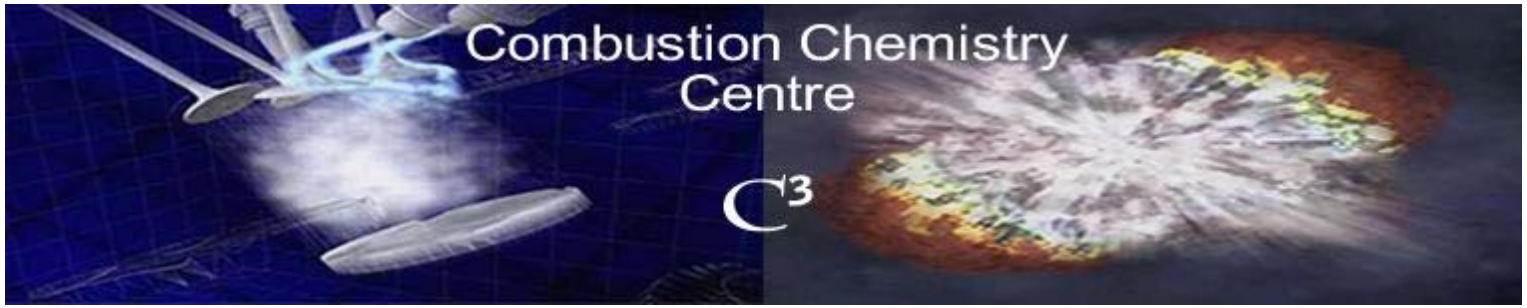


Detailed chemical kinetic mechanisms for combustion

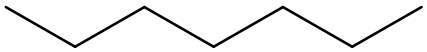
Dr. Henry Curran

Combustion Chemistry Centre
National University of Ireland Galway

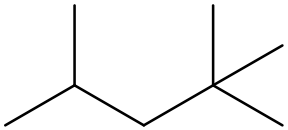
MULTI AGENCY COORDINATION COMMITTEE FOR COMBUSTION RESEARCH (MACCCR)
FUELS RESEARCH REVIEW
Los Angeles, CA
15-17 September 2009

Develop chemical kinetic models

- Gasoline
  - n-heptane

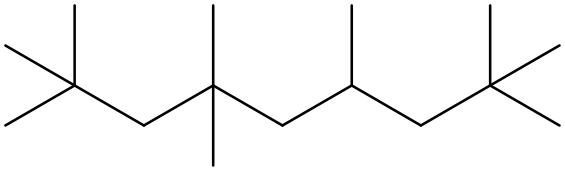


  - iso-octane

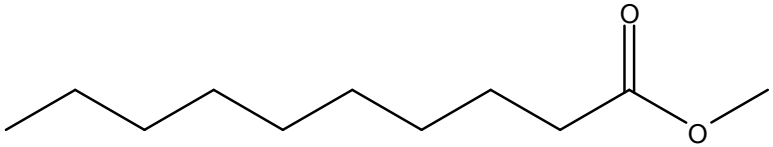


- Diesel
  - n-cetane

  - iso-cetane

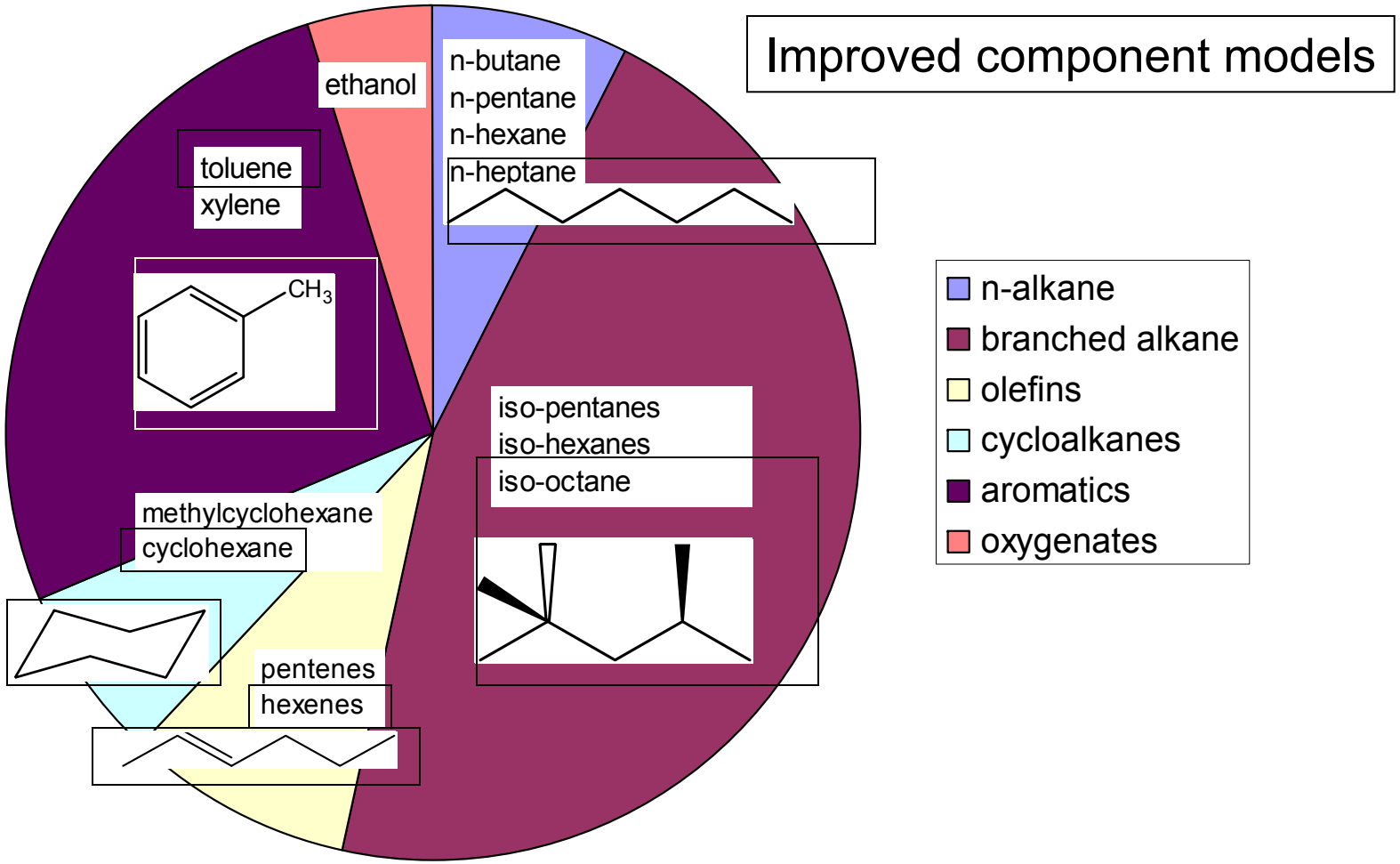


- Biodiesel

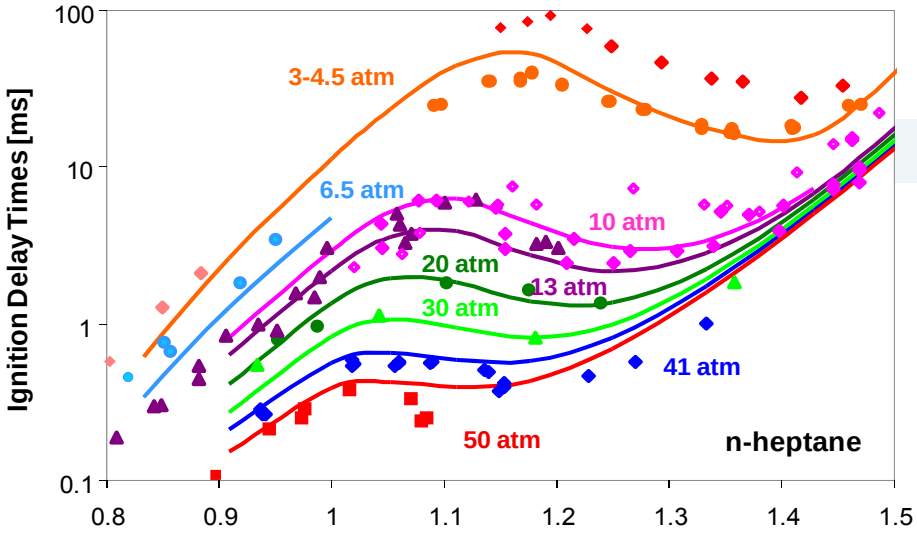


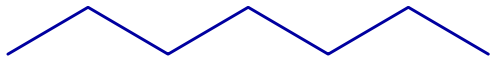
- Gas Turbines smaller HCs

Recent improvements to fuel surrogate models: Gasoline



PRF ignition over a wide temperature and pressure range



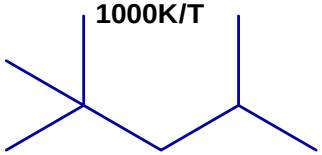


n-heptane:

P = 3 - 50 atm

T = 650K - 1200K

Φ = 1

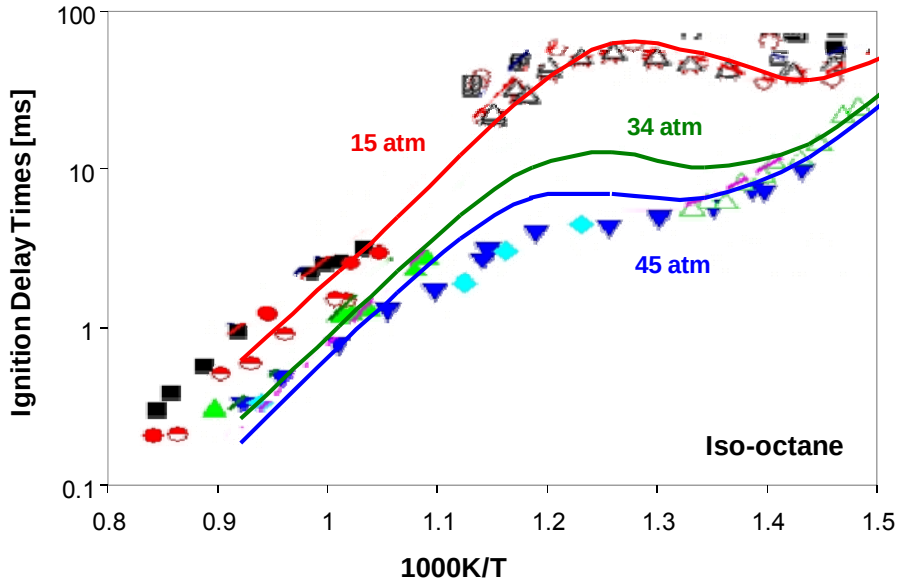


iso-octane:

P = 15 - 45 atm

T = 650K - 1150K

Φ= *1*



Experimental data: Minetti R., M. Carlier, M. Ribaucour, E. Therssen, L. R. Sochet (1995); H.K.Ciezki, G. Adomeit (1993); Gauthier B.M., D.F. Davidson, R.K. Hanson (2004); Mittal G. and C. J. Sung,(2007); Minetti R., M. Carlier, M. Ribaucour, E. Therssen, L.R. Sochet (1996); K. Fieweger, R. Blumenthal, G. Adomeit (1997).

Gasoline surrogates

Gasoline surrogate	Composition liquid volume (%)				Octane number
	Ethanol	Iso-octane	n-Heptane	Toluene	
Surrogate A	40.0	37.8	10.2	12.0	98.75
Surrogate B	20.0	62.0	18.0	–	92.0
Surrogate C	–	69.0	17.0	14.0	87.0

L.R. Cancino, M. Fikri, A.A.M. Oliveira, C. Schulz, Proc. Combust. Inst. 32 (2009) 501−508.

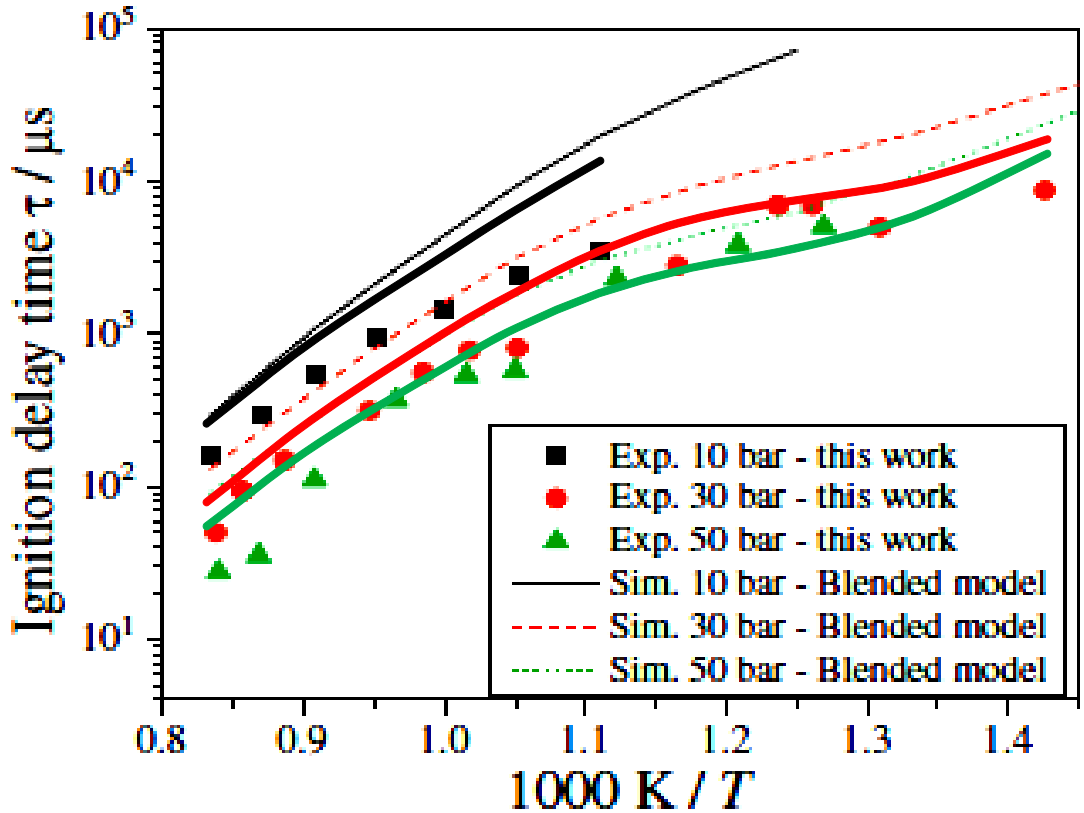


Fig. 2. Simulation and experimental results for surrogate A ignition delay times in air. $\phi = 1.0$, $p = 10$, 30, and 50 bar (see Tables 1 and 2 for composition and sub-mechanisms models).

