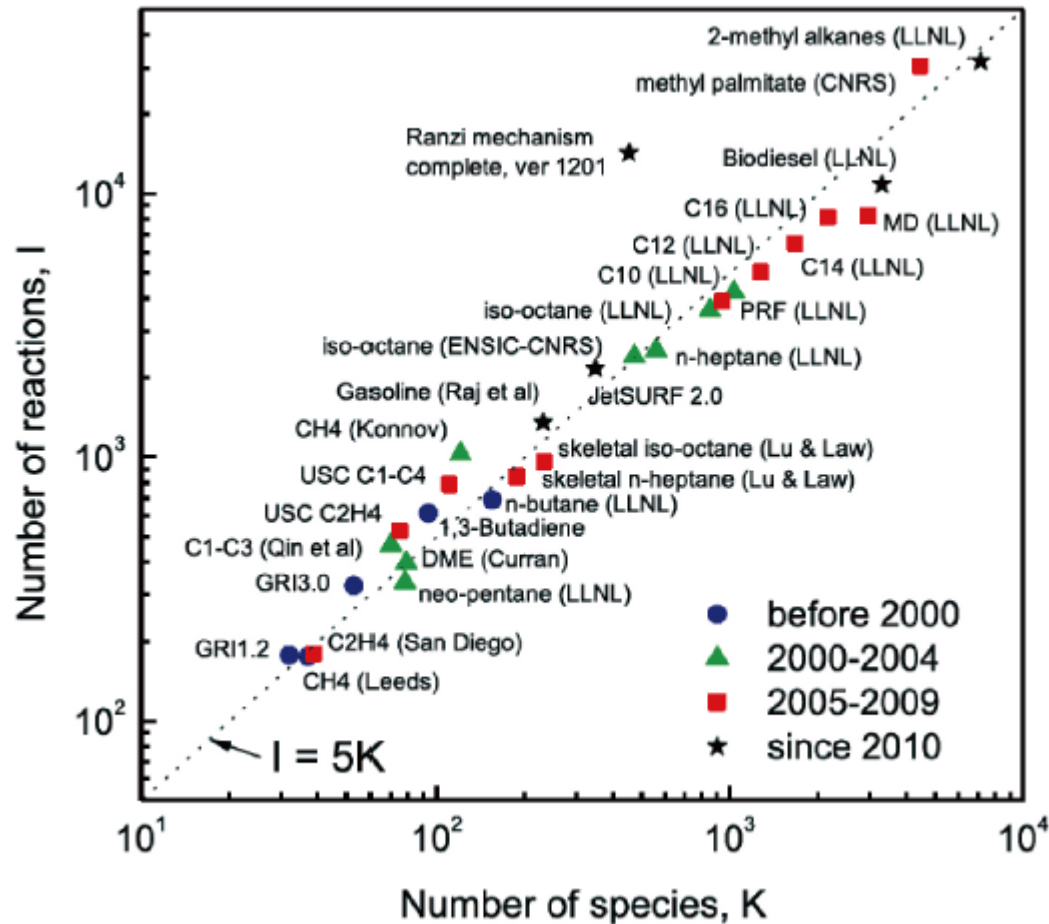


Topic 6

Chemical mechanisms

Examine ways in which mechanisms are constructed, their dependence on rate and thermodynamic data, their evaluation using experimental targets and the optimization of component rate constants using direct and indirect data

Numbers of species and reactions in mechanisms for combustion of hydrocarbon fuels (Lu and Law, Prog En Comb Sci, 2009, 35, 192, updated Yuan et al, Science China (Chemistry), 2017, 60, 1391)



- Larger mechanisms require thousands of rate constants.
- Can't measure them all - calculation essential

Hierarchical approach to combustion mechanisms

- Westbrook and Dryer, Proc. Comb. Inst. 18 (1981) 749-766, Prog. Energy Combust. Sci. 10 (1981) 1-57. Construction of comprehensive, hierarchical chemical mechanisms.
- Build mechanisms up with increasing complexity - O_2 + (i) H_2 (ii) CO/H_2O (iii) CH_4
- Use evaluated rate data where available

Examples of $\text{H}_2 + \text{O}_2$ mechanisms

- Li et al. Int J Chem Kinet 36, (2004) 566-575 based on earlier mechanism by Mueller et al. Updated Burke et al, Int J Chem Kinet 44: 444-474, 2012
- Konnov, Combustion and Flame 152 (2008) 507-528. Examination of uncertainties in rate coefficients based on earlier (2004)mechanism
- Hong et al., Comb and Flame, 158, (2011) 633-644
- Keromnes et al Comb and Flame 160 (2013) 995-1011.

Testing mechanisms against global observables: Li et al

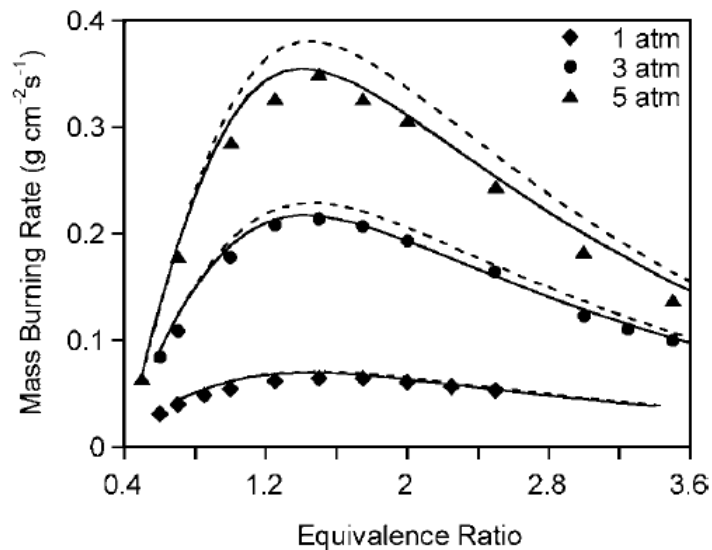


Figure 7 Laminar flame mass burning rate at 1, 3, and 5 atm for $\text{H}_2/\text{O}_2/\text{He}$ mixture ($\text{O}_2:\text{He} = 1:7$). Symbols: experimental data [7]; solid lines: the present model; dashed lines: the model of Mueller et al. [1].

