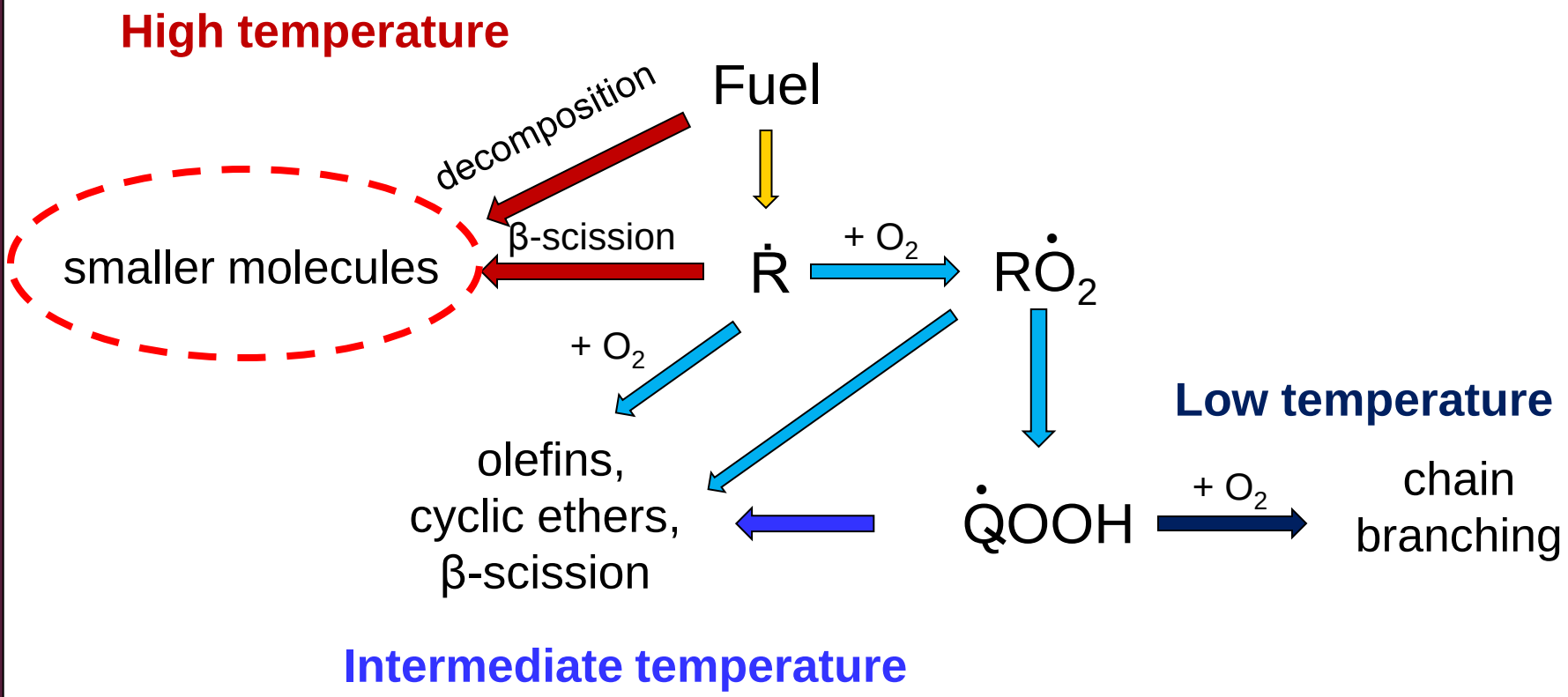
General reaction scheme



Sub-mechanism

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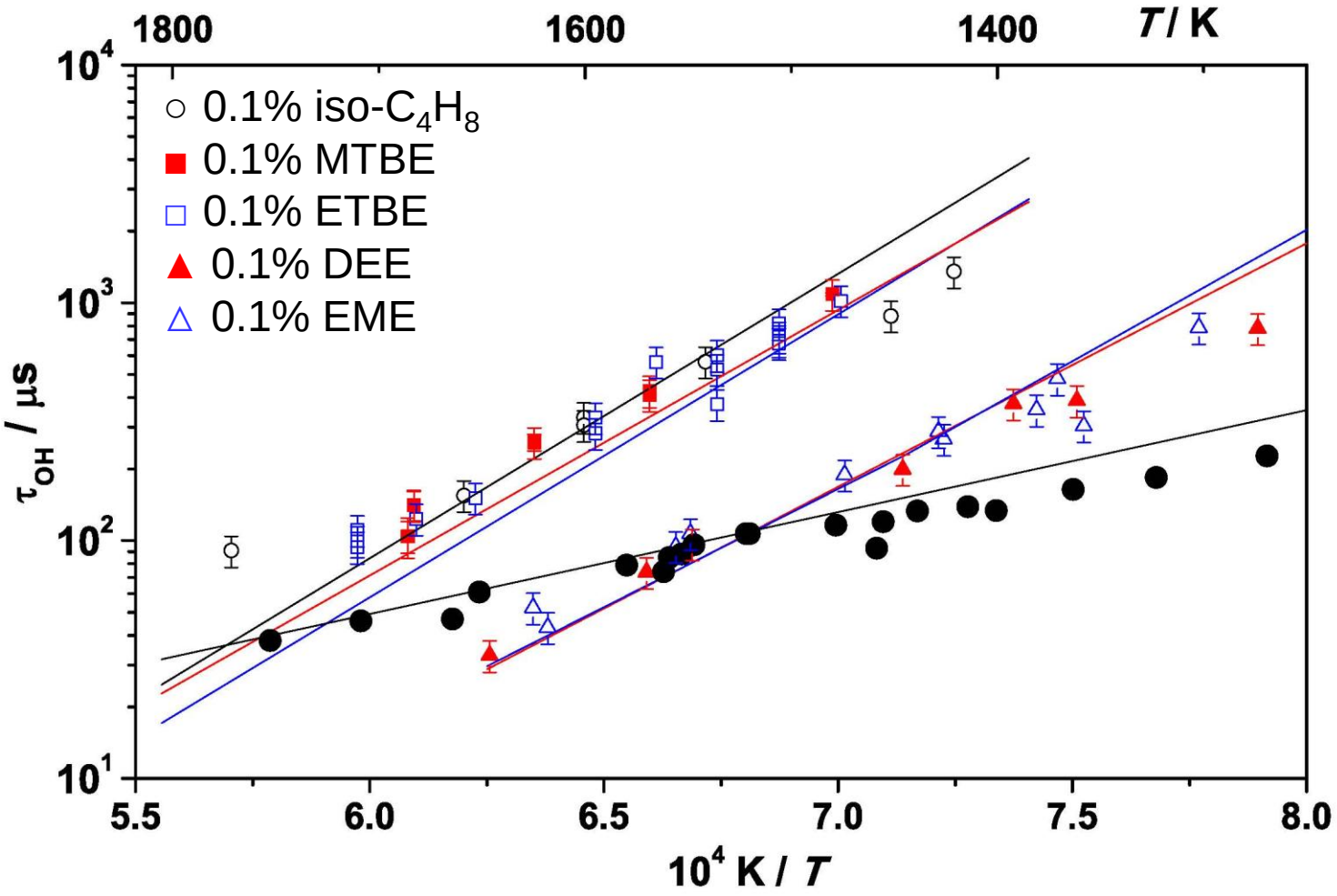
Reactivity of ethers

- 1% H_2, 1% O_2 in Ar, p_5 = 1.4–2.6 atm



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

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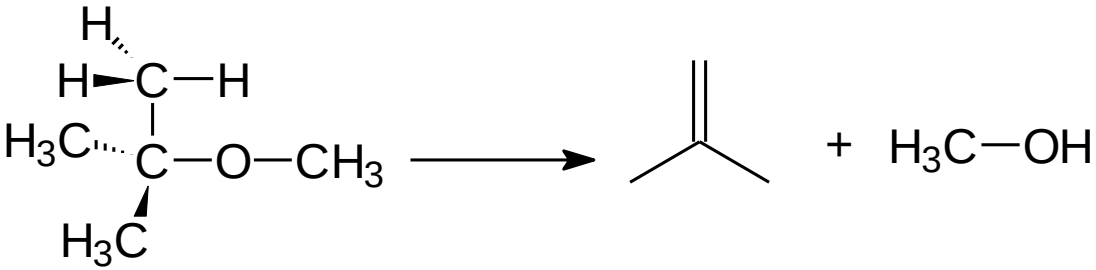
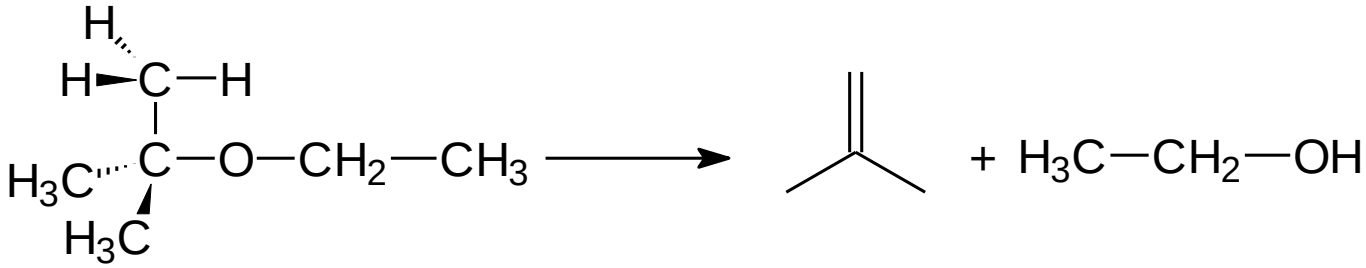
Ether molecular elimination



MTBE isobutene + methanol

$k = 1.70 \times 10^{14}$ 0. 60800. s^{-1}



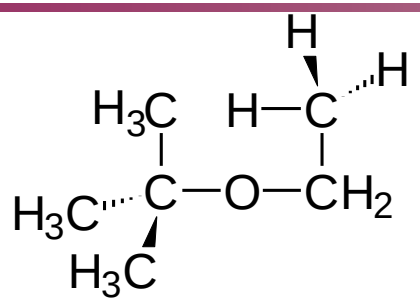
ETBE isobutene + ethanol

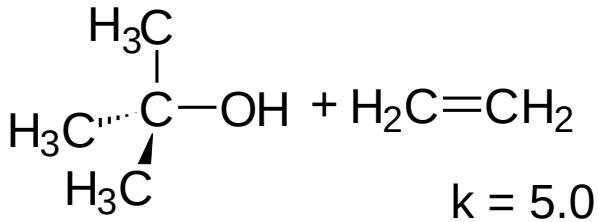
$k = 1.70 \times 10^{14}$ 0. 60600. s^{-1}

