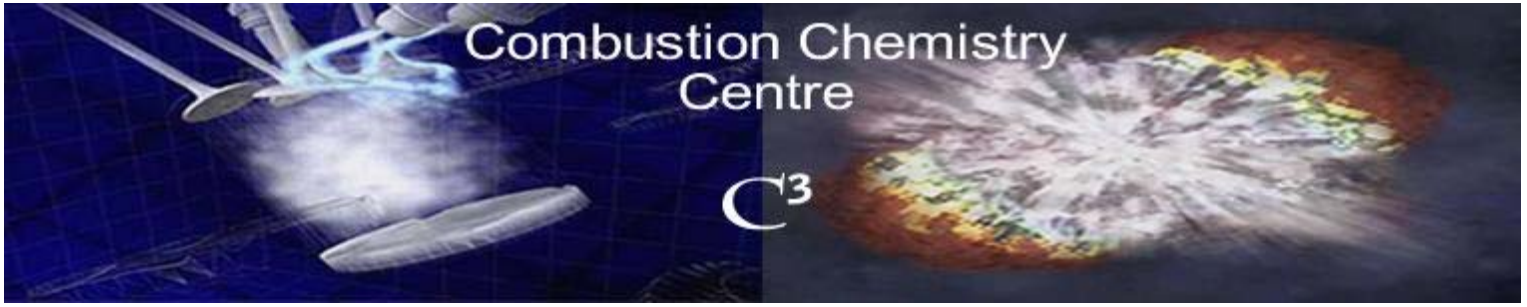

Uncertainties in Important Reactions for Propene Oxidation

S.M. Burke, H.J. Curran

Combustion Chemistry Centre,

NUI Galway, Ireland

4th IWMRRF San Francisco June 19—21, 2013.

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Why propene?

- Formed in high concentration from larger HC and oxygenated HC molecules
- On oxidation generates high concentrations of allyl radicals
- Involved in the formation of aromatic and poly-aromatic HC species

Introduction

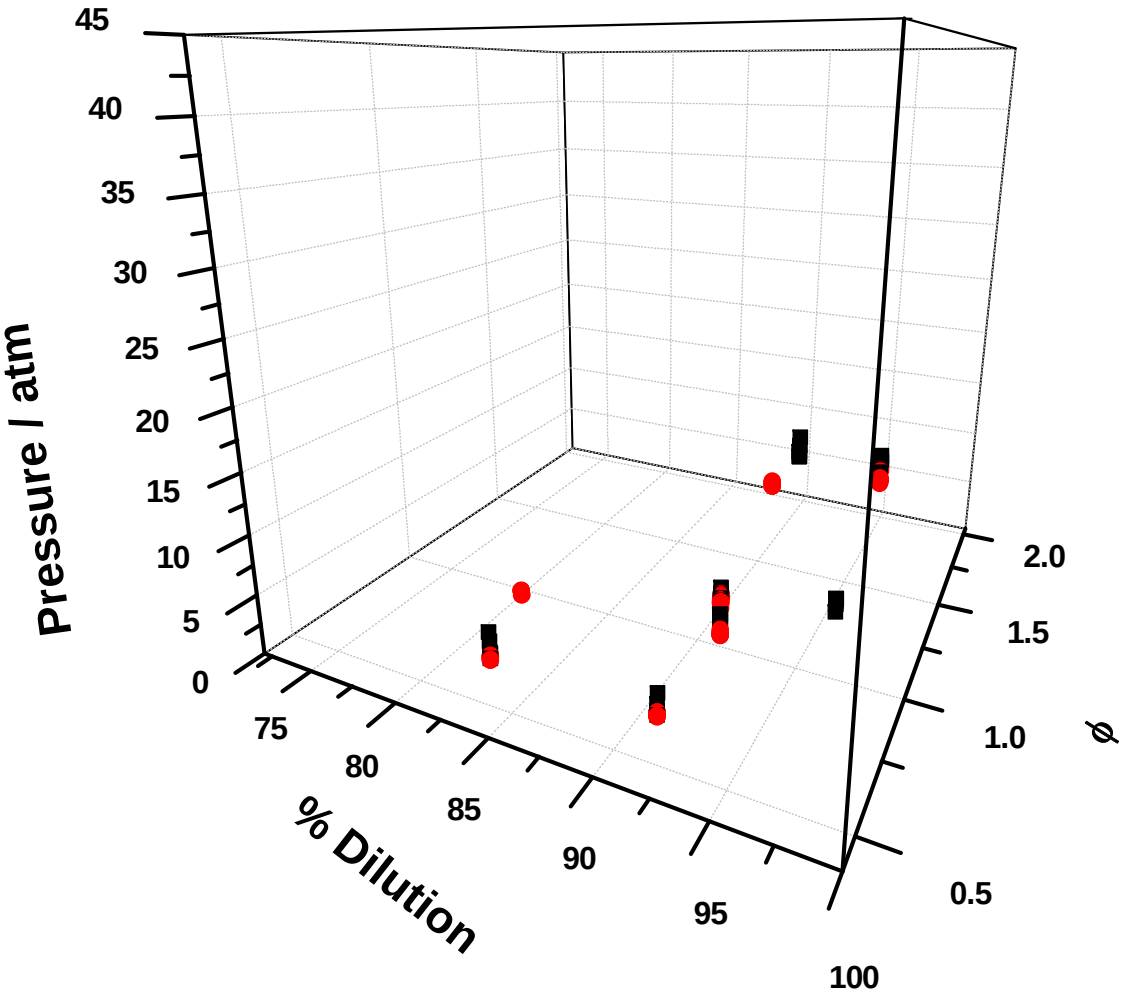
- Detailed chemical kinetic mechanism for propene
  - 324 species and 1803 reactions
  - Including new C_2 sub-mechanism (Aramco Mech 1.3) validated for:
    - CH_4, C_2H_6, C_2H_4, C_2H_2, CH_2O, CH_3OH, CH_3CHO, C_2H_5OH
- Measured/ab-initio rate constants if possible
- Validated against available literature data and new experimental data

Range of validation

Current data available in the literature	Shock Tube	Jet-Stirred Reactor	Flow Reactor	Flame Speed
	✓	✓	✓	✓
Temperature / K	1270–1840	900–1400	1180–1210	293–425
Pressure (atm)	0.95–7.02	1–8	1.0	1–5

- New ignition delay time and speciation data
  - Lower temperatures and higher pressures than previously published

Current ignition delay data



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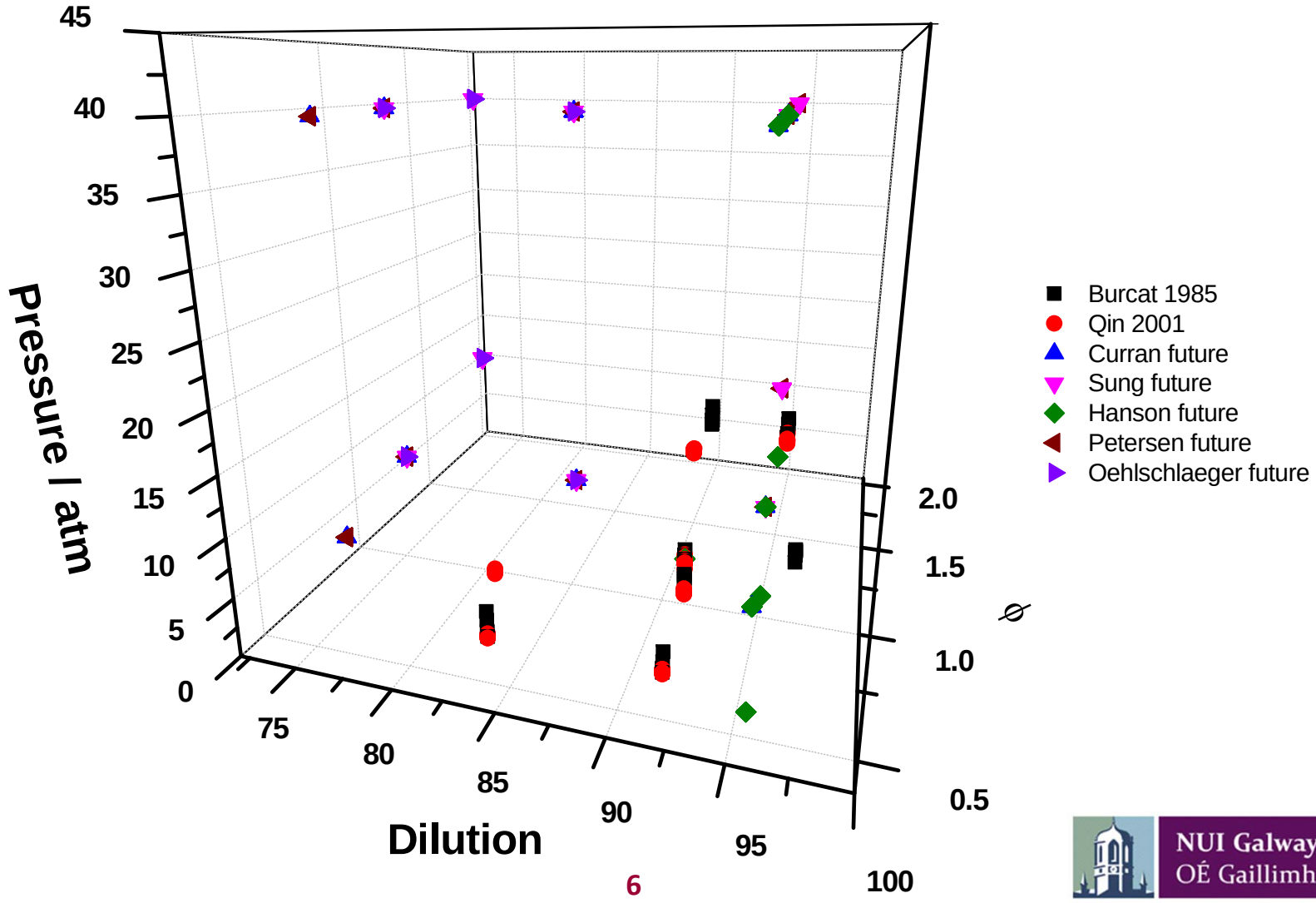
New data ignition delay time

- New shock tube and rapid compression machine ignition delay time data higher pressures (10–40 atm) and lower temperatures (700–1300 K)



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Previous jet-stirred reactor data