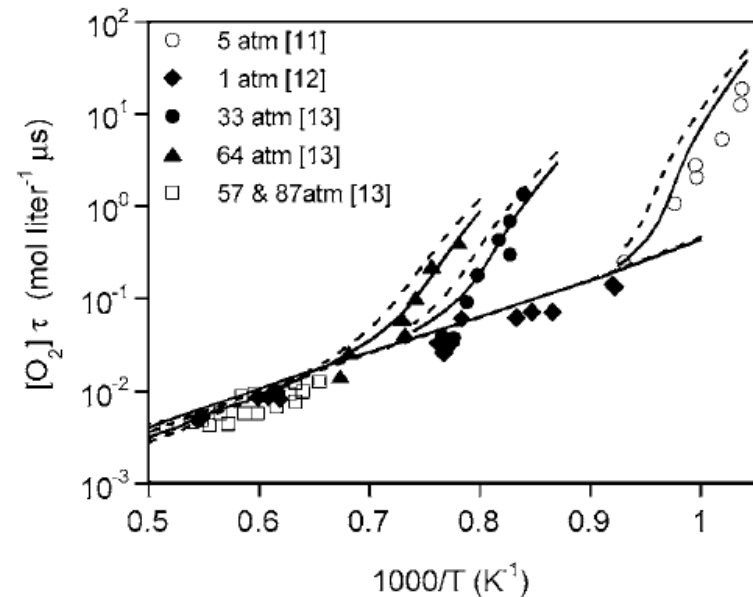
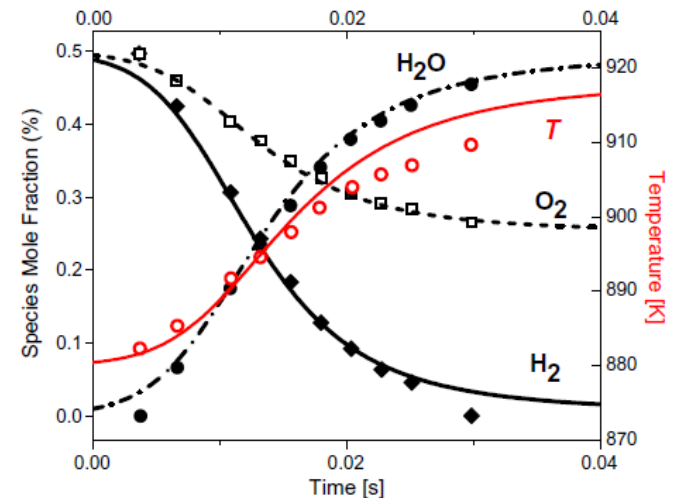
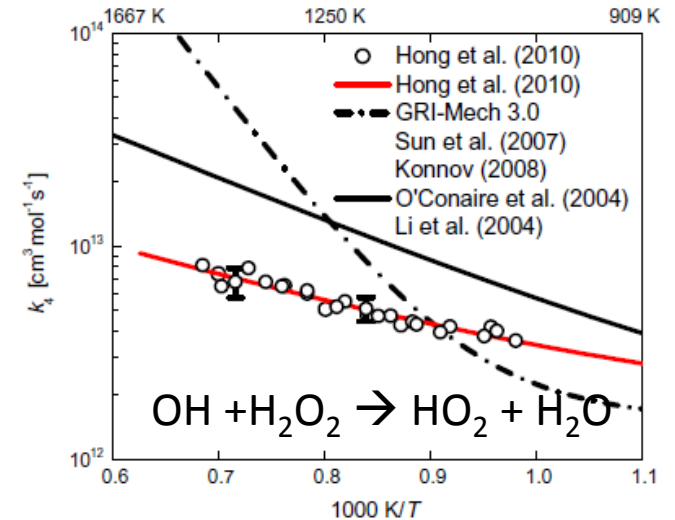
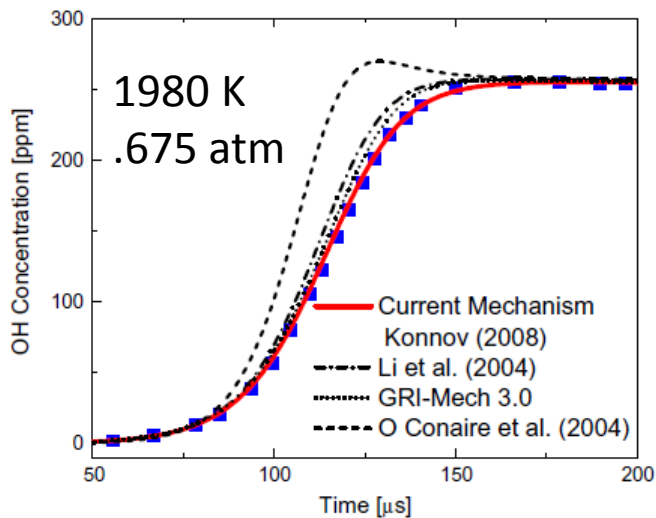
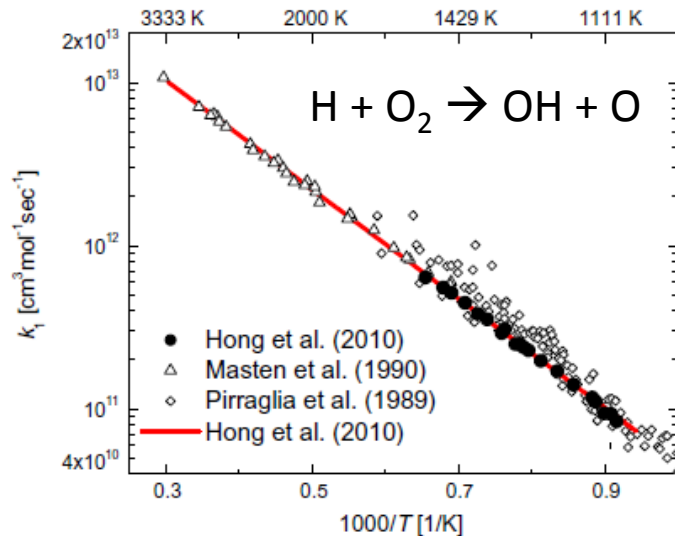


