

From Experiment to CFD; Ongoing Work at the Combustion Chemistry Centre

Kenji Yasunaga

Work areas

- ▶ Experiments
- ▶ Modelling and simulation
- ▶ Quantum chemistry

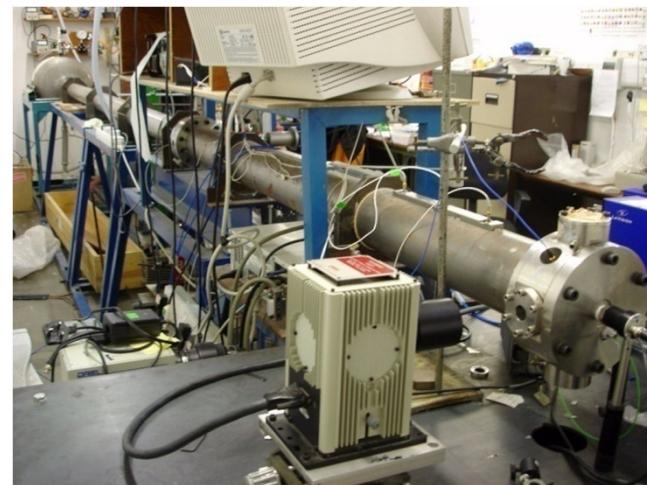
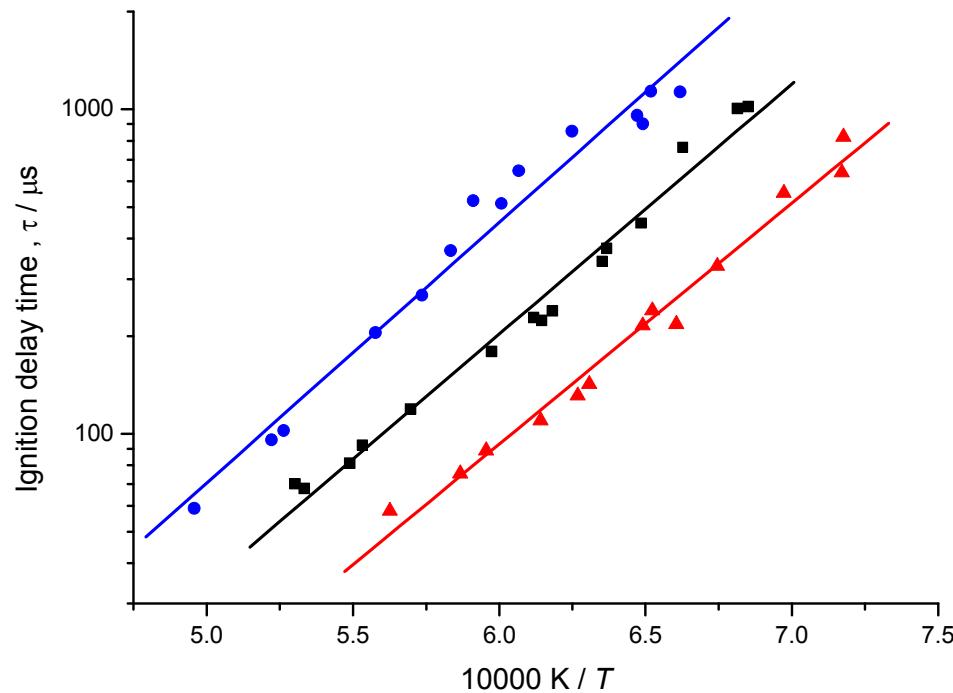
Experimental facilities

- ▶ Old
 - ▶ Shock tube #1
 - ▶ Low pressure, unheated, ...
 - ▶ Rapid compression machine #1
 - ▶ Twin piston, well understood, ...
- ▶ New
 - ▶ Shock tube #2
 - ▶ Hi-pressure, heated

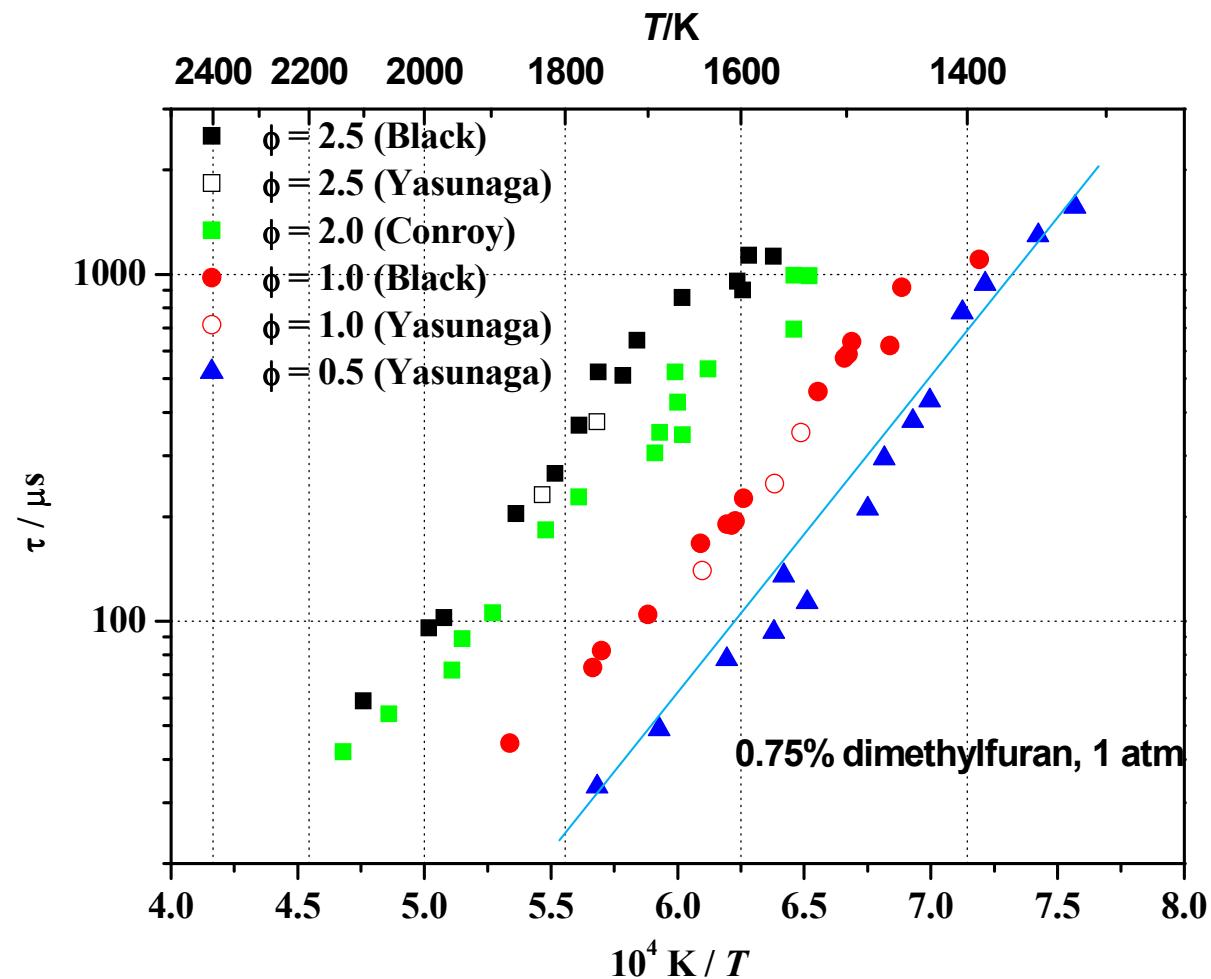
Results from ST#1 (Montréal 2008)