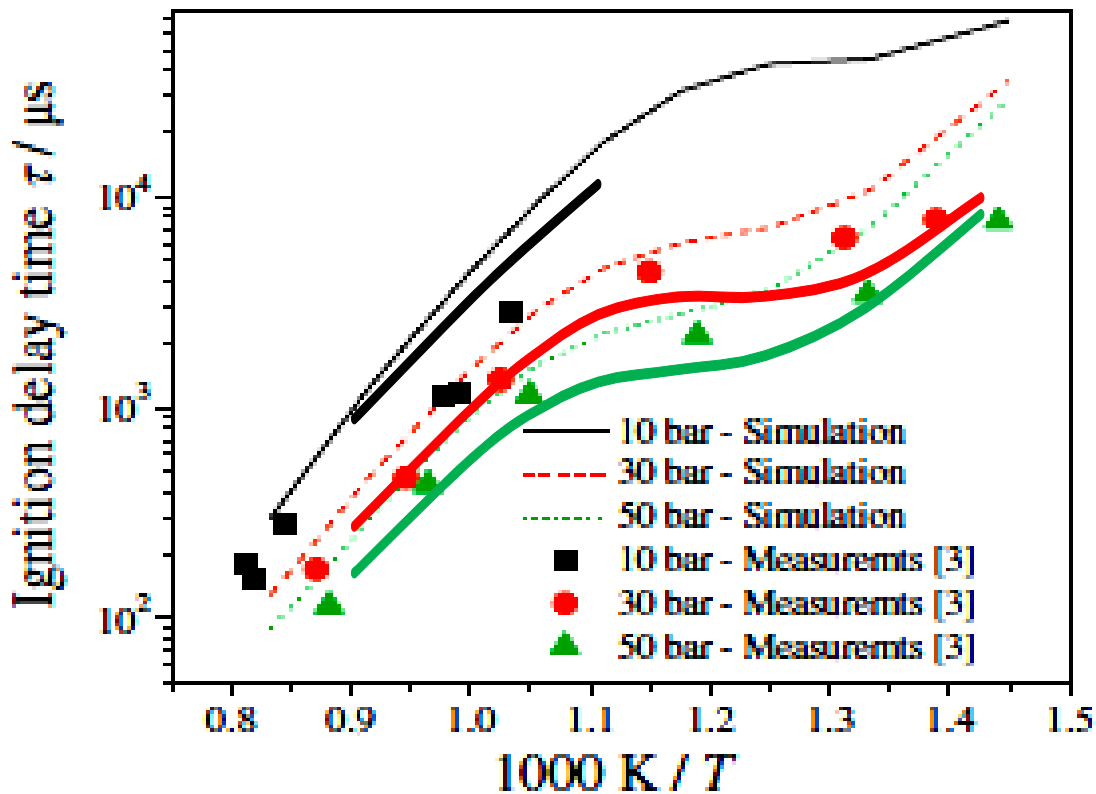


Fig. 3. Simulation and experimental results (from [3]) for surrogate B ignition delay times in air. $\phi = 1.0$ (see Tables 1 and 2 for composition and sub-mechanisms models).

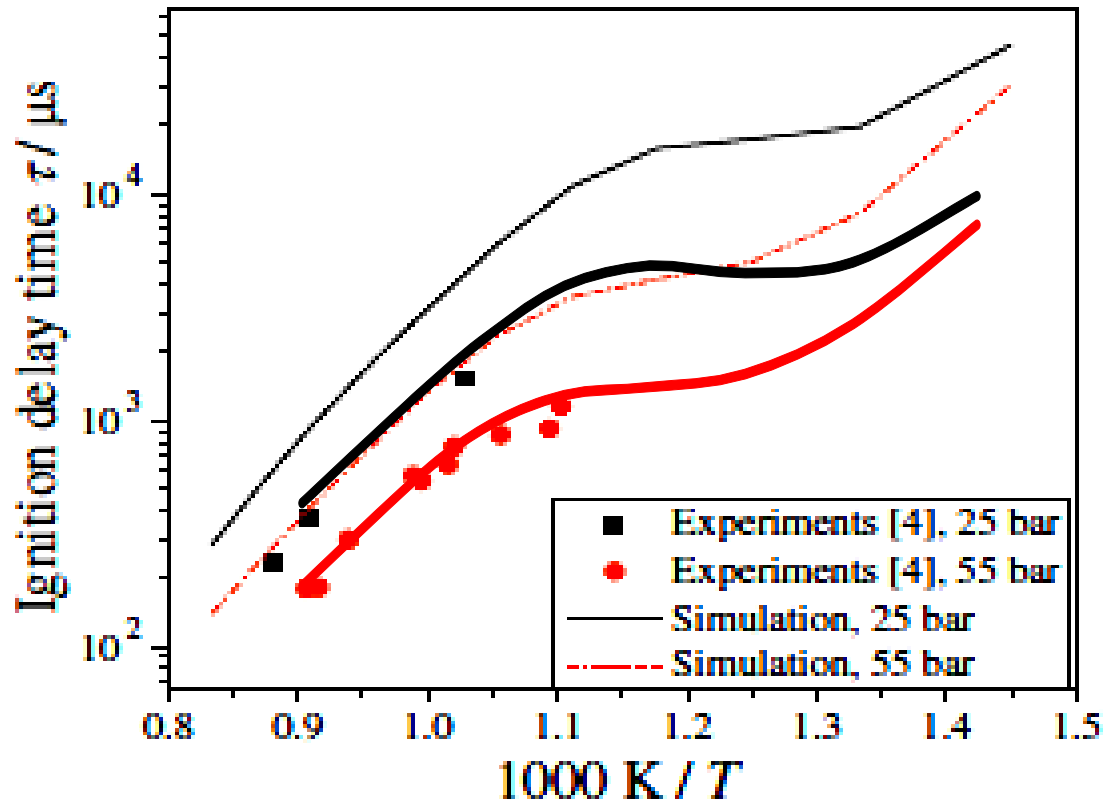


Fig. 4. Simulation and experimental results (from [4]) for surrogate C ignition delay times in air. $\phi = 1.0$ (see Tables 1 and 2 for composition and sub-mechanisms models).

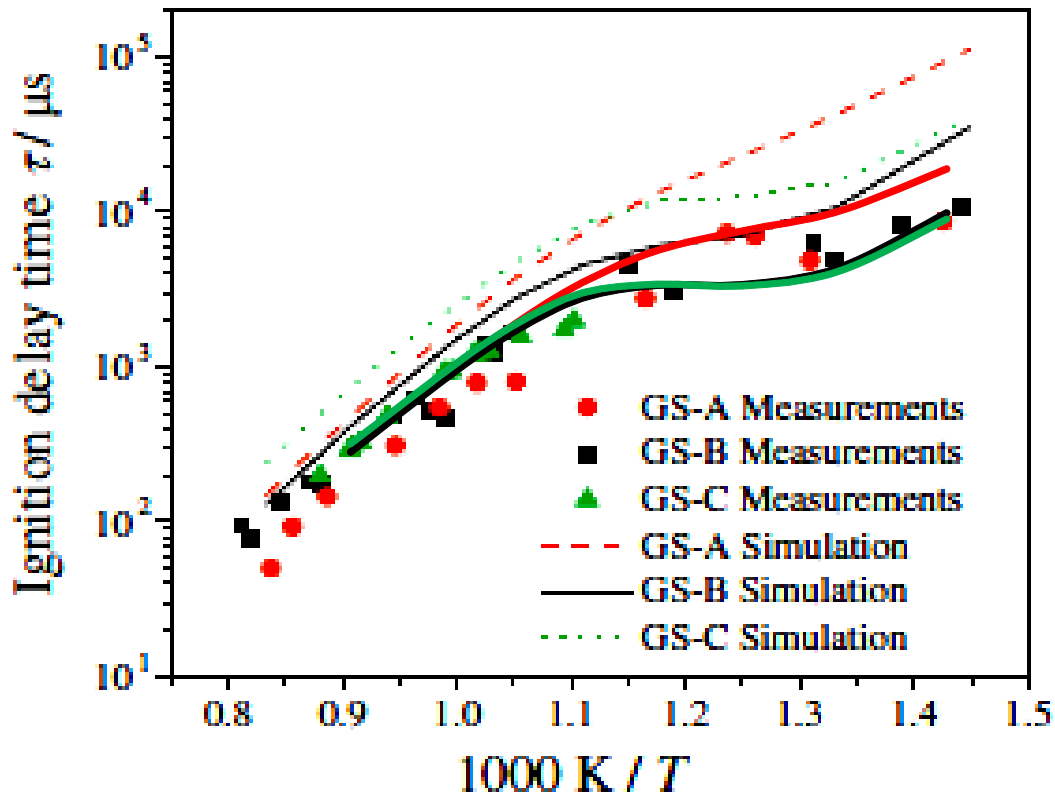
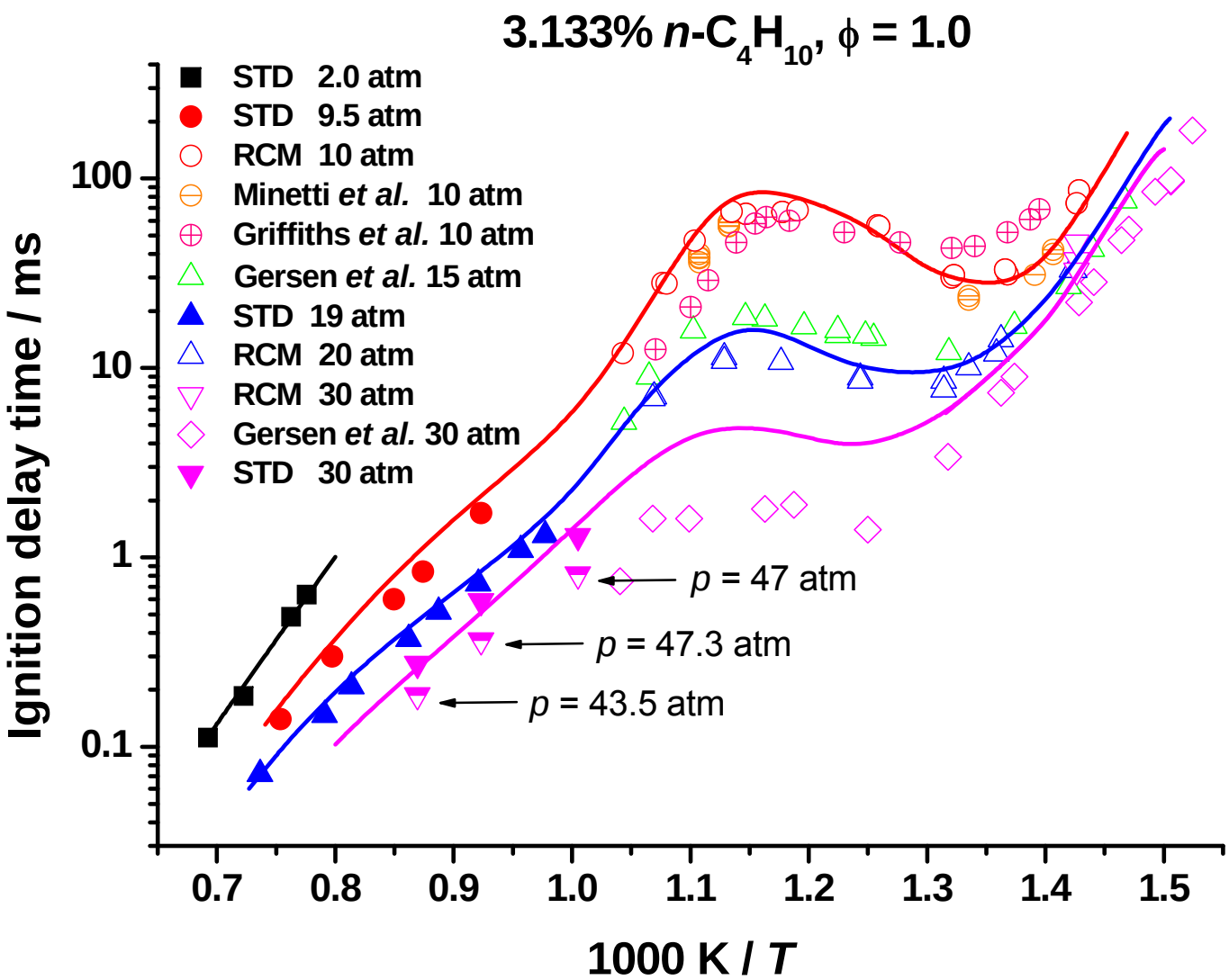
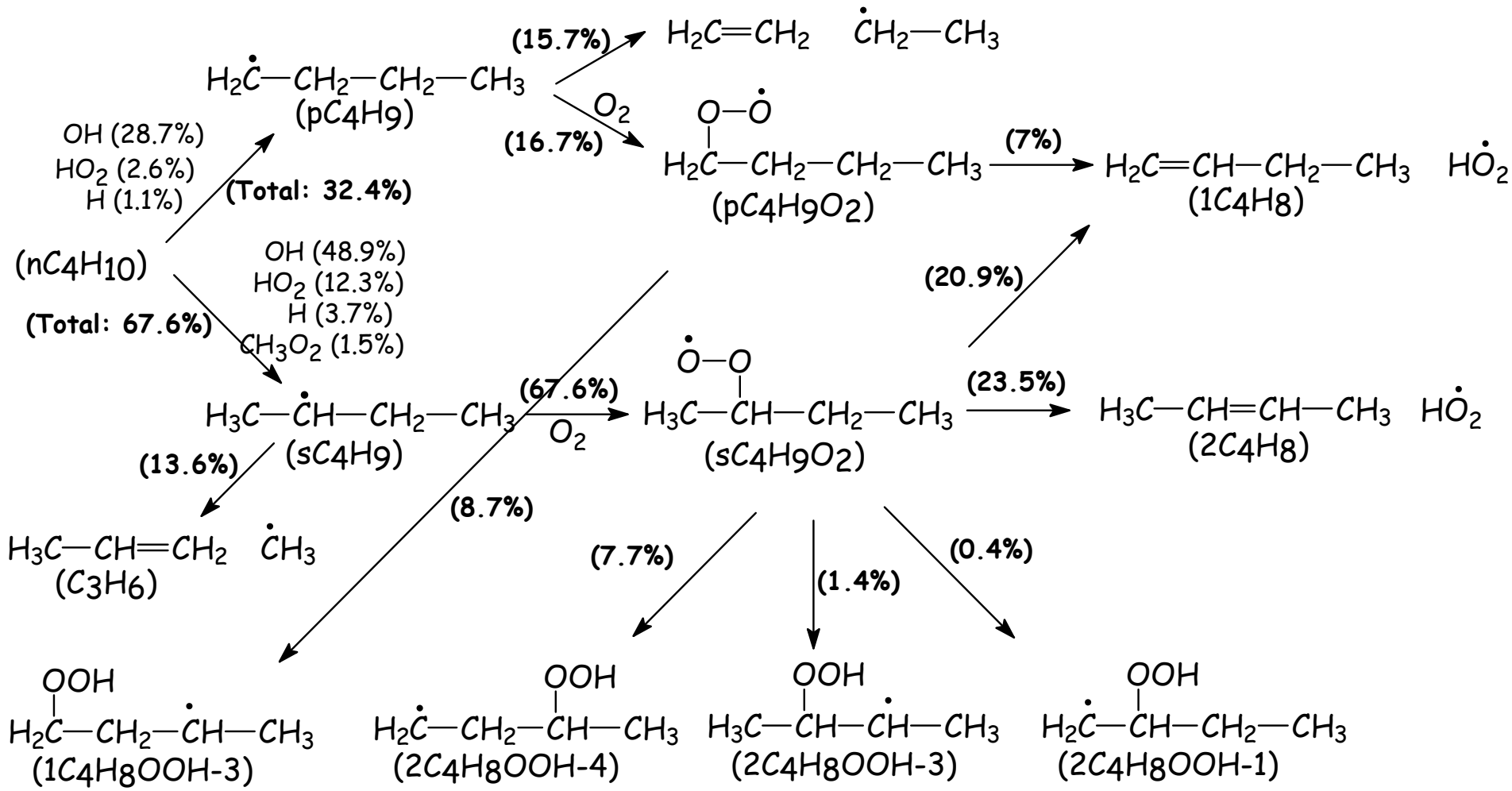