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

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

Ether molecular elimination

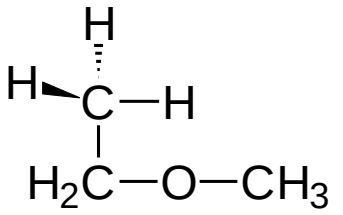


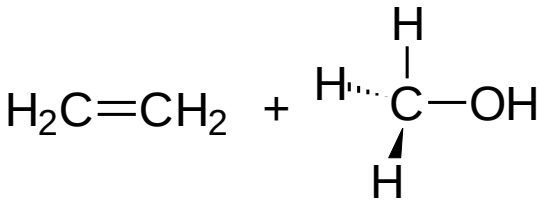


$k = 5.0 \times 10^{13}\ 0.\ 63400.\ s^{-1}$

ETBE

tert-butanol + ethylene

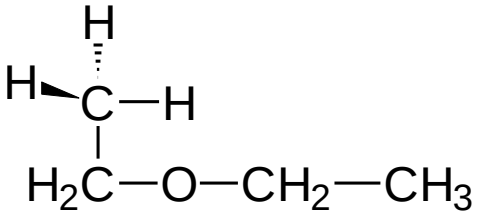


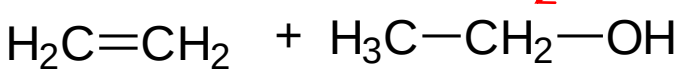


EME

ethylene + methanol

$k = 5.0 \times 10^{13}\ 0.\ 65200.\ s^{-1}$





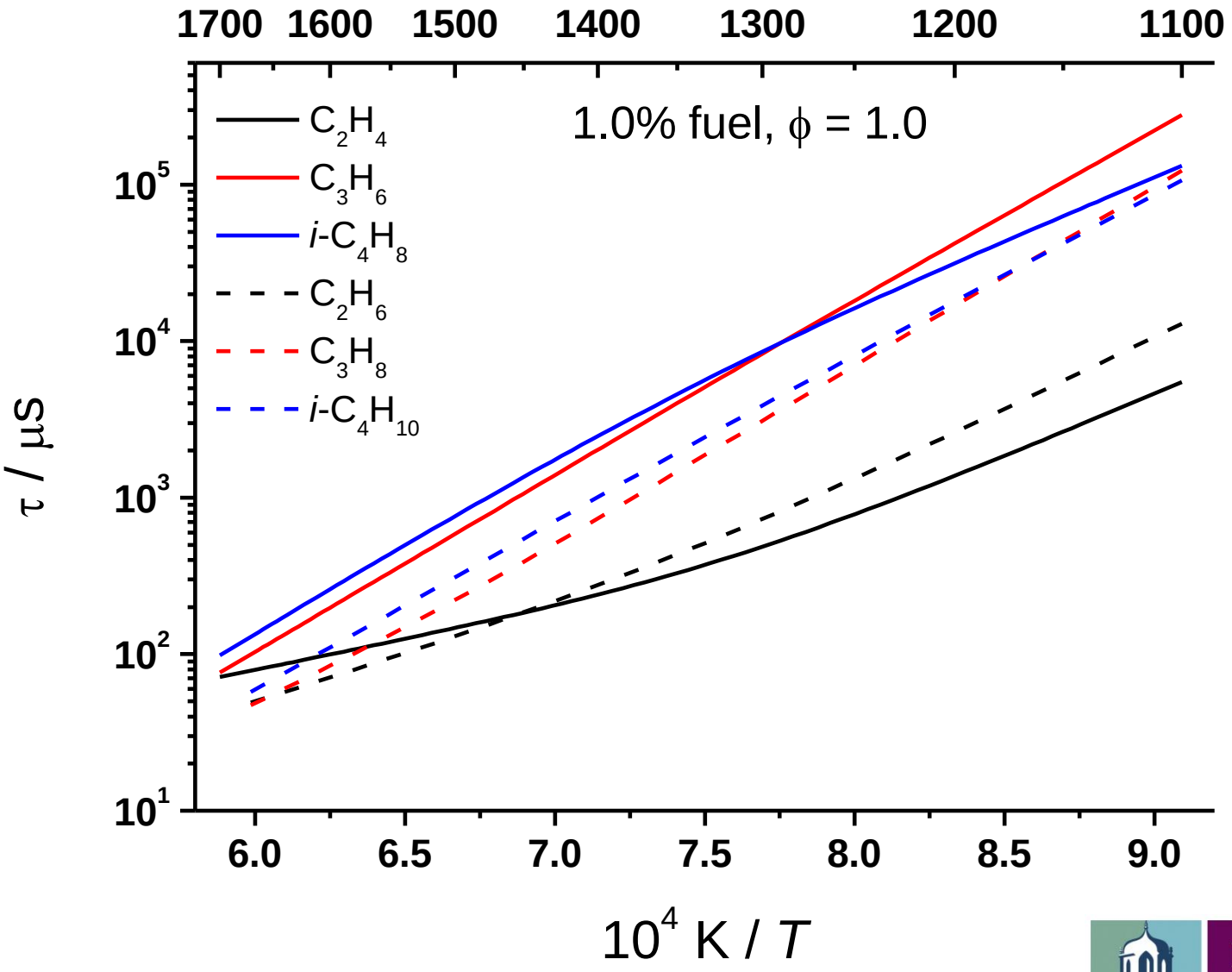
DEE

ethylene + ethanol

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

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

Ethylene is very fast to ignite



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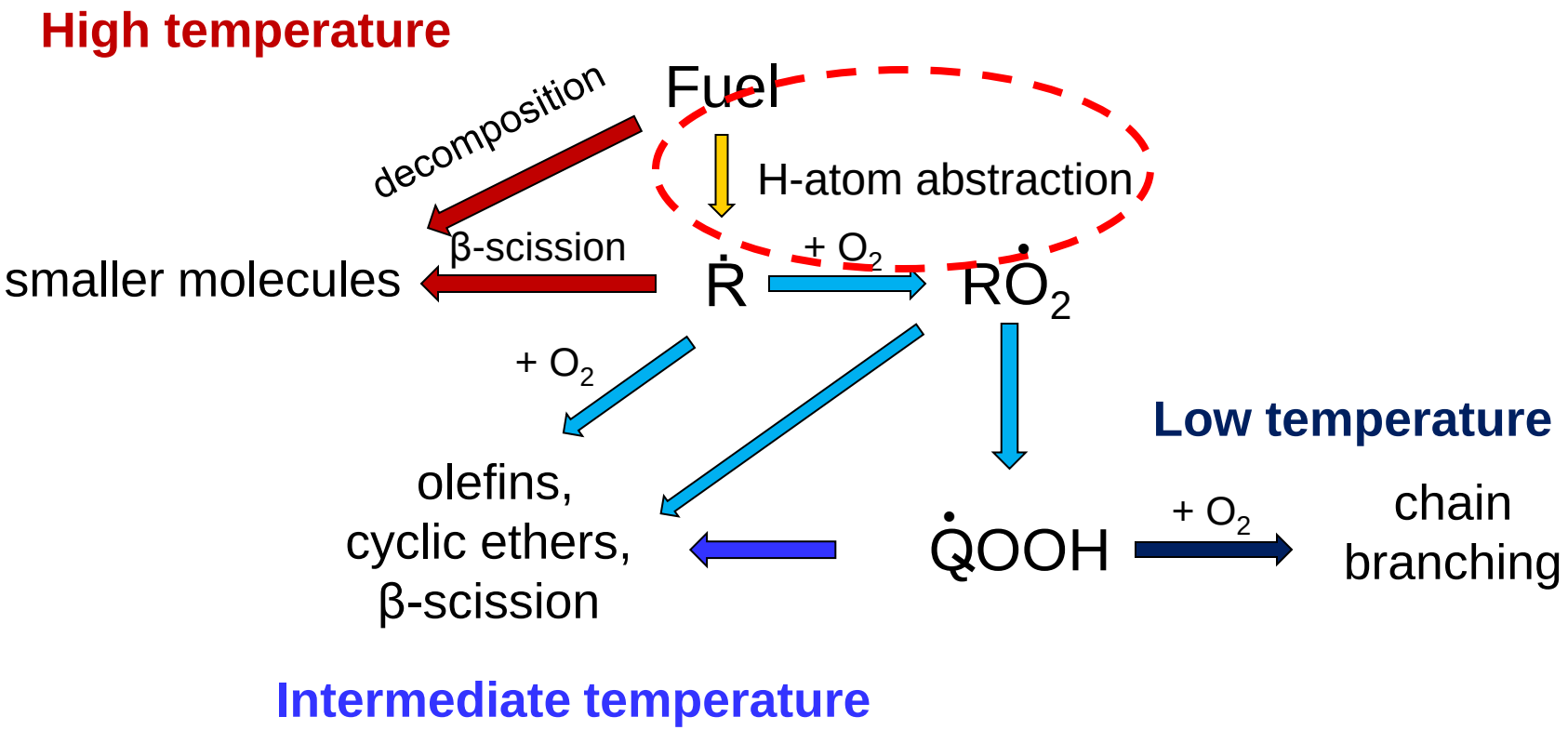
General reaction scheme



H-atom abstraction reactions

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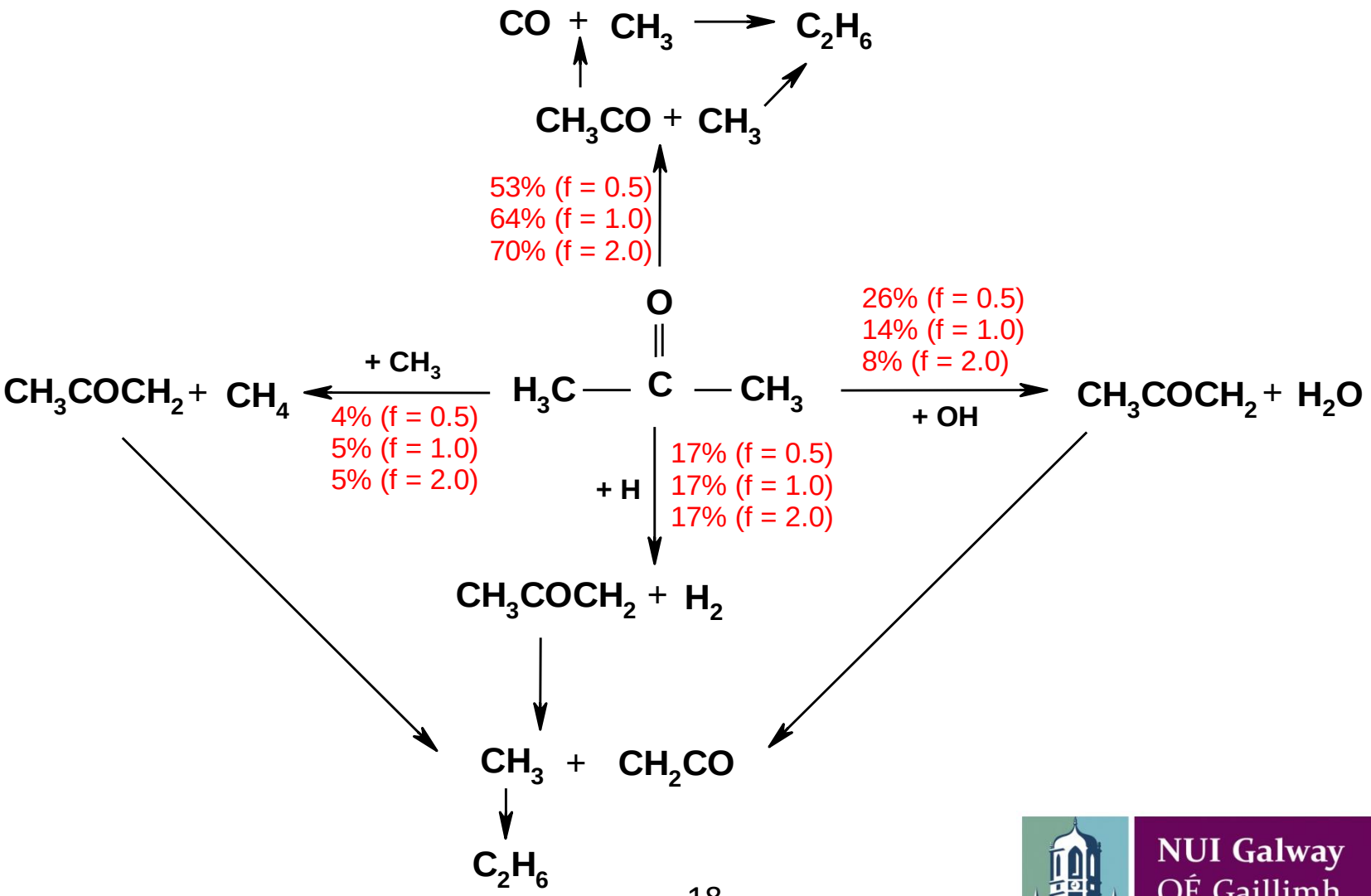
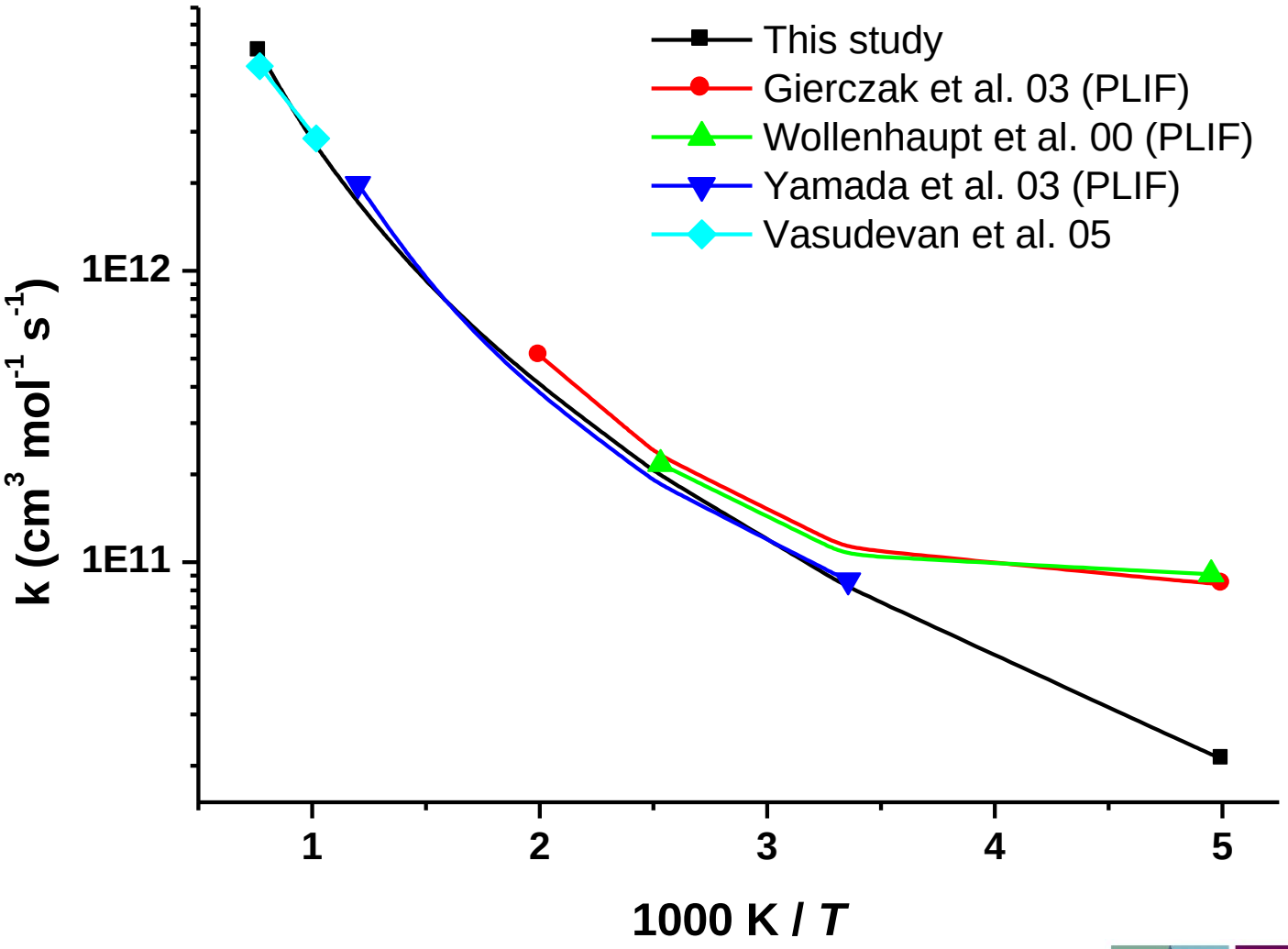
Acetone: Low *p*, High *T*