► 2,5-dimethylfuran vs n-butanol vs ethanol

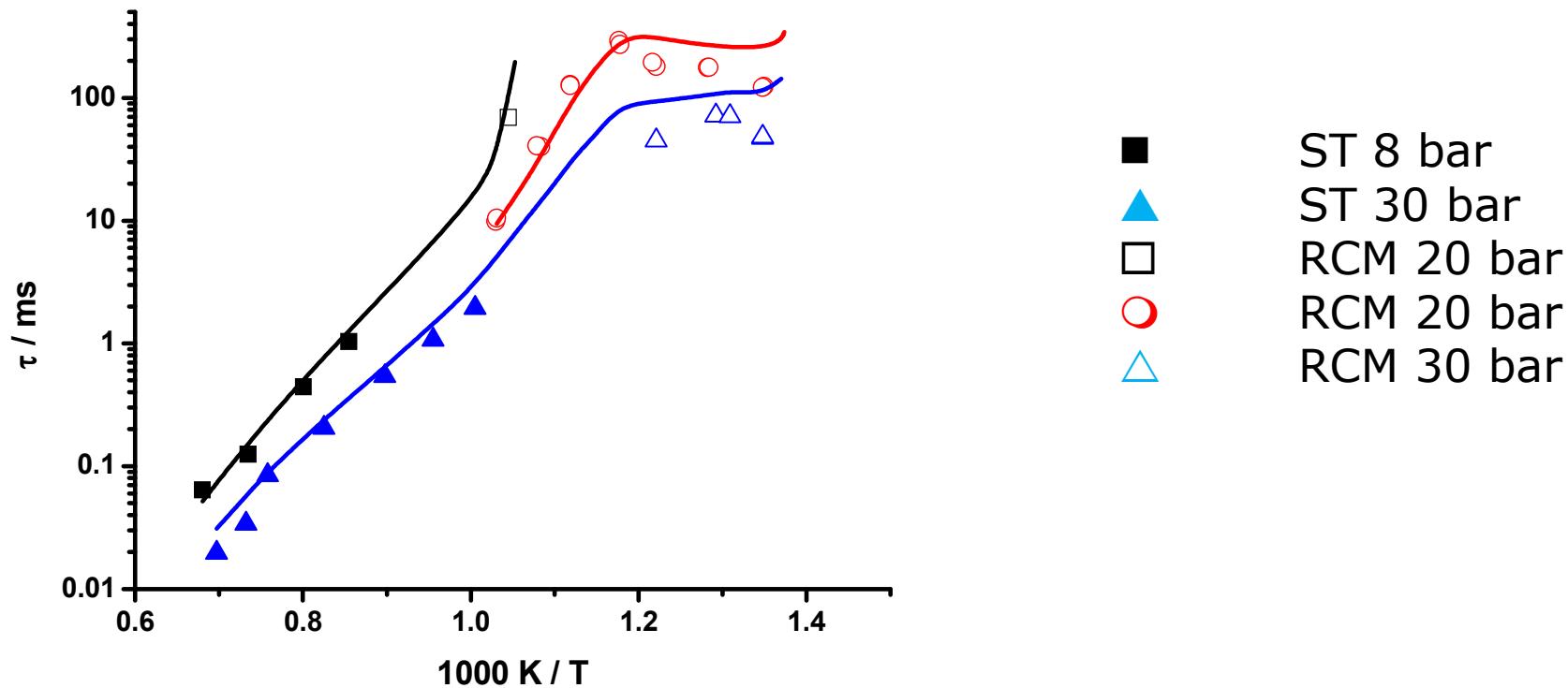
- 0.75% fuel: 2.25%O₂, balance Ar
- Reflected shock pressure 1.0 atm



Unpublished 2,5-dimethylfuran



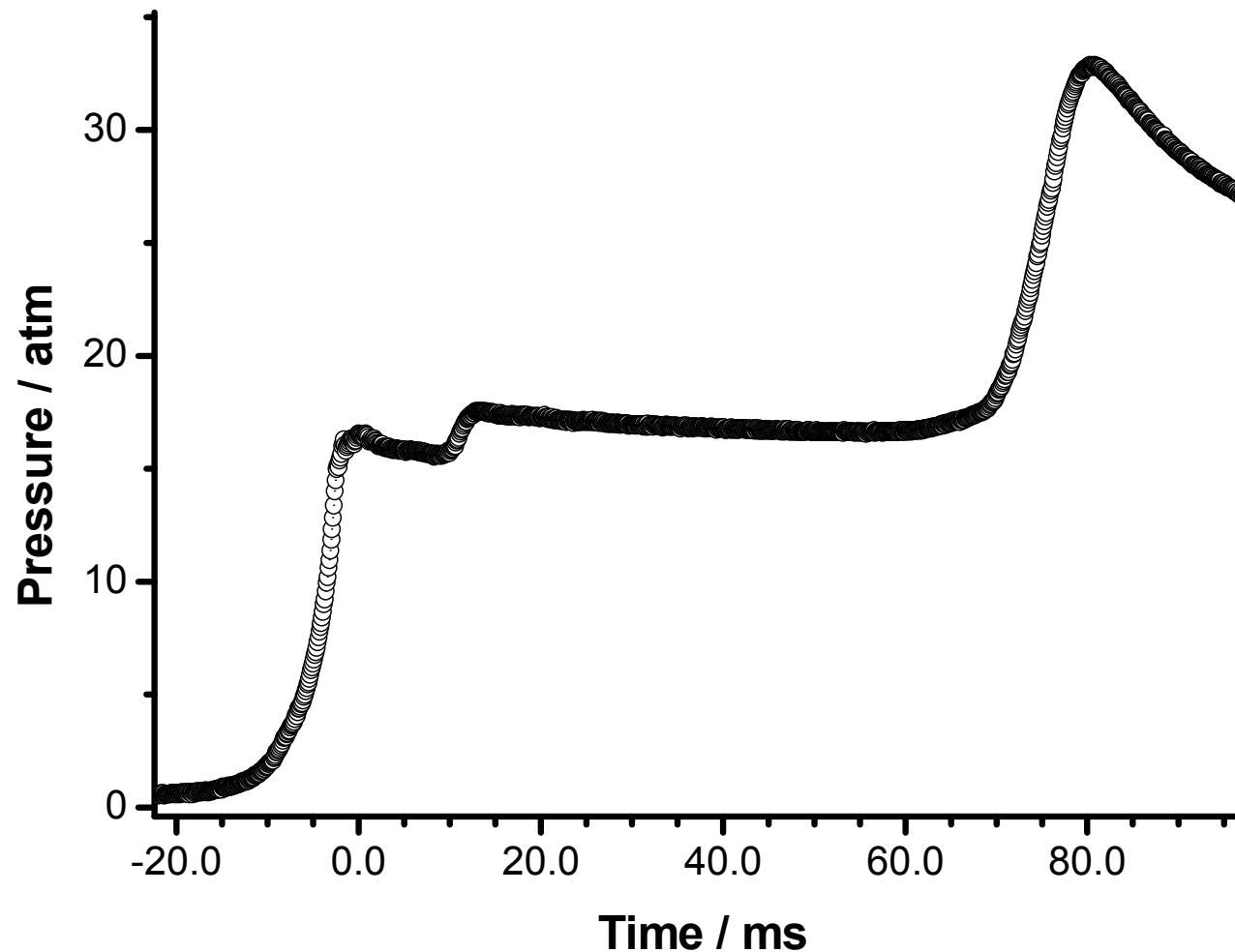
Old RCM (Darren Healy)



- ▶ 5.1% CH_4 , 1.09% C_2H_6 , 1.09% C_3H_8 , 19.47% O_2 and 73.25% diluent, $\phi = 0.5$ in "air".
- ▶ Combust. & Flame 2008, 155, 441; ibid. 451. 153, 316

Low- T chemistry (Peter O'Toole)

80:20 CH₄:CH₃OCH₃ $\phi=0.5$, $T_c=715\text{K}$ O₂/N₂



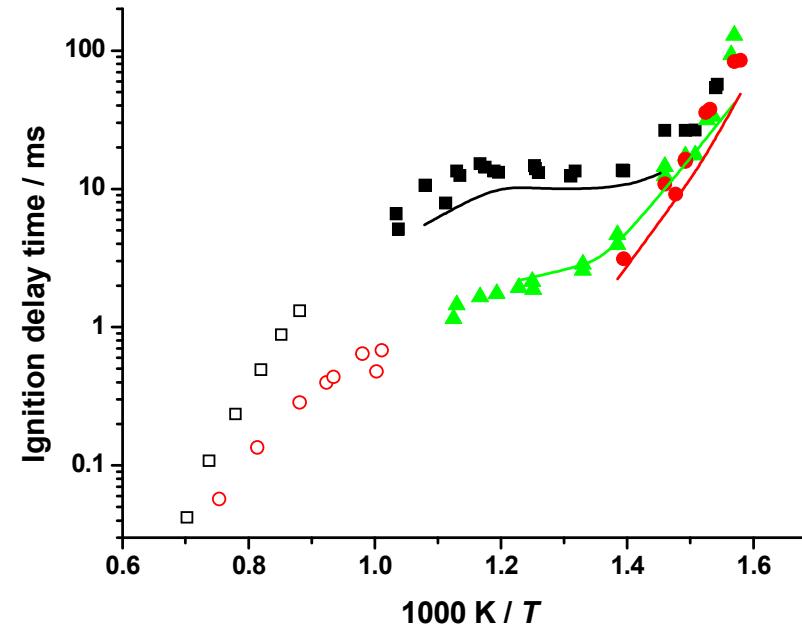
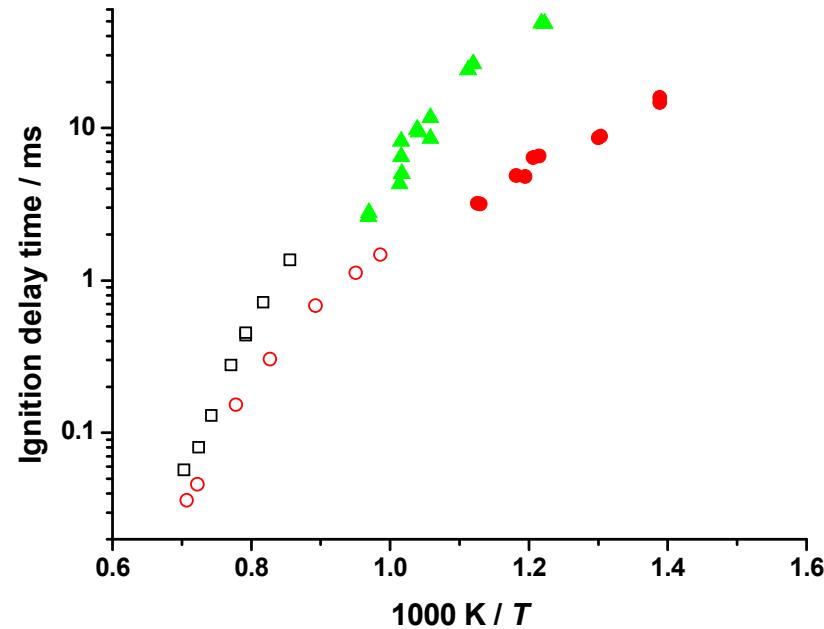
Natural gas/DME blends [60%CH₄:40% DME]