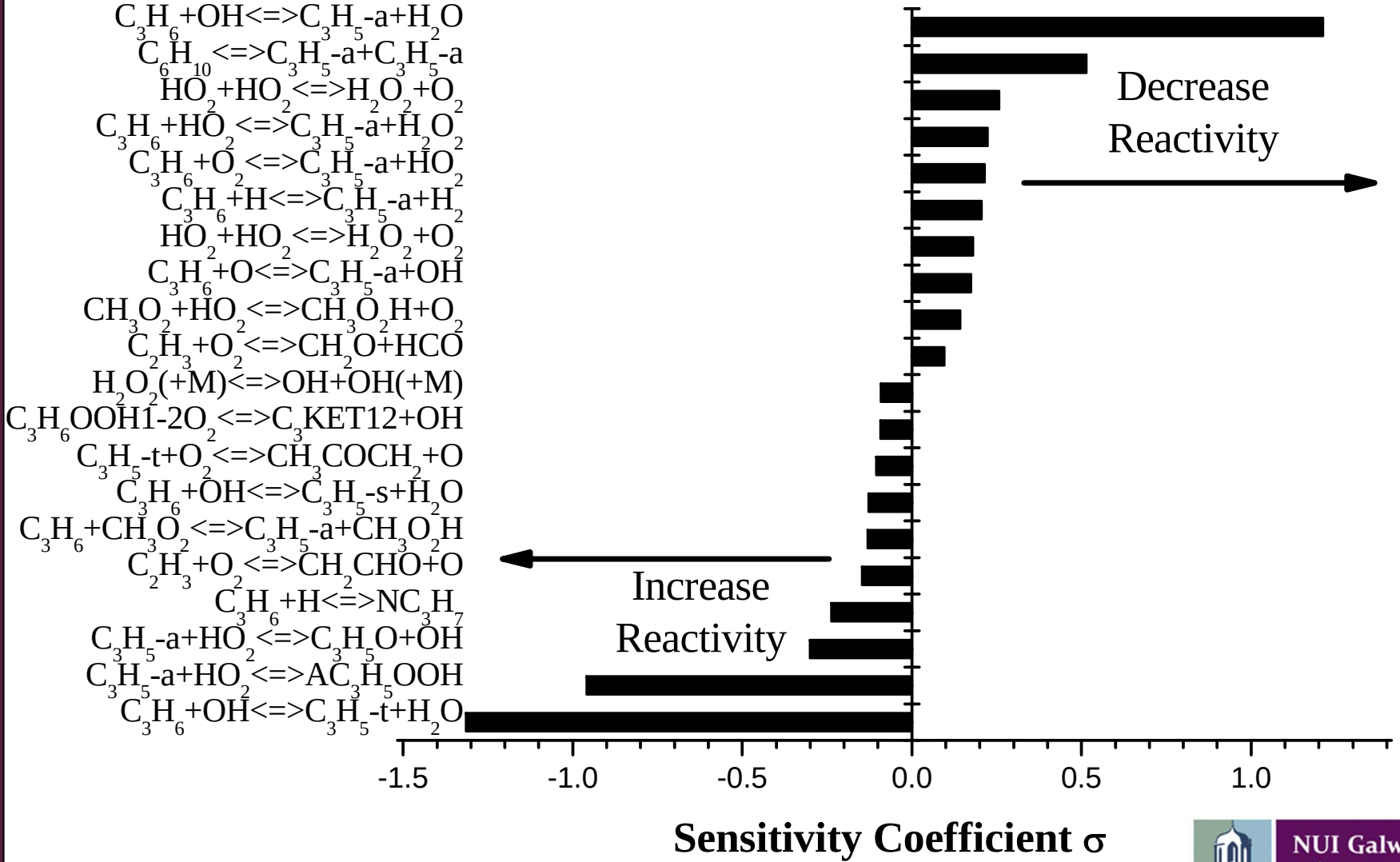
- Previous JSR studies Dagaut and co-workers
  - Le Cong 2010 C_3H_6 and $C_3H_6/CO_2/H_2O$
    - Temperature = 950–1450 K
    - ϕ = 0.5–2.0
    - τ = 0.12 s
    - Pressure: 1 atm
    - Species profiles for: O_2, CO, CO_2, H_2O, CH_4, C_2H_4, C_2H_2, C_3H_6
  - Dagaut 1988 and 1992
    - Temperature: 900 –1200 K
    - Pressure = 1–8 atm
    - τ = 0.05–1.80 s
    - Species profiles for: C_3H_6, H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_2H_2, CH_3CHO,

New jet-stirred reactor data

- New JSR data
  - Frédérique Battin-Leclerc Nancy, France
    - Temperature = 800–1100 K
    - ϕ = 0.64–2.19
    - τ = 2 s
    - Pressure: 1 atm
    - Species profiles for: O_2, CO, CO_2, CH_4, C_2H_4, C_2H_2, C_2H_6, C_3H_6, C_3H_8, C_3H_4-a, C_3H_4-p, CH_3CHO, CH_3OH, C_4H_8-1, C_4H_6, C_3H_6O1-2, C_2H_3CHO, C_2H_5CHO , CH_3COCH_3, C_6H_6, C_6H_{10}

Sensitivity Analysis—C_3H_6

4.46% fuel in air, ϕ = 1.0, 40 atm, 800 K



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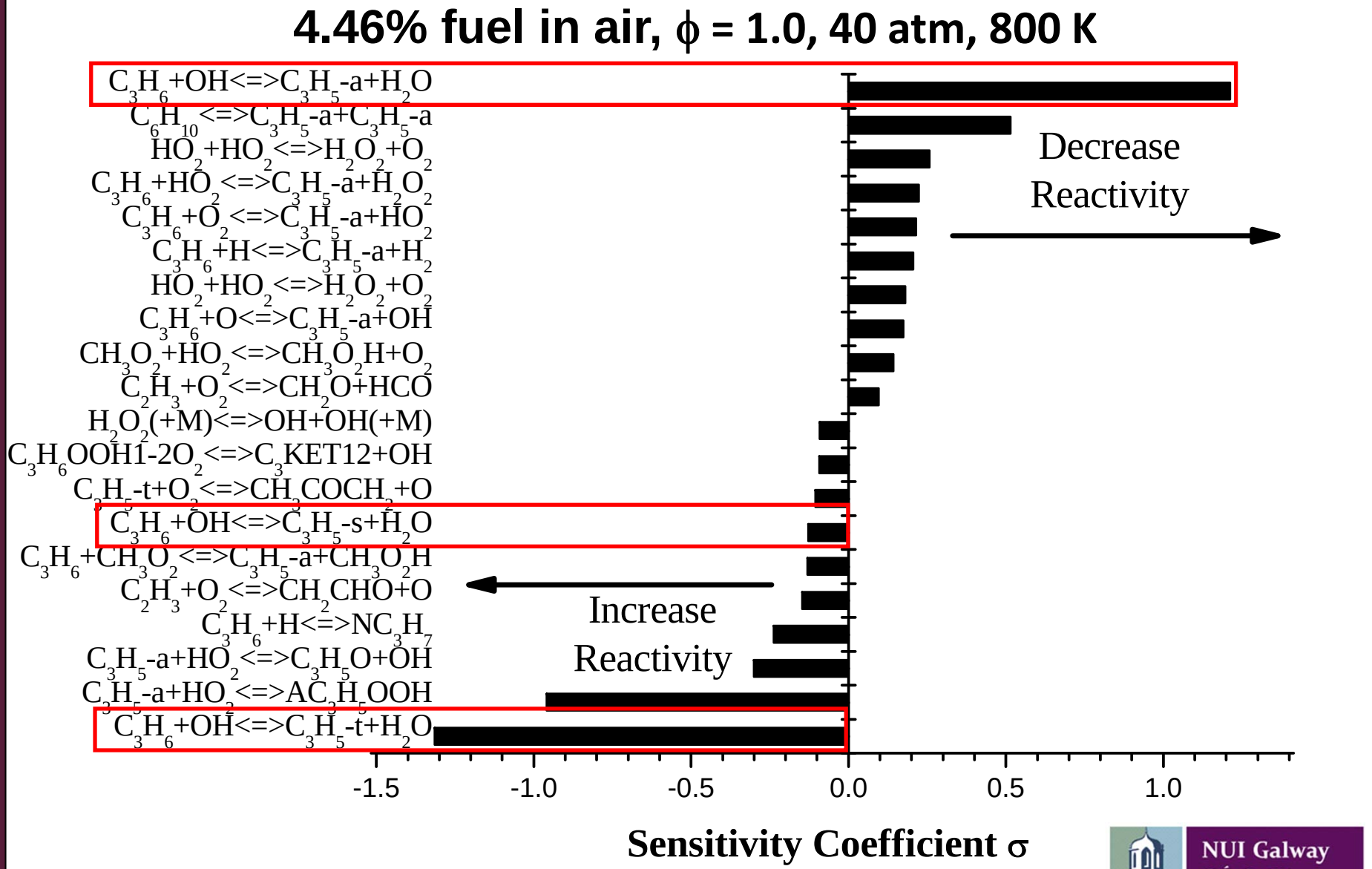
Sensitivity Analysis—C_3H_6



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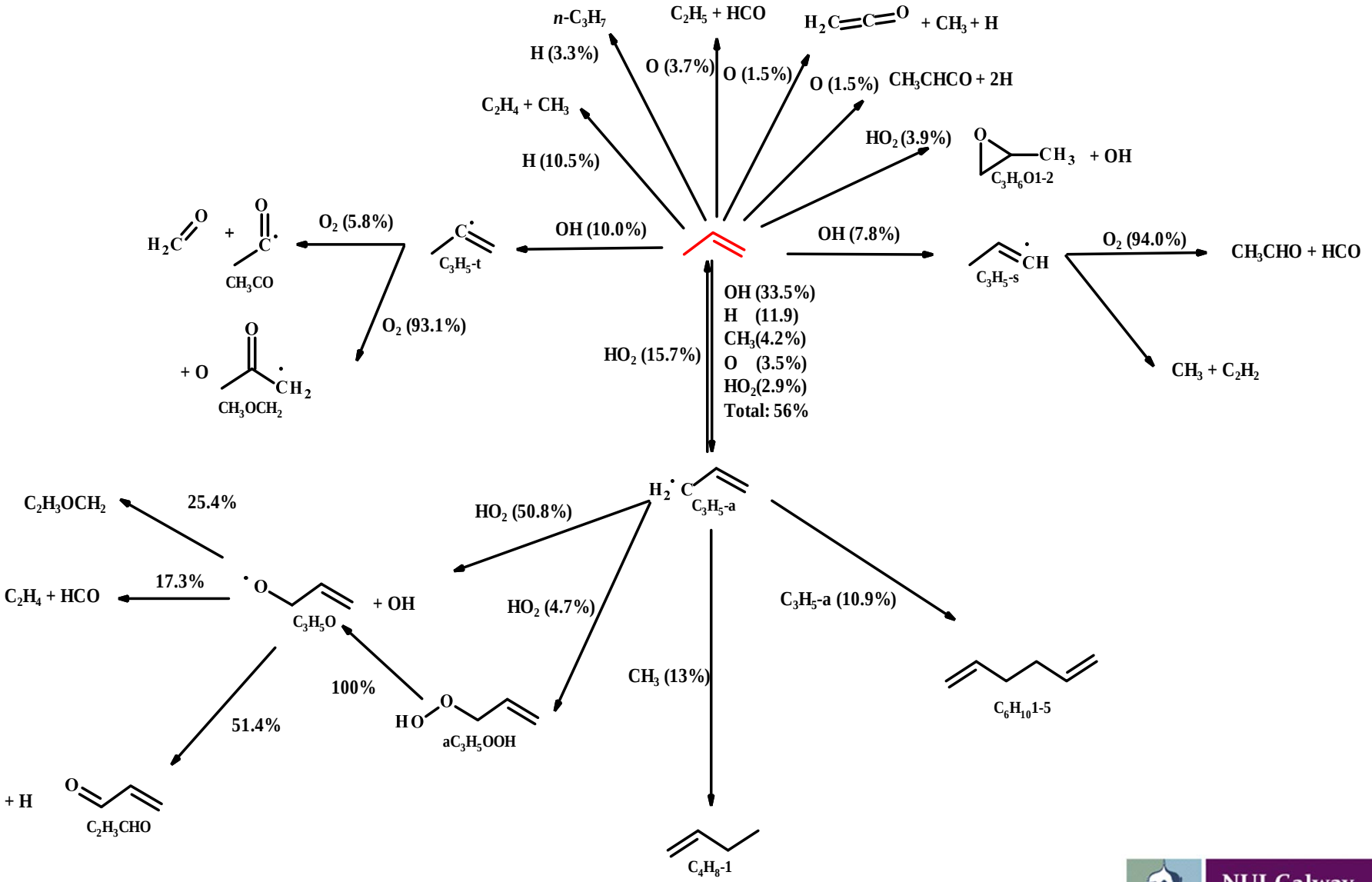
Rate of production analysis
JSR 900 K, τ = 2 s, 50% Fuel consumption