Figure 11 Ignition delay of $\text{H}_2/\text{O}_2/\text{Ar}$ mixtures in shock tubes. Initial conditions: $\text{H}_2 = 8.0\%$, $\text{O}_2 = 2.0\%$ at 5 atm [11]; $\text{H}_2 = 1.0\%$, $\text{O}_2 = 2.0\%$ at 1 atm [12]; $\text{H}_2 = 2.0\%$, $\text{O}_2 = 1.0\%$ at 33, 57, 64, and 87 atm [13]. Symbols: experimental data [11–13]; solid lines: the present model; dashed lines: Mueller et al. [1]. Ignition delay time for the cases of Ref. [11] is defined by the maximum of OH concentration; for Ref. [12], as the time when OH concentration reaches 1×10^{-6} mol/L; and for Ref. [13], by the maximum of $\frac{d[\text{OH}]}{dt}$.

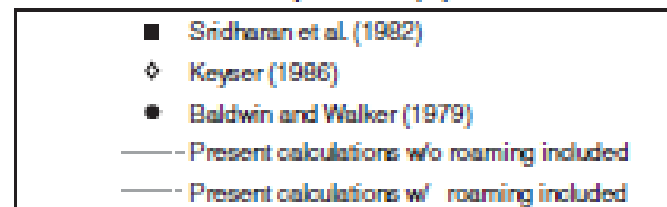
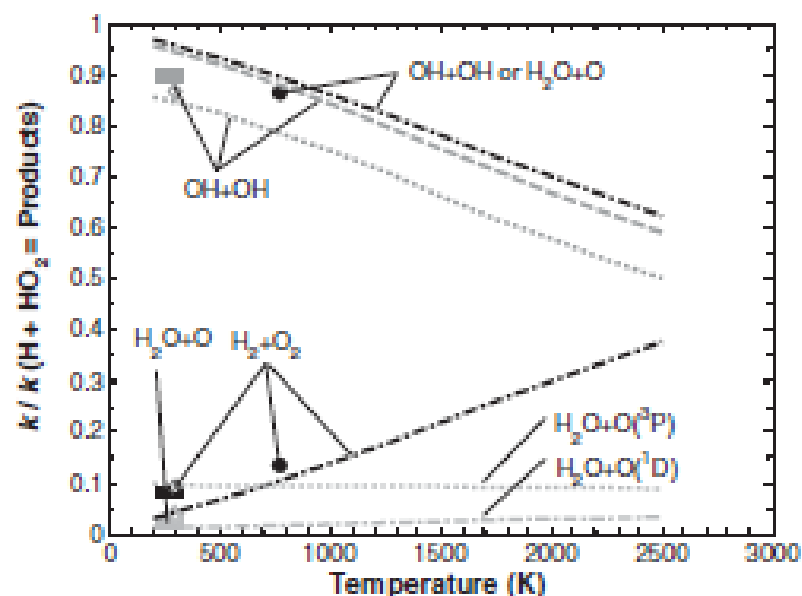
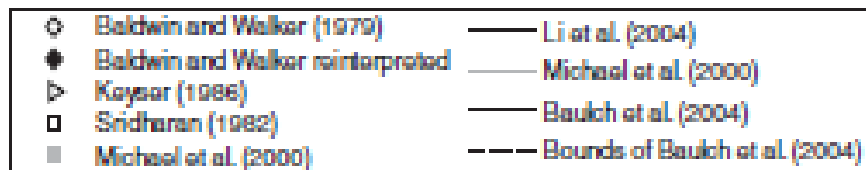
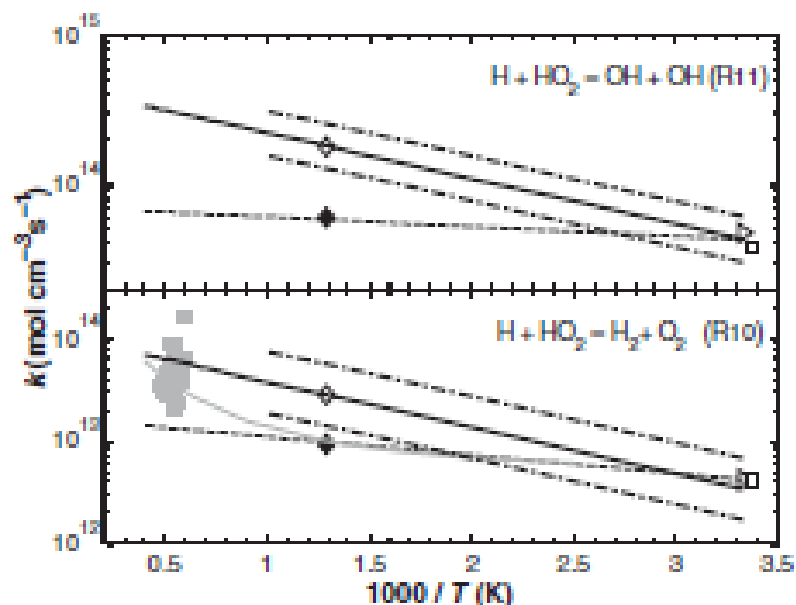
Hong et al.