1.25% fuel, 22% fuel conversion, T = 1400 K, p = 1 atm



$CH_3COCH_3 + OH = CH_3COCH_2 + H_2O$



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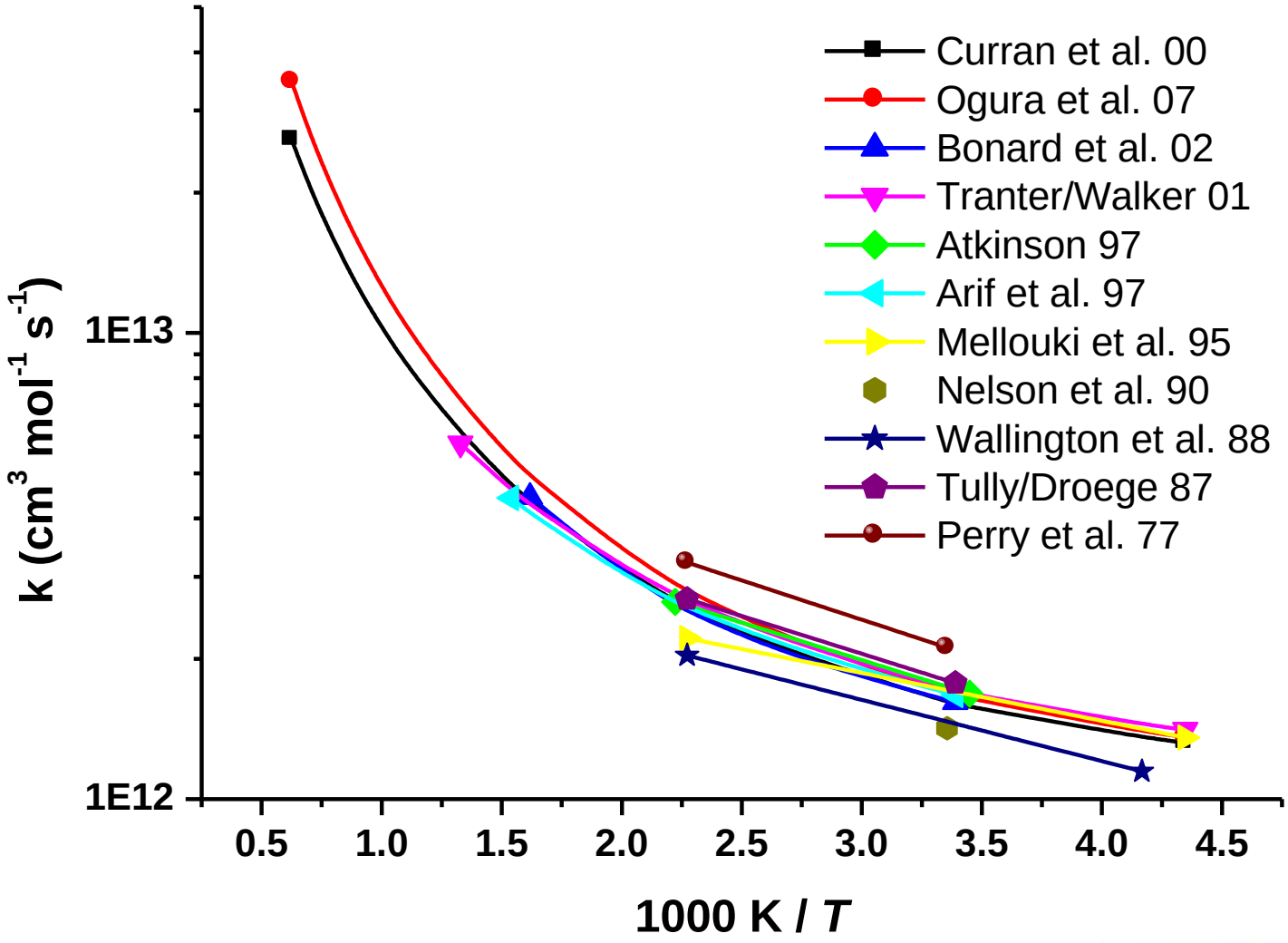
$CH_3OCH_3 + OH = CH_3OCH_2 + H_2O$



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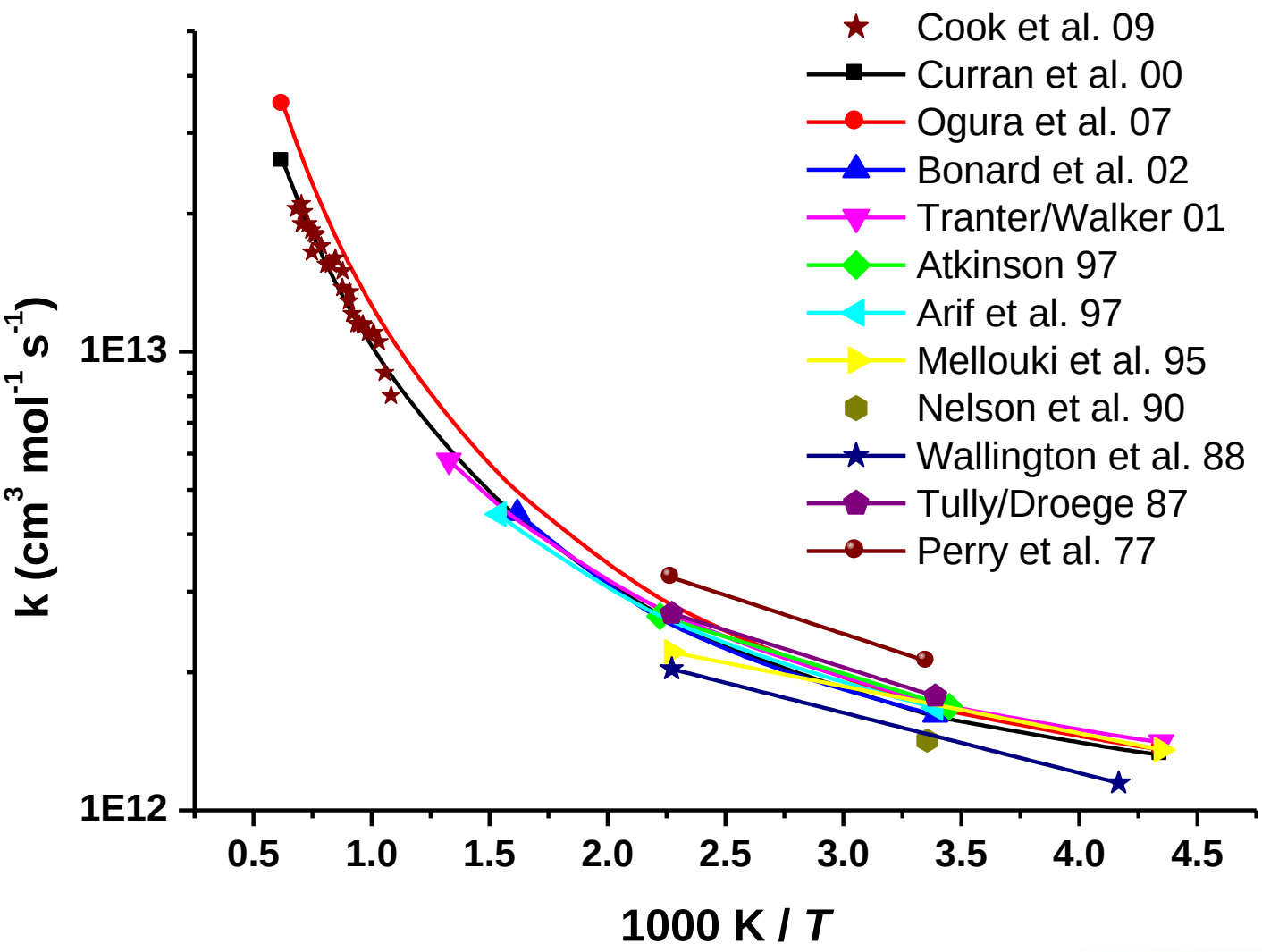
$CH_3OCH_3 + OH = CH_3OCH_2 + H_2O$



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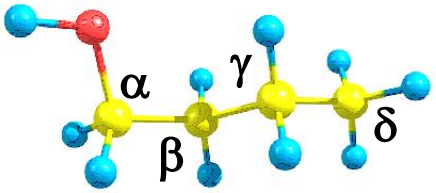
H-atom Abstraction

- *n*-Butanol + •OH/HO_2•

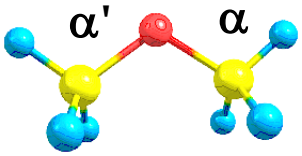


C-W. Zhou, J. M. Simmie, H. J. Curran. *Combust. & Flame*, **2011** *158* 726−731.
C-W. Zhou, J. M. Simmie, H. J. Curran. *Int. J. Chem. Kinet.*, **2012** *44* 155−164.