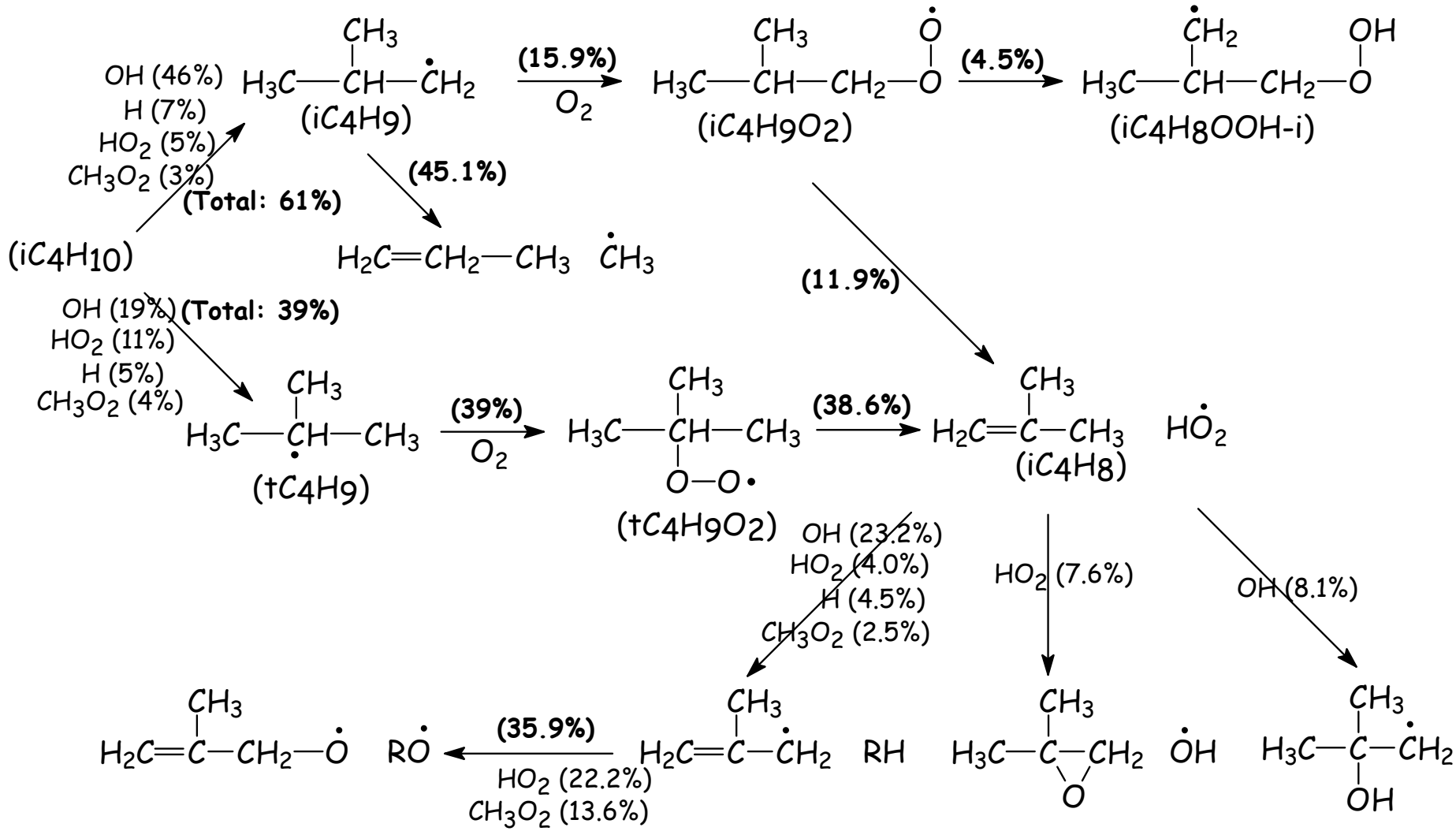
Fig. 5. Simulation and experimental results for all surrogates/air ignition delay times at $p_5 = 30$ bar. $\phi = 1.0$ (see Tables 1 and 2 for composition and sub-mechanisms models).

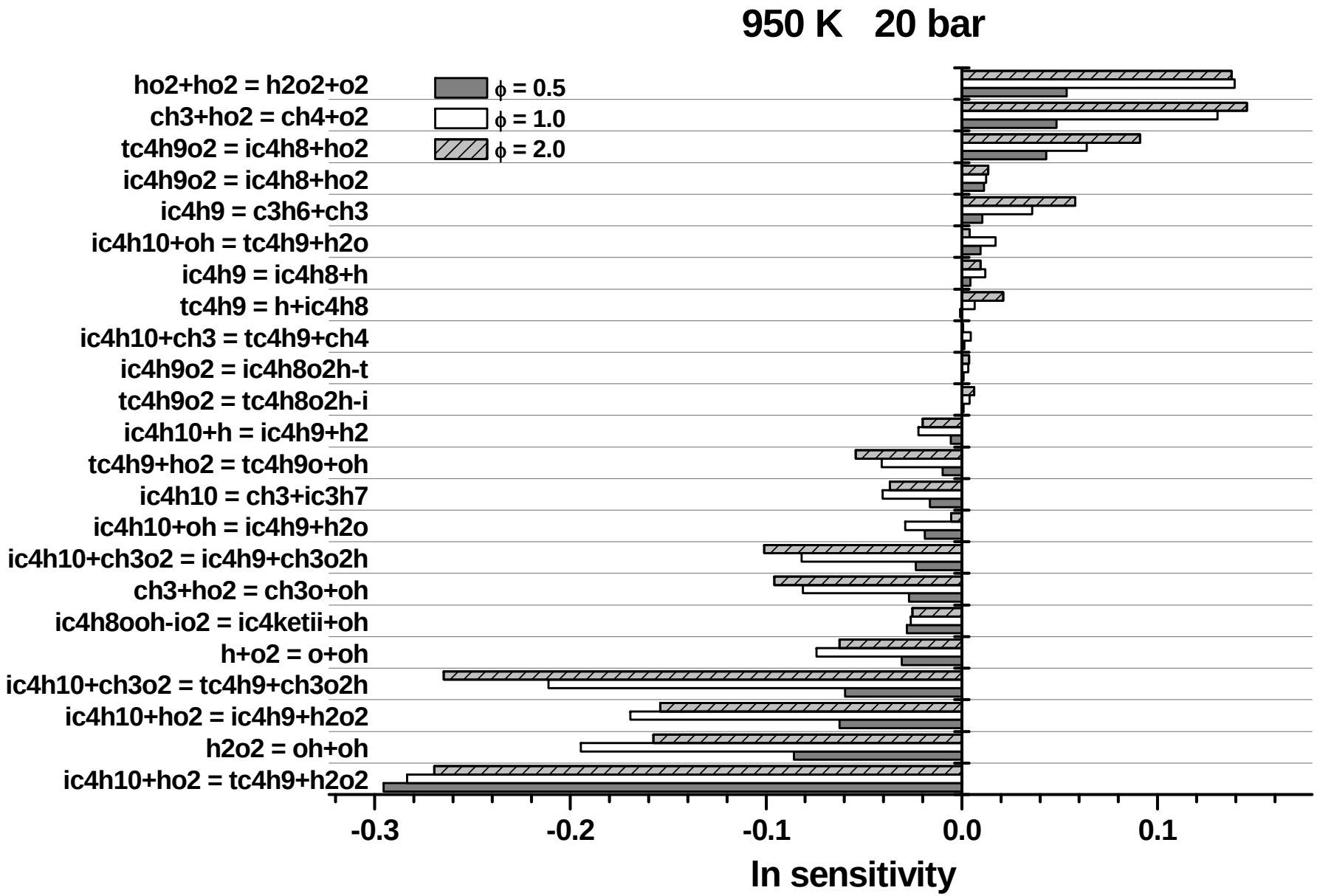

3.133% n-C4H10, ϕ = 1.0
STD 2.0 atm
STD 9.5 atm
RCM 10 atm
Minetti et al. 10 atm
Griffiths et al. 10 atm
Gersen et al. 15 atm
STD 19 atm
RCM 20 atm
RCM 30 atm
Gersen et al. 30 atm
STD 30 atm
p = 47 atm
p = 47.3 atm
p = 43.5 atm
Ignition delay time / ms
100
10
1
0.1
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1000 K / T