Revised mechanism using own shock tube data on
 $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$, $\text{H}_2\text{O}_2 + \text{M}$, $\text{OH} + \text{H}_2\text{O}_2$, $\text{OH} + \text{HO}_2$



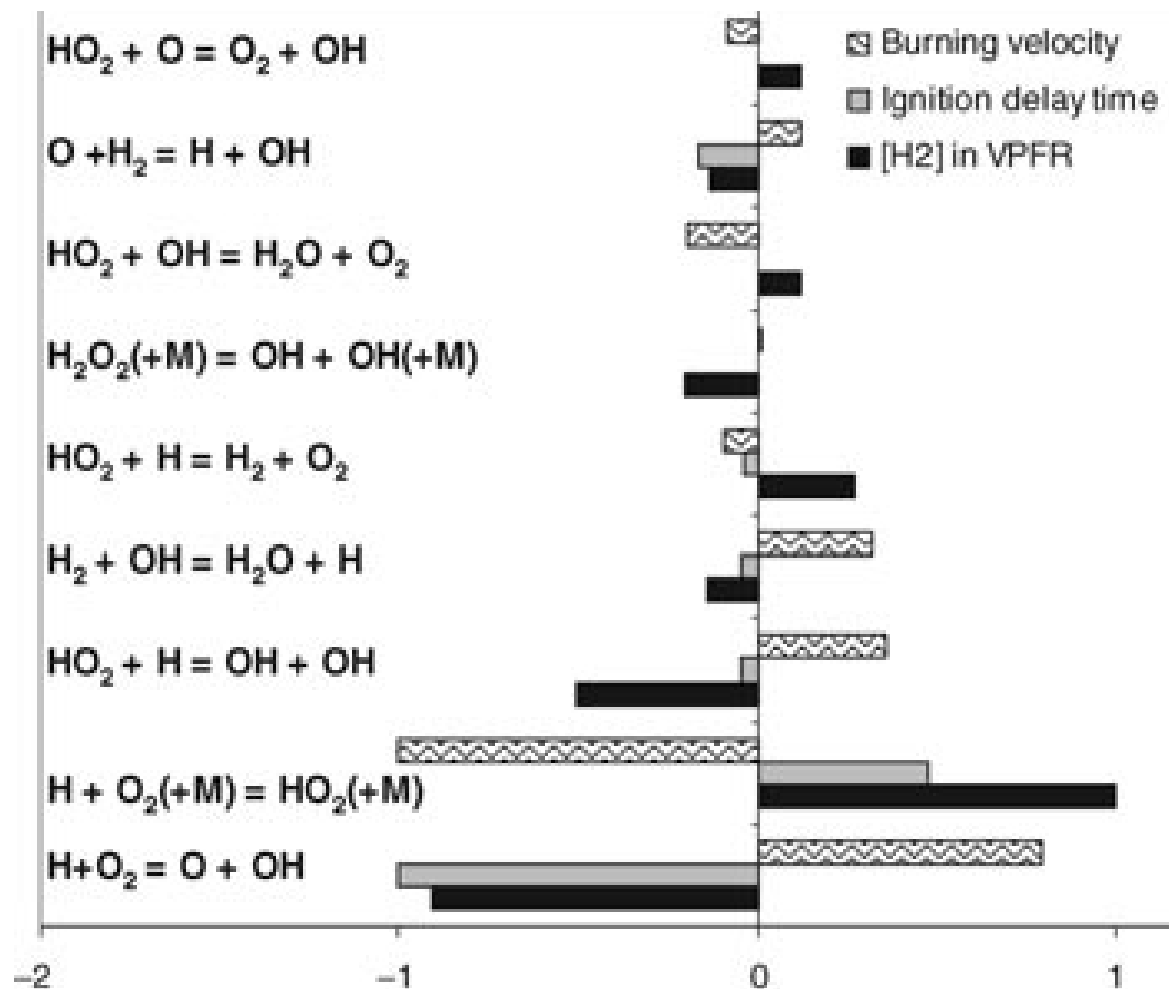
Species profiles, 880 K, 0.3 atm

Burke et al.



Branching ratios

Sensitivity analysis (Burke et al)



A Hierarchical and Comparative Kinetic Modeling Study of C1-C2 Hydrocarbon and Oxygenated Fuels

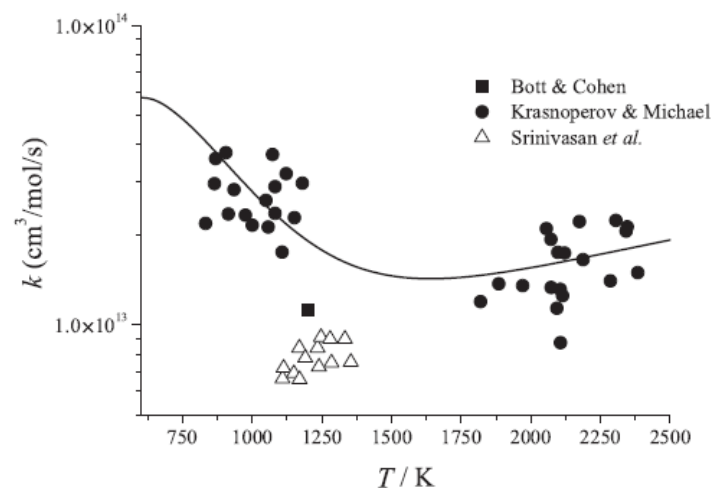
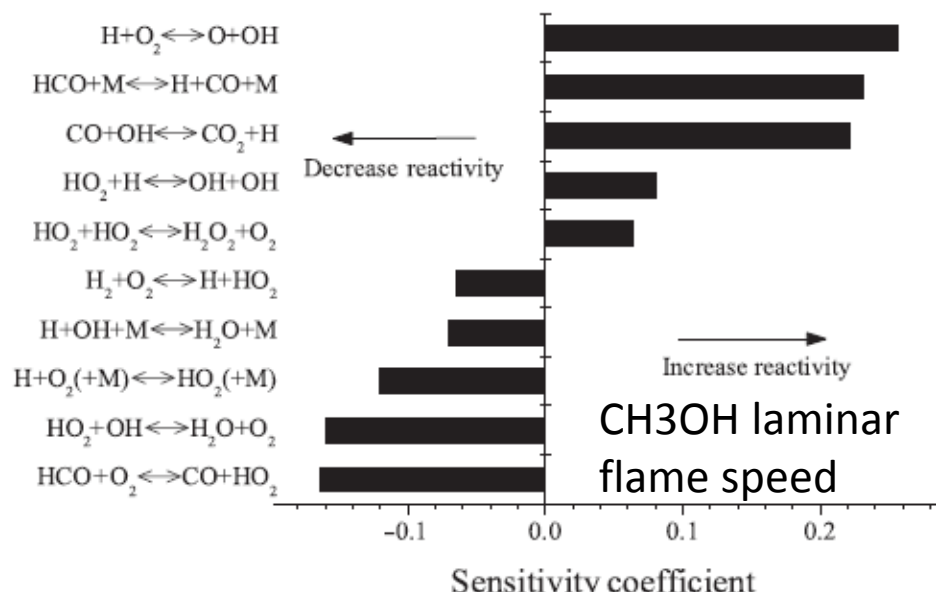
Metcalfe et al, Int J Chem Kinet, 45, 638 (2013)