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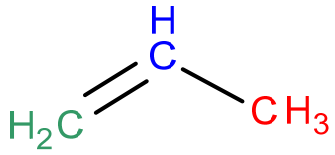
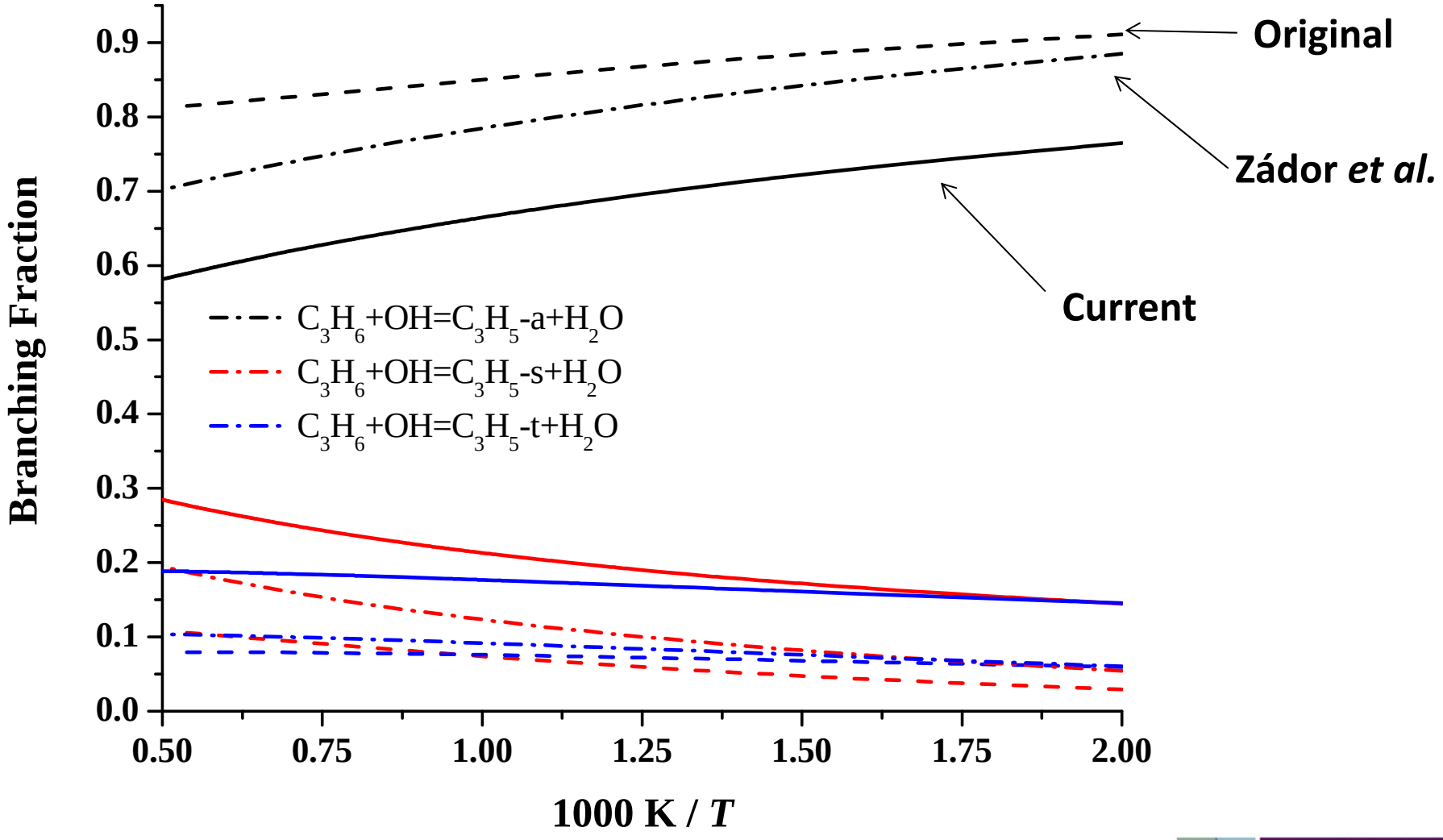
Branching ratio sensitivity



- Allyl (C_3H_5-a)
  - Resonantly stabilised
  - Can undergo recombination (C_6H_{10} / C_4H_8-1)
  - Chain **Terminating**
- Propen-2-yl (C_3H_5-t)
  - Reacts with O_2
  - Chain **Branching**
- Propen-1-yl (C_3H_5-s)
  - Reacts with O_2
  - Chain **Propagating**

Branching ratio C_3H_6 + ȮH



Zádor *et al. Phys. Chem. Chem. Phys.*, **2009**, *11*, 11040-11053

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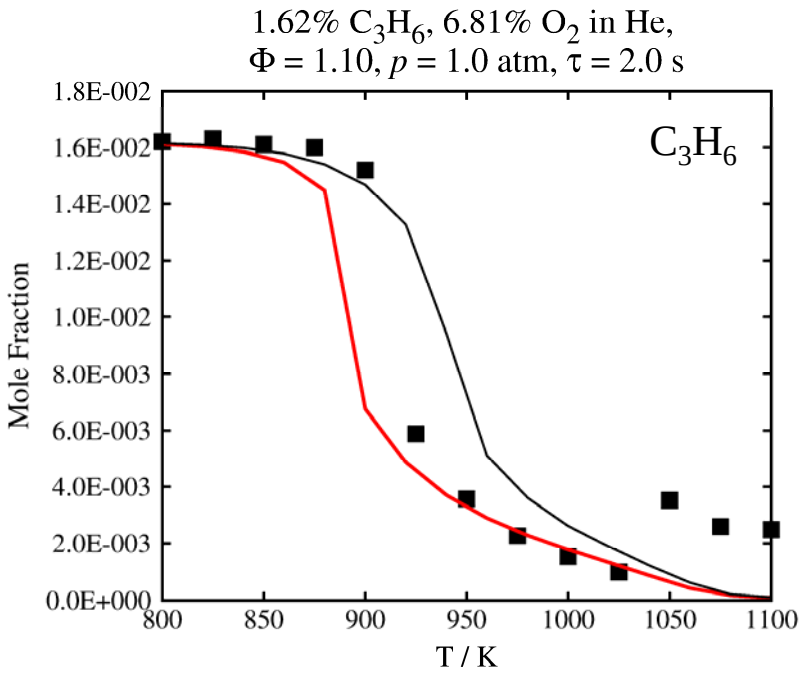
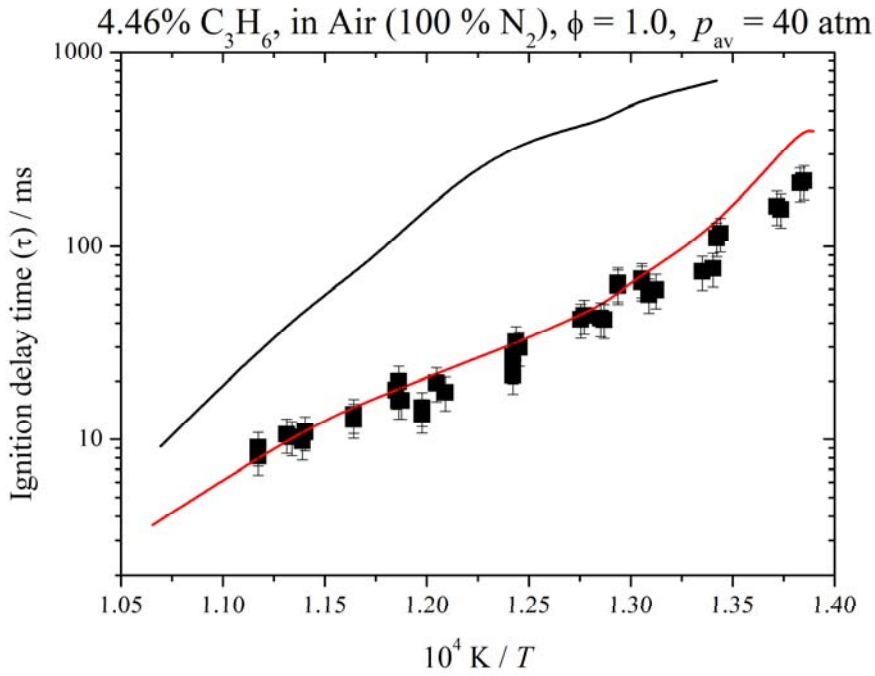
Effect of C_3H_6 + ȮH branching ratio

JSR 1 atm



Nancy JSR (new data)

Ignition delay time 40 atm



NUI Galway RCM (new data)

Current

Zádor et al.

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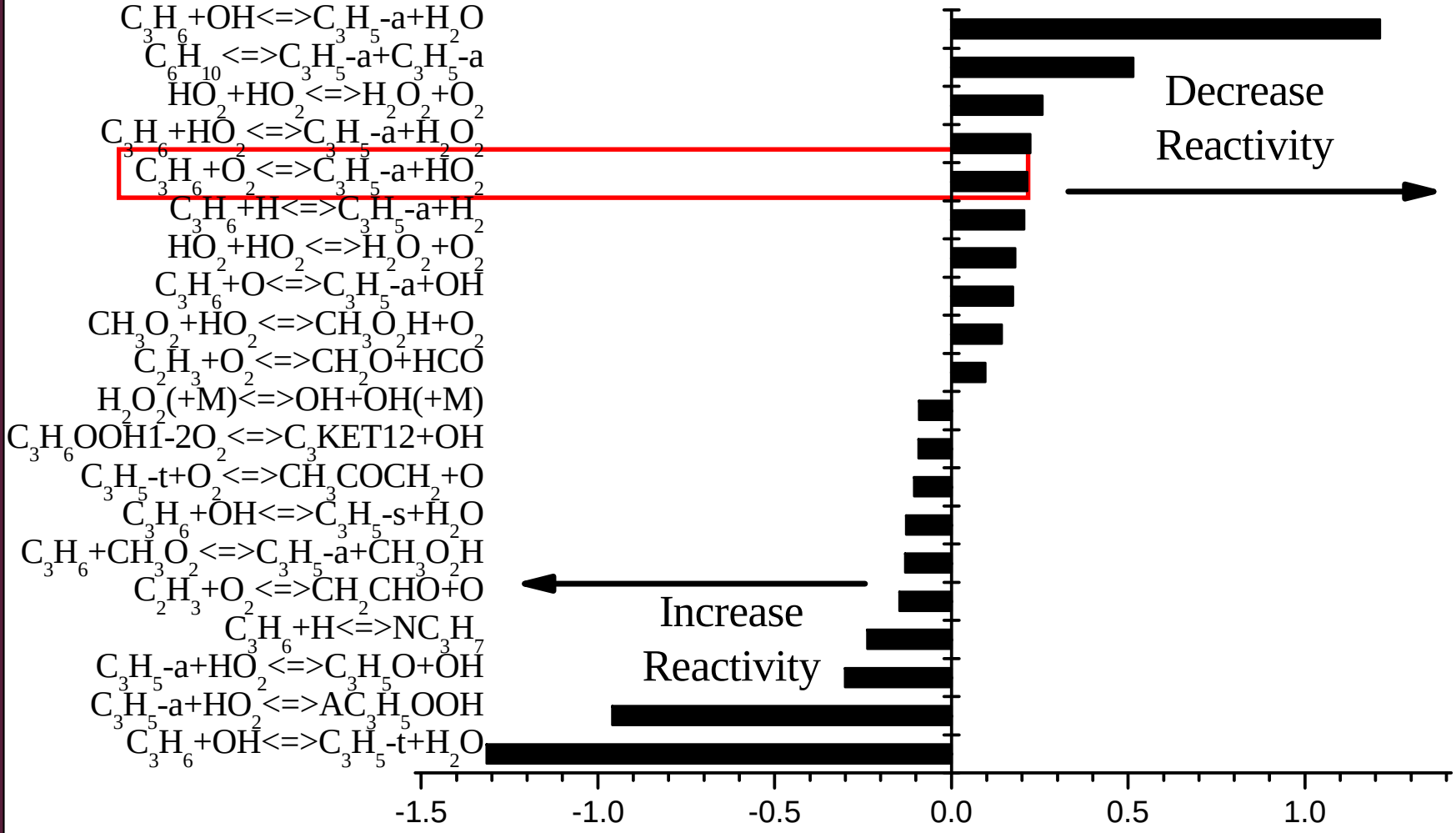
Sensitivity Analysis—C_3H_6