Left: $\phi=0.3$

Right: $\phi=1.0$

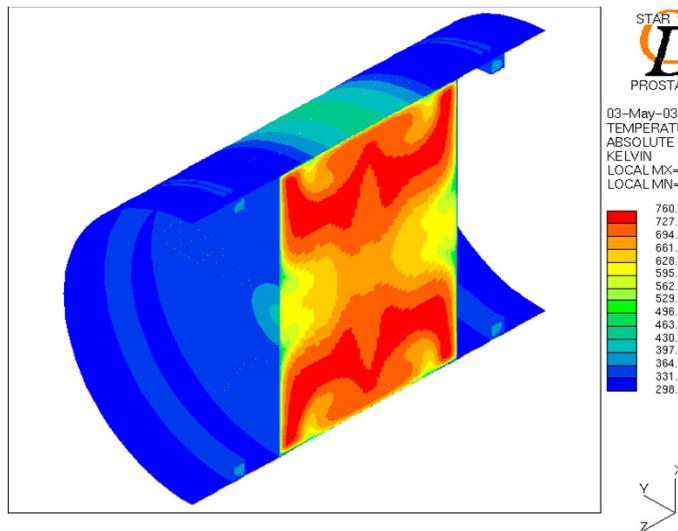
ST □ 7 ○ 30

RCM ■ 7 ▲ 15 ● 30

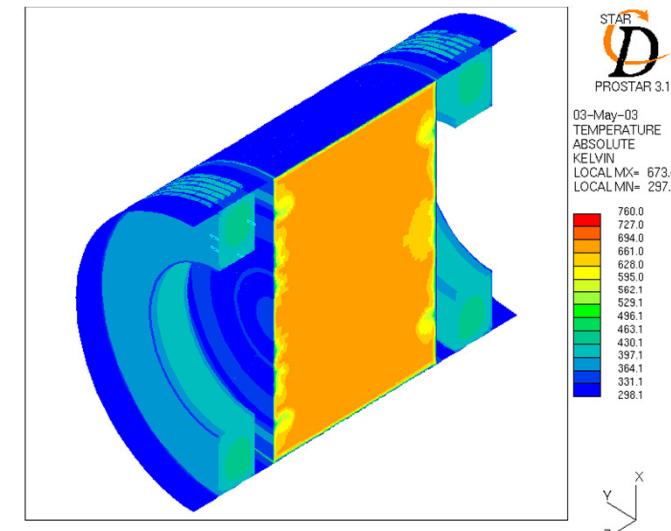


CFD of unique machine (Judith Würmel)

Poor crevice

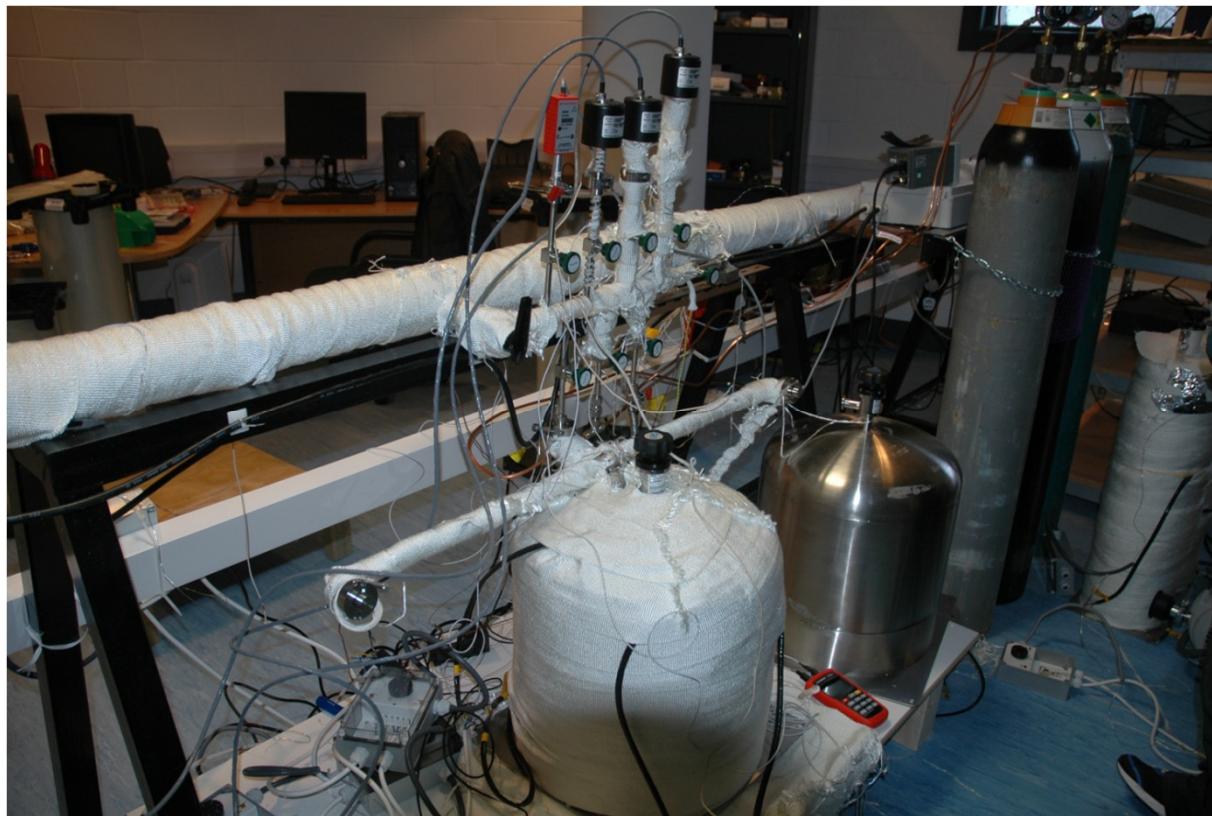


Good crevice

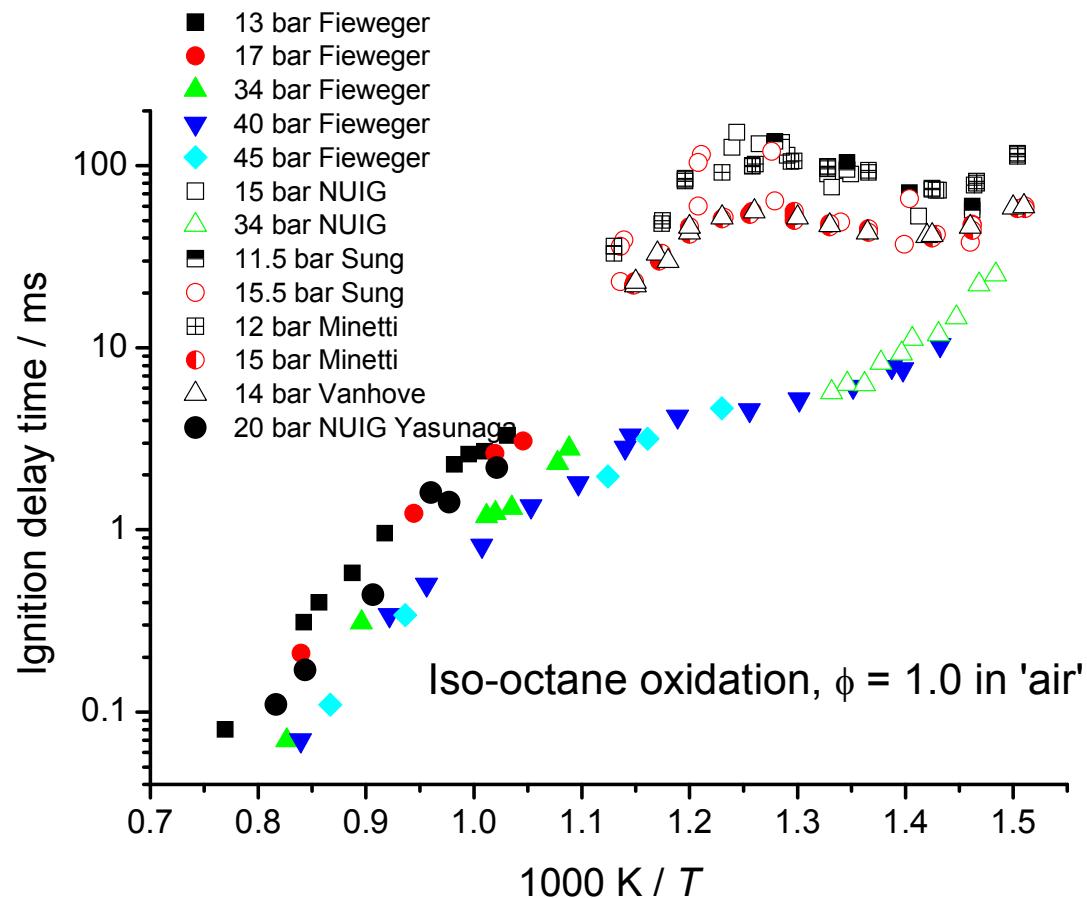


New ST (Colin Tobin, Christine Conroy)