n-Butane oxidation ϕ = 1, 830 K, 20 atm, 20% consumption

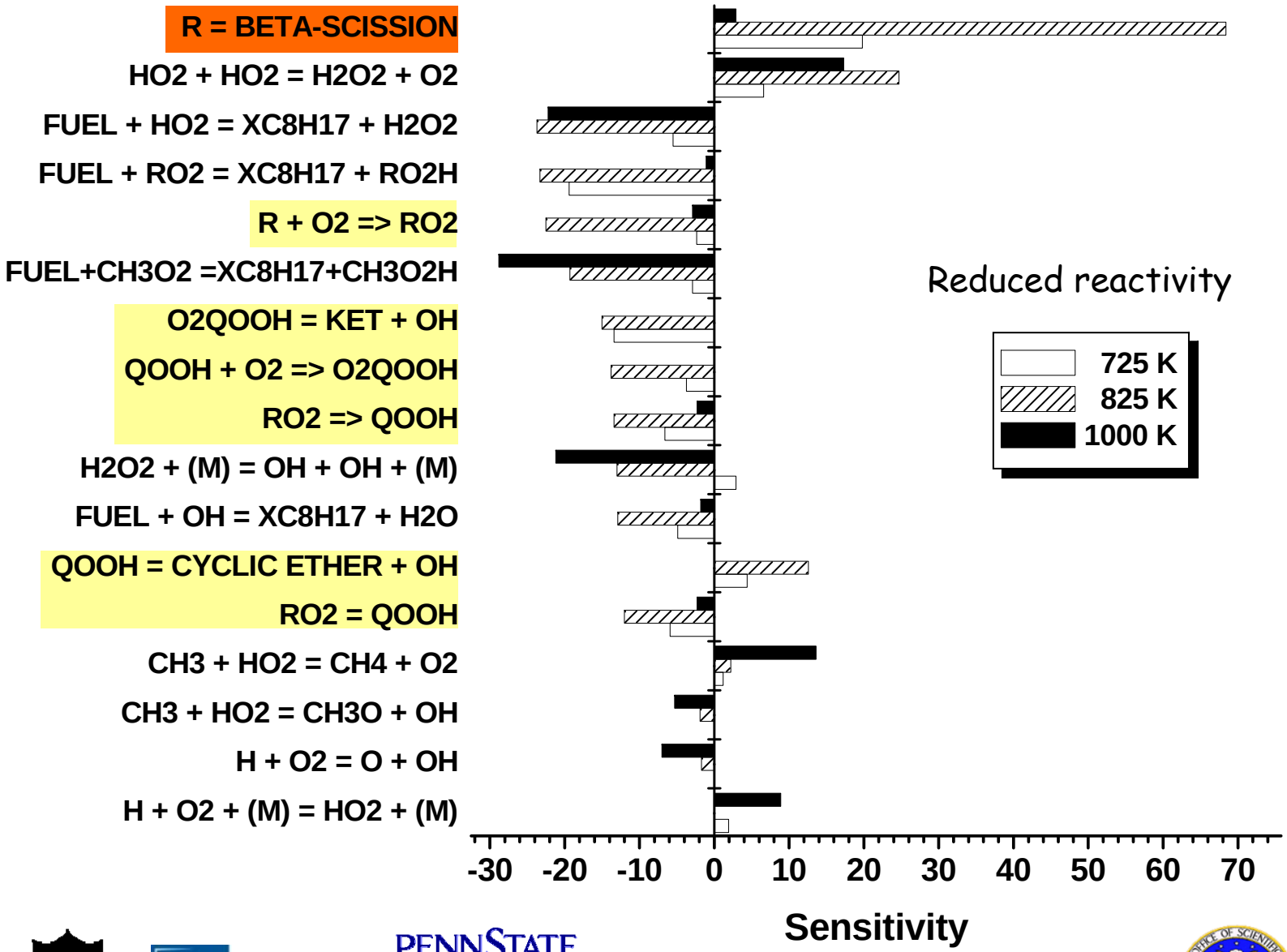


iso-Butane oxidation ϕ = 1, 875 K, 10 atm, 15% consumption

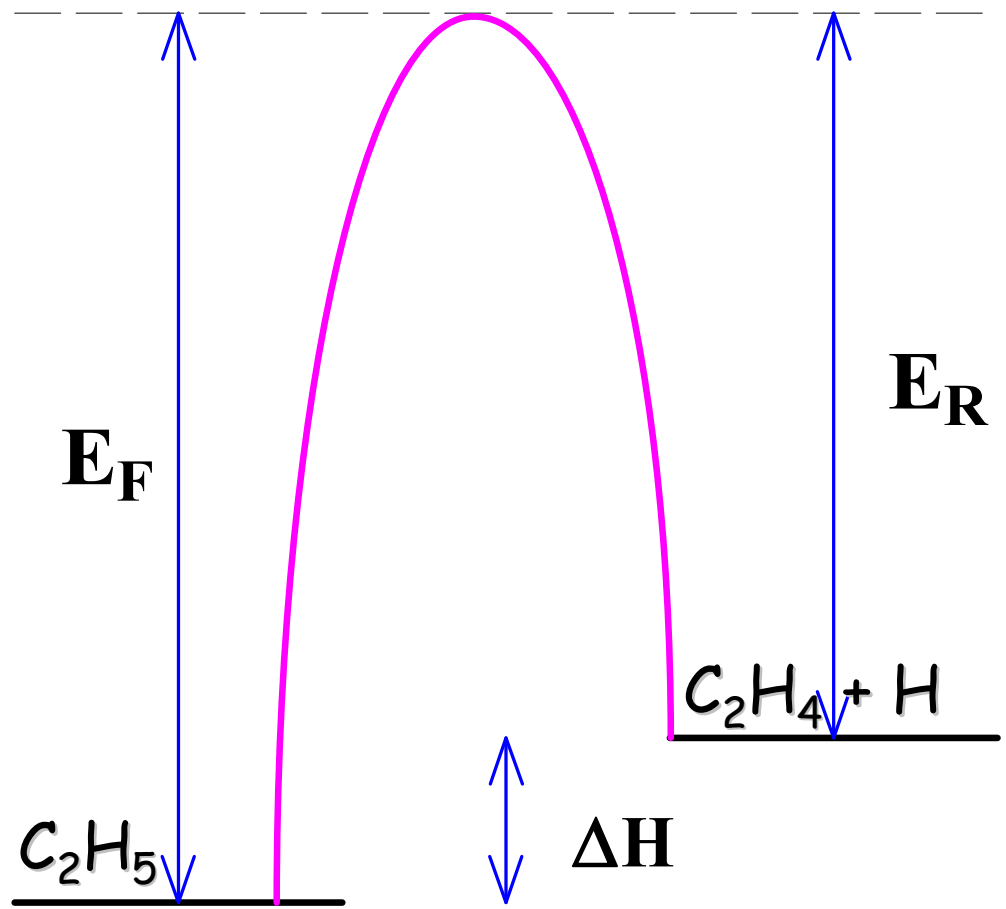



950 K 20 bar
ho2+ho2 = h2o2+o2
ch3+ho2 = ch4+o2
tc4h9o2 = ic4h8+ho2
ic4h9o2 = ic4h8+ho2
ic4h9 = c3h6+ch3
ic4h10+oh = tc4h9+h2o
ic4h9 = ic4h8+h
tc4h9 = h+ic4h8
ic4h10+ch3 = tc4h9+ch4
ic4h9o2 = ic4h8o2h-t
tc4h9o2 = tc4h8o2h-i
ic4h10+h = ic4h9+h2
tc4h9+ho2 = tc4h9o+oh
ic4h10 = ch3+ic3h7
ic4h10+oh = ic4h9+h2o
ic4h10+ch3o2 = ic4h9+ch3o2h
ch3+ho2 = ch3o+oh
ic4h8ooh-io2 = ic4ketii+oh
h+o2 = o+oh
ic4h10+ch3o2 = tc4h9+ch3o2h
ic4h10+ho2 = ic4h9+h2o2
h2o2 = oh+oh
ic4h10+ho2 = tc4h9+h2o2
ϕ = 0.5
ϕ = 1.0
ϕ = 2.0
-0.3
-0.2
-0.1
0.0
0.1
ln sensitivity