4.46% fuel in air, ϕ = 1.0, 40 atm, 800 K



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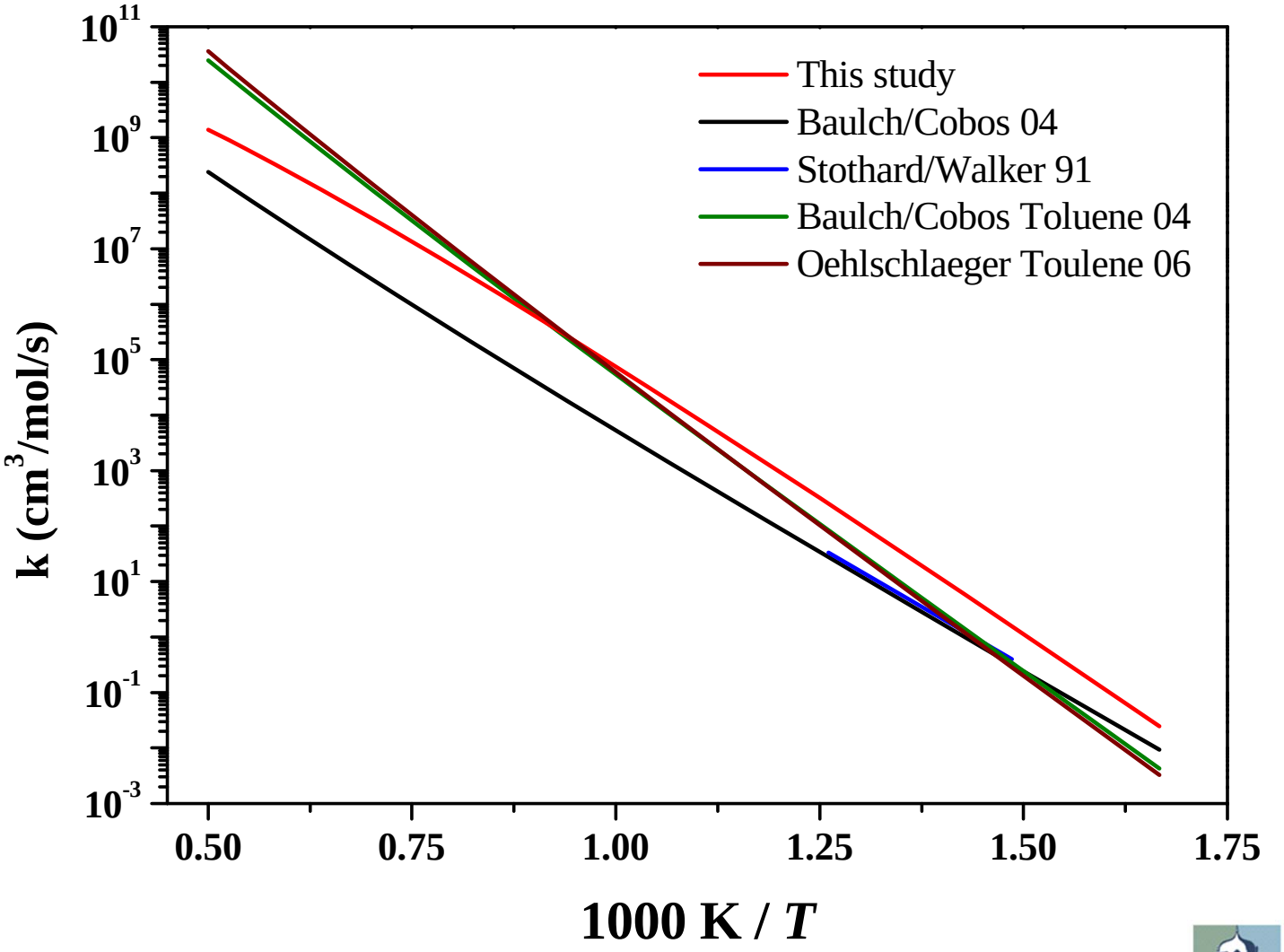
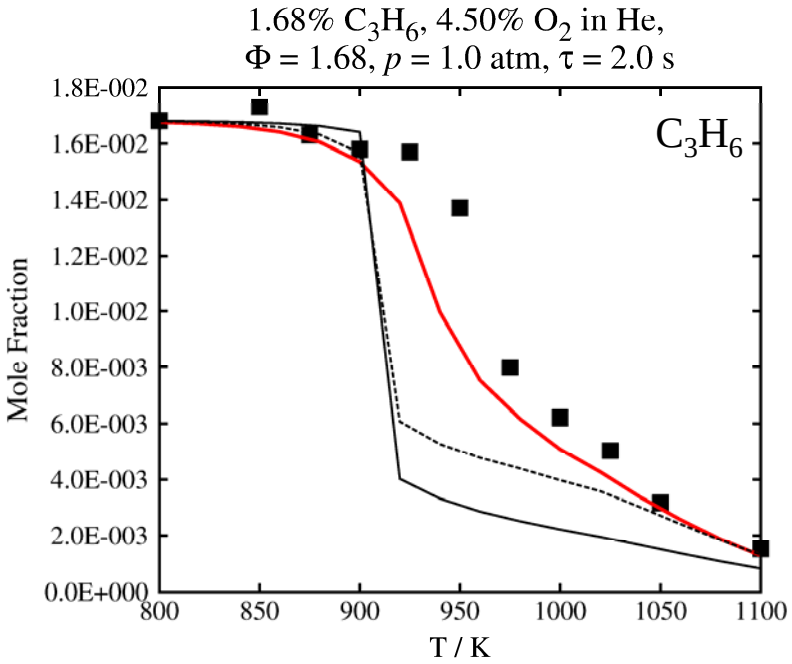
$C_3H_6 + O_2 = \dot{C}_3H_5\text{-a} + H\dot{O}_2$



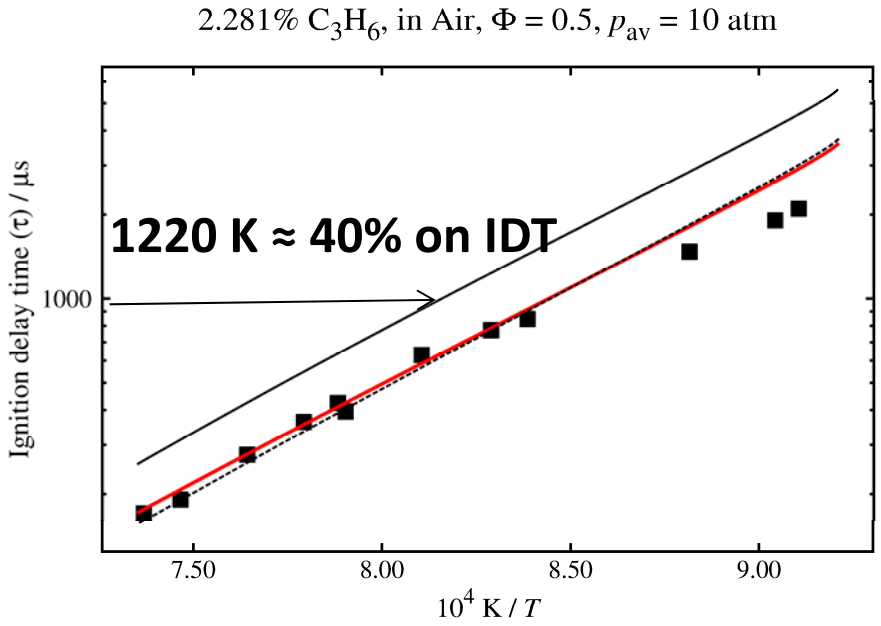
NUI Galway
OÉ Gaillimh

Effect of $C_3H_6 + O_2 = \dot{C}_3H_5\text{-a} + H\dot{O}_2$

JSR (new Nancy)



Shock tube (new NUIG)



Red: Current

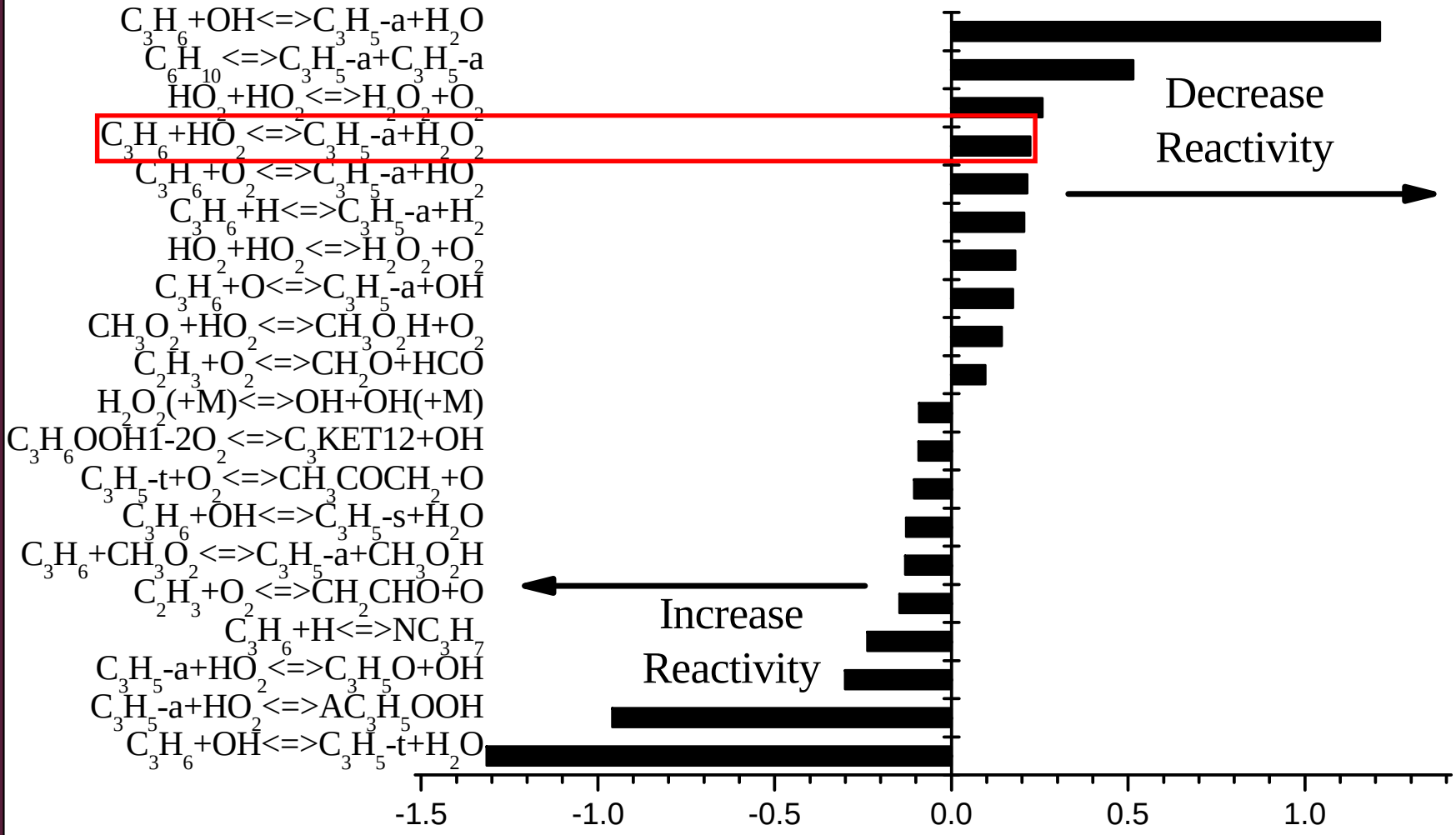
Solid Black: Baulch/Cobos C_3H_6

Dashed Black: Baulch/Cobos Toluene

NUI Galway
OÉ Gaillimh

Sensitivity Analysis—C_3H_6

4.46% fuel in air, ϕ = 1.0, 40 atm, 800 K



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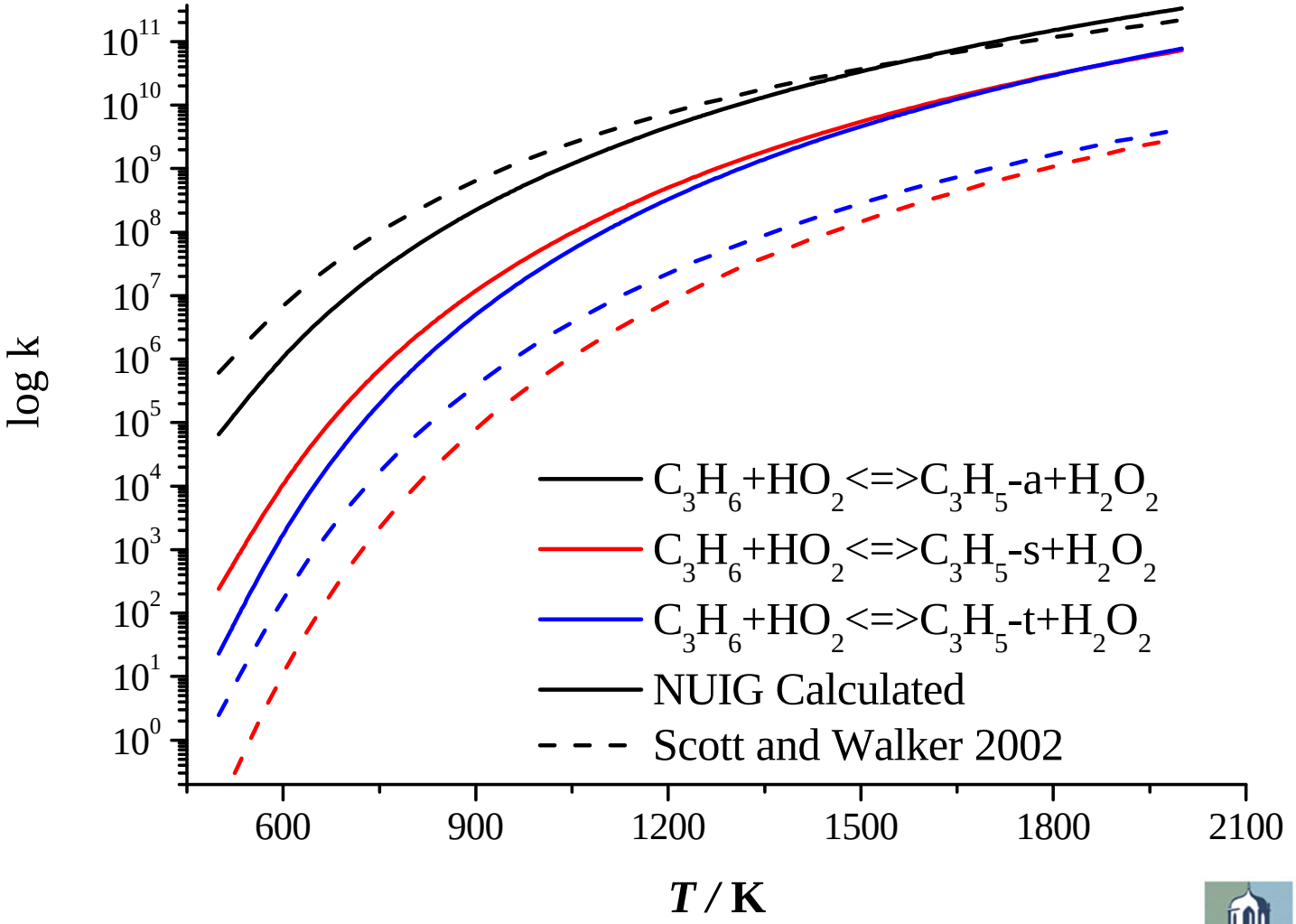
$C_3H_6 + H\dot{O}_2$