Table I Range of Experimental Devices Used for Mechanism Validation

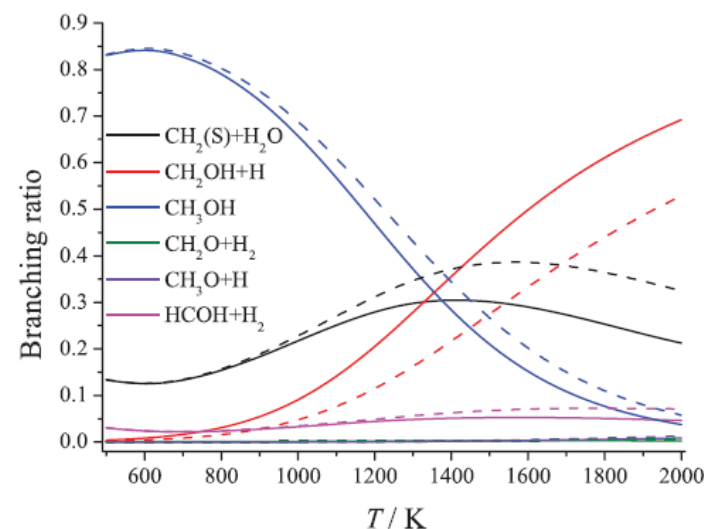
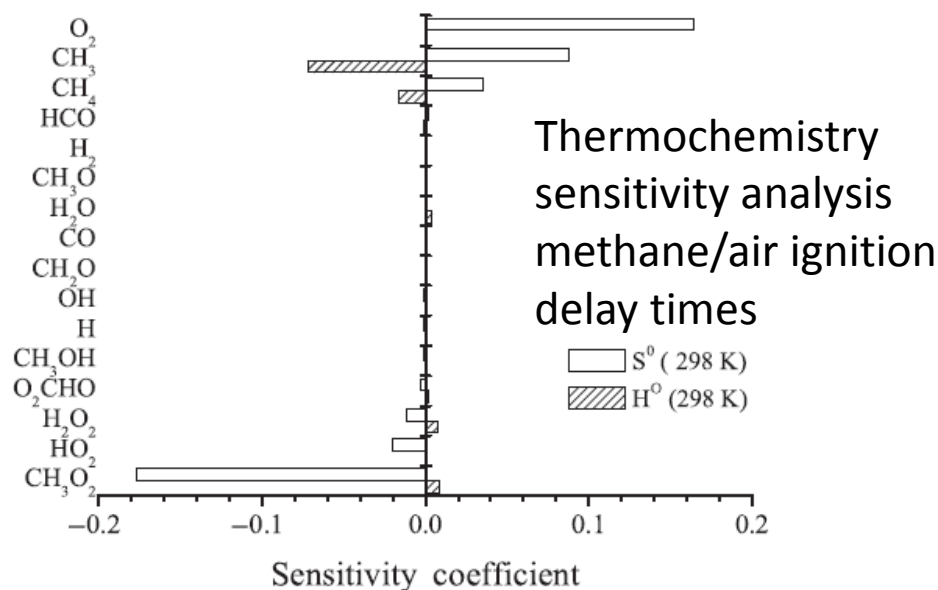
Fuel	Shock Tube	Jet-Stirred Reactor	Flow Reactor	Flame Speed	Flame Speciation
Methane	✓	✓	✓	✓	
Ethane	✓	✓		✓	
Ethylene	✓	✓	✓	✓	✓
Acetylene	✓	✓	✓	✓	✓
Formaldehyde			✓		✓
Acetaldehyde	✓	✓	✓		
Methanol	✓	✓	✓	✓	
Ethanol	✓	✓	✓	✓	✓
Methane/ethane	✓	✓		✓	
Temperature (K)	833–2500	800–1260	600–1400	295–600	300–2300
Pressure (atm)	0.65–260	1–10	1.0–59.22	1–10	0.026–0.05
Equivalence ratio (ϕ)	0.06–6.0	0.25–5.0	0.05–5.0	0.4–2.2	0.75–2.4

- Mechanisms evaluated using ignition delays, laminar burning velocities and flame speeds,

Examples of sensitivity analyses and optimised rate data



Recommended $k(\text{CH}_3 + \text{OH})$



Reaction channels in $\text{CH}_3 + \text{OH}$ vs theory

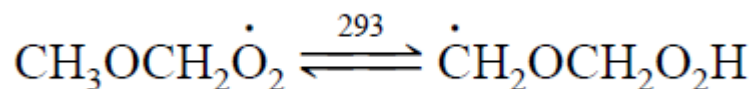
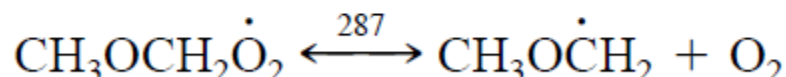
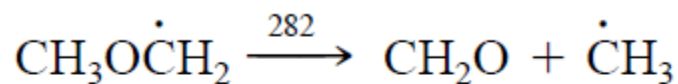
More complex mechanisms 1.