- ▶ Diameter: 6.3 cm Driver: 3 m Test: 5.73 m
- ▶ Reflected shock p_5 70 bar Initial T_1 135°C



New ST (Kenji Yasunaga)



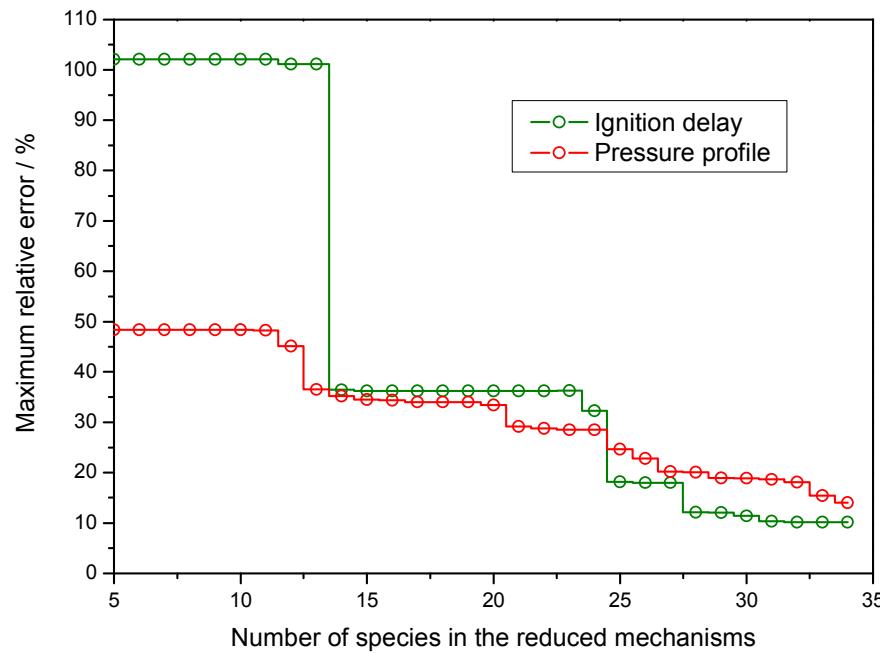
Modelling (Zeynep Serinyel, Sinéad Burke)

- ▶ Natural gas C₀ to C₅ chemistry + biofuel blends
 - ▶ High-pressure & low temperatures
- ▶ High molecular weight HCs
 - ▶ Low volatility ⇔ heated STs, RCMs,
- ▶ Bio-fuels
 - ▶ Structural features R-C(O)OR'
 - ▶ Methyl formate HC(O)OCH₃
 - ▶ Higher alcohols
 - ▶ n-butanol, ...
- ▶ Next-generation biofuels
 - ▶ 2,5-Dimethylfuran

Mechanism reduction [I. Gy. Zsély & Tibor Nagy]

Natural gas mechanism
(NUIG C4_49)

230 species, 1327 rxns



90% methane and 10% propane

Lean and stoichiometric

Gas turbine relevant conditions

Temperatures: 876–1,465 K

Pressures: 10–40 atm

Grouping of 30 experiments to
form 6 regimes

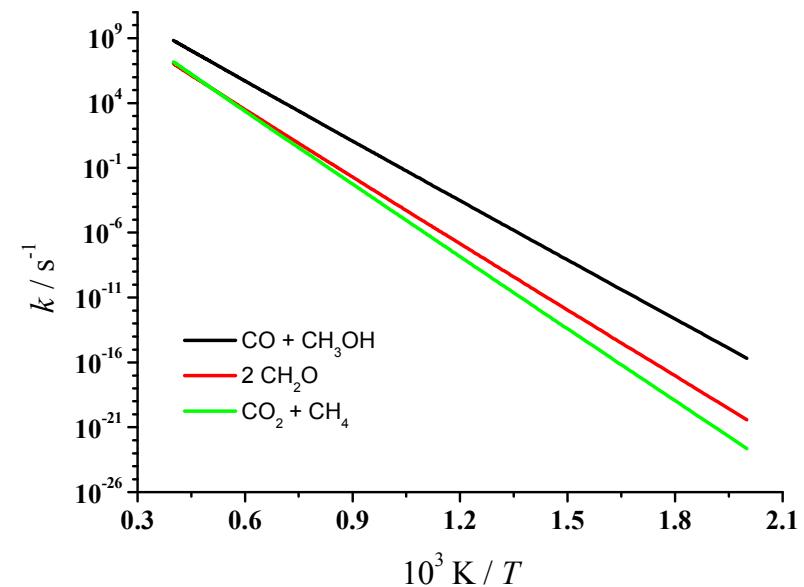
Quantum chemistry

Enols C=C-OH

- ▶ Only one stable enol known
 - ▶ Detected in $\text{CH}_2=\text{CH}_2$ flames **Taatjes 2005**
 - ▶ Astrochemists 2001
 - ▶ Mechanism: $>\text{C}=\text{C}< + \cdot\text{OH}$
 - ▶ Ubiquitous – O- and N-cpds.
 - ▶ Exhaust gases?
 - ▶ Ethenol \Rightarrow shortfall in RCOOH in urban air
 - ▶ **Archibald 2007** assumed 2:1 $\text{CH}_3\text{CHO}:\text{CH}_2=\text{CH(OH)}$
 - ▶ In alcohols?
 - ▶ Iso-butanol 60:40 ethanal:ethenol ratio **Qi et al. 2007**
- $$\text{H}\cdot + \text{CH}_3\text{CHO} \leftarrow \text{CH}_3\cdot\text{CHOH} \rightarrow \text{CH}_2=\text{CH(OH)} + \text{H}\cdot$$
- ▶ We compute a 3.1 ratio at 1,000K
 - J. Phys. Chem. A (2009) 113(27): 7834-7845.