- Theoretically calculated at NUI Galway



Scott and Walker C&F 129(4) 365--377 2002

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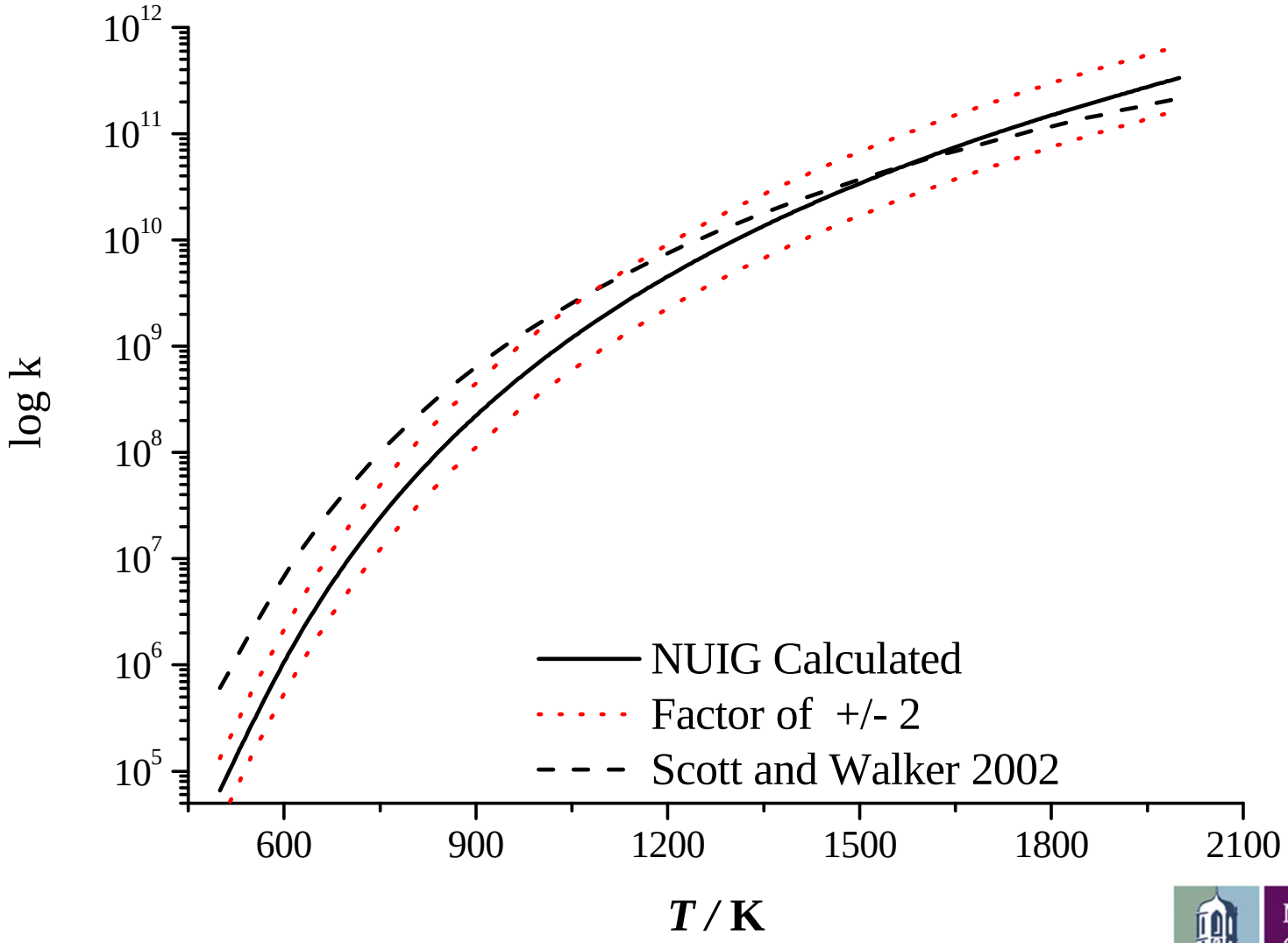
$C_3H_6 + H\dot{O}_2 \Leftrightarrow \dot{C}_3H_5\text{-a} + H_2O_2$



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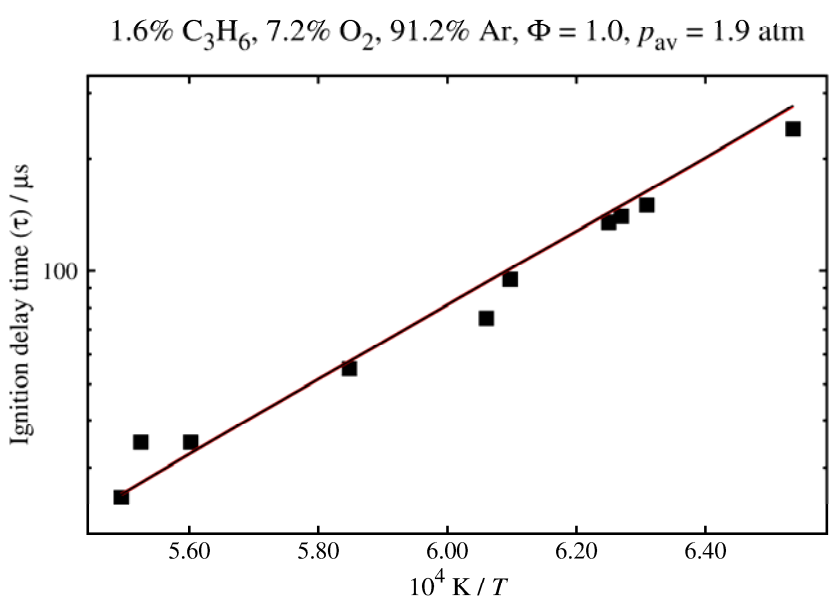
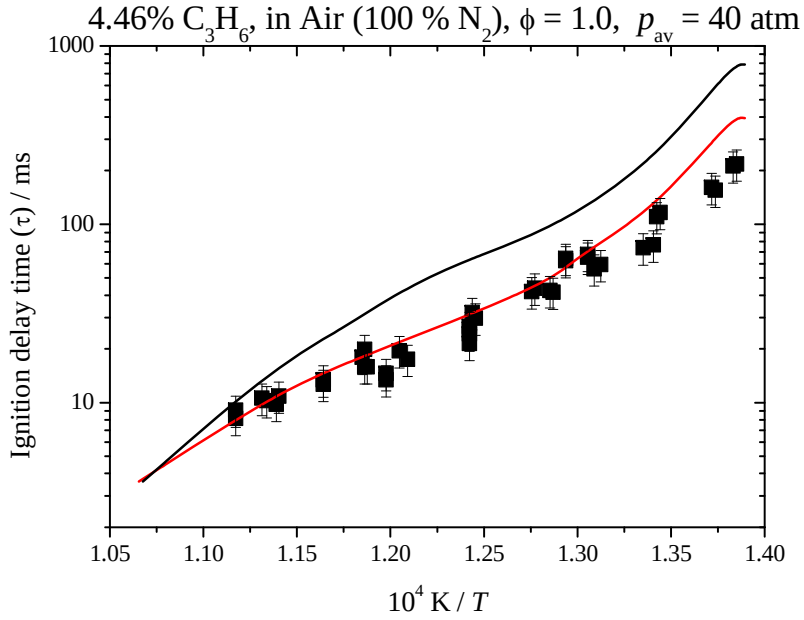
Effect of $C_3H_6 + H\dot{O}_2$

- Large effect at high pressure in the RCM
- Little effect at lower pressures in the shock tube





Qin et al. 2001

NUI Galway RCM (new data)

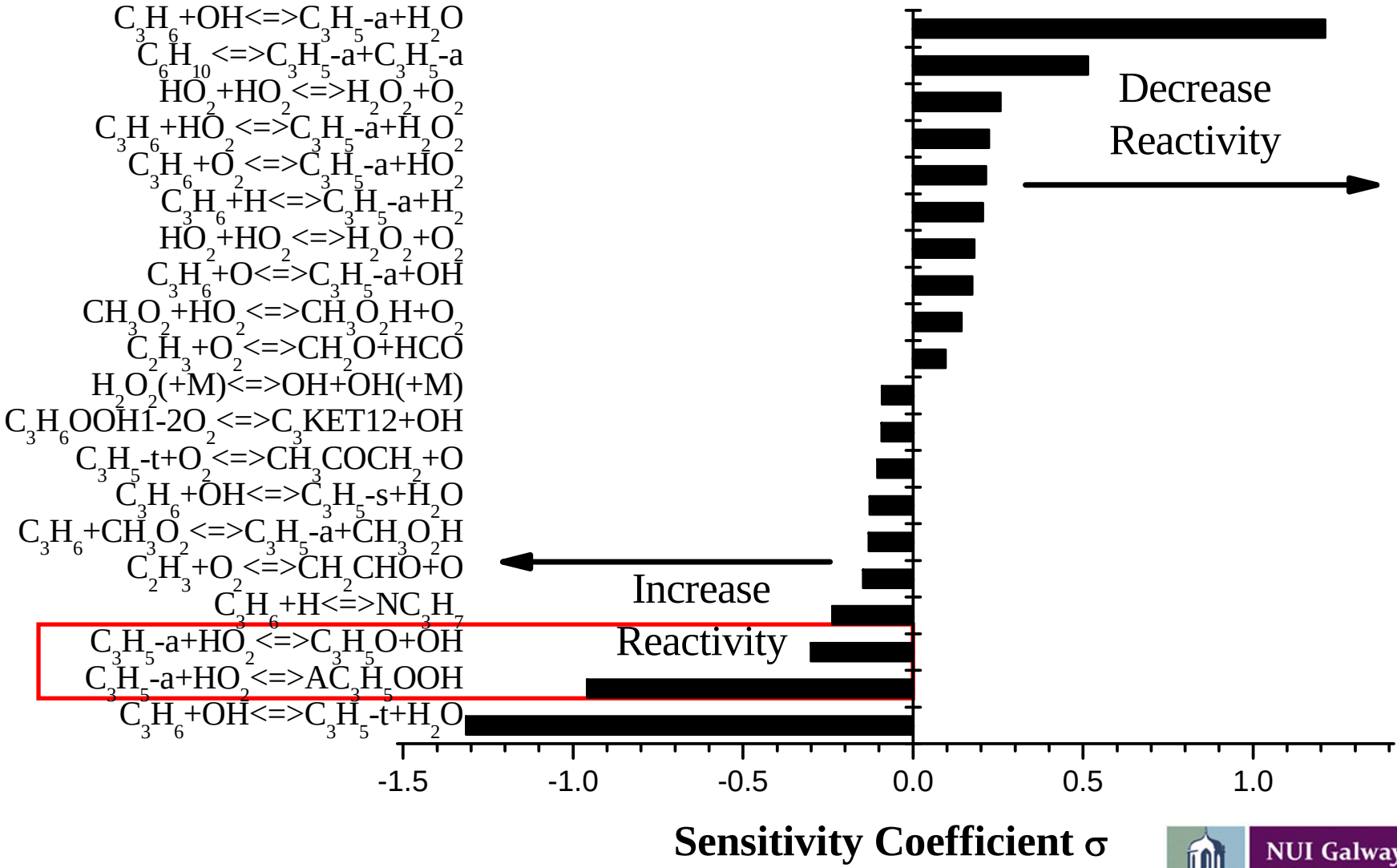
Current

Previous

NUI Galway
OÉ Gaillimh

Sensitivity Analysis—C_3H_6

4.46% fuel in air, ϕ = 1.0, 40 atm, 800 K



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

- Allyl + $H\dot{O}_2$ system (adopted Goldsmith *et al.)*

C_3H_5-a+HO_2<=>C_3H_5O+OH
C_3H_5-a+HO_2<=>AC_3H_5OOH
C_3H_5-a+HO_2<=>C_2H_3CHO+H_2O
AC_3H_5OOH<=>C_2H_3CHO+H_2O
AC_3H_5OOH<=>C_3H_5O+OH