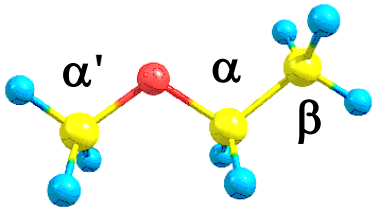
- *n*-Butanol + $\dot{C}H_3$ (Imperial College London: Prof. Alex Taylor)

D. Katsikadakos, C-W. Zhou, J. M. Simmie, H. J. Curran, P.A. Hunt,
Y. Hardalupas, A.M.K.P. Taylor. *Proc. Comb. Inst.,* 2012. Paper 4D03 Thursday 2nd August.

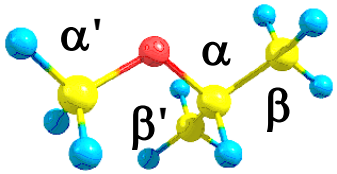
- Ethers + •OH



DME



EME



iPME

C-W. Zhou, J.M. Simmie, H.J. Curran
Phys. Chem. Chem. Phys. **2010** *12* 7221−7233.

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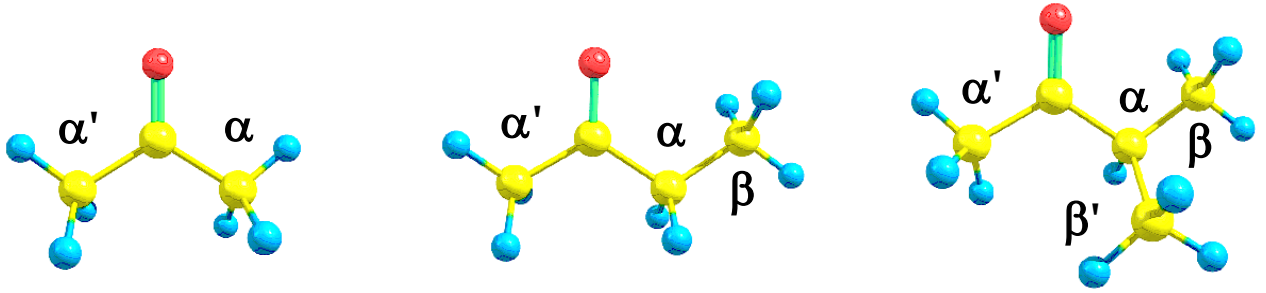
H-atom Abstraction

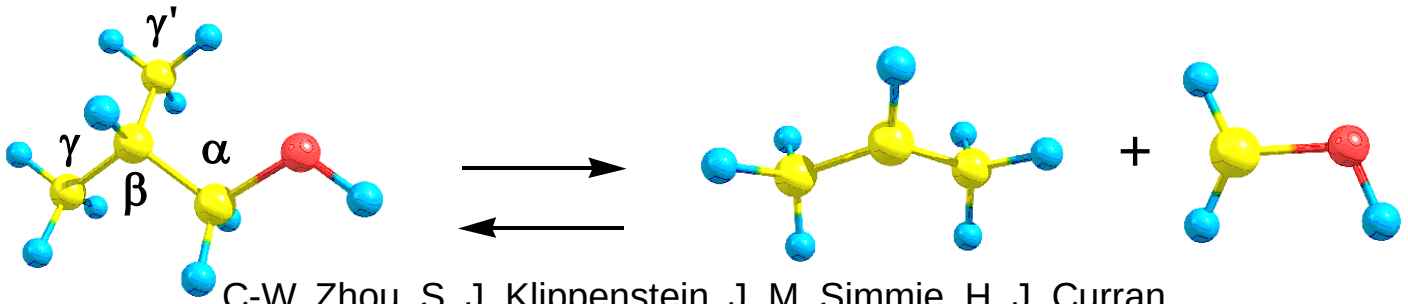
- Ketones + •OH



DMK EMK iPMK

C-W. Zhou, J. M. Simmie, H. J. Curran. *Phys. Chem. Chem. Phys*. **2011** *13* 11175−11192.

- *iso*-Butanol decomposition and related $(CH_3)_2\dot{C}H + \dot{C}H_2OH$ reaction (Argonne National Laboratory: Dr. Stephen Klippenstein)



C-W. Zhou, S. J. Klippenstein, J. M. Simmie, H. J. Curran
Proc. Comb. Inst., **2012** *in press*
Paper : 4D05 Thursday 2nd August

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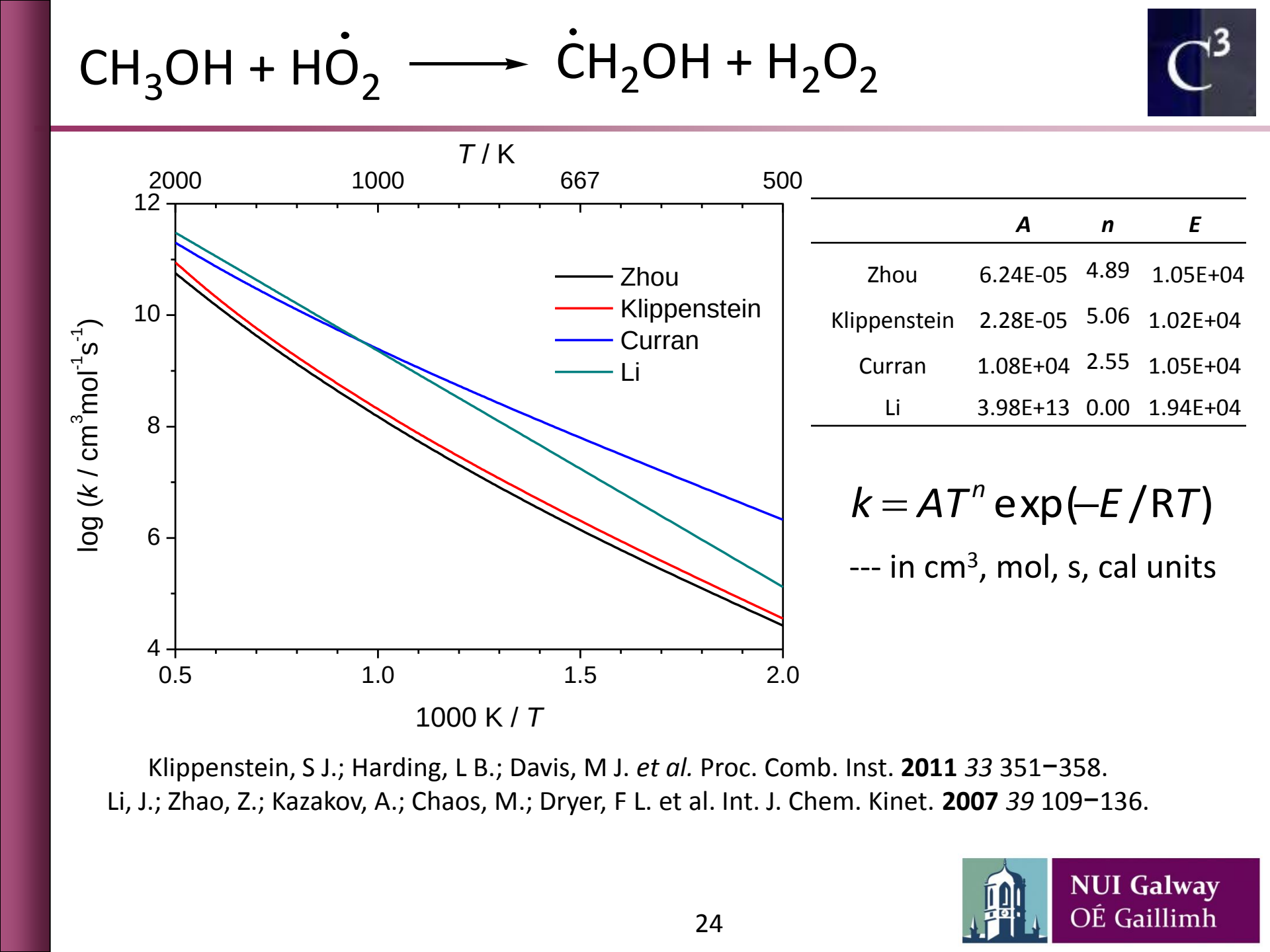


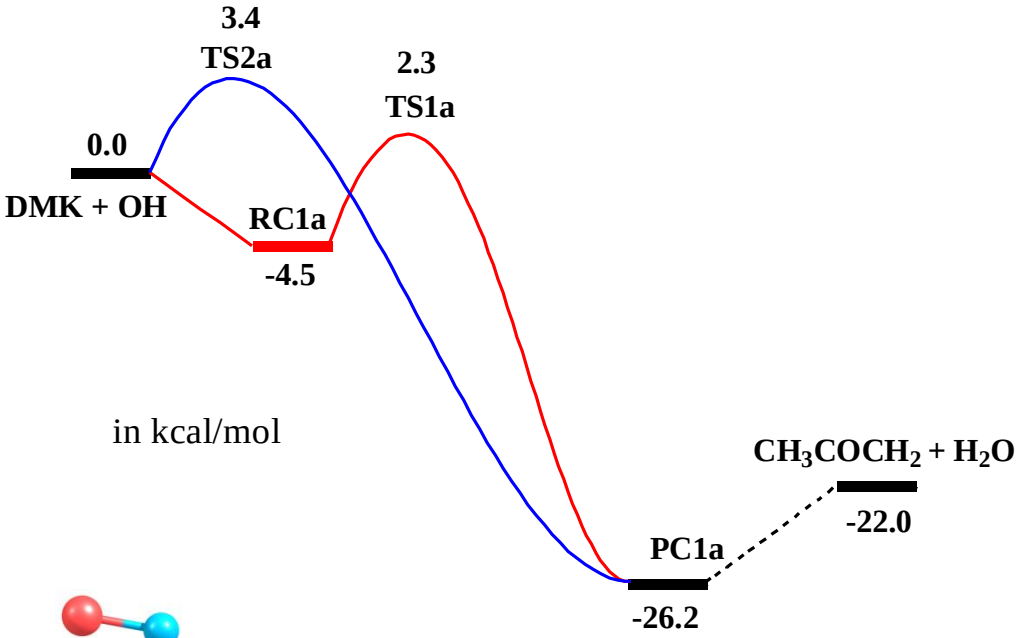
	A	*n*	*E*
Zhou	6.24E-05	4.89	1.05E+04
Klippenstein	2.28E-05	5.06	1.02E+04
Curran	1.08E+04	2.55	1.05E+04
Li	3.98E+13	0.00	1.94E+04

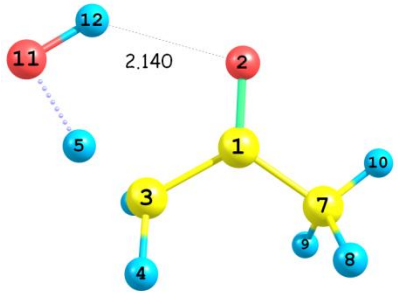
$$k = AT^n \exp(-E/RT)$$

--- in cm^3, mol, s, cal units

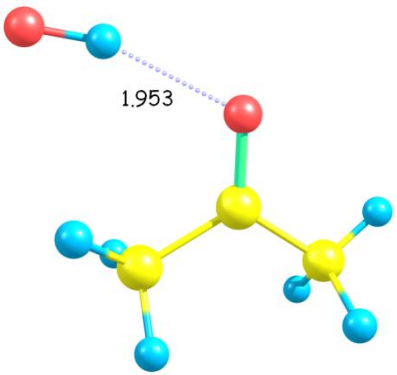
Klippenstein, S J.; Harding, L B.; Davis, M J. *et al.* Proc. Comb. Inst. **2011** *33* 351−358.
Li, J.; Zhao, Z.; Kazakov, A.; Chaos, M.; Dryer, F L. et al. Int. J. Chem. Kinet. **2007** *39* 109−136.