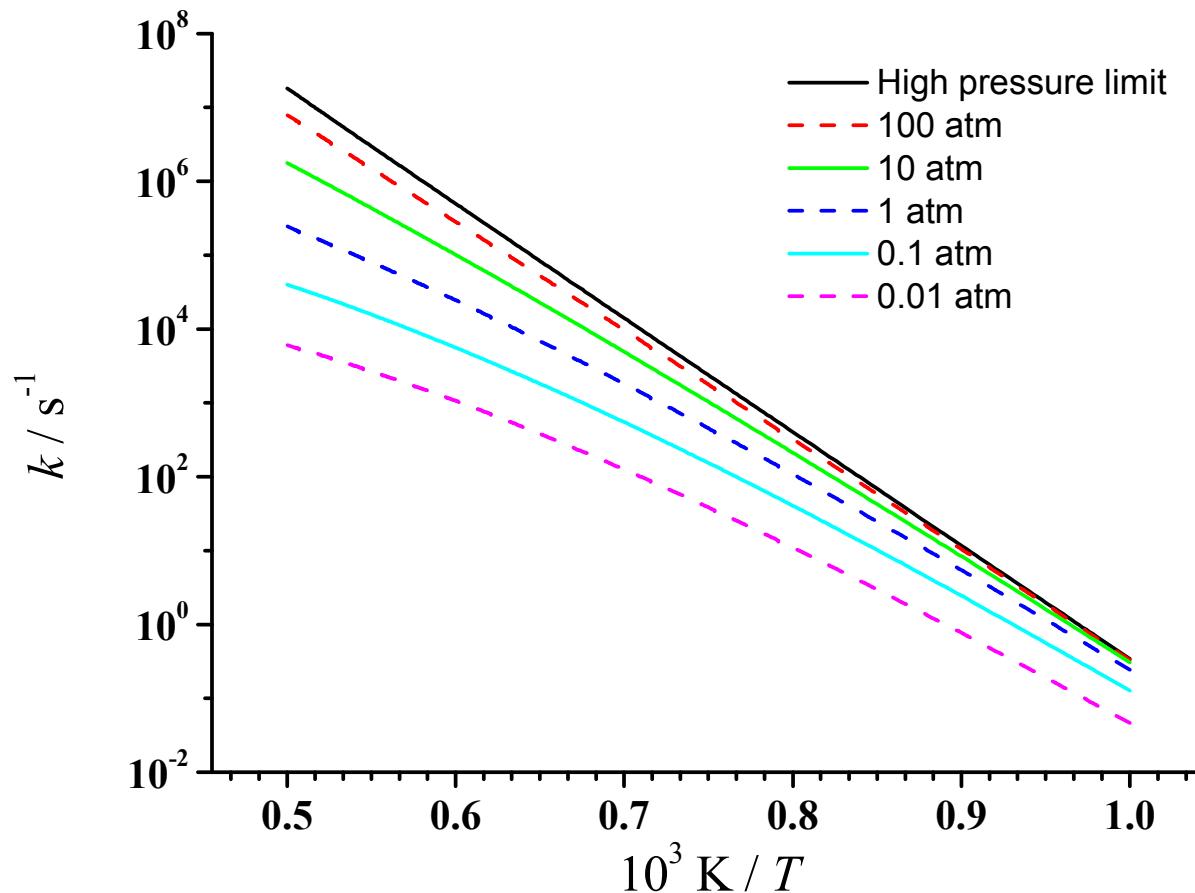
Methyl formate decomposition

- ▶ Multilevel methods: CBS-QB3 and APNO, G3
 - ▶ Zero-point corrected electronic energies (0K)
 - ▶ Barriers to reaction & reaction enthalpy
- ▶ $\text{HCOOCH}_3 \rightarrow \text{CO} + \text{CH}_3\text{OH}$
 $285.5 \pm 4.1 \text{ kJ/mol}$
- ▶ $\text{HCOOCH}_3 \rightarrow 2\text{CH}_2\text{O}$
 $321.2 \pm 1.8 \text{ kJ/mol}$
- ▶ $\text{HCOOCH}_3 \rightarrow \text{CO}_2 + \text{CH}_4$
 $348.3 \pm 3.5 \text{ kJ/mol}$



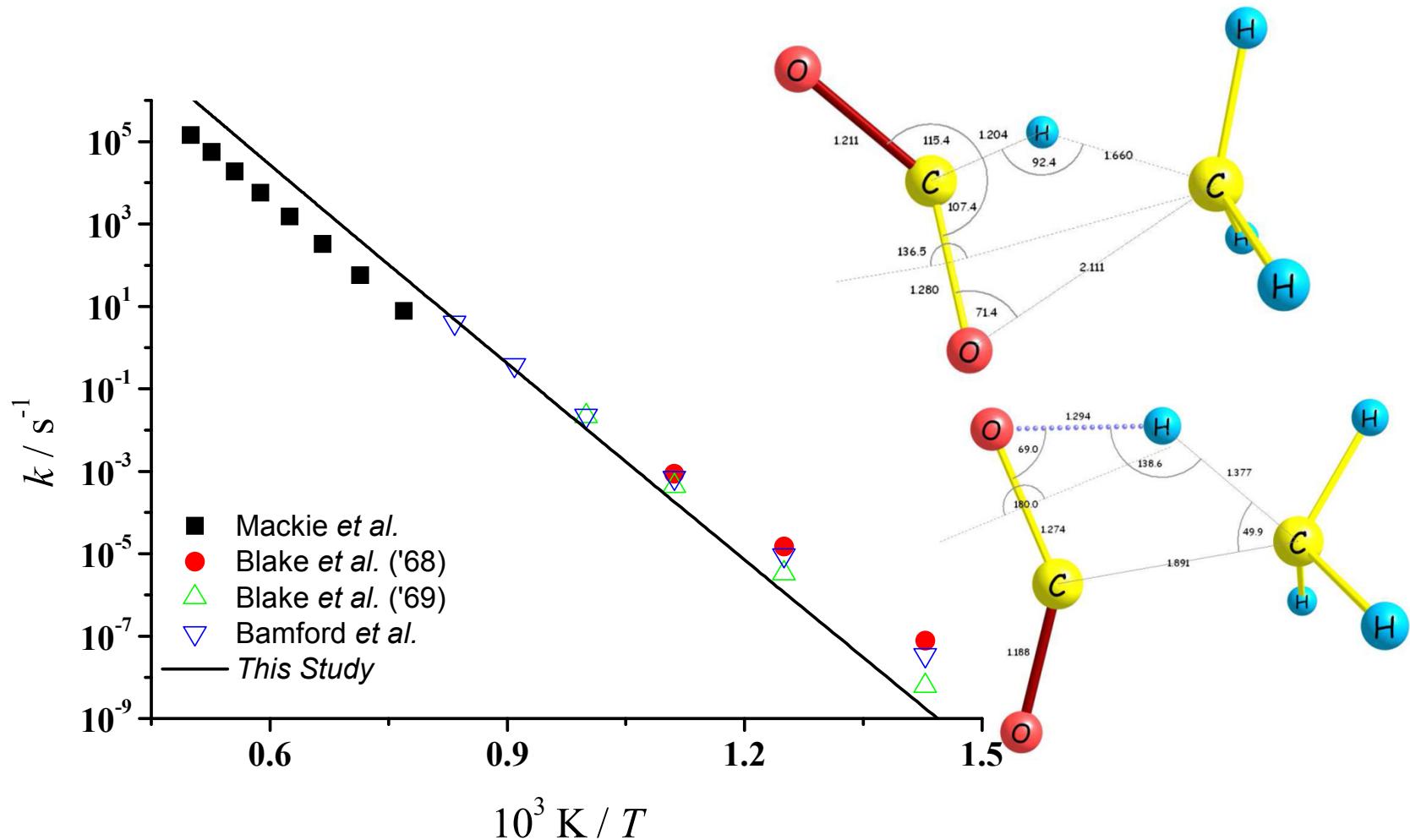


Time-dependent solution of master equation



Kinetics: $\text{CH}_3\text{COOH} \Rightarrow \text{CH}_4 + \text{CO}_2$

$\text{TS} \sim \text{TS}$ for $\text{HCOOCH}_3 \Rightarrow \text{CH}_4 + \text{CO}_2$