$C_2H_3OCH_2$<=>C_2H_3+CH_2O
$C_2H_3OCH_2$<=>CH_2CH_2CHO
$C_2H_3OCH_2$<=>C_2H_3CHO+H
$C_2H_3OCH_2$<=>C_2H_4+HCO
CH_2CH_2CHO<=>C_2H_3+CH_2O

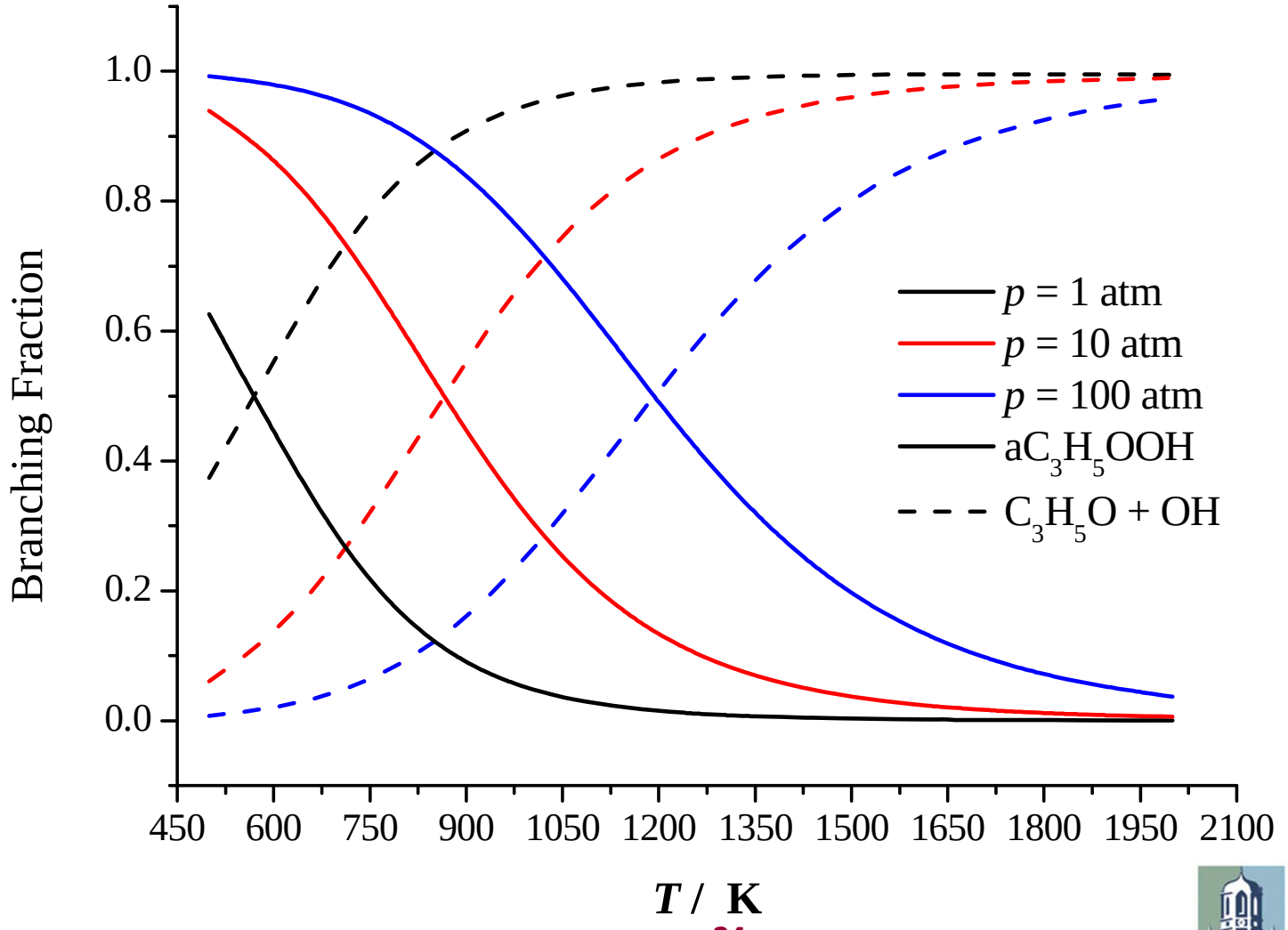
C_3H_5O<=>C_2H_3+CH_2O
C_3H_5O<=>$C_2H_3OCH_2$
C_3H_5O<=>CH_2CH_2CHO
C_3H_5O<=>C_2H_3CHO+H
C_3H_5O<=>C_2H_4+HCO

CH_2CH_2CHO<=>C_2H_3CHO+H
CH_2CH_2CHO<=>C_2H_4+HCO
C_2H_3+CH_2O<=>C_2H_3CHO+H
C_2H_3+CH_2O<=>C_2H_4+HCO

Goldsmith et al .Proc. Comb. Inst., **2011***, 33*, 273–282.

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

Allyl ($\dot{C}_3H_5$-a) + $H\dot{O}_2$ branching fraction at 1, 10 and 100 atm



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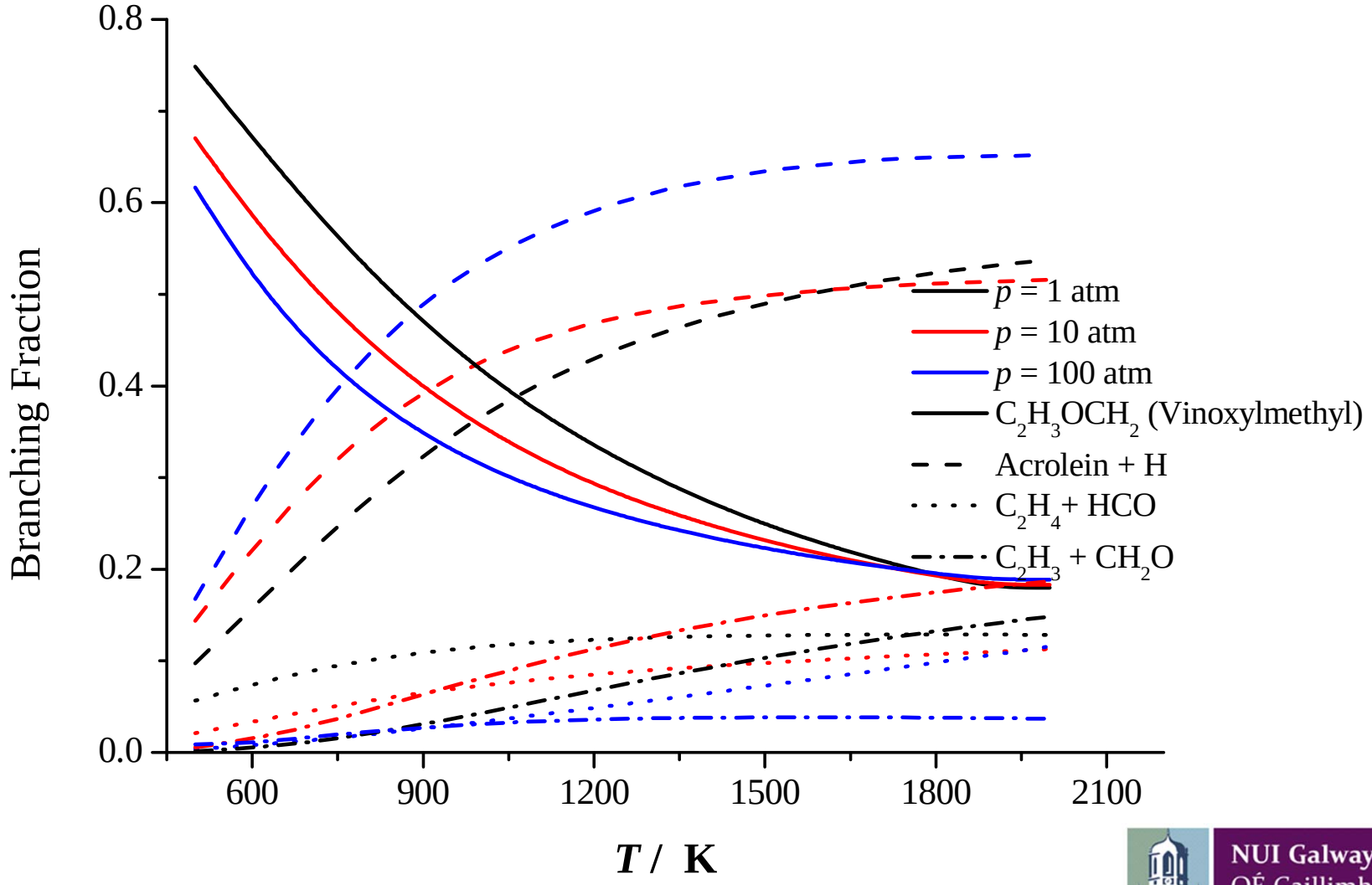
$\dot{C}_3H_5$-a + $H\dot{O}_2$

Alloxy ($C_3H_5\dot{O}$) decomposition branching fraction at 1, 10 and 100 atm



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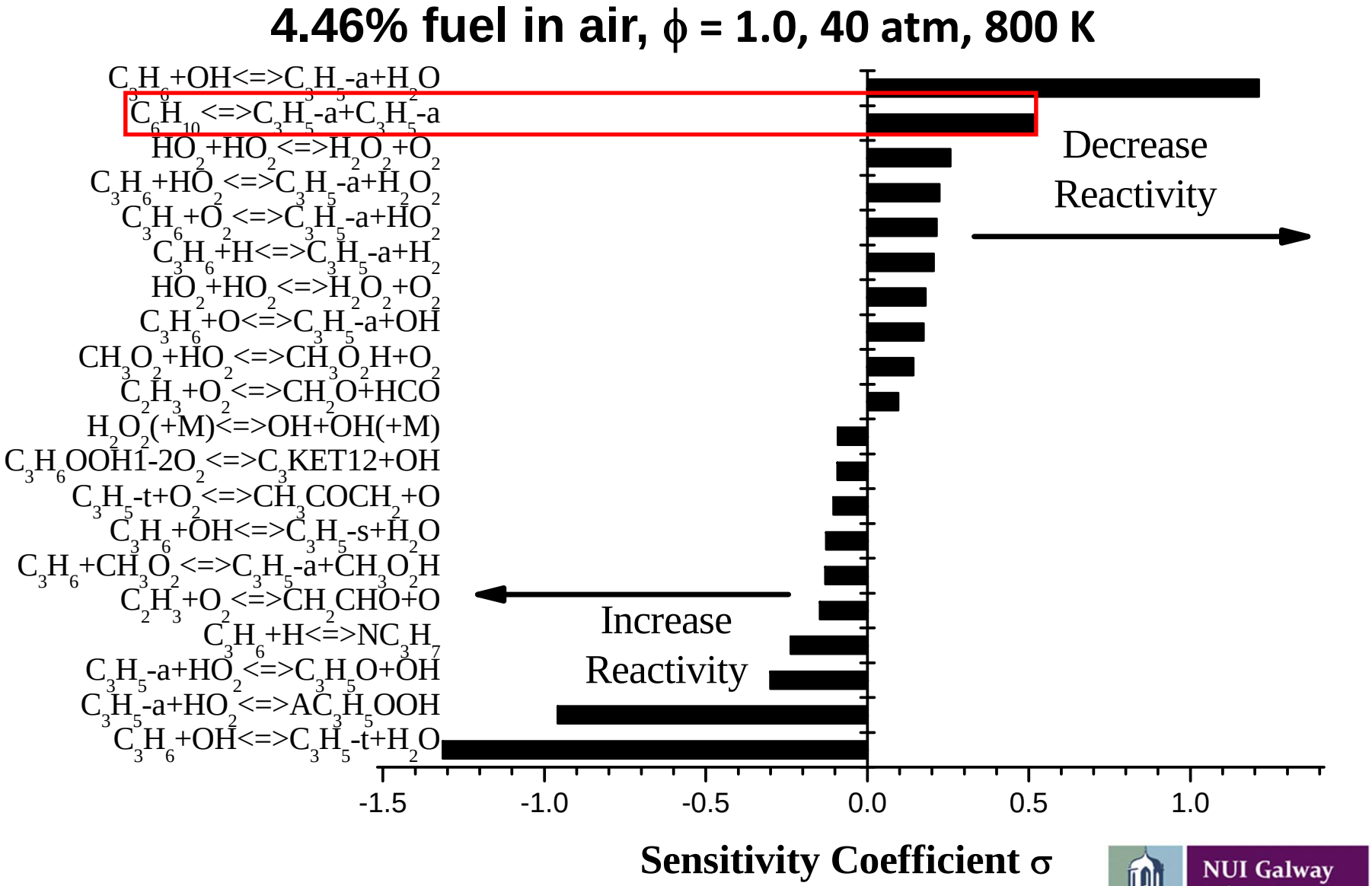
Sensitivity Analysis—C_3H_6