High *p*, low *T*: iC_8H_{18}, ϕ = 1.0 in air, P = 40 atm

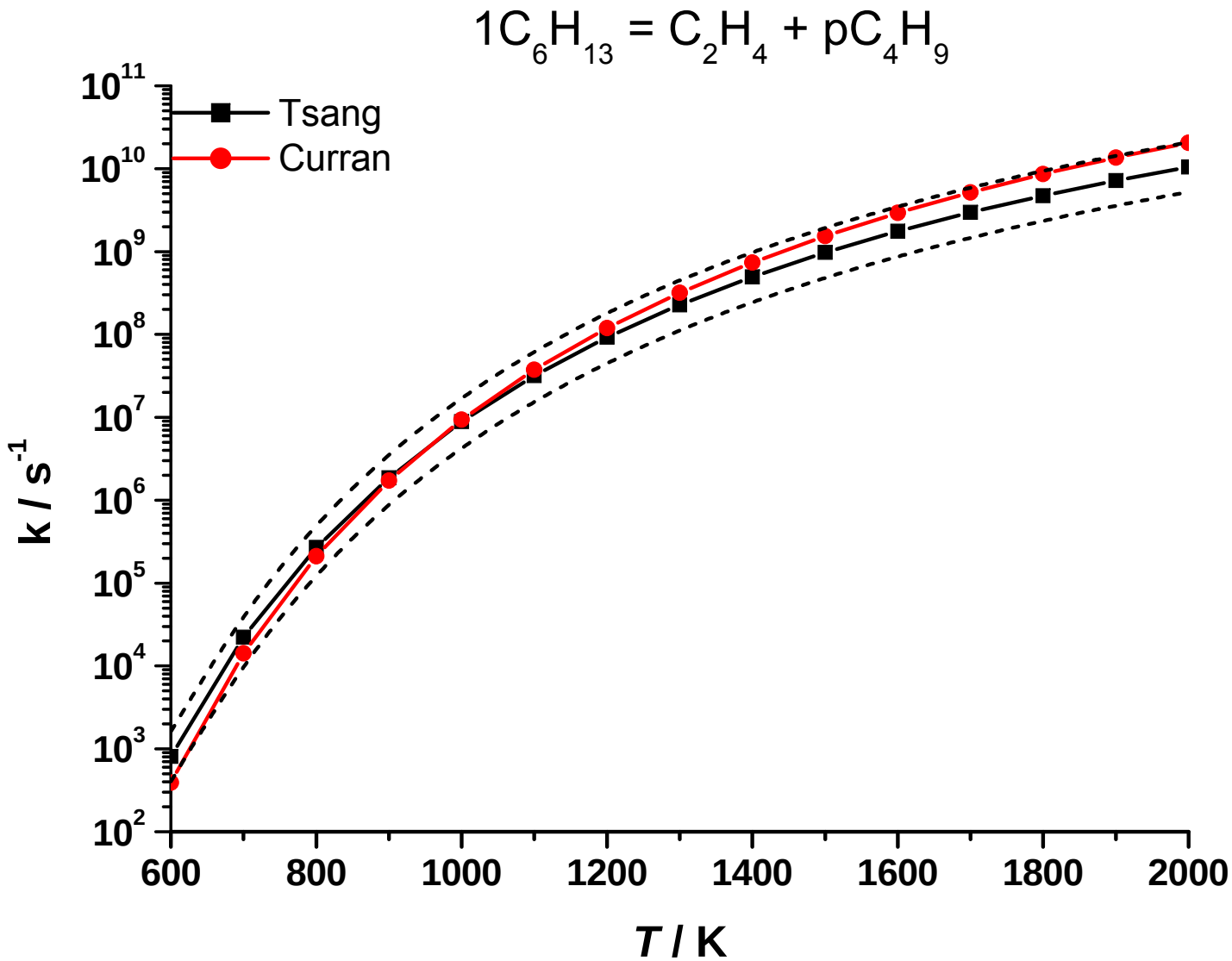


Alkyl radical decomposition

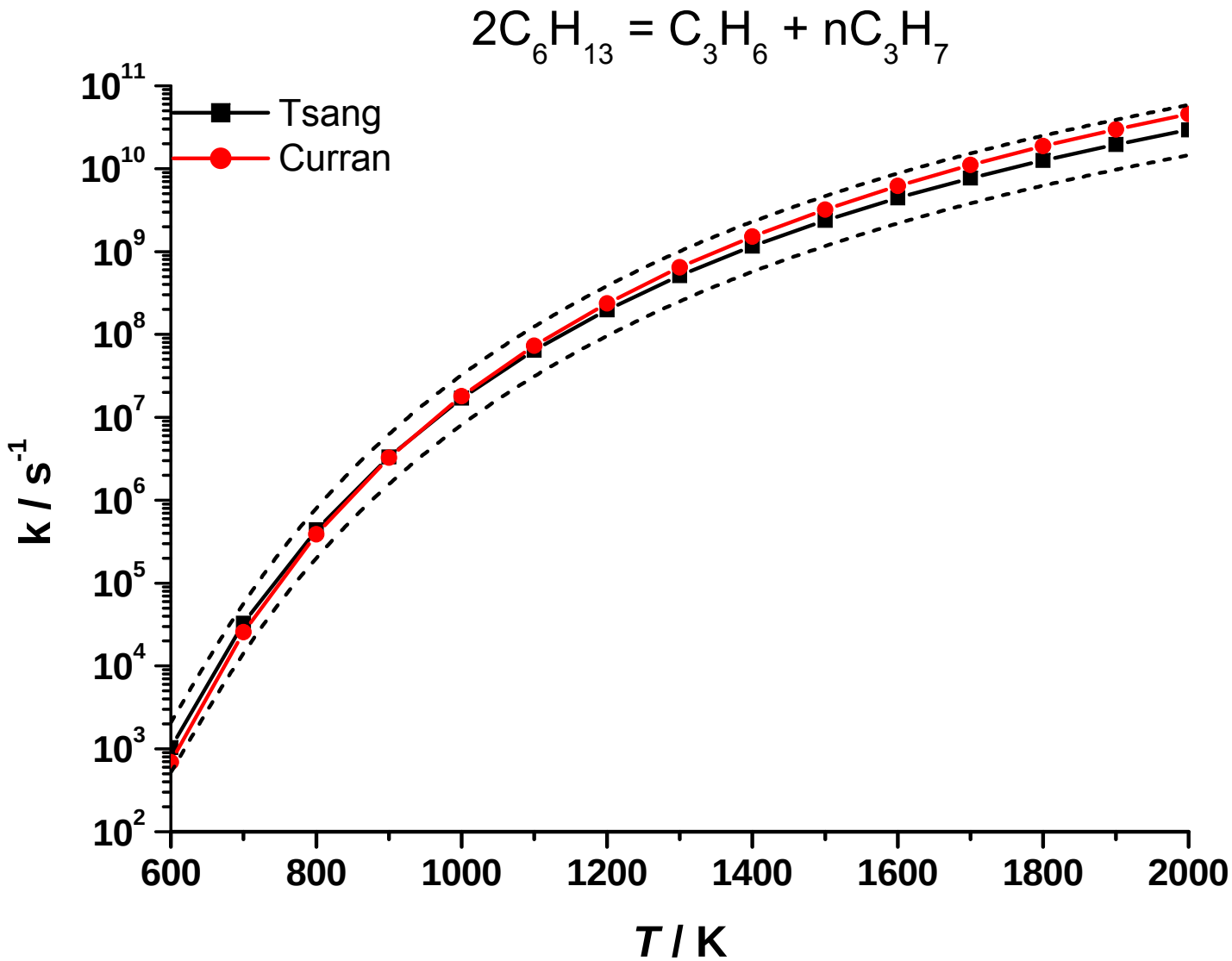


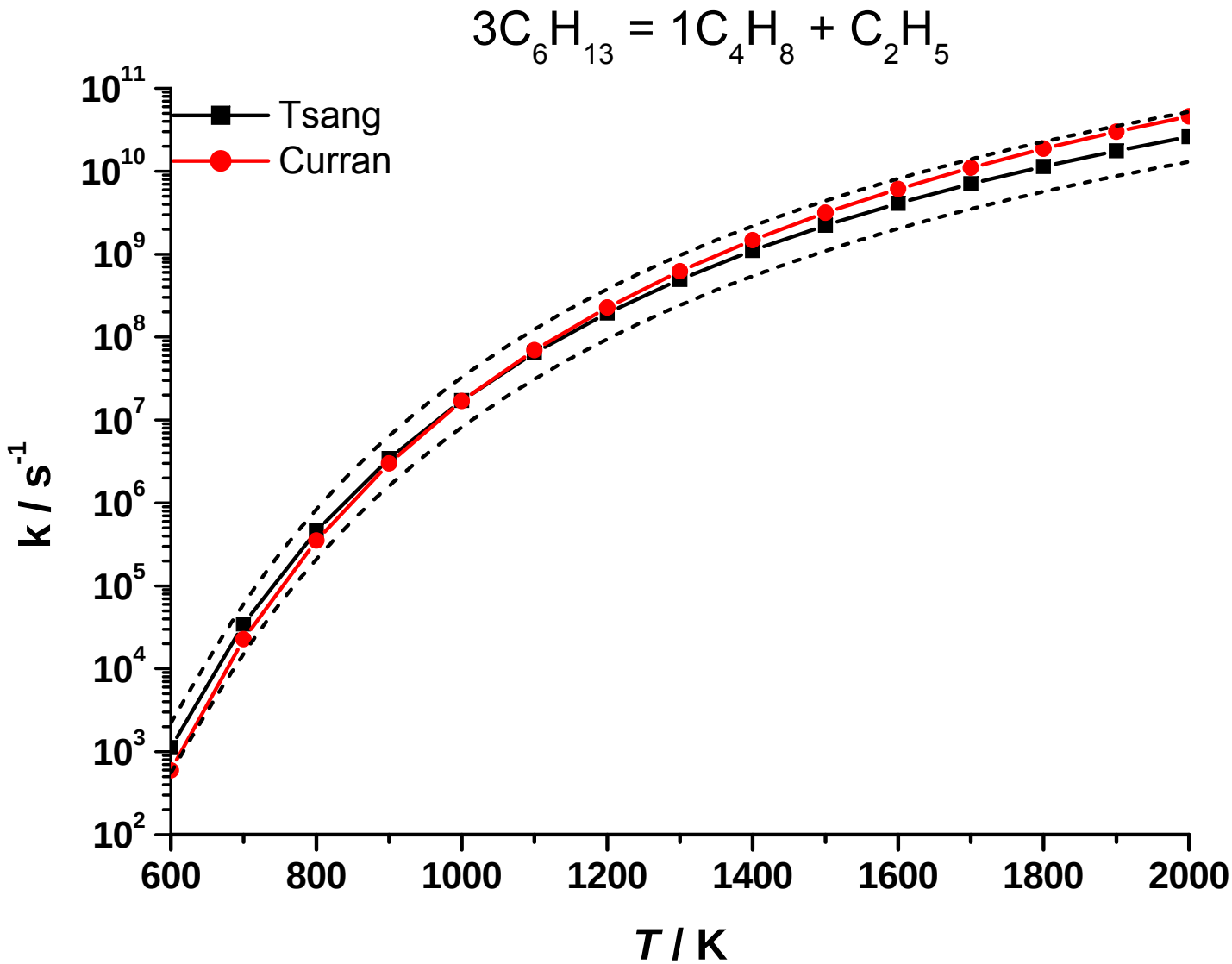
Alkyl radical decomposition

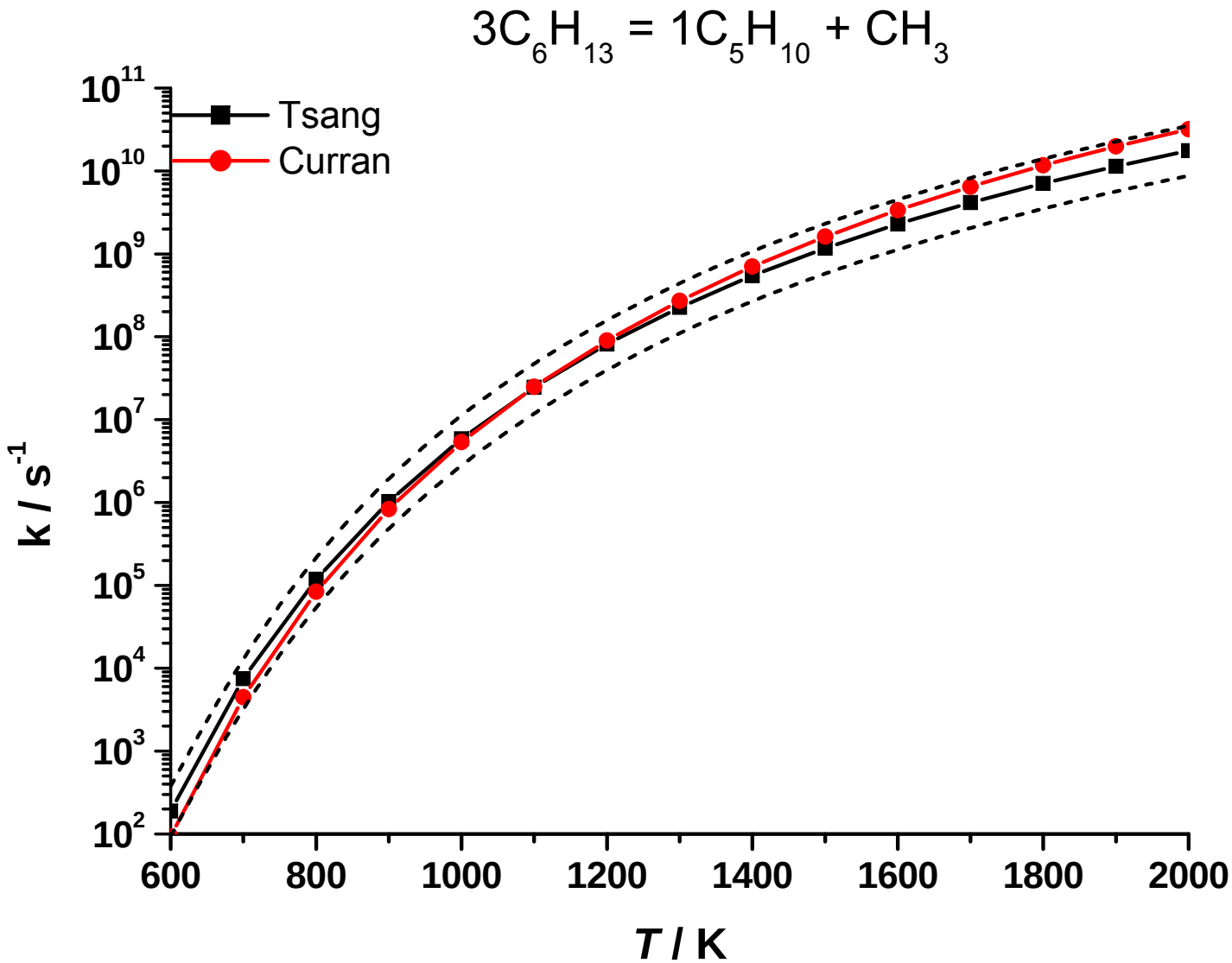
Reaction	A-factor	T^n	Ea (cal/mol)
$C_2H_4 + CH_3 = nC_3H_7$	1.76×10^4	2.48	6130.
$C_2H_4 + C_2H_5 = nC_4H_9$	1.00×10^4	2.48	6130.
$C_2H_4 + nC_3H_7 = 1C_5H_{11}$	5.71×10^3	2.48	6130.
$C_2H_4 + nC_4H_9 = 1C_6H_{11}$	3.26×10^3	2.48	6130.
$C_2H_4 + 1C_5H_{11} = 1C_7H_{15}$	1.86×10^3	2.48	6130.
$iC_4H_8 + tC_4H_9 = cC_8H_{17}$	6.09×10^2	2.48	6130.
$C_3H_6 + CH_3 = iC_4H_9$	1.89×10^3	2.67	6850.
$iC_4H_8 + iC_4H_9 = aC_8H_{17}$	6.09×10^2	2.48	8520.



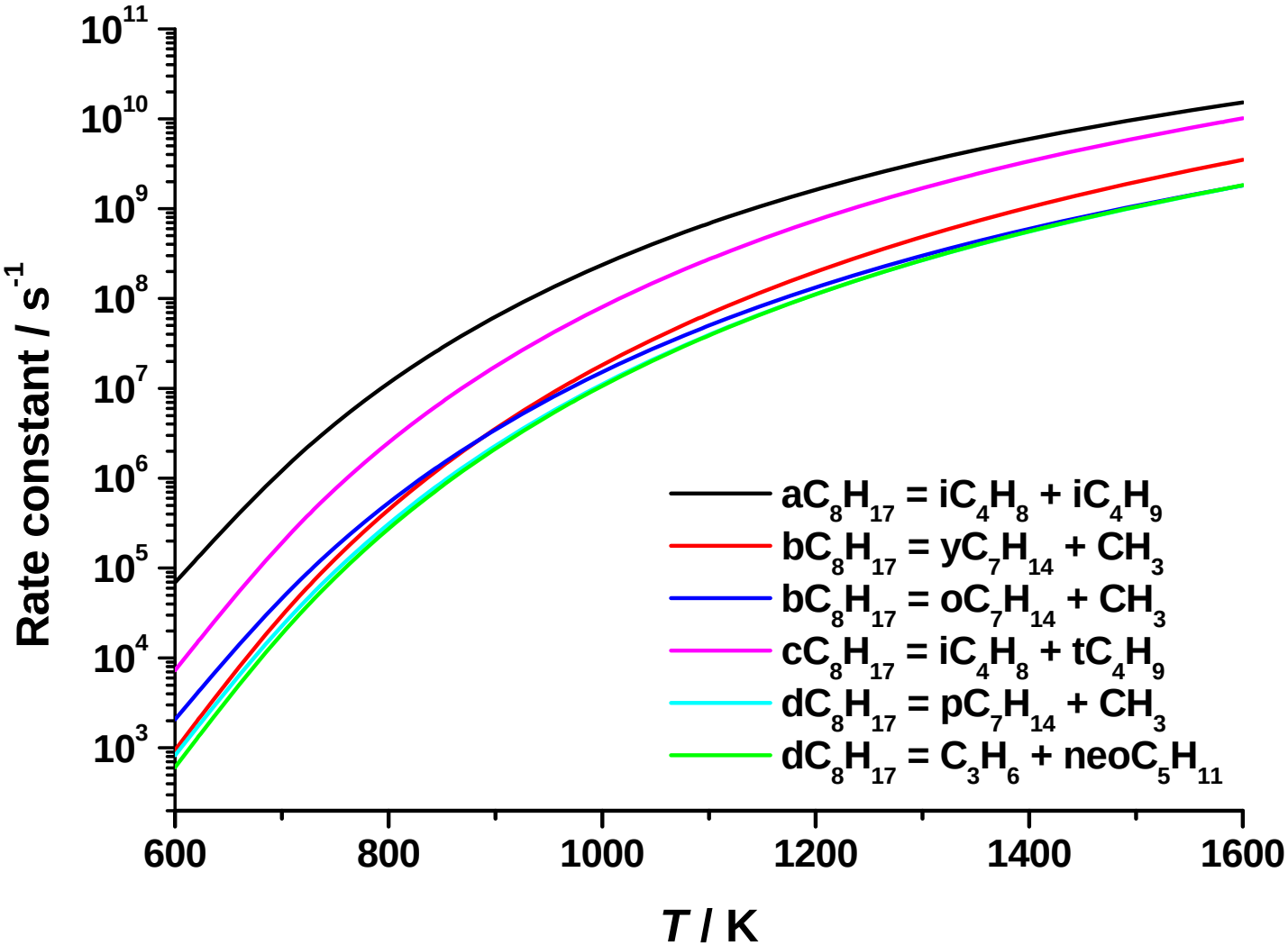
Wing Tsang, James A. Walker, Jeffrey A. Manion, ***Proc Combust. Inst. 32 (2009) 131-138.***


$2C_6H_{13} = C_3H_6 + nC_3H_7$
Tsang
Curran
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
10^{4}
10^{3}
10^{2}
k / s^{-1}
600
800
1000
1200
1400
1600
1800
2000
T / K

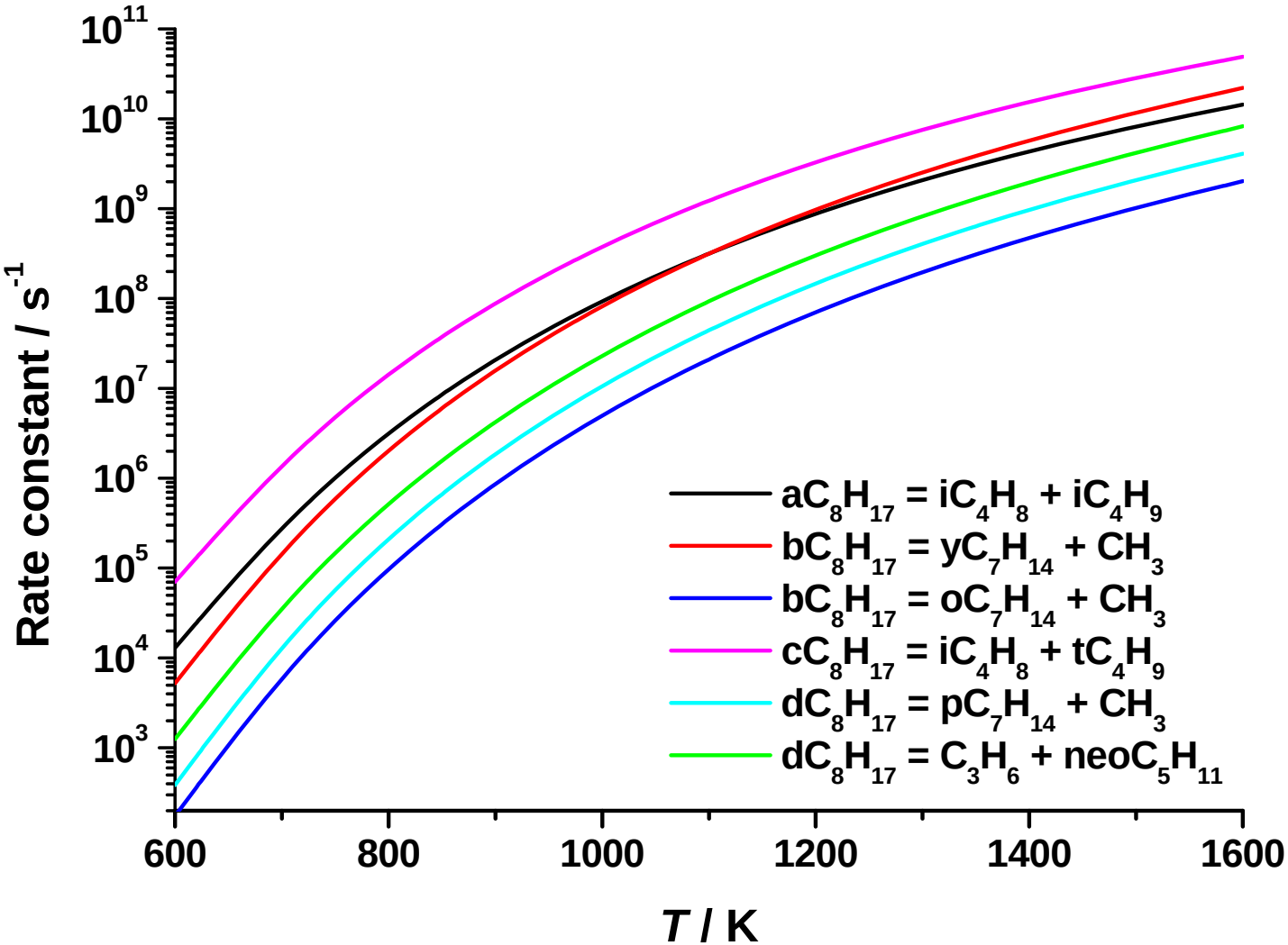

$3C_6H_{13} = 1C_4H_8 + C_2H_5$
Tsang
Curran
k / s^{-1}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
10^{4}
10^{3}
10^{2}
600
800
1000
1200
1400
1600
1800
2000
T / K

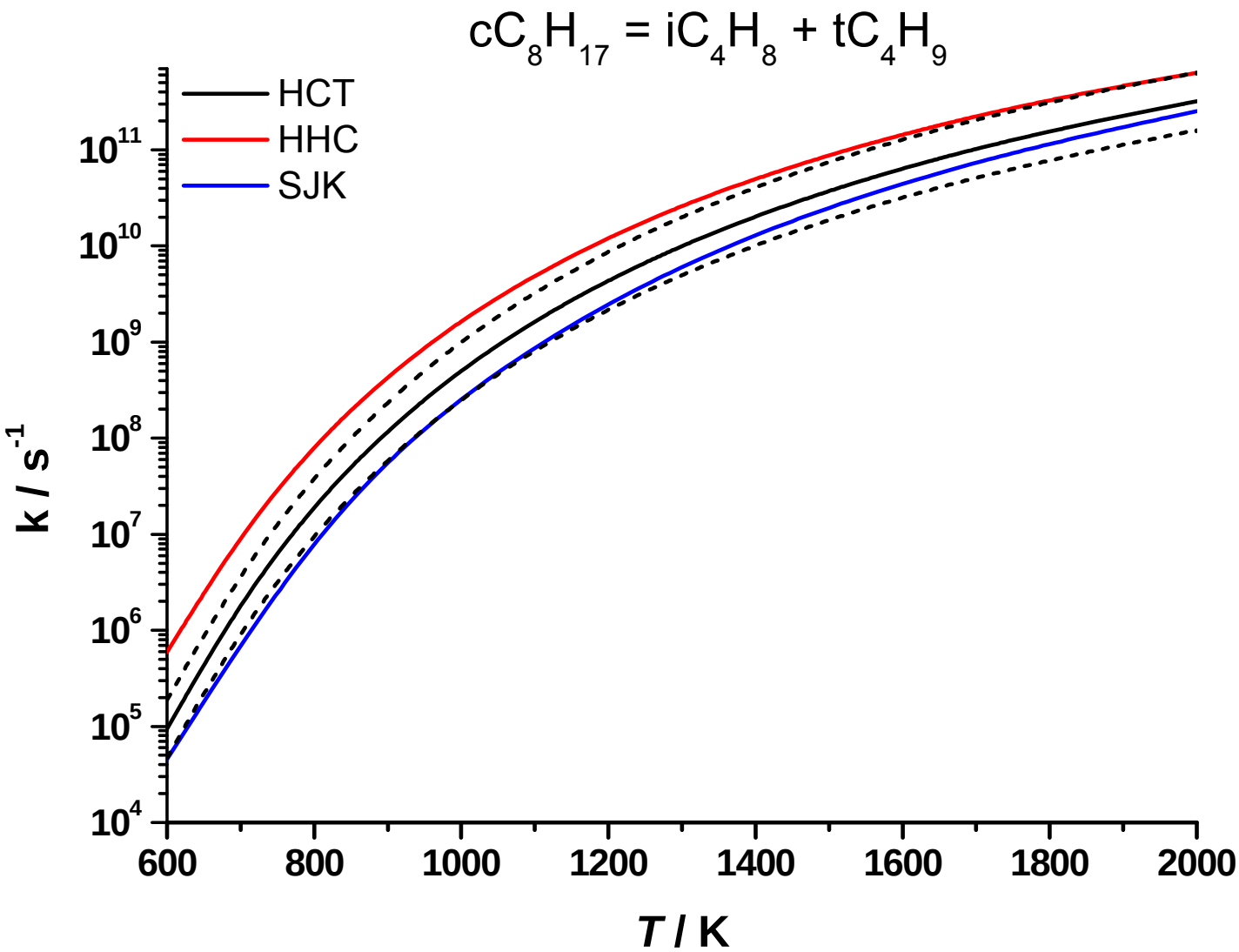

$3C_6H_{13} = 1C_5H_{10} + CH_3$
Tsang
Curran
k / s^{-1}
10^{11}
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
10^{4}
10^{3}
10^{2}
600
800
1000
1200
1400
1600
1800
2000
T / K