Acetone: α' hydrogen reactivity

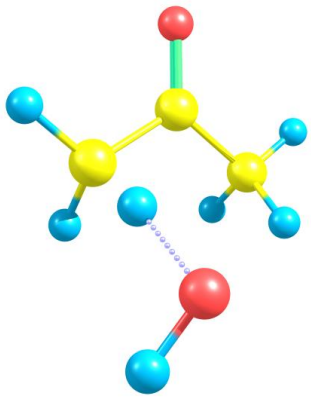




TS1a

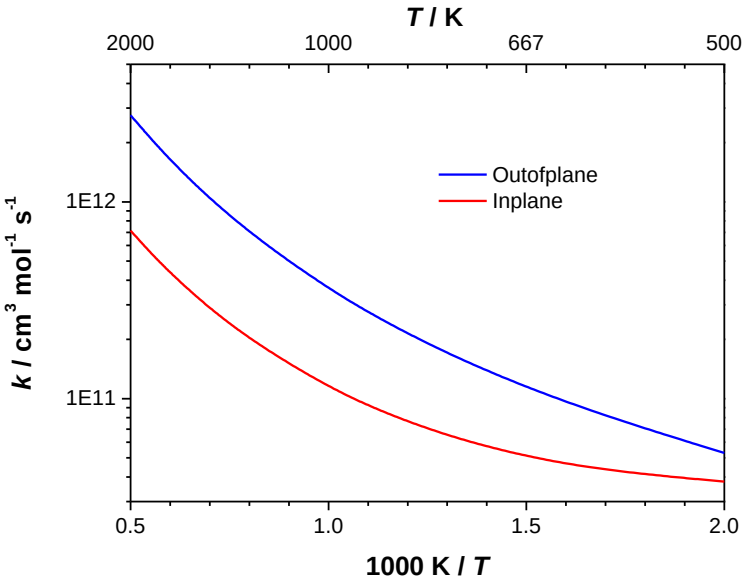


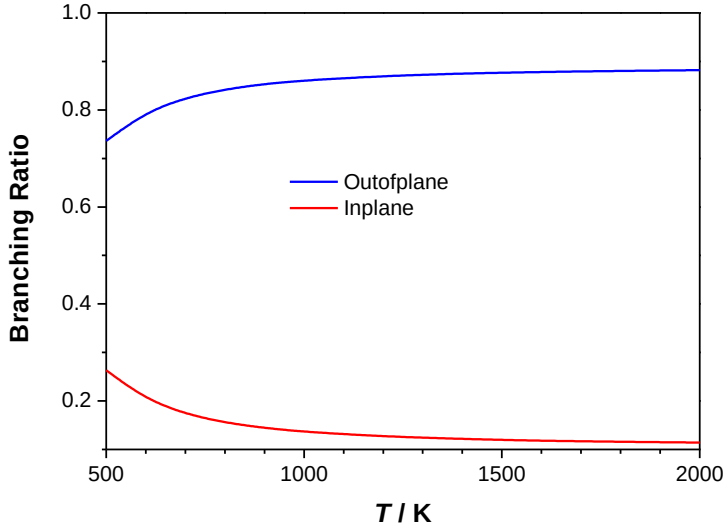
RC1a

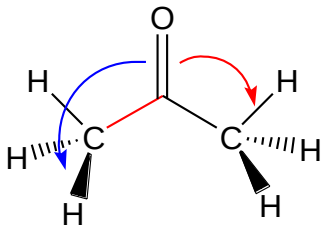


TS2a

Acetone: α' hydrogen reactivity





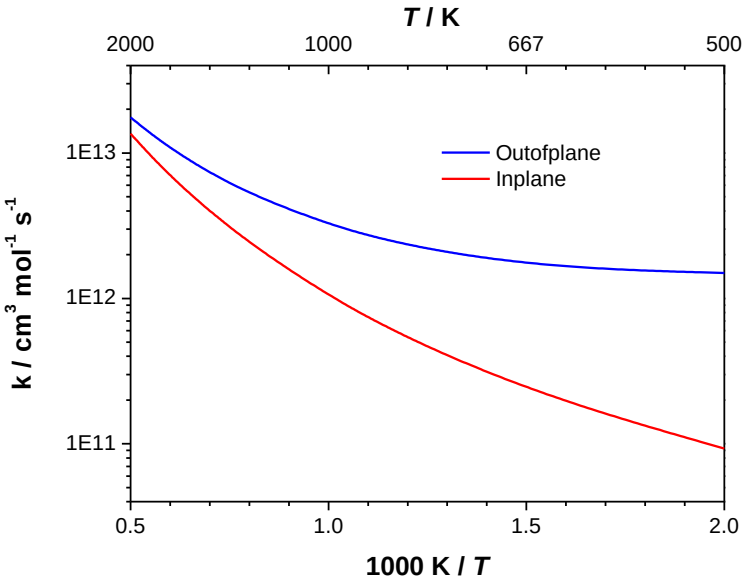


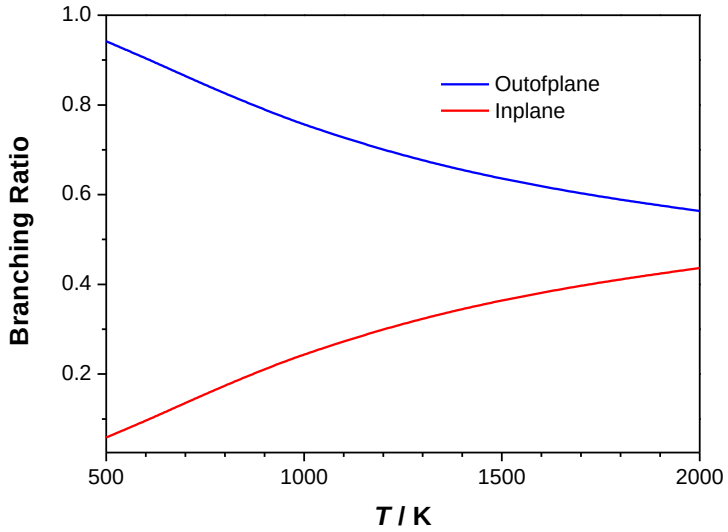
- Electron delocalization from π(CO) to σ*(CH_{in}) and σ*(CH_{out}) is different

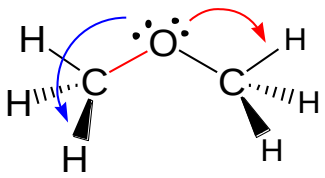
ΔE_{CT} = 2.0 kcal/mol

ΔE_{CT} = 0.0 kcal/mol

α' hydrogen reactivity in DME







ΔE_{CT} = 4.9 kcal/mol

ΔE_{CT} = 1.7 kcal/mol

- Electron delocalization from oxygen lone pairs to σ*(CH_{out}) weaken the BDE of out-of-plane CH bond by 5.0 kcal/mol.

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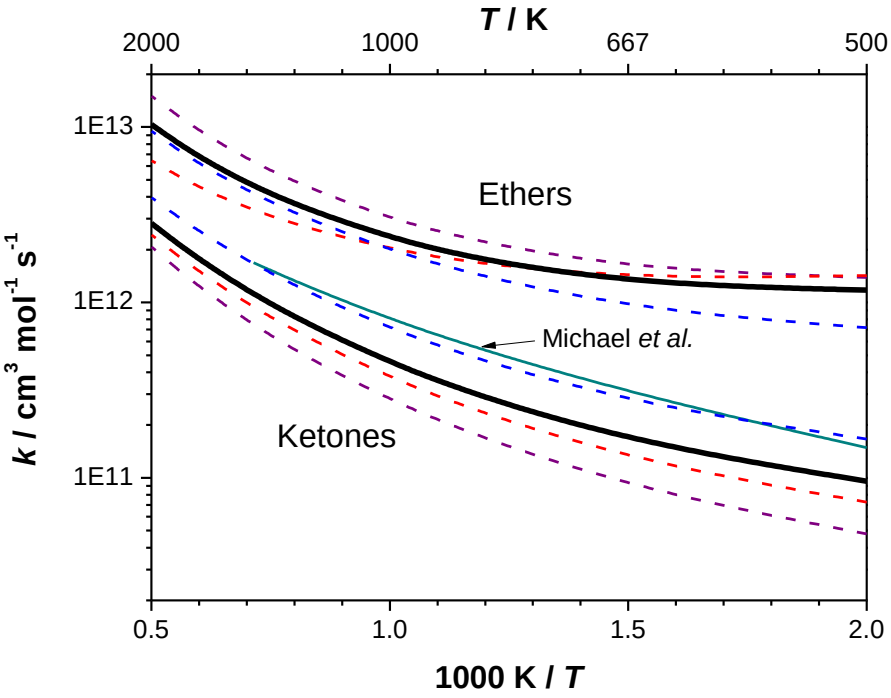
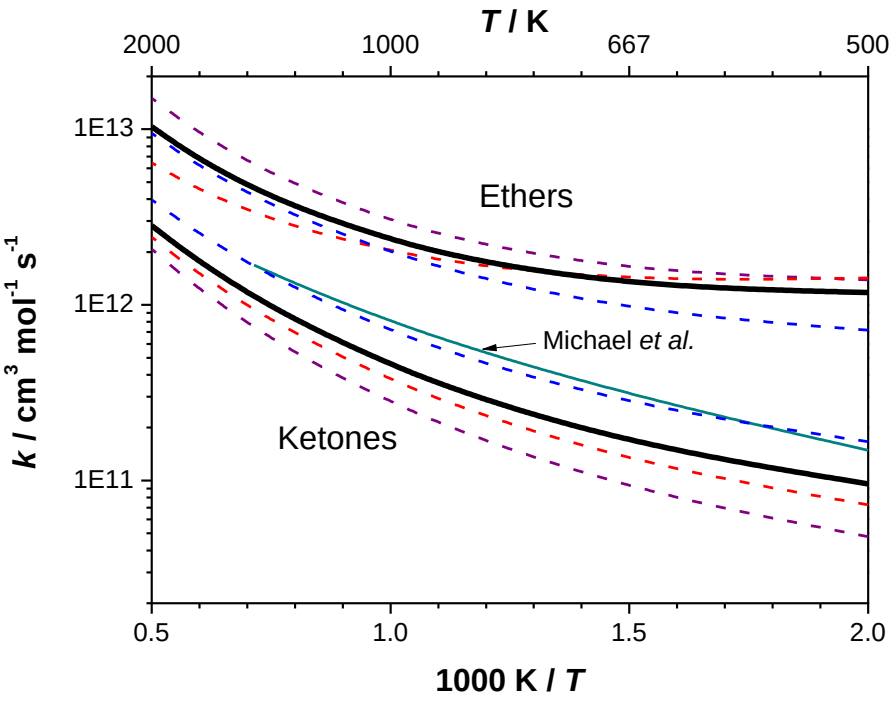
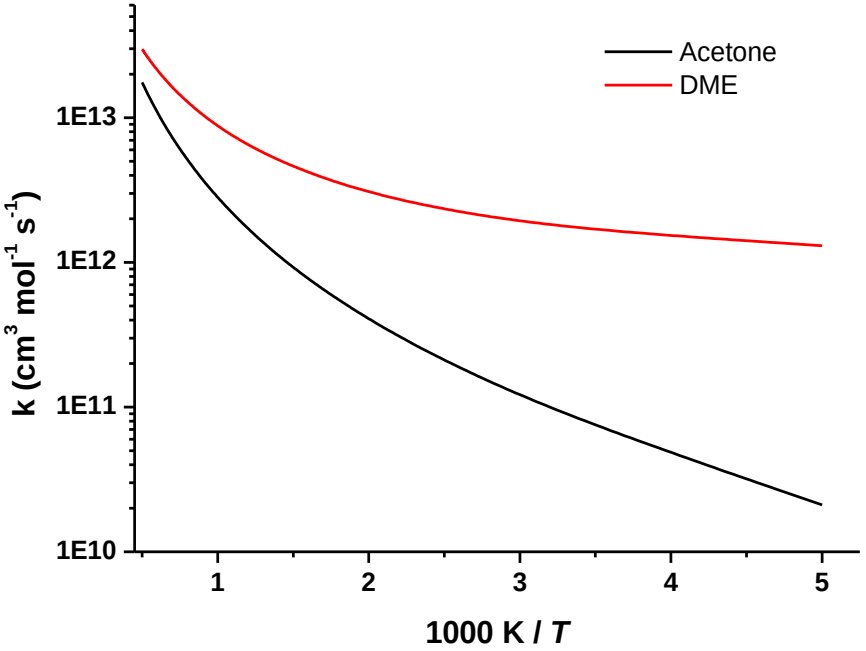
α' Reactivity Compared to Alkanes