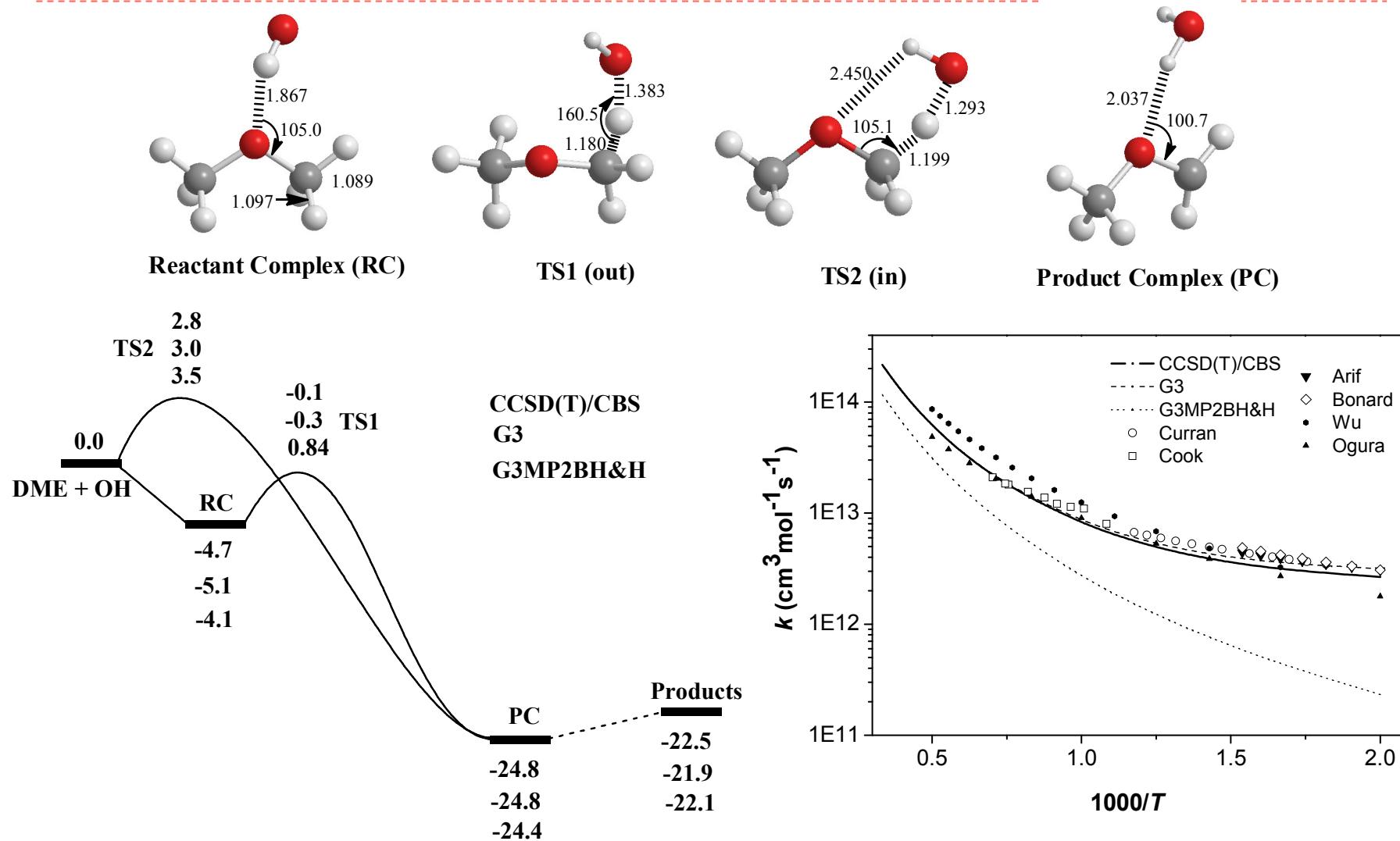


H-abstraction by $\cdot\text{OH}$, HO_2^\bullet , et cetera

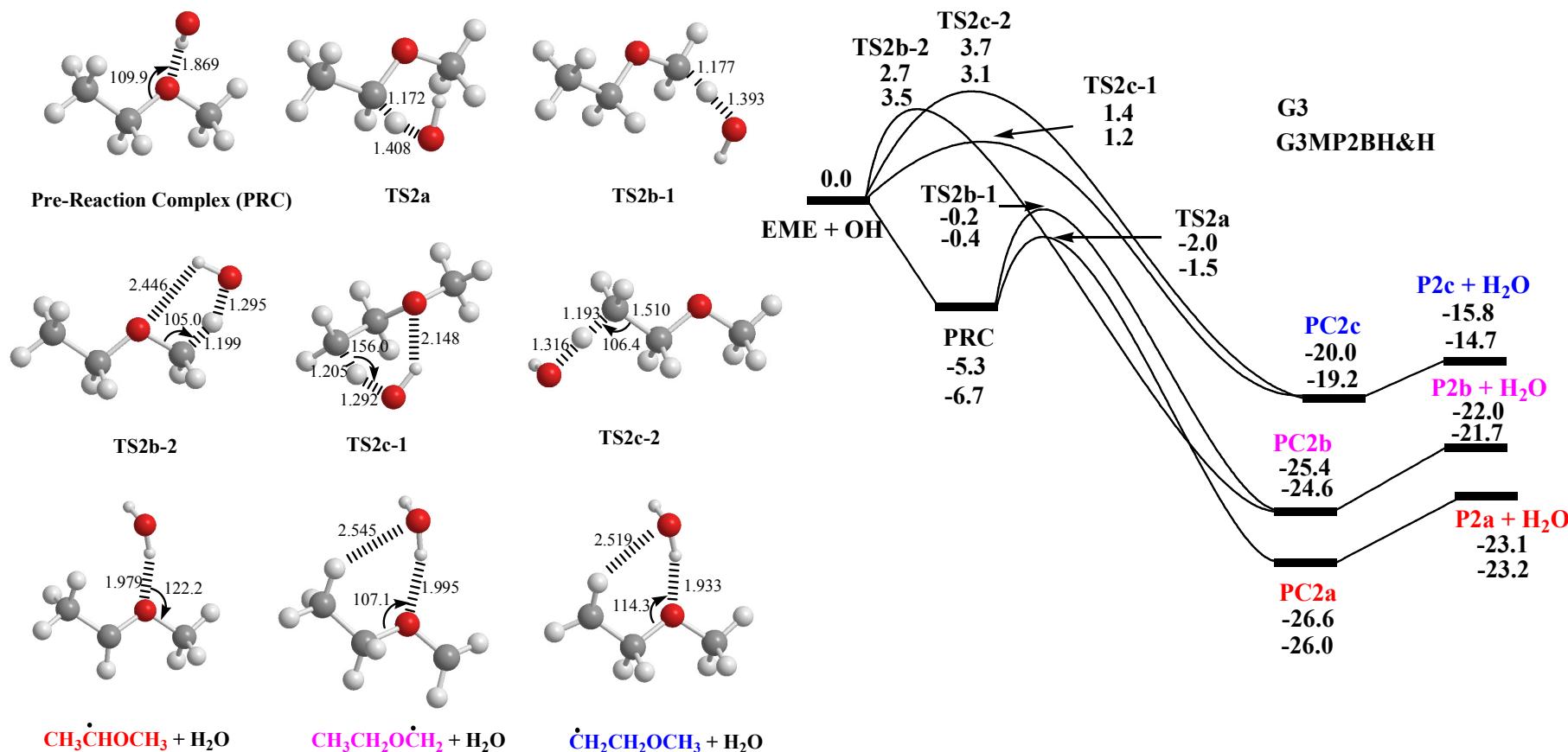
- ▶ From hydrocarbons
 - ▶ Primary
 - ▶ Secondary
 - ▶ Tertiary
- ▶ How does O-atom influence abstraction?
 - ▶ Alcohols
 - ▶ n-Butanol [HO_2^\bullet J. Comp. Chem. in press]
 - ▶ Ethers: DME, EME, iPME
 - ▶ Energetics: Coupled cluster in the basis set limit
 - ▶ Kinetics: RRKM, VRC-TST, Eckart tunneling
 - ▶ Furans

$\cdot\text{OH} + \text{Dimethyl ether}$ [Chong-Wen Zhou]

$$k / \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 2.74 T^{3.94} \exp(1,534/T)$$

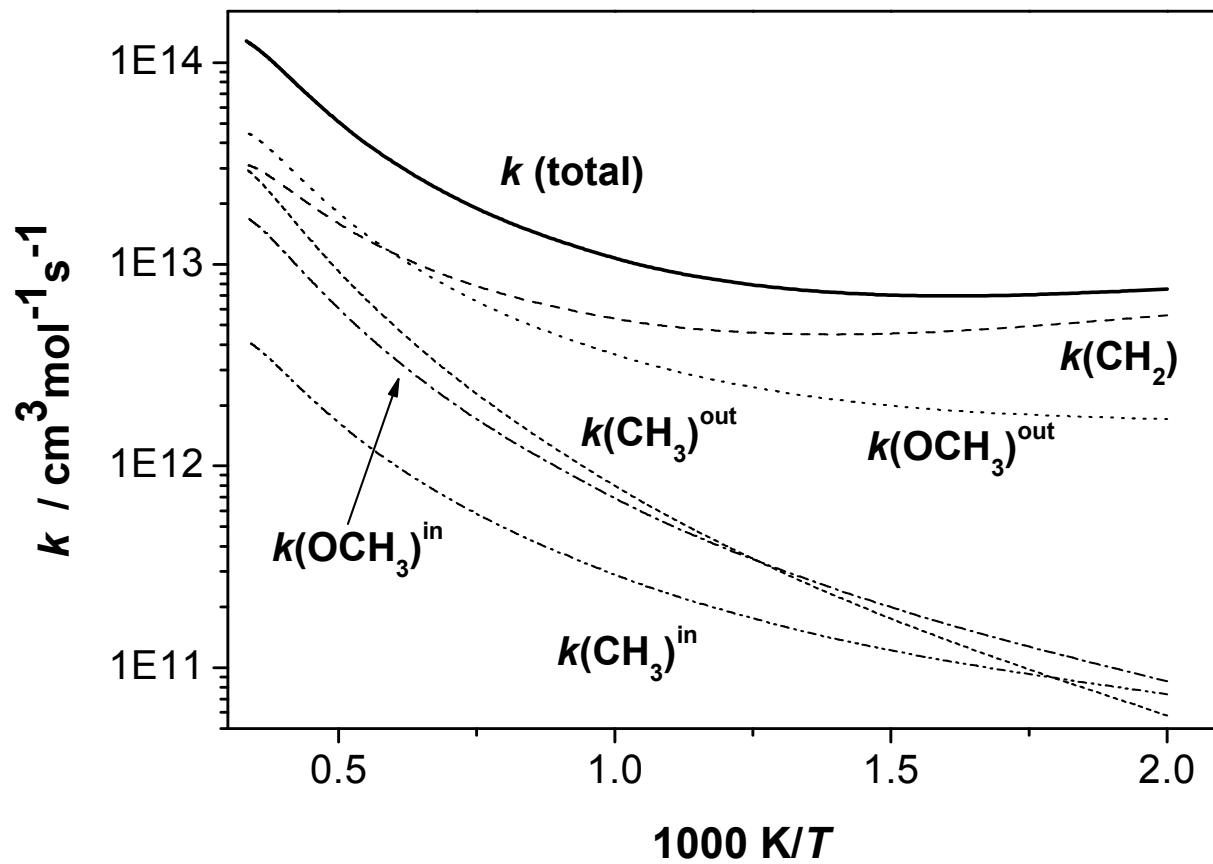


$\cdot\text{OH} + \text{CH}_3\text{CH}_2\text{OCH}_3$



$$k(\text{total}) / \text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 20.9 T^{3.61} \exp(2,060/T)$$

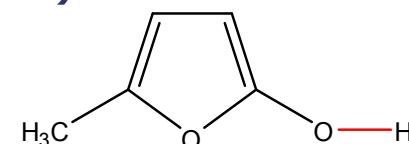
Branching $\text{CH}_3\text{CH}_2\text{OCH}_3$ versus $\text{CH}_3\text{CH}_2\text{OCH}_3$ $\text{CH}_2/\text{OCH}_3 = 3.4 - 0.43 \ln T + 1,120/T$



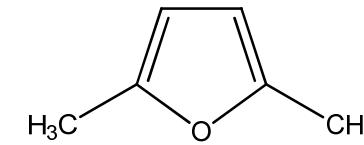
Alkyl furans

Quite different to toluene, xylenes, ..