Alkyl radical decomposition

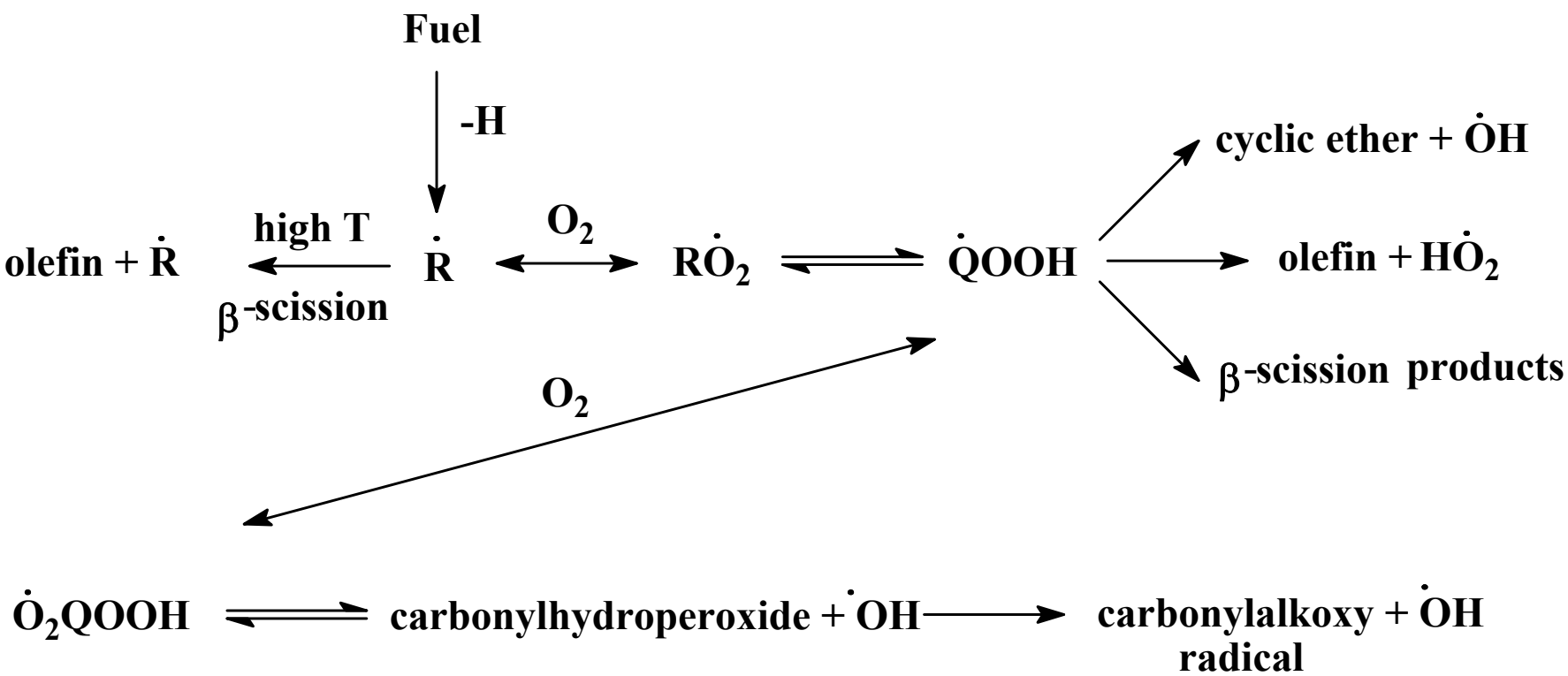


Alkyl radical decomposition




cC8H17 = iC4H8 + tC4H9
HCT
HHC
SJK
k / s-1
10^11
10^10
10^9
10^8
10^7
10^6
10^5
10^4
600
800
1000
1200
1400
1600
1800
2000
T / K

Fuel Oxidation Reaction Scheme



New/modified reaction classes

- 1. $O_2QOOH \rightleftharpoons$ Alt. H-atom isomerisation
- 2. $O_2QOOH \rightarrow$ cyclic ether + OH
- 3. $RO_2 + OH \rightarrow RO + HO_2$
- 4. $RO_2 + HO_2 \rightarrow ROOH + O_2$
- 5. $RO_2 \rightleftharpoons QOOH$
- 6. $O_2QOOH \rightleftharpoons$ carbonylhydroperoxide + OH
- 7. QOOH intramolecular isomerisation
- 8. $RO_2 \rightarrow$ Olefin + HO_2 (concerted elimination)

Large distribution of products species

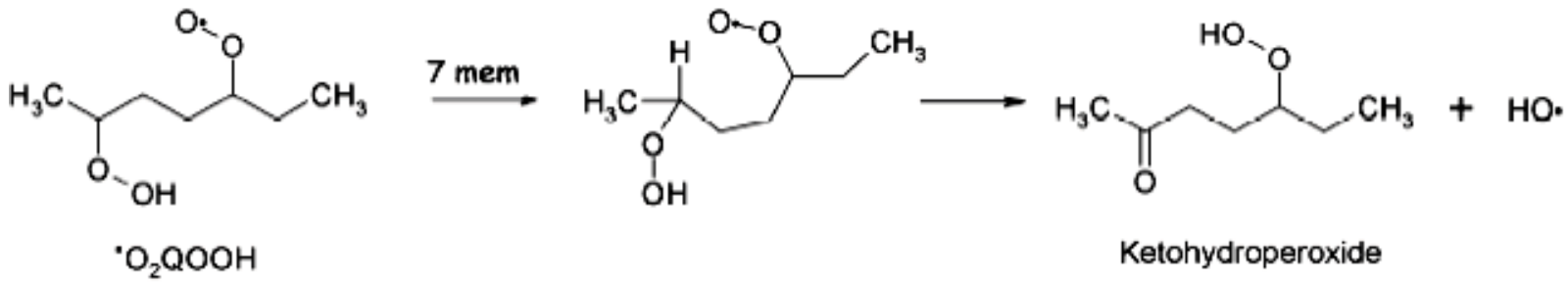
M.S. Kurman, R.H. Natelson, N.P. Cernansky, D.L. Miller

6th US National Combustion Meeting, Paper 23G2 2009

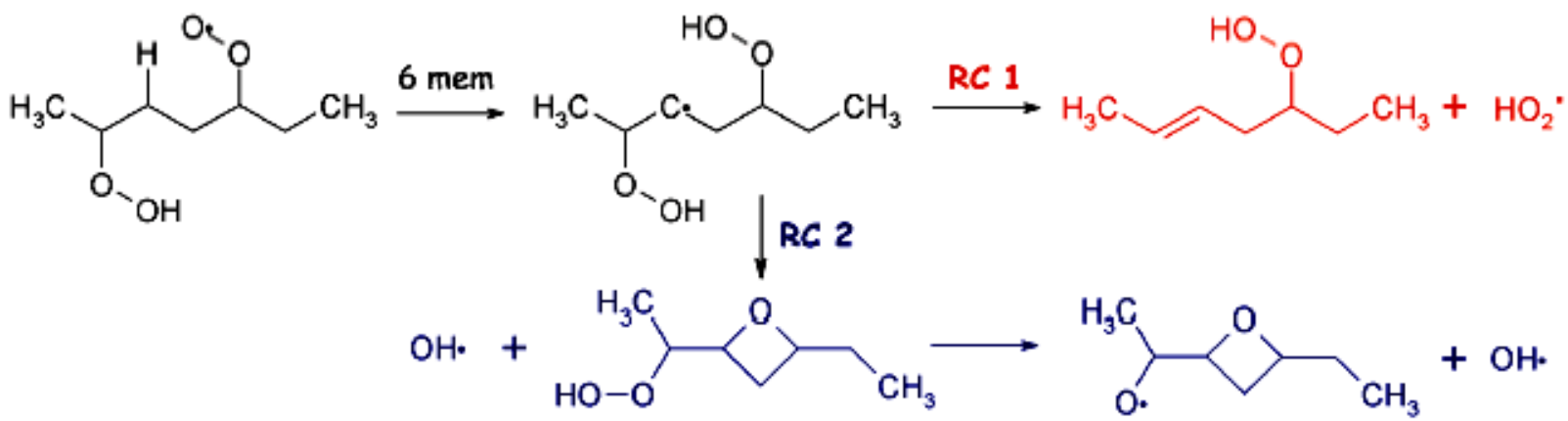
- Alkanes, alkenes, alkynes, dienes, cycloalkenes, alcohols, aldehydes, ketones, diones, carboxylic acids, cyclic ethers, lactones, non-cyclic ethers and esters, dioxins and other species.

- Many of these species are included in current mechanisms but some are not.