Oxidation of C1-C5 Alkane Quinternary Natural Gas Mixtures at High Pressures *Energy Fuels* 2010, 24, 1521-1528

- Rapid compression machine and shock tube
- detailed chemical kinetic mechanism
- . Mixtures of $\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8/\text{n-C}_4\text{H}_{10}/\text{n-C}_5\text{H}_{12}$ studied in the temperature range 630-1550 K, in the pressure range 8-30 bar, and at equivalence ratios of 0.5, 1.0, and 2.0 in air
- Mechanism: NUIG Combustion Chemistry Centre, Natural Gas III mechanism, 2011. Available at <http://c3.nuigalway.ie/naturalgas3.html>. (See more recent developments later in lecture)

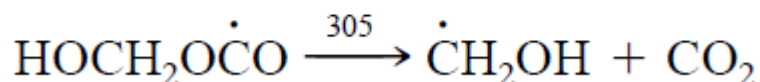
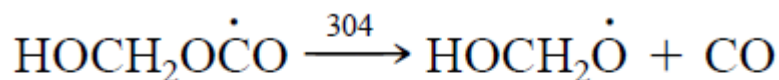
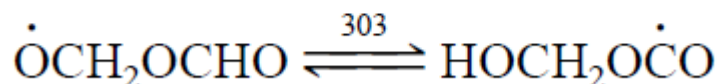
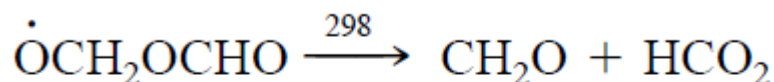
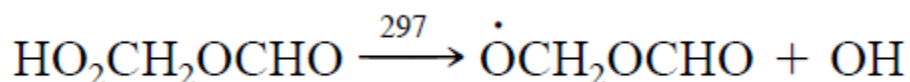
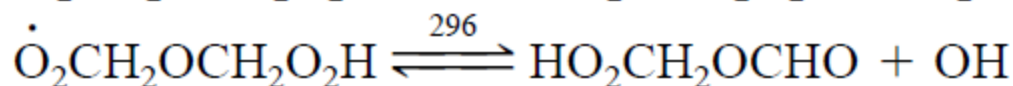
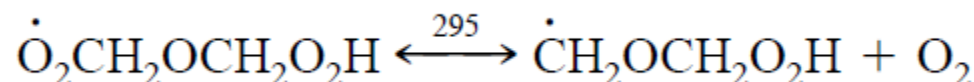
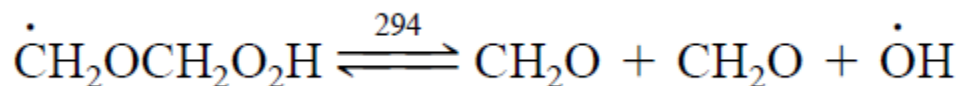
More complex mechanisms 2.

Curran et al, low T dimethyl ether oxidation



$$\varepsilon_a = \Delta H_{\text{rxn}} + \text{ring strain} + E_{\text{abst}}$$

$$E_{\text{abst}} = 12.7 + (\Delta H_{\text{rxn}} \times 0.37)$$



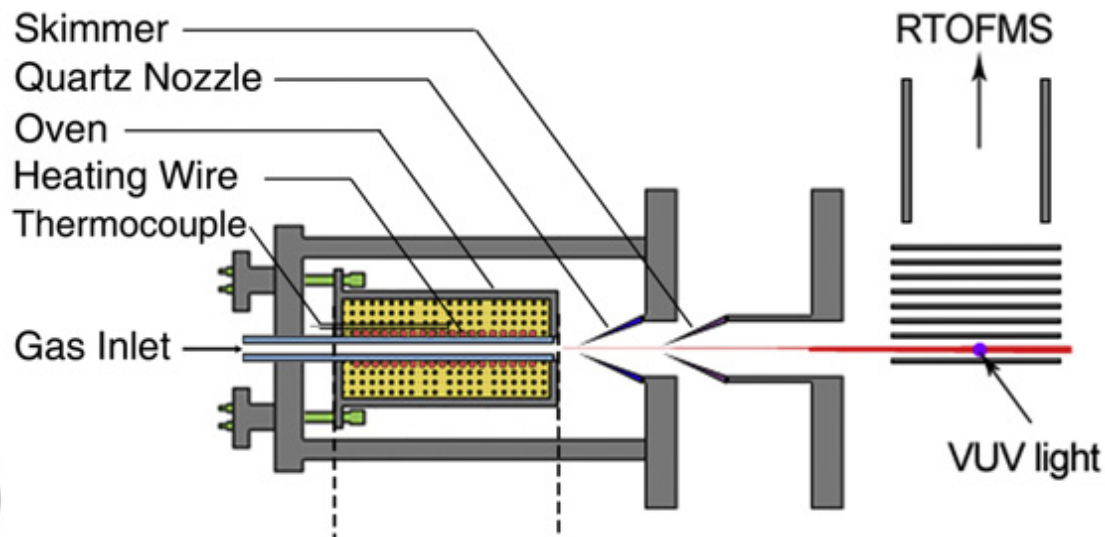
Most of rate coefficients have not been measured and were estimated - e.g. through relations with thermodynamic data.