- Ethers
  - Oxygen lone pairs accelerate reactivity of α' hydrogen compared to alkane
  - Growing size of the α-side has no influence on reactivity of α' hydrogen atoms
- Ketones
  - α' H-atom is less reactive than primary H-atom in alkanes
  - Growing size of the α-side will accelerate reactivity of α' H-atoms

Comparative Reactivity





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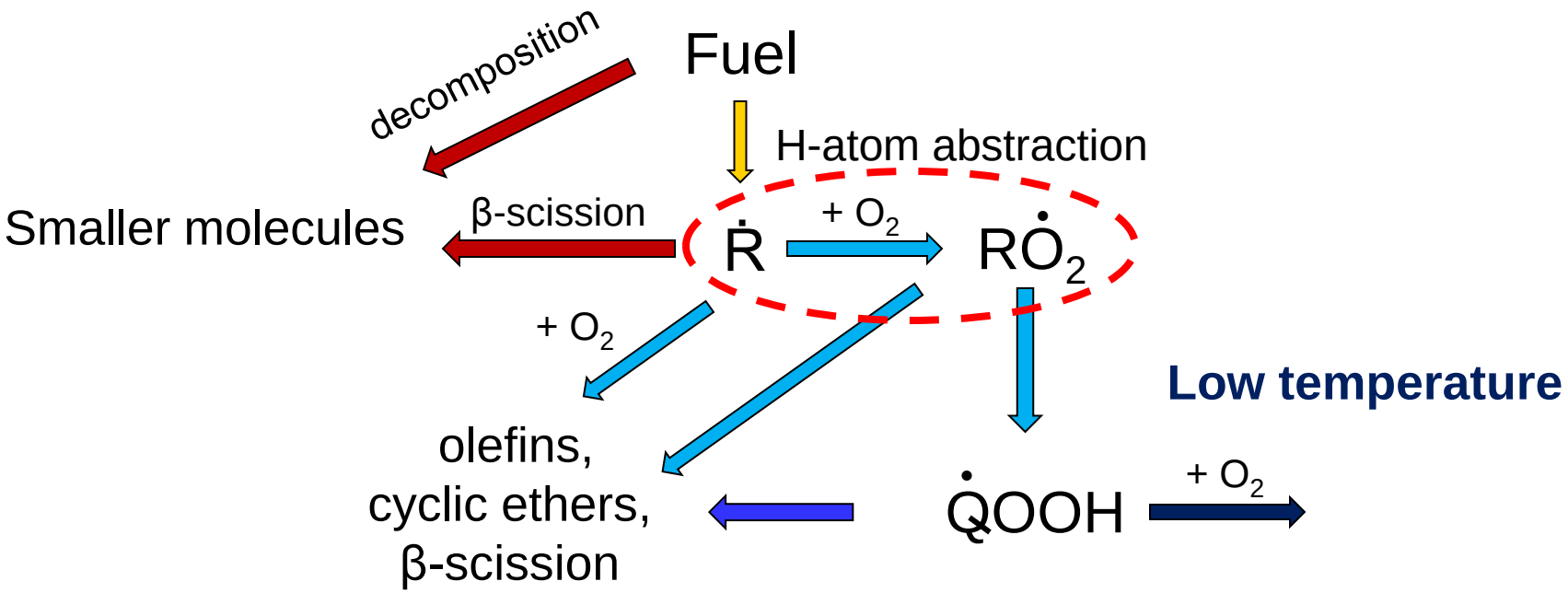
General reaction scheme

High temperature



Intermediate temperature

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Low-temperature chemistry

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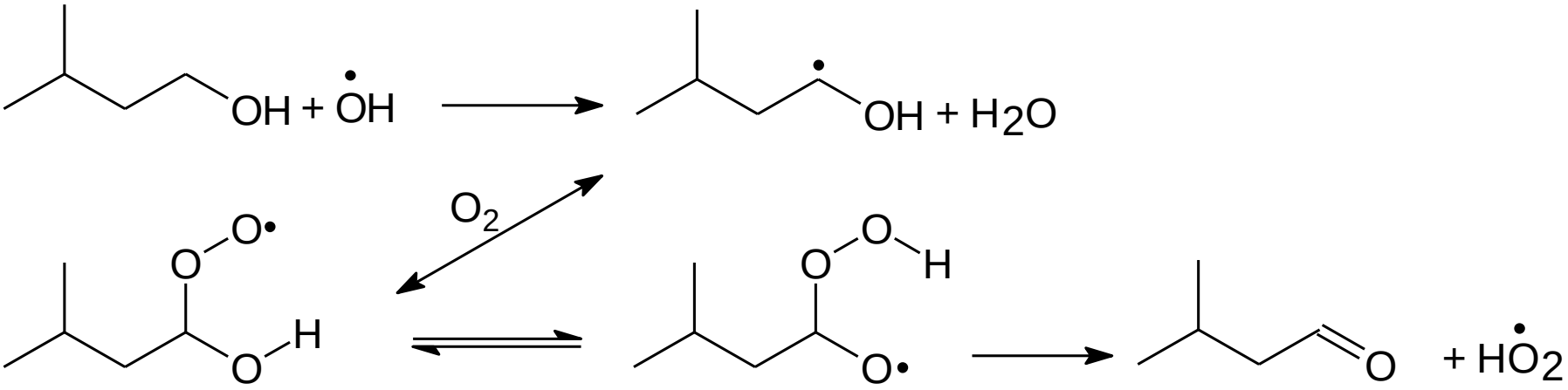
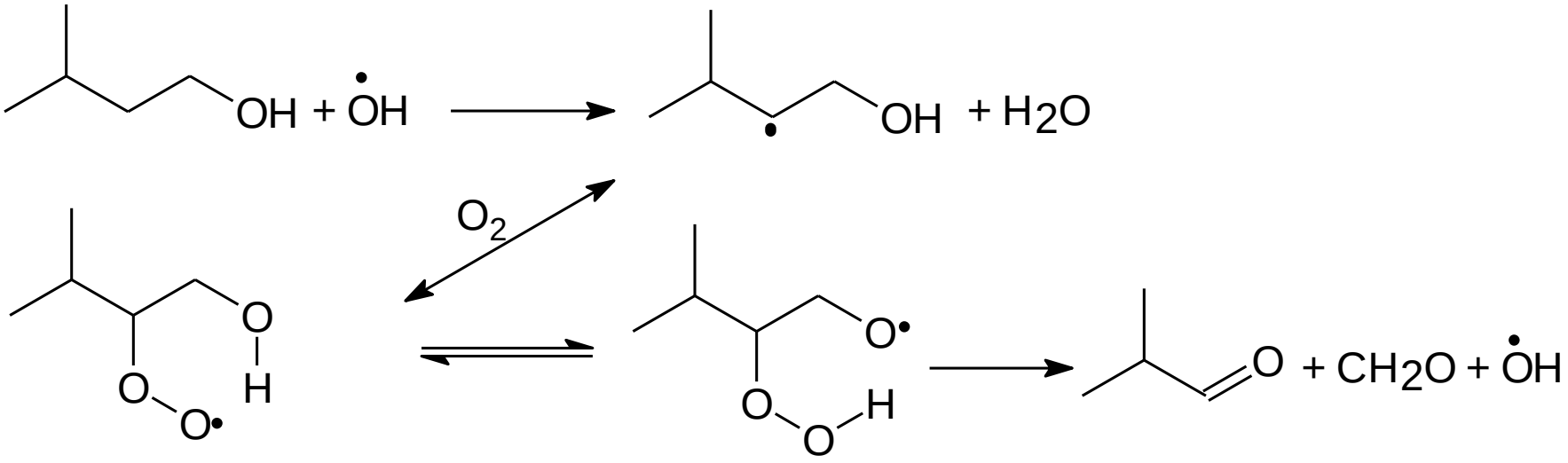
Alcohol Oxidation

Aldehyde formation from α-radical + O_2

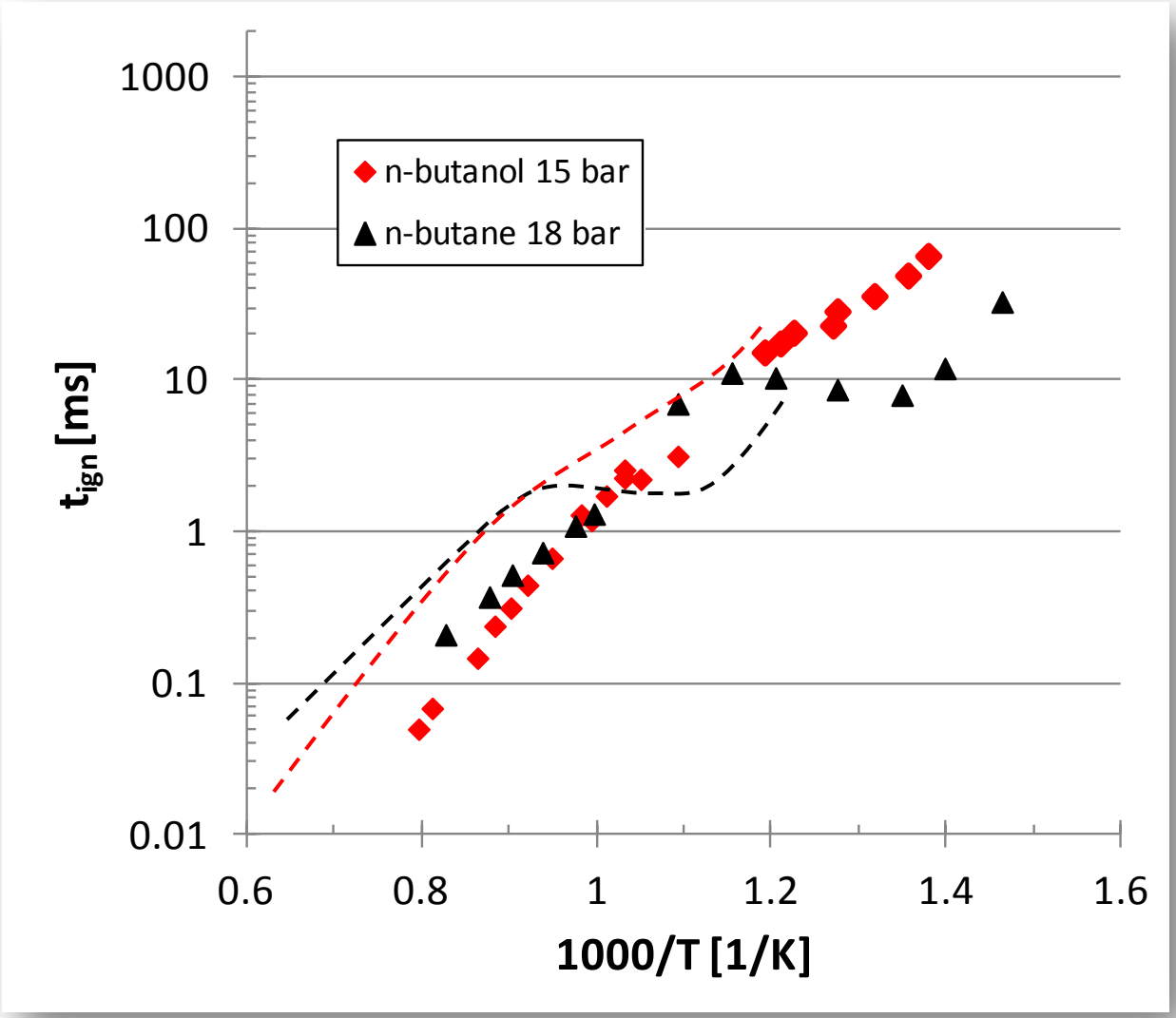


Alcohol Oxidation

Waddington mechanism (β-radical + O_2)