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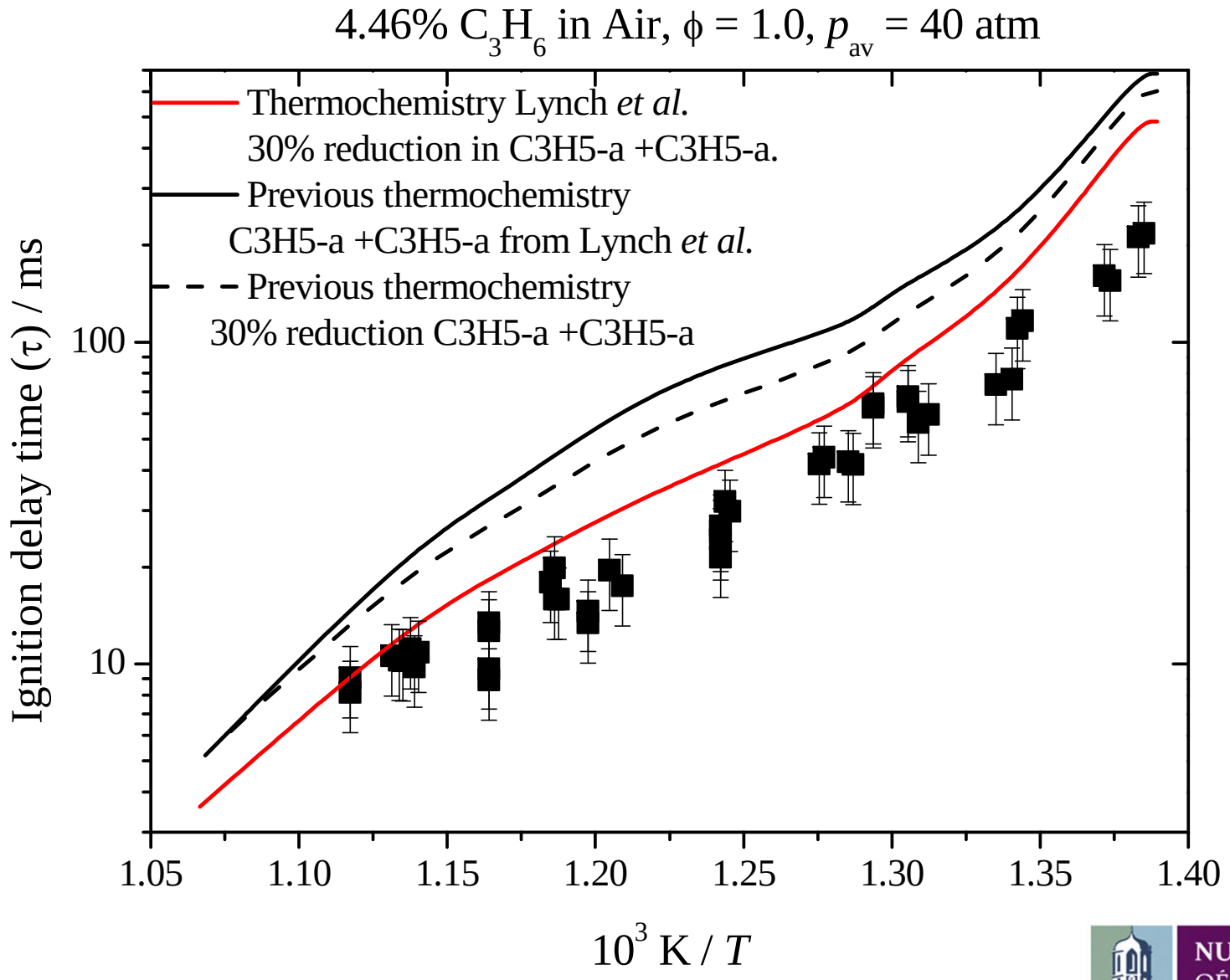
$\dot{C}_3H_5$-a + $\dot{C}_3H_5$-a



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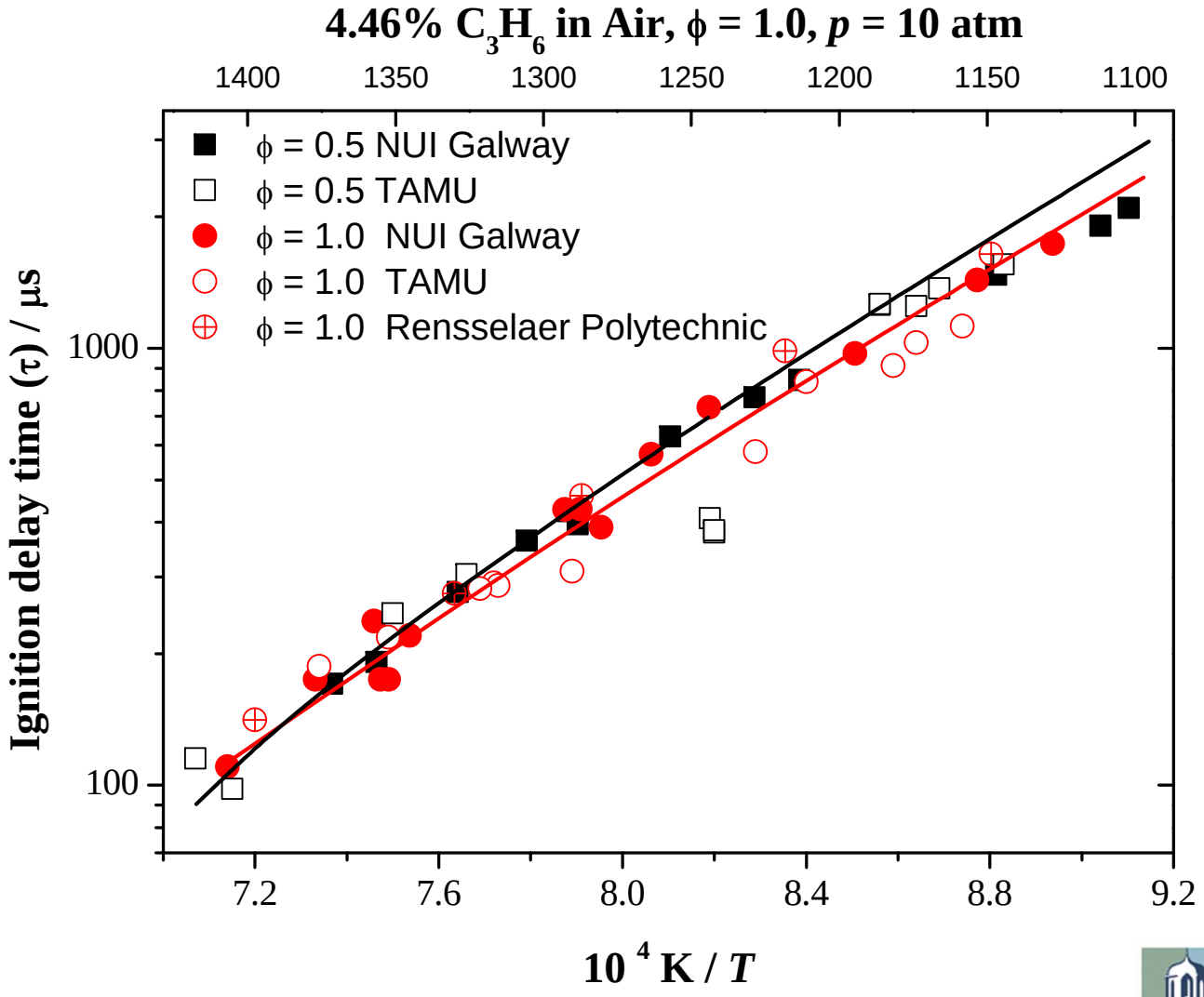
Other rate constants changed

- $C_3H_6+CH_3$ (both addition and abstraction)
  - Applied a pressure dependent treatment of the addition pathway
  - Estimated rate constant for the abstraction channel based on a values from Tsang and an NUI Galway calculation
- C_3H_6+H (both addition and abstraction)
  - Applied a pressure dependent treatment of the addition pathway
  - Estimated rate constant from Curran for abstraction
- C_3H_6+O (both addition and abstraction)
  - Altered the branching ratio of the abstraction reaction
  - Addition channel analogy with C_2H_4
- C_3H_5-a decomp. (from Miller *et al.*) J. Phys. Chem. A, 2008, 112, 9429-9438
- C_3H_5-s+O_2
  - Analogy with C_2H_4
- C_3H_4 chemistry (from Hansen *et al.*) Combust. Flame, 2009, 156, 2153-2164

Other Validation

- Shock tube at 10 atm



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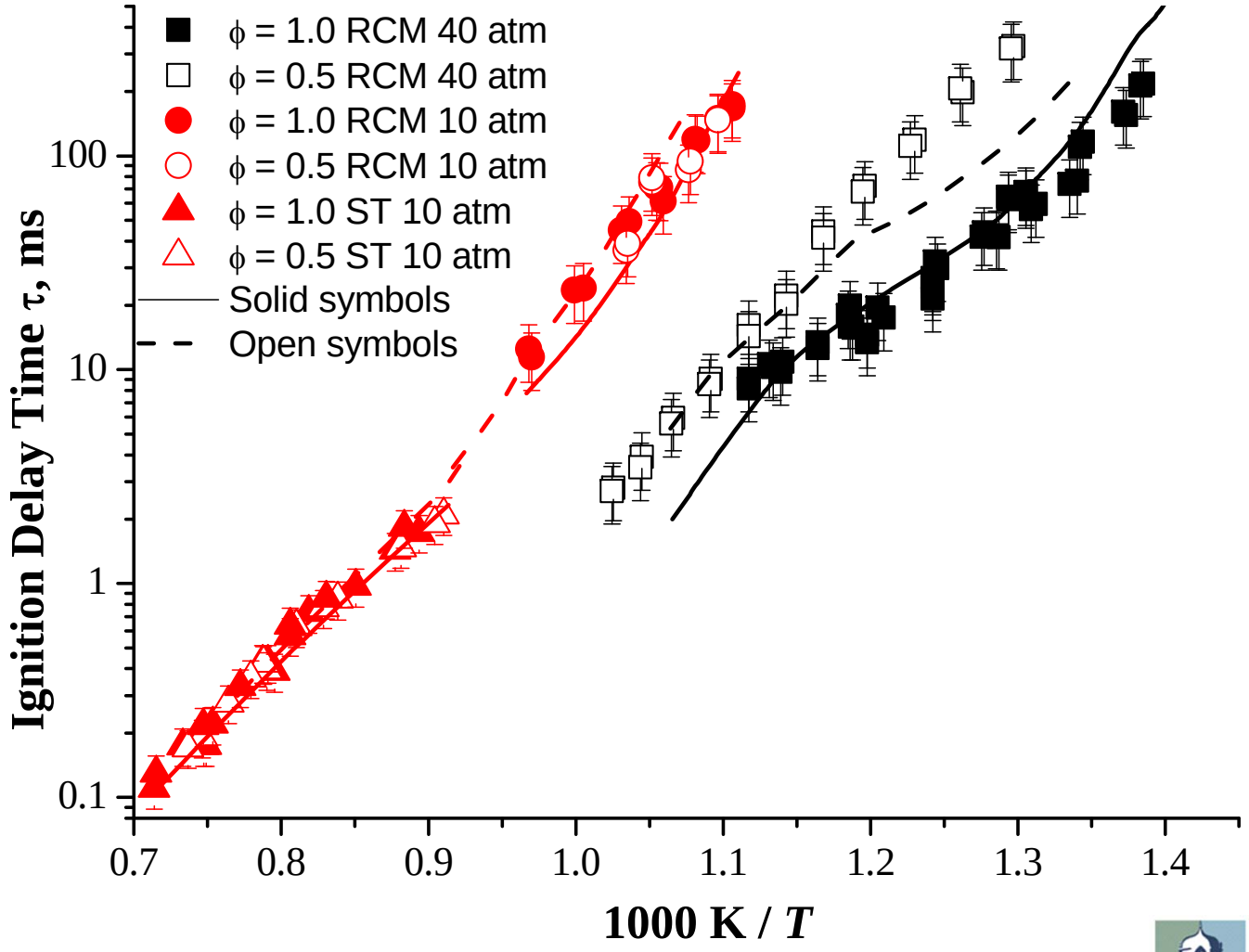
Other Validation