Int J Chem Kinet, 2000, 32, 741

See discussion in Topic 7

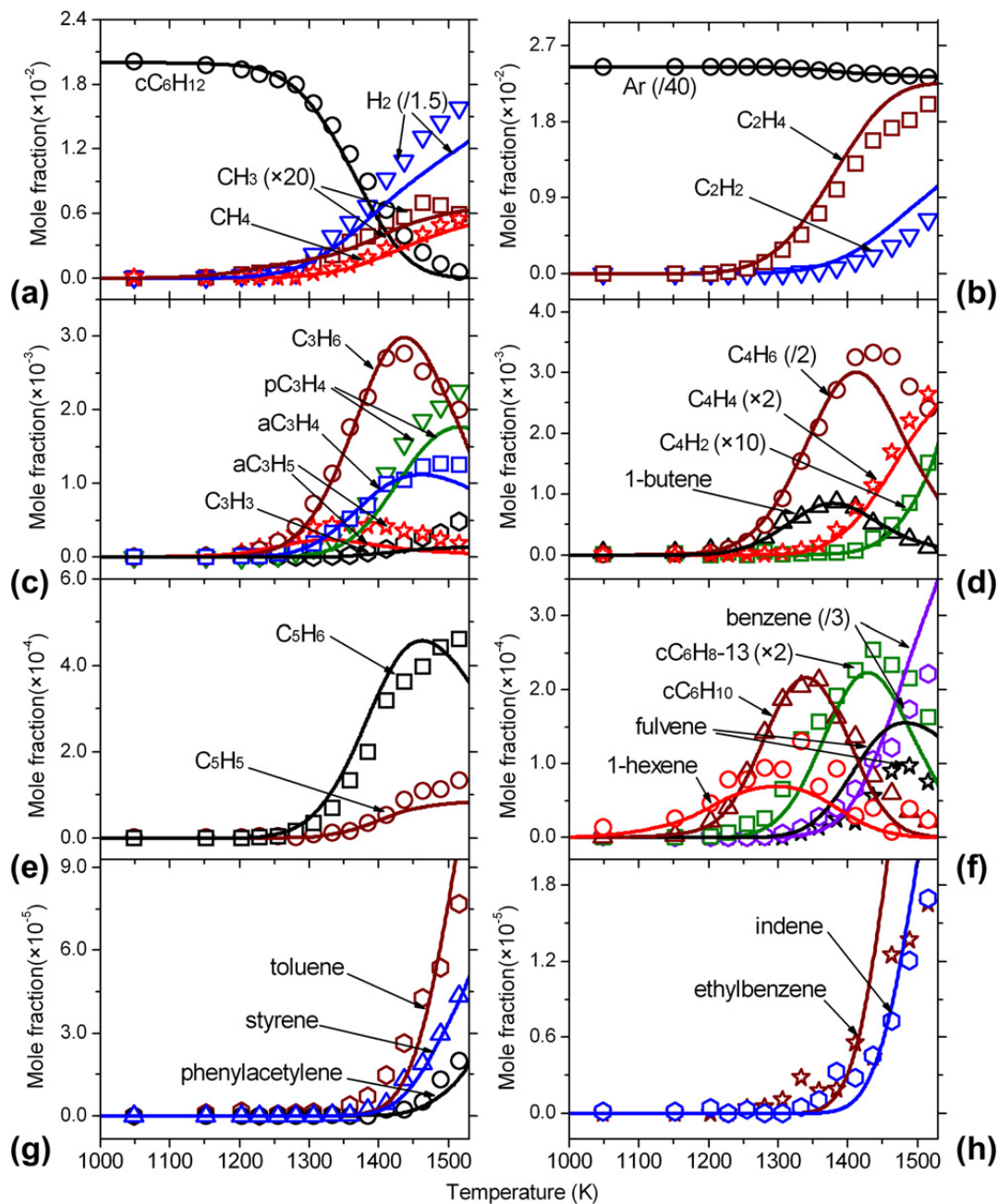
Larger Molecules 1. Cyclohexane pyrolysis

Wang et al, Comb and Flame 159 (2012) 2243-2253



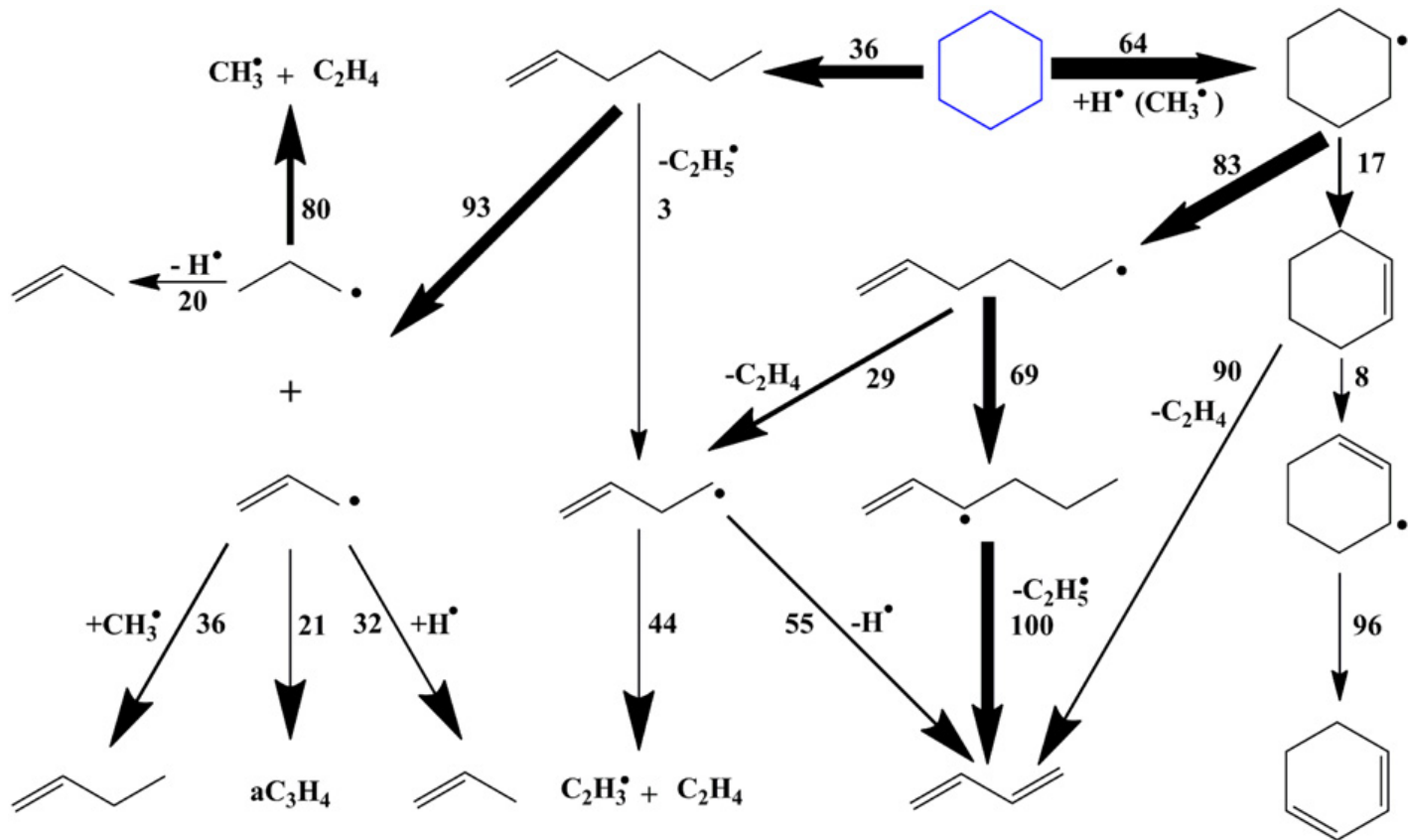
- Heated flow reactor, 950 to 1520 K, synchrotron VUV photoionization mass spectrometry.
- 30 species identified by photoionization efficiency (PIE) spectra, including some radicals like methyl, propargyl, allyl and cyclopentadienyl radicals, and stable products (e.g., 1-hexene, benzene and some aromatics).