Comparison: Alcohol/Alkane Oxidation



Effect of chain length

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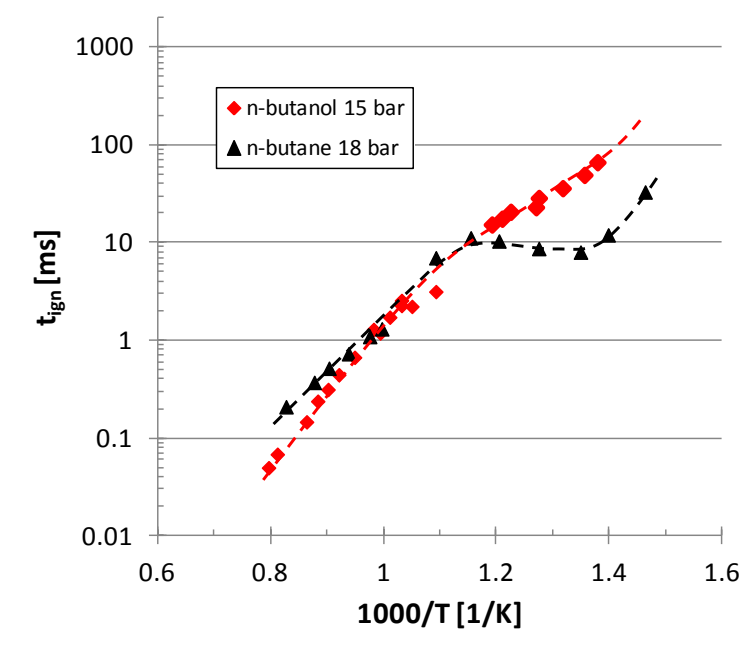
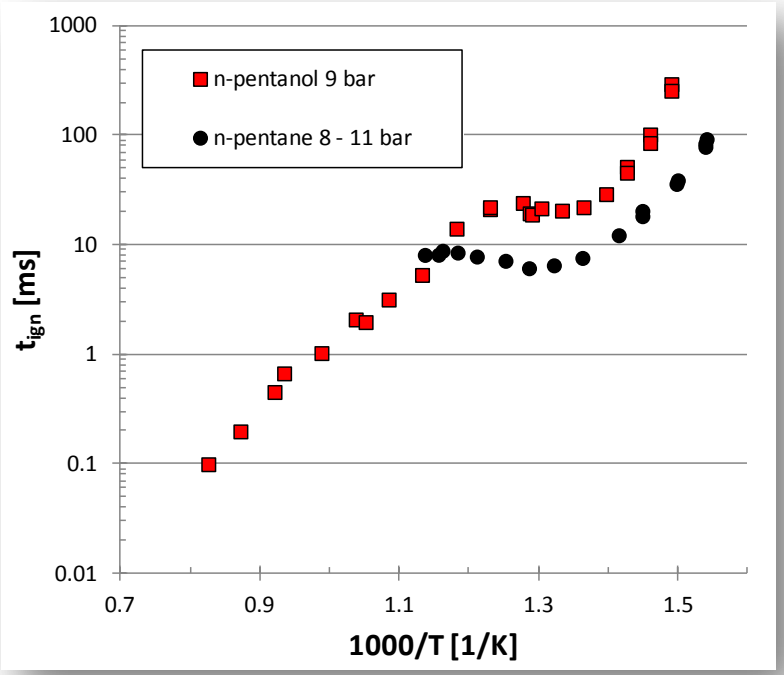
Alcohol Oxidation

Effect of chain length on influence of functional group

n-Butanol vs *n*-Butane

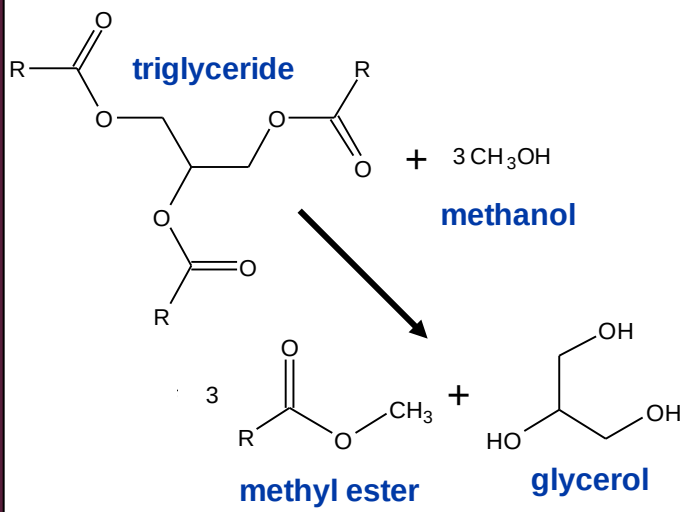


n-Pentanol vs *n*-Pentane



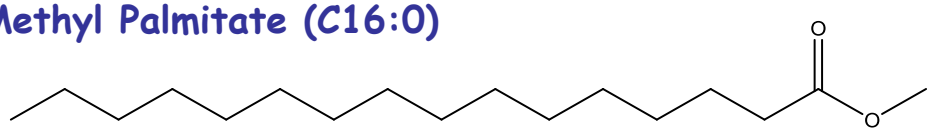
Heufer *et al.* Proc. Comb. Inst. (2012) in press.
Paper 4D06, Thursday 2nd August

Soybean and rapeseed derived biodiesels have only 5 principal components

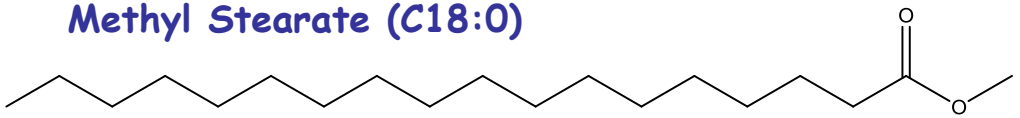


Fatty acid methyl esters (FAMEs):

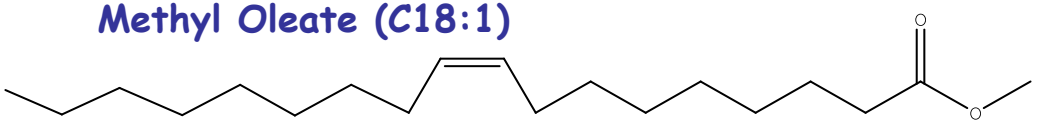
Methyl Palmitate (C16:0)



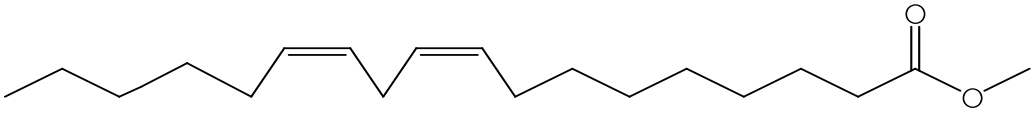
Methyl Stearate (C18:0)



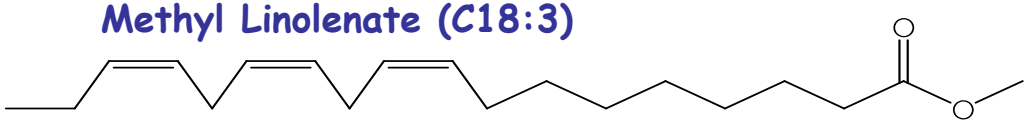
Methyl Oleate (C18:1)

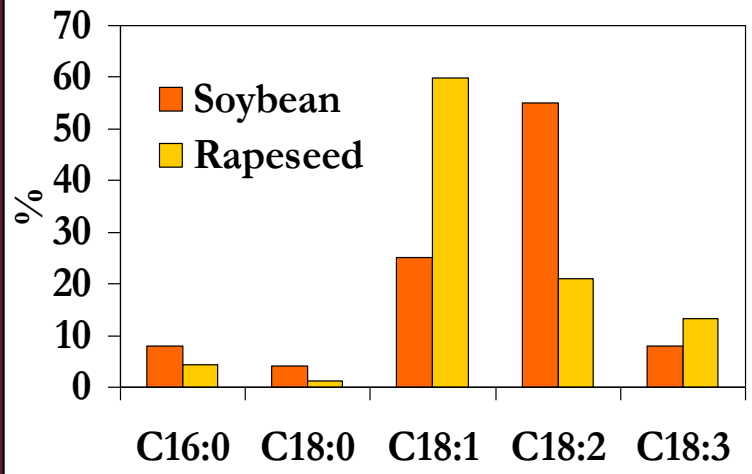


Methyl Linoleate (C18:2)



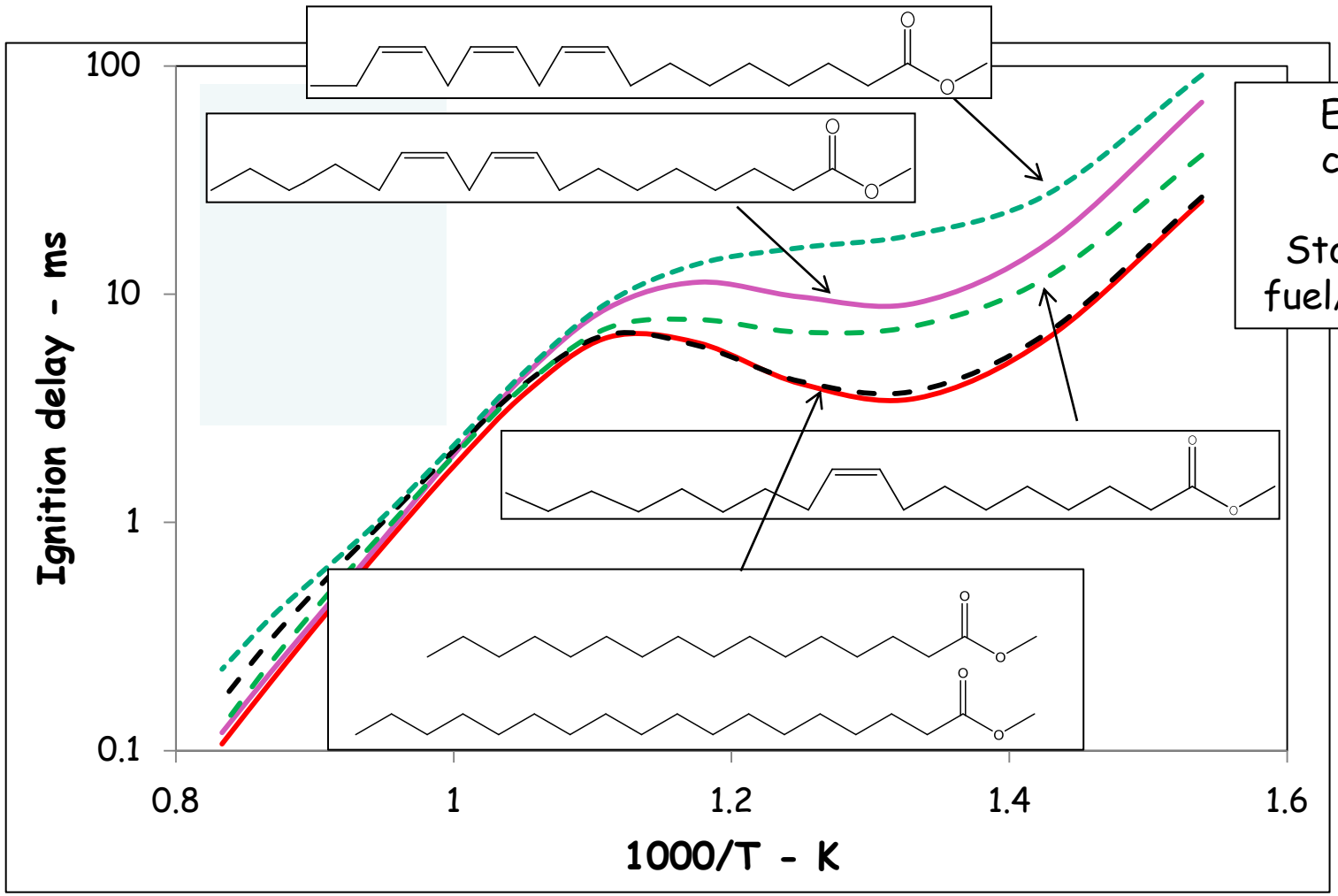
Methyl Linolenate (C18:3)