$O_2QOOH \rightleftharpoons$ alternative isomerisation

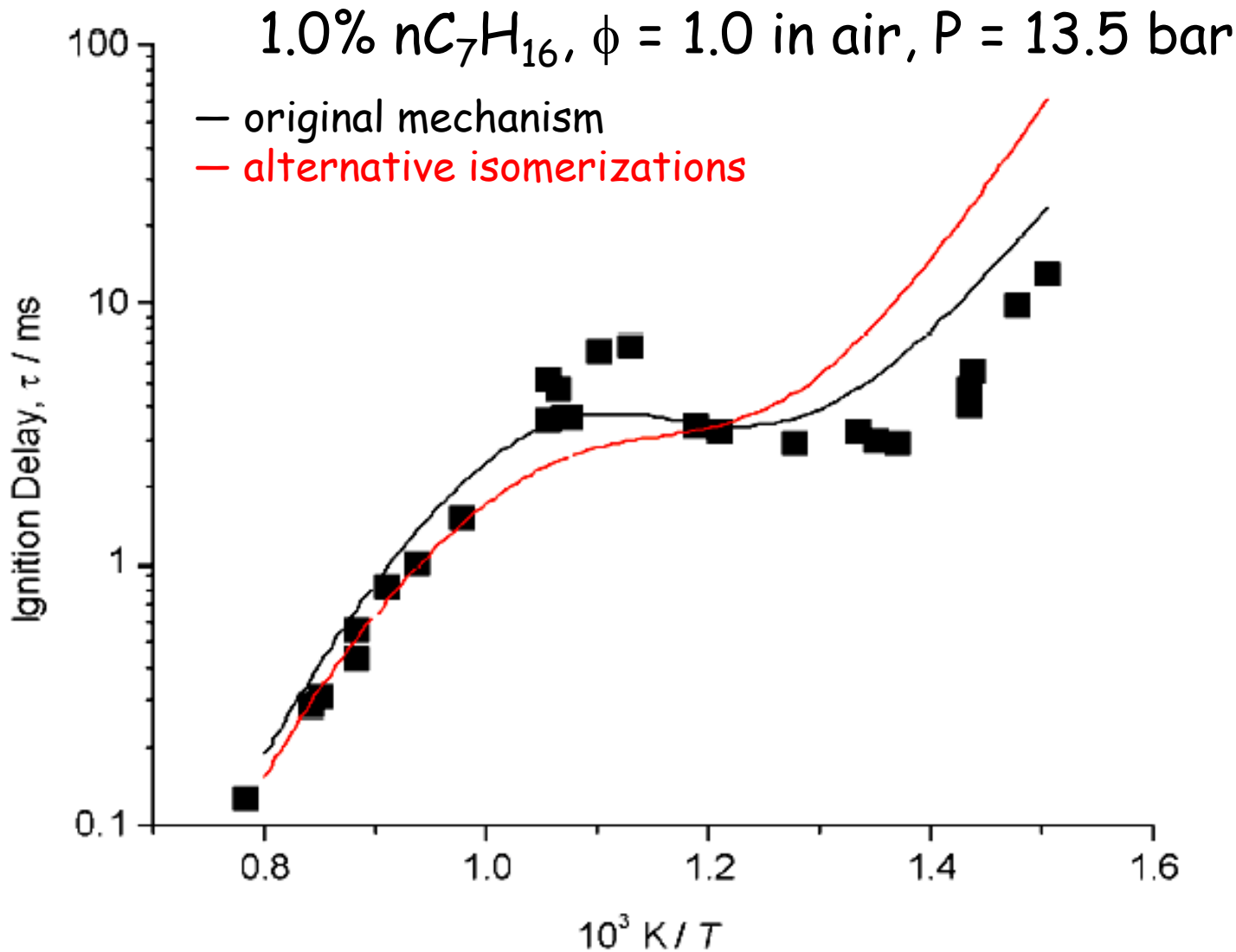


Conventional chemistry

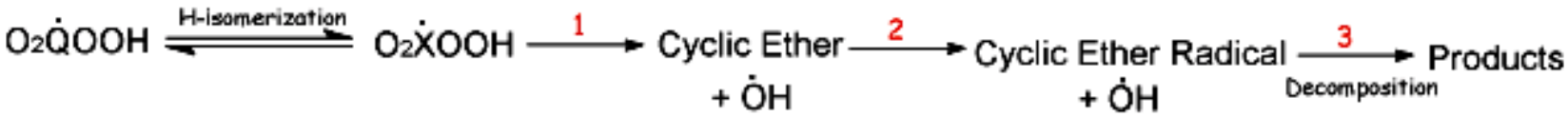


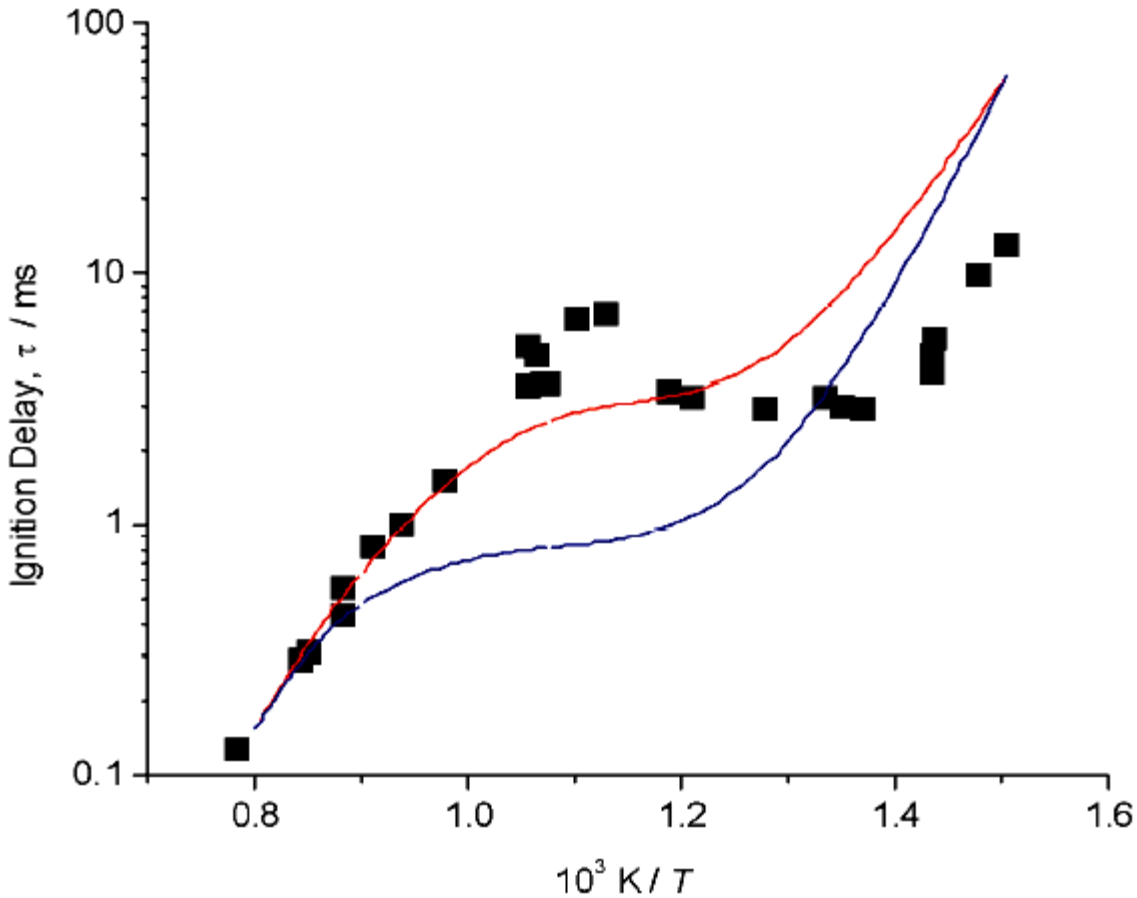
Alternative chemistry

$O_2QOOH \rightleftharpoons$ alternative isomerisation

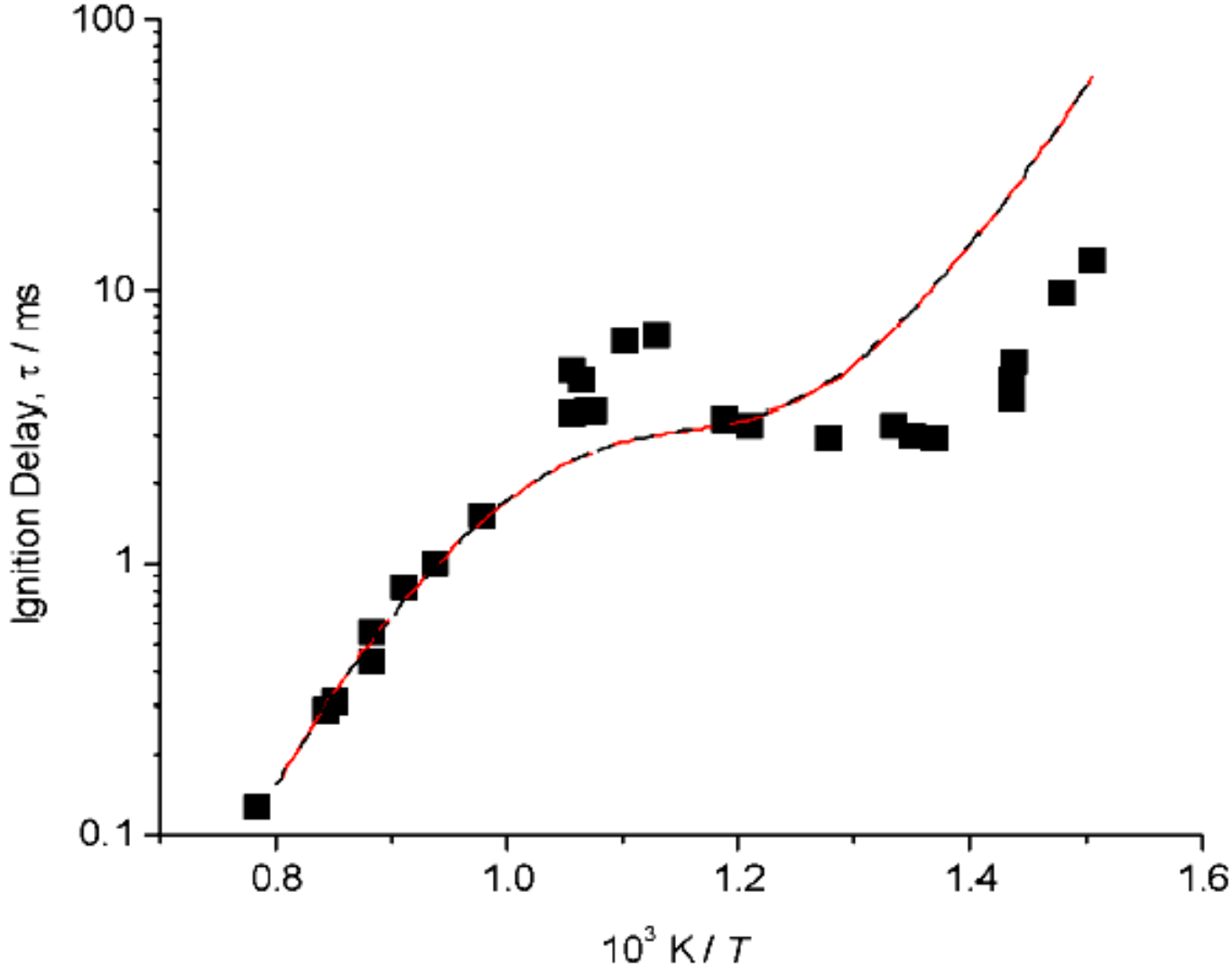


$O_2QOOH \rightarrow$ cyclic ether + OH

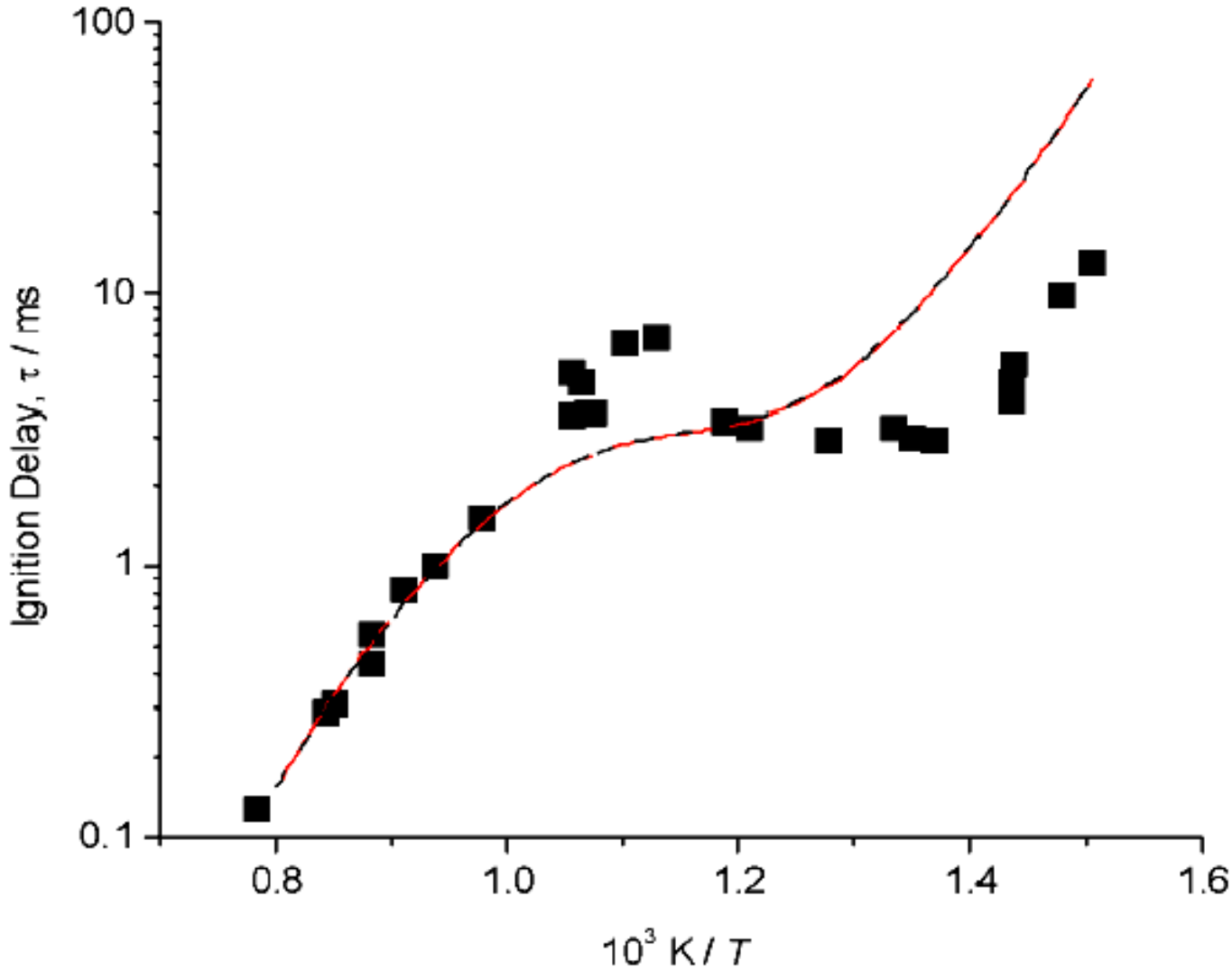




$RO_2 + OH \rightarrow RO + HO_2$



$RO_2 + HO_2 \rightarrow ROOH + O_2$



$$RO_2 \rightleftharpoons QOOH$$

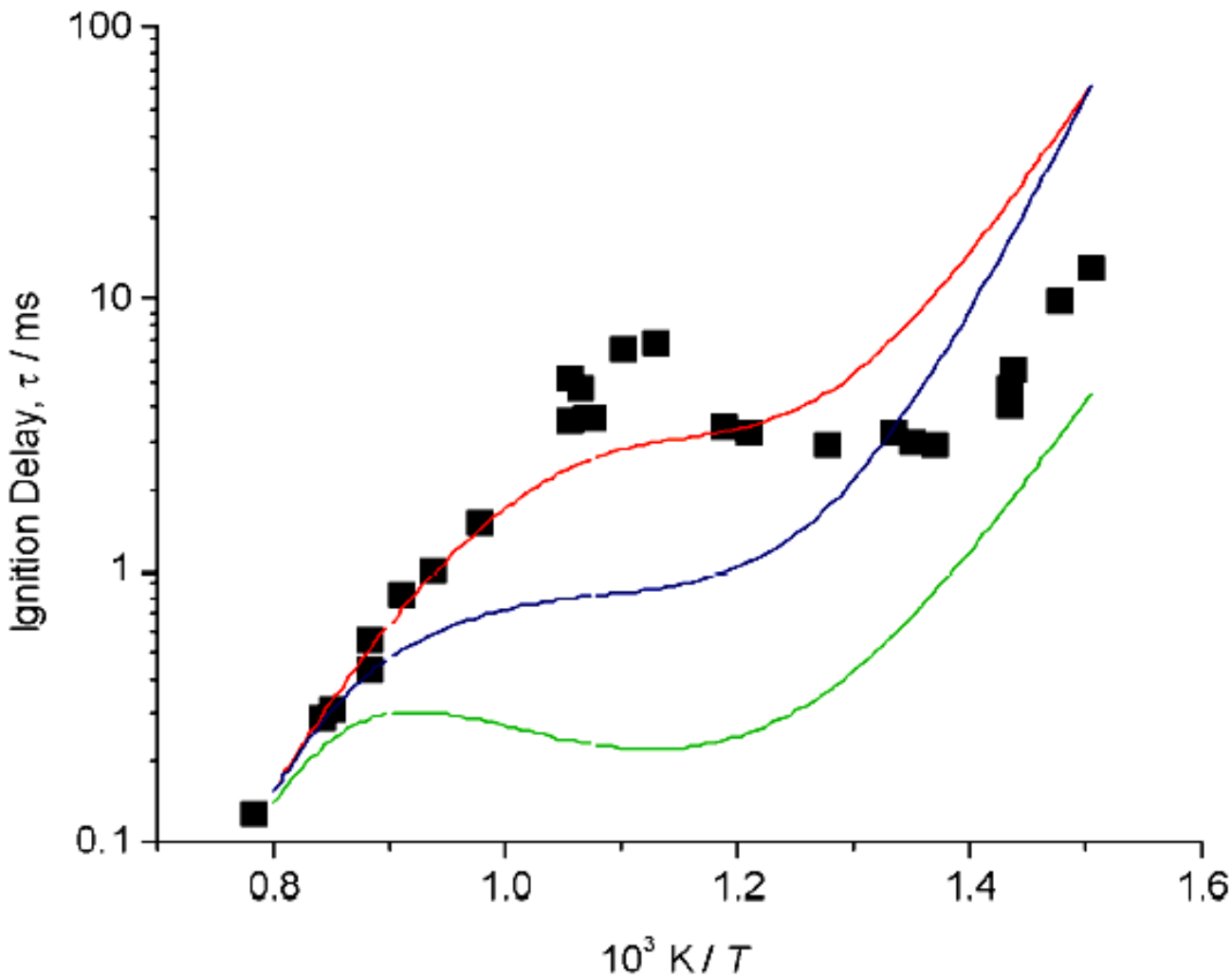
$$O_2QOOH \rightleftharpoons \text{carbonylhydroperoxide} + OH$$