- Shock tube and RCM at 10 and 40 atm



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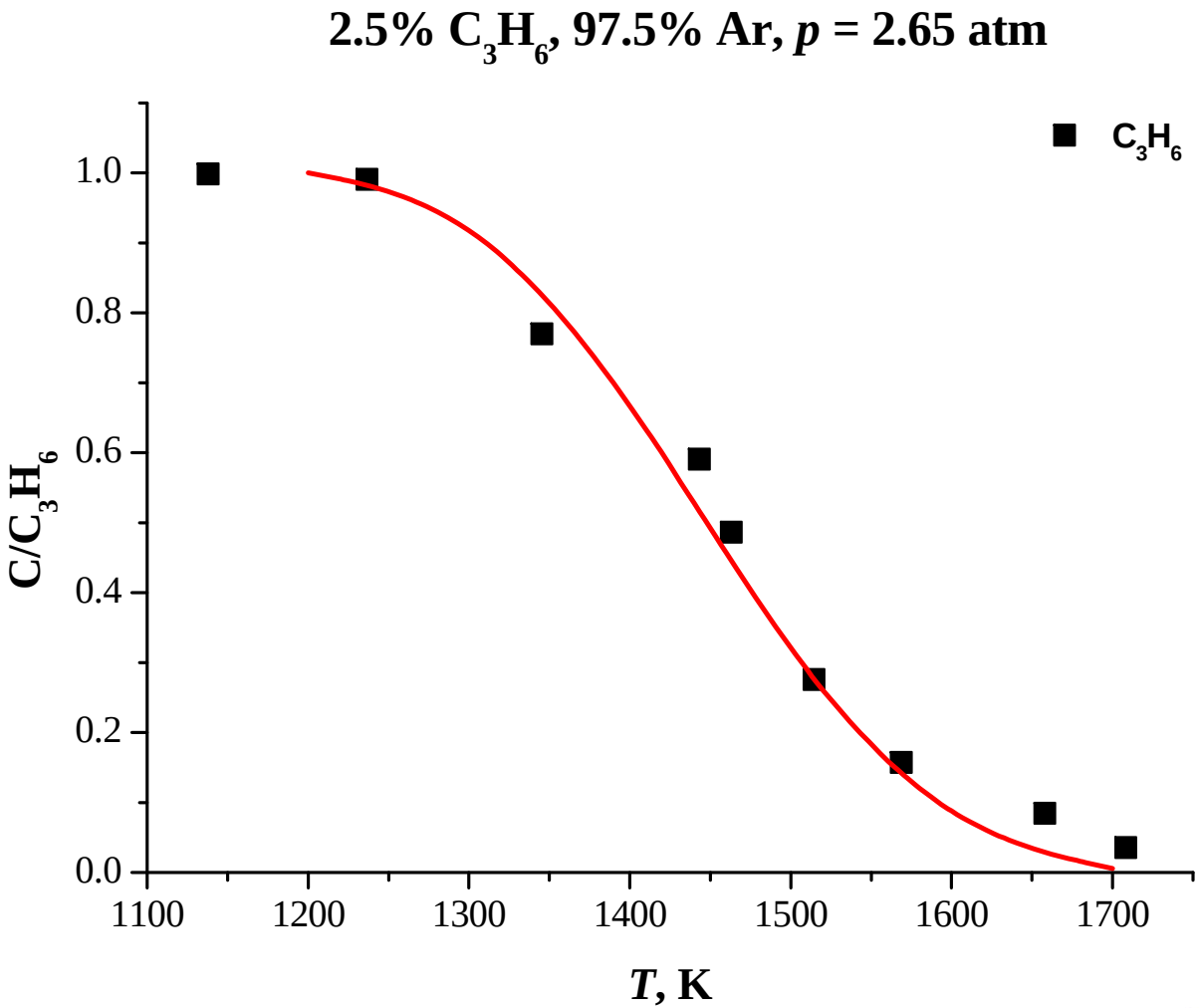
Other Validation

- Pyrolysis data from Hidaka *et al.* 1992



Hidaka et al. Int. J. Chem. Kinet., **1992**, *24*, 761-780

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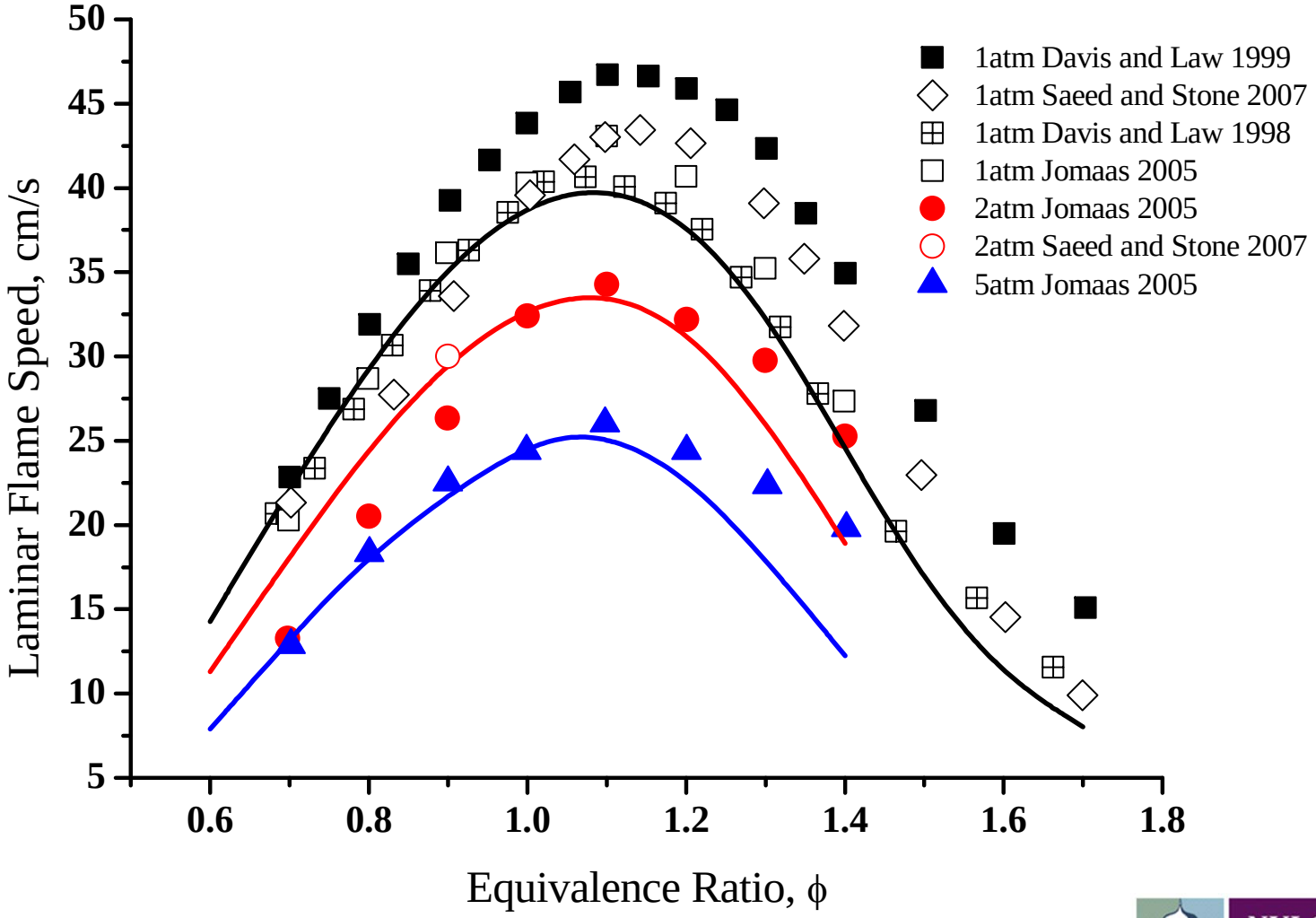
Other Validation

- Flame speed



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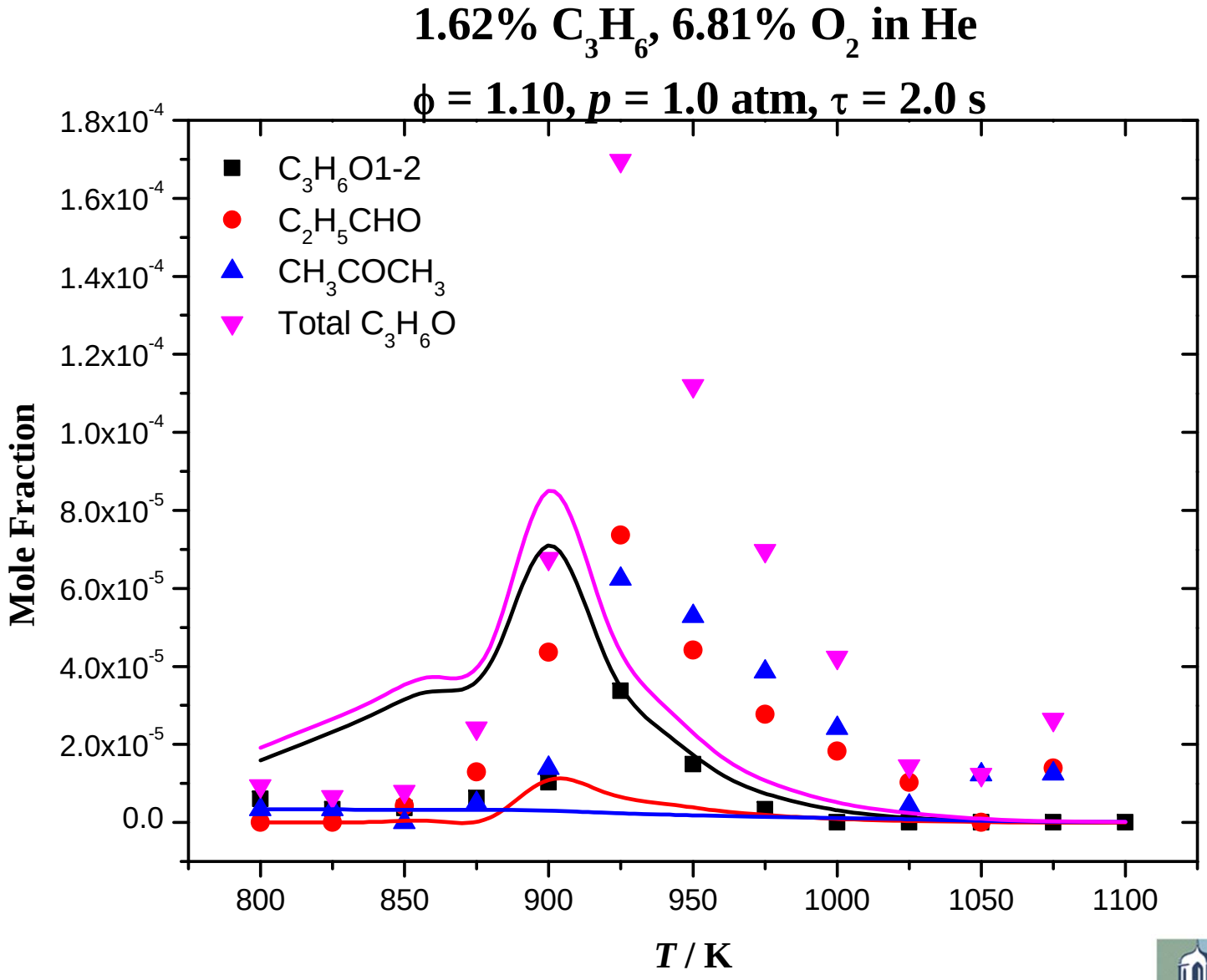
Under-prediction of C_3H_6O in JSR



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