Westbrook *et al.* Proc. Comb. Inst. (2012) in press.
Paper 3D03 Wednesday 1st August

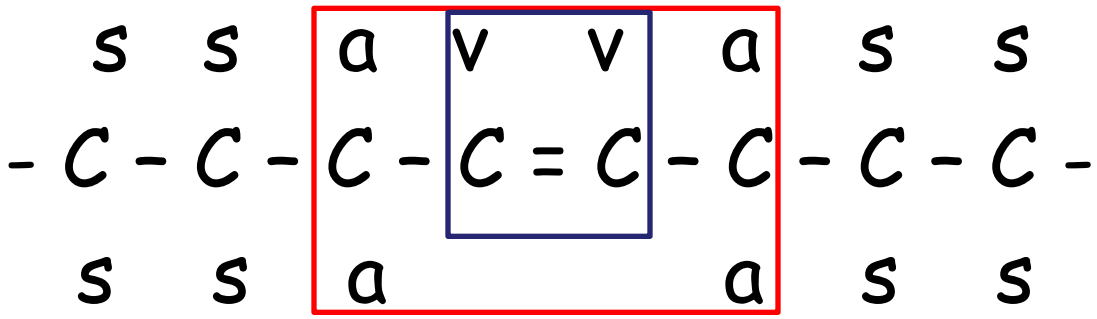
Biodiesel components ignite in order of number of double bonds



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

Westbrook *et al. Proc.* Comb. Inst. (2012) in press.
Paper 3D03 Wednesday 1st August

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

Westbrook *et al. Proc.* Comb. Inst. (2012) in press.
Paper 3D03 Wednesday 1st August

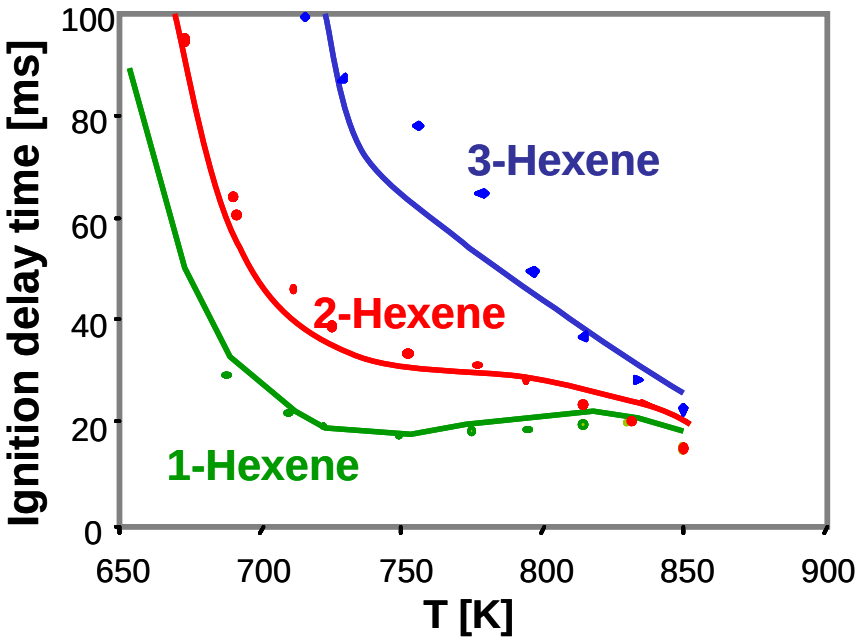
Observed same effect in hydrocarbon fuels: hexenes

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 155 (2008) 756—772.

Novel fuels

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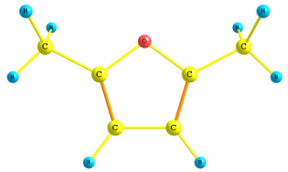
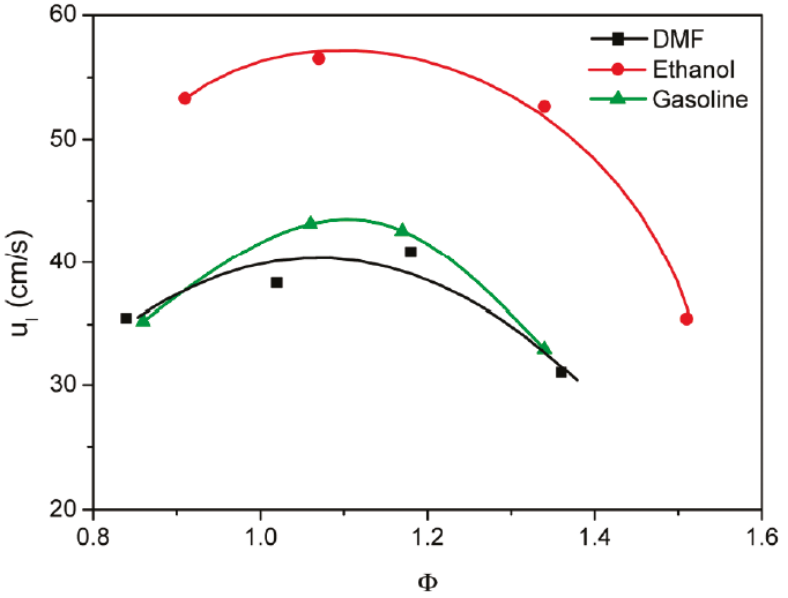
Furans vs bio-ethanol



- Promising Next Generation Biofuels
  - Roman-Leshkov et al., Nature (2007) *447:* 982-985. (2nd generation)
- Novel renewable production process
  - Biomass (lignocellulosic) feedstock not destined for human/animal consumption
  - Highly efficient
  - Large scale and low cost
- Desirable physicochemical properties
  - Higher energy density (40%)
  - Direct combustion in unmodified engine
  - RON = 119
  - Lower aqueous solubility and less volatile



Laminar Flame Speed Measurements of DMF, Ethanol and Gasoline, Tian et al., Energy Fuels, **2010**

Energy Densities:

- Gasoline: 35 MJ/L
- 2,5-DMF: 31 MJ/L
- Bio-Ethanol: 23 MJ/L

Session 1: Monday morning: "Kinetics of Cyclic Ethers"

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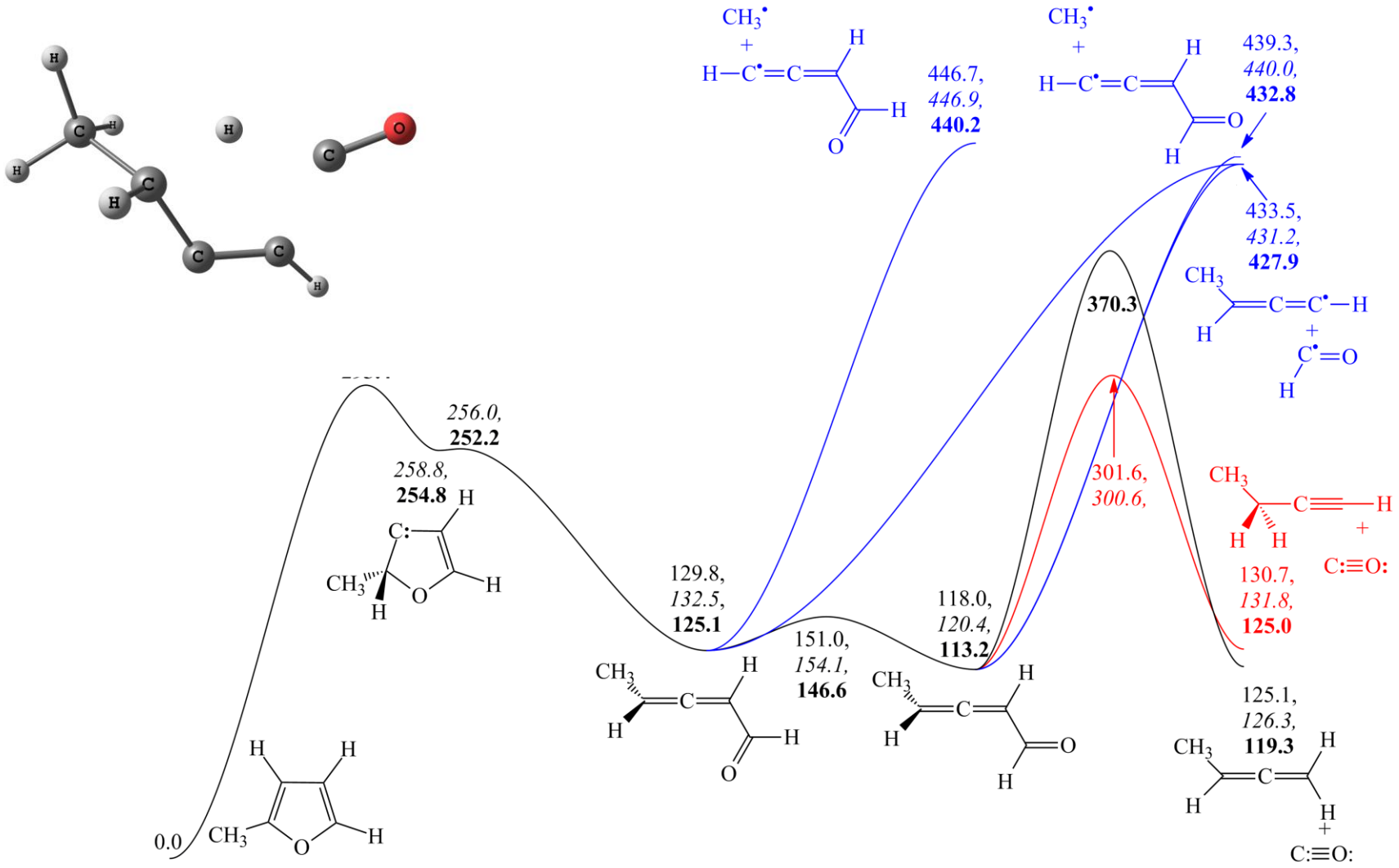
2MF: Unimolecular Decomposition



Energies (0 K, kJ / mol) CBS-QB3, *CBS-APNO*, **G3**

Somers et al. Comb. Inst. (2012) in press. Paper1D01 Monday 30th July

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Conclusions

- General chemical reaction schemes of HCs can be applied to oxygenated fuels
- Details of oxygenated fuel combustion are quite different!