- R. Sumathi and W.H. Green
  - *ab-initio* calculations at the CBS-QB3 level

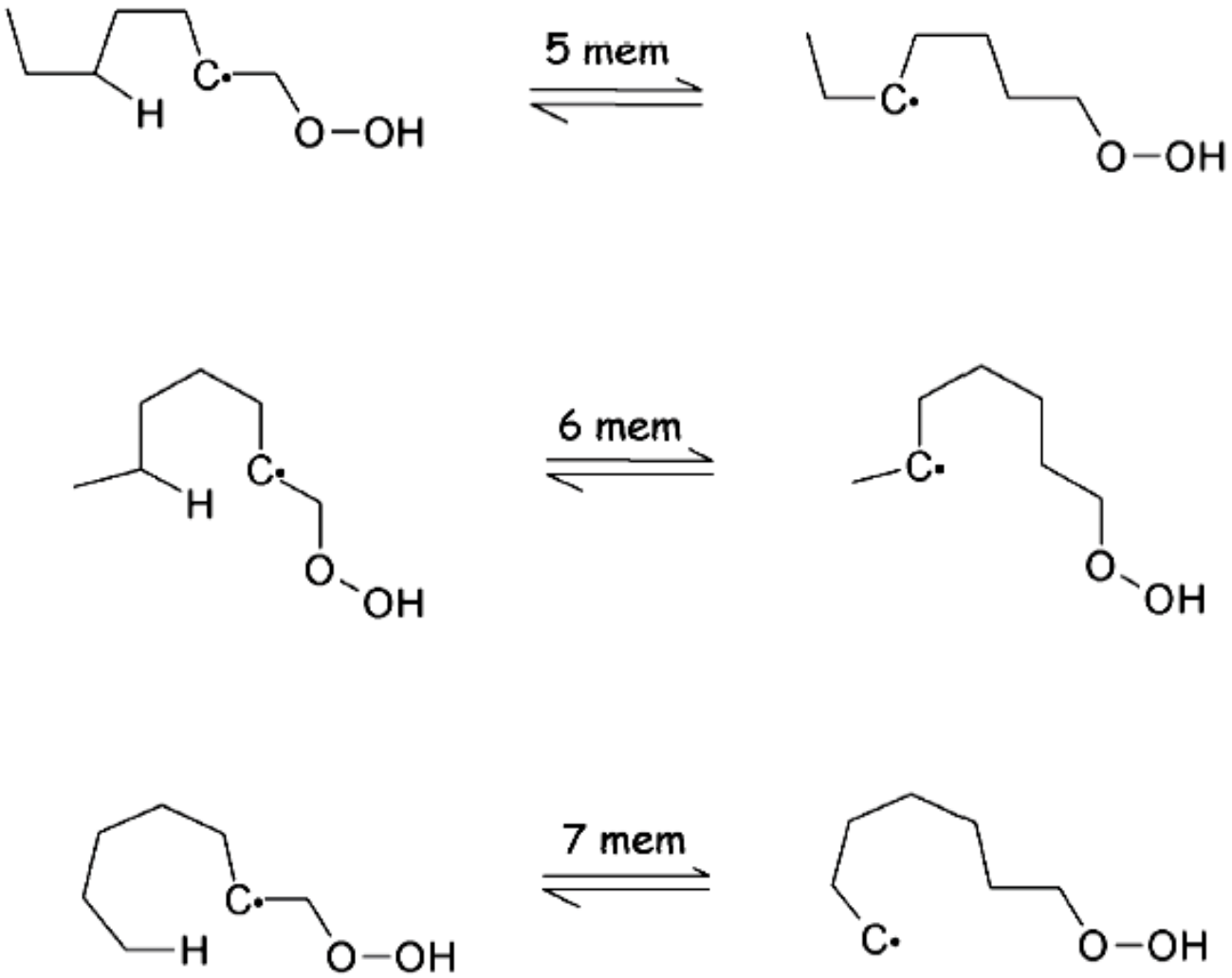
- Rate constants for isomerization significantly faster (x 10) than present Curran recommendations

$RO_2 \rightleftharpoons QOOH$

$O_2QOOH \rightleftharpoons$ carbonylhydroperoxide + OH



QOOH Intramolecular isomerisation



QOOH Intramolecular isomerisation

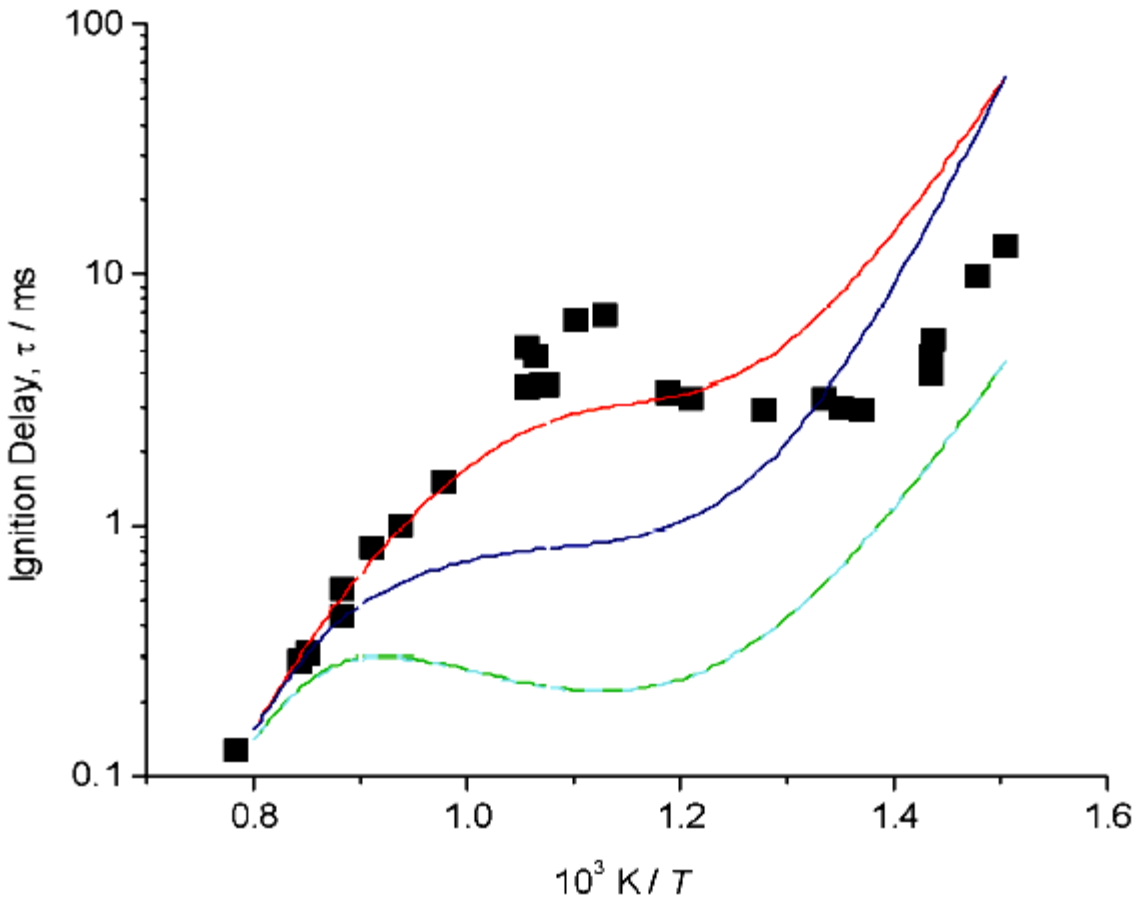


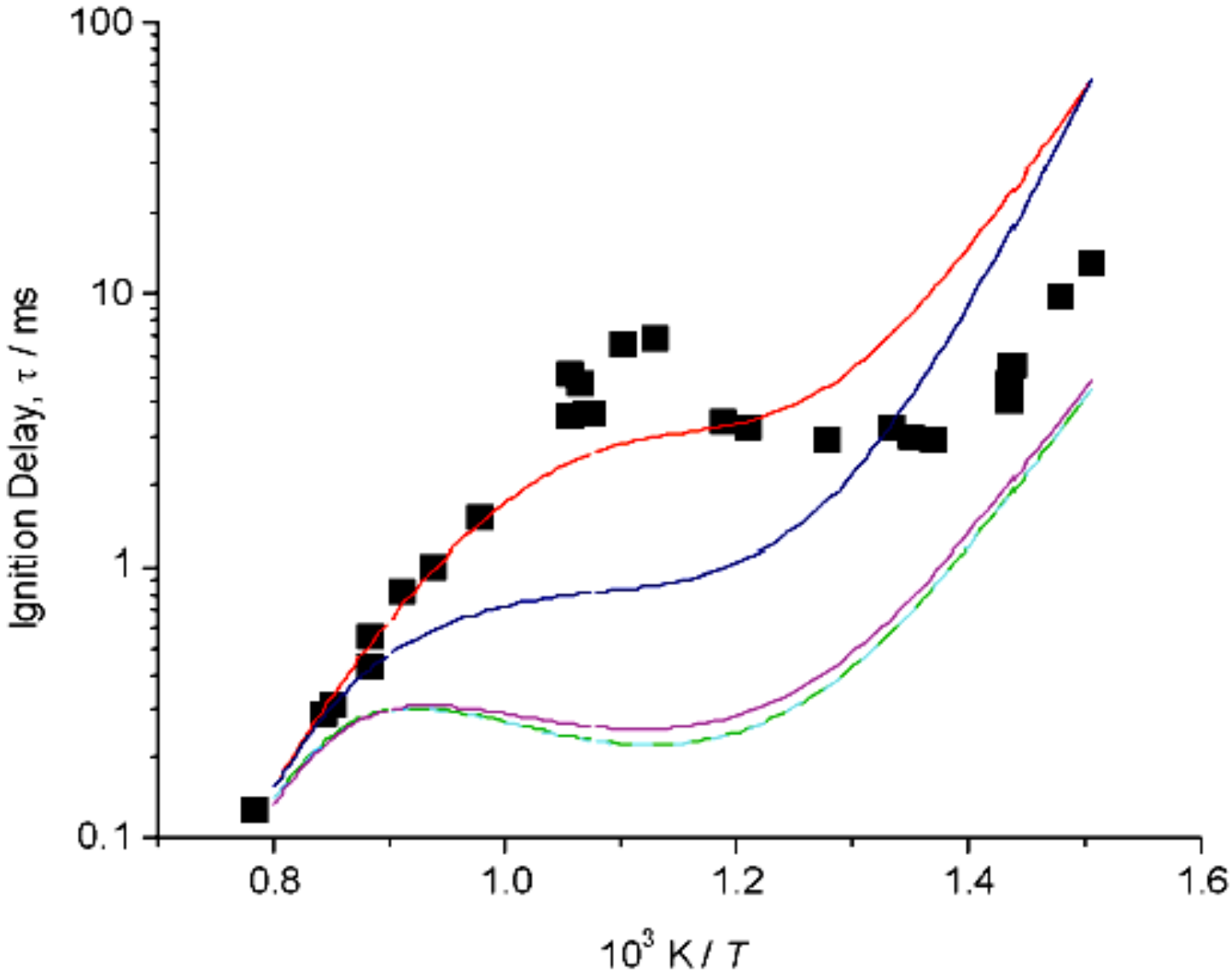
Figure 5.13: *n*-Heptane, $\phi = 1.0$ and ~ 13.5 bar: ■ Ciezki *et al* [58], — *this study* plus reaction class 1, — reaction class 1 *and* 2, — reaction class 1, 2, 5 and 6, - - - reaction class 1, 2, 5, 6 *and* 7.

$RO_2 \rightarrow$ olefin + HO_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.

$RO_2 \rightarrow$ olefin + HO_2

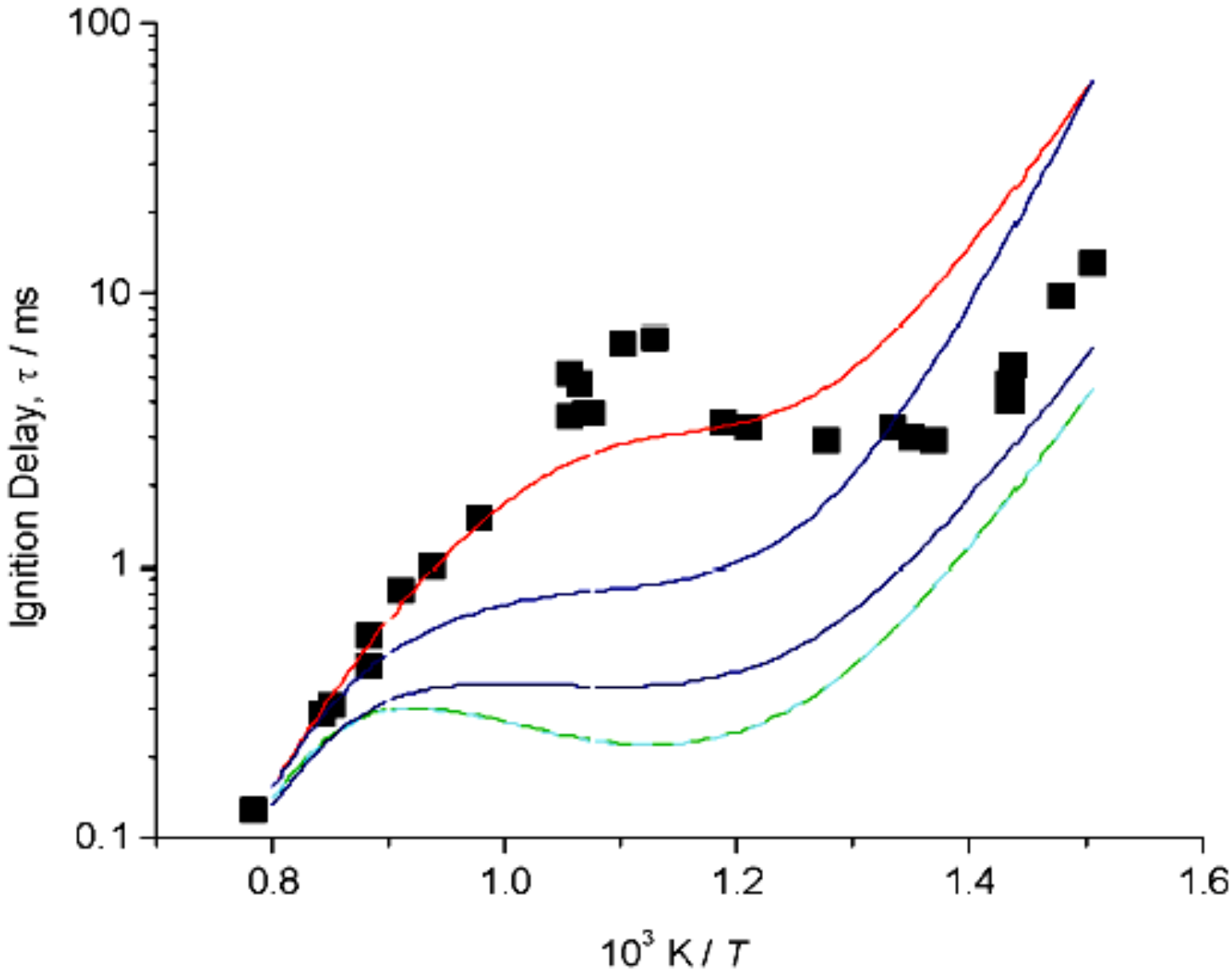


$RO_2 \rightarrow$ olefin + HO_2

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.

$RO_2 \rightarrow$ olefin + HO_2



Conclusions

- Many improvements in the PRF mechanisms
- Large HC mechanism development stemming from smaller species
- Additional reactions are occurring
  - These reactions can have a large influence on overall reactivity
  - Current mechanisms capture large features
    - ignition delay times
    - Speciation
  - Added complexity will lead to enormous mechanisms

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