- ▶ Very strong ring-carbon hydrogen bonds
 - ▶ **505** vs 472 (benzene)
- ▶ Very strong ring-carbon methyl bonds
 - ▶ **480** vs 427 (toluene)
- ▶ Weak Ring-CH₂—H bonds
 - ▶ **360** vs 376 (toluene)
- ▶ Extremely weak ring-carbon-**O—H** bond
 - ▶ **268** vs 366 (HO—H) or 206 (·OO—H)
- ▶ J Phys Chem A 2009, 113, 5128

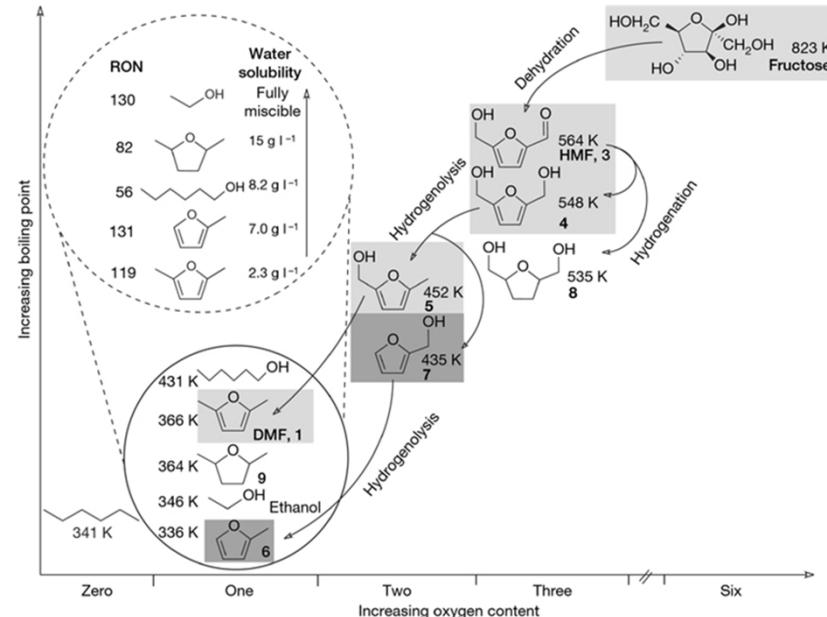


Why 2,5-dimethylfuran?



Next-generation bio-fuel

- ▶ Production
 - ▶ From biomass [Nature 2007]
- ▶ Properties
 - ▶ RON 119, water insoluble
- ▶ Chemistry unknown
 - ▶ ST pyrolysis (Lifshitz *et al.*)
 - ▶ Rich flames by VUV-MBMS (Wu *et al.* C&F 2009, 156, 1365)
 - Methyl radical to 2-methylnaphthalene(!)
 - ▶ ST ignition delays (Black *et al.* 32nd Combustion Symposium)
 - ▶ JSR oxidation (Dagaut & Togbé; CNRS Orléans)



•OH abstraction barriers

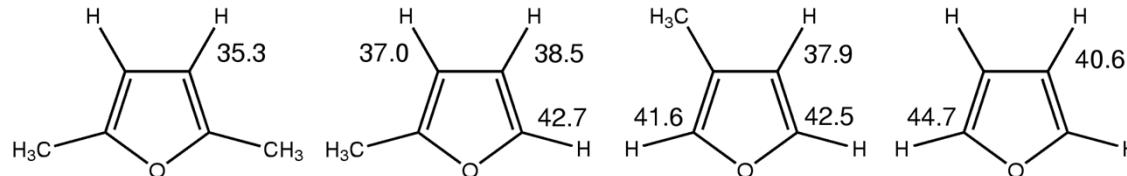


Figure 13: Barriers, G3(0K), to H-atom abstraction by $\cdot\text{OH}$ radical

Table 3: Barriers to H-abstraction by hydroxyl radical

Radical Product	$\Delta E^\ddagger(0\text{K})^a / \text{kJ mol}^{-1}$			Lit. ref.
	CBS-QB3	CBS-APNO	G3	
<i>Abstraction from furan ring</i>				
DMF3R	21.5	22.9	35.3	—
2MF3R	23.2	—	37.0	120.2 ^c
2MF4R	24.3	—	38.5	36.4 ^c
2MF5R	28.2	—	42.7	113.5 ^c
3MF2R	27.9	—	41.6	45.2 ^b
3MF4R	23.9	25.4	37.9	39.9 ^b
3MF5R	27.7	—	42.5	48.9 ^b
F2R	29.7	—	44.7	49.6 ^d
F3R	—	—	40.6	45.8 ^d
<i>Abstraction from methyl group</i>				
DMF2R	—	—	15.5	—
2MF2R	—	—	16.5	13.1 ^c
3MF3R	—	—	7.4	12.1 ^b

^aIncludes ZPE ^bAverage of G3MP2 & G3MP2B3¹⁶ ^cG3MP2B3(298.15K)¹⁷ ^dG3MP2³⁴

Pre-reaction complex

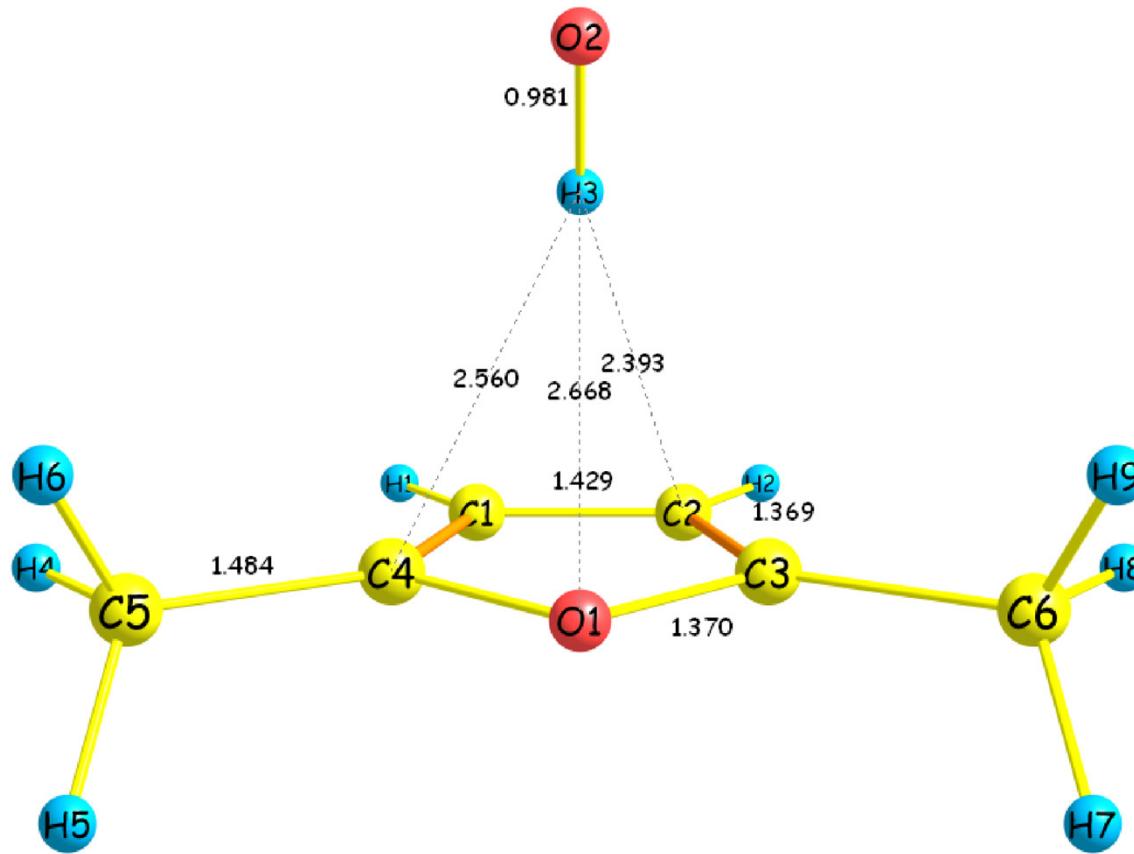


Figure 16: Pre-reaction complex formed by 25DMF + $\cdot\text{OH}$; G3 geometry $\angle\text{OHO} = 117.6^\circ$

H-abstraction by $\cdot\text{H}$, $\text{HO}_2\cdot$, O, O_2 , ...

Zero-point corrected electronic energies

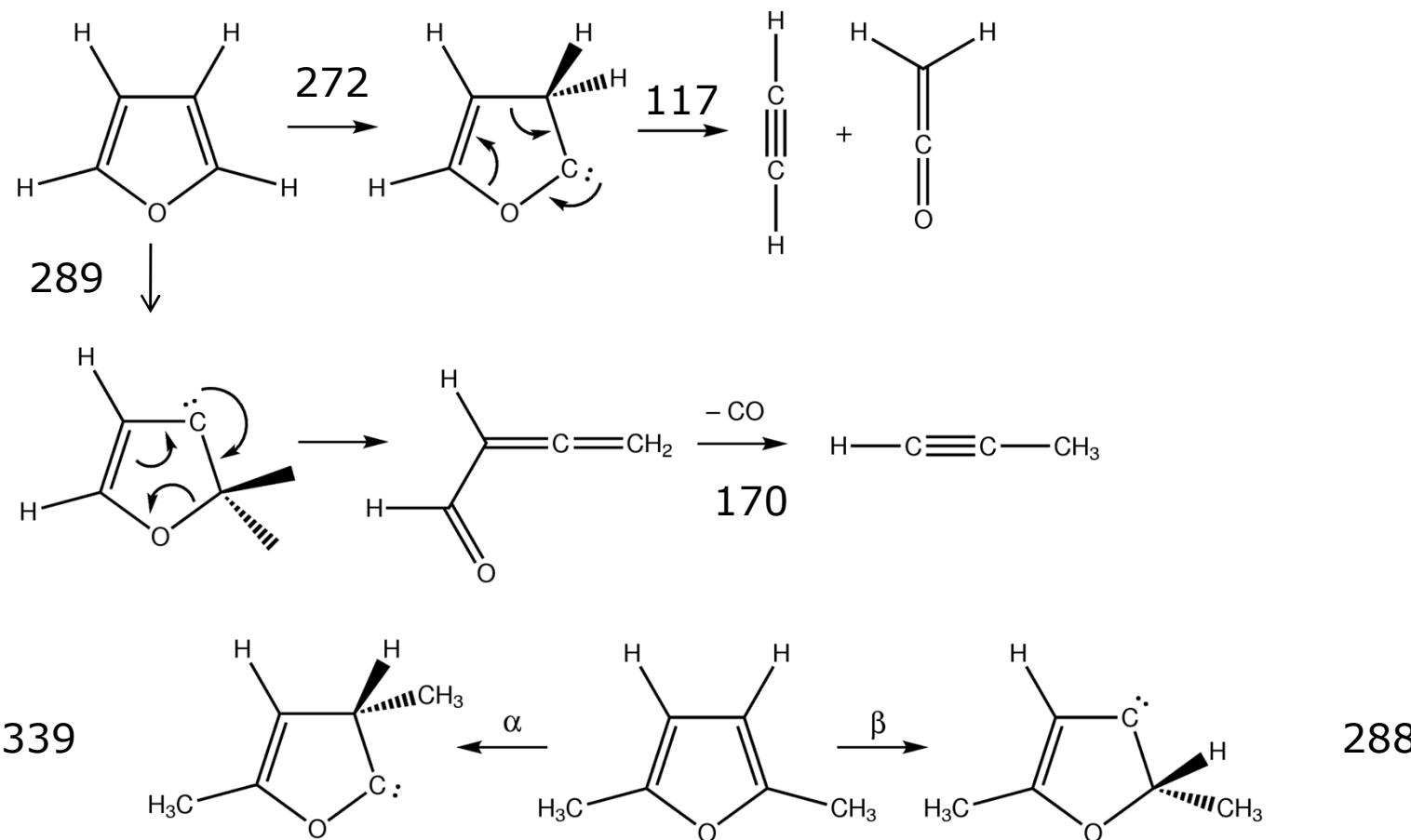
► From	-CH ₃	ring-H
► OH	16	35
► H	29	88
► HO ₂	57	130
► O	12	65
► O ₂	148	260

TS < ΔE (rxn)

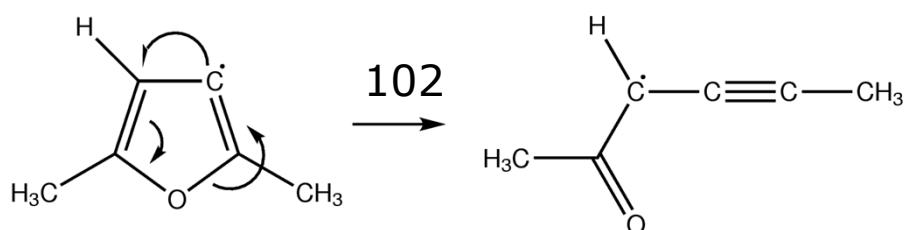
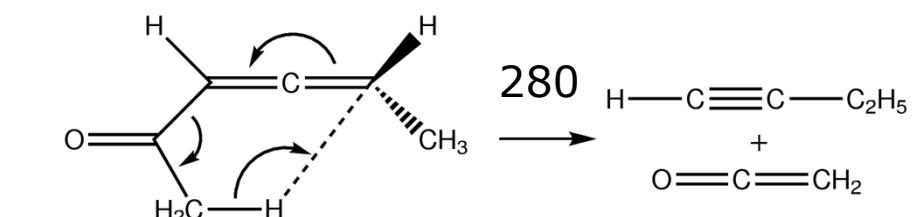
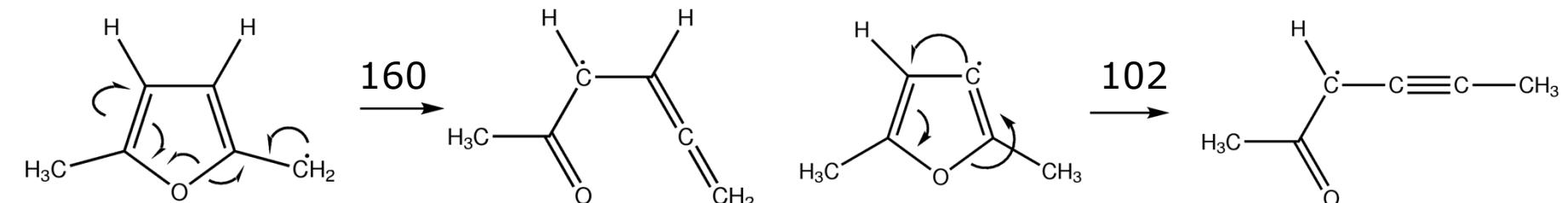
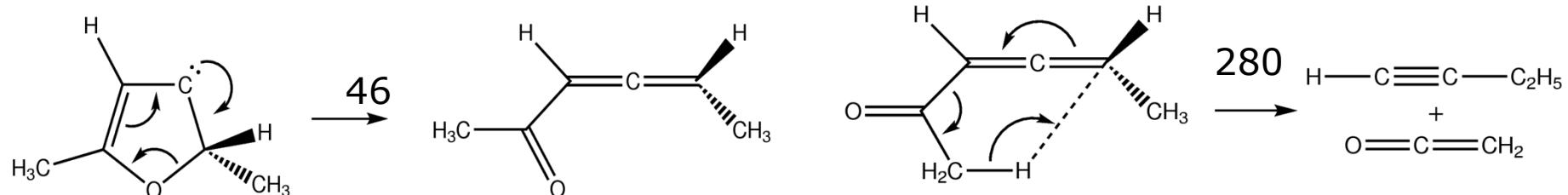
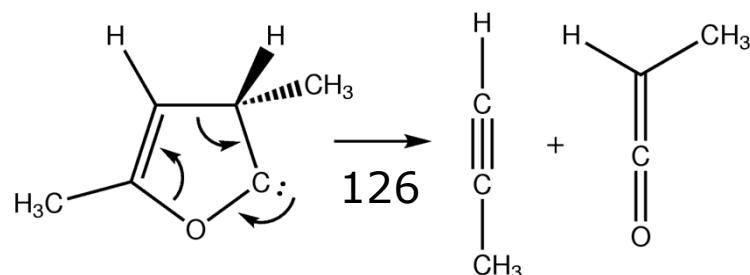
Initial decompositions

Vasiliou *et al.* J Phys Chem A 2009, 113, 8540

Flow reactor 1,600K; acetylene, ketene, CO & propyne



More



Not detected by Wu

Major projects (from September 2009)

- ▶ National

- ▶ Science Foundation Ireland
- ▶ Higher Education Authority
- ▶ IRCSET

- ▶ International

- ▶ FP7 EU Project: Gas Turbine Network

- ▶ Industrial

- ▶ North American gas turbine manufacturer
- ▶ French automotive manufacturer
- ▶ Middle Eastern oil company



Henry Curran



John Simmie