Observed products vs temperature



- Open symbols - experiment; full lines simulations
- Mechanism based on earlier work at Hefei and on A High-temperature Chemical Kinetic Model of n-alkane (up to n-dodecane), Cyclohexane, and Methyl-, ethyl-, n-propyl and n-butyl-cyclohexane Oxidation at High Temperatures, JetSurF Version 2.0, September 19, 2010. <http://melchior.usc.edu/JetSurF/JetSurF2.0>.

Rate of production analysis of cyclohexane pyrolysis at 1360 K

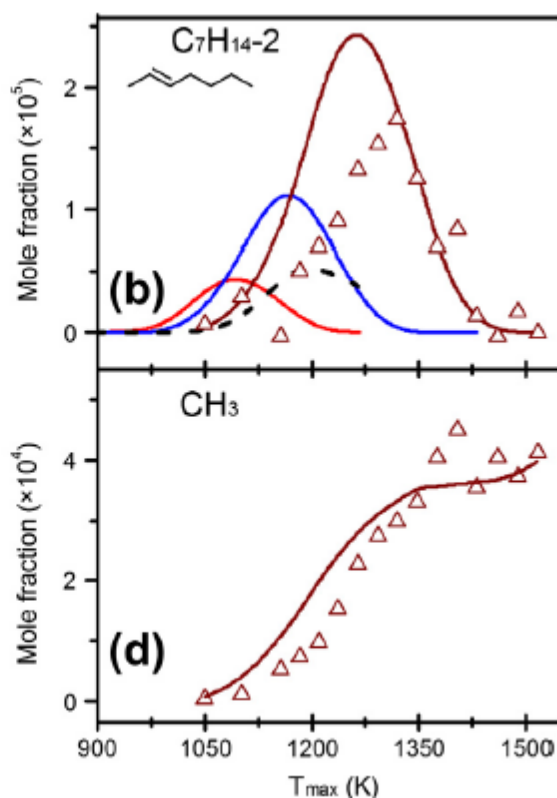
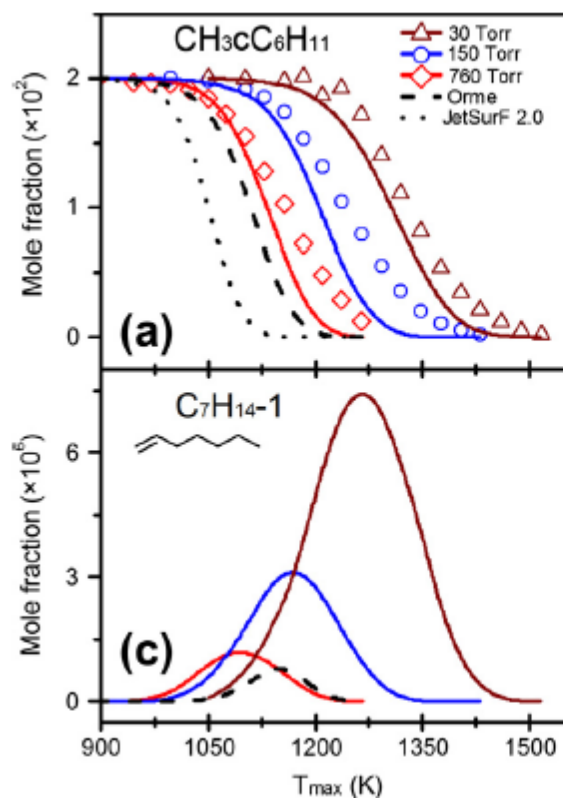


- Thickness of arrows denotes relative rate, numbers show percentage conversion

Larger molecules 2

Experimental and kinetic modeling study on methylcyclohexane pyrolysis and combustion, Wang et al, Comb and Flame, 161 (2014) 84-100

- synchrotron vacuum ultraviolet photoionization mass spectrometry combined with molecular-beam sampling was used to investigate the species formed during the pyrolysis of methylcyclohexane and in premixed flame of methylcyclohexane.



Solid lines: Wang et al mechanisms
Other mechanisms at 760 Torr

Mechanism based on cyclohexane mechanism; development also included Theoretical calculations of abstraction by H

Comprehensive mechanisms:

1. AramcoMech2.0

- Kinetic and thermochemical properties of a large number of C_1 - C_4 based hydrocarbon and oxygenated fuels over a wide range of experimental conditions. Developed by Curran et al., at NUI Galway.
- Developed in a hierarchical way 'from the bottom up', starting with a H_2/O_2 sub-mechanism, followed by a C_1 sub-mechanism and has grown to include larger carbon species such as ethane, ethylene, acetylene, allene, propyne, propene, n-butane, isobutane, isobutene, 1-butene and 2-butene, and oxygenated species including formaldehyde, acetaldehyde, methanol, ethanol, and dimethyl ether.
- Validated against a large array of experimental measurements including data from shock tubes, rapid compression machines, flames, jet-stirred and plug-flow reactors.

References

- Y. Li, et al. The Oxidation of 2-Butene: A High Pressure Ignition Delay, Kinetic Modeling Study and Reactivity Comparison with Isobutene and 1-Butene Proceedings of the Combustion Institute (2017) 36(1)403-411.
- C-W. Zhou et al. " A Comprehensive experimental and modeling study of isobutene oxidation", Combust. Flame (2016) 167 353-379.
- U. Burke, et al., " A Detailed Chemical Kinetic Modeling, Ignition Delay time and Jet-Stirred Reactor Study of Methanol Oxidation", Combust. Flame (2016) 165 125-136.
- S.M. Burke, et al. , " An experimental and modeling study of propene oxidation. Part 2: Ignition delay time and flame speed measurements", Combust. Flame (2015) 162(2) 296-314.
- S.M. Burke et al. , " An experimental and modeling study of propene oxidation. Part 1: Speciation measurements in jet-stirred and flow reactors", Combust. Flame (2014) 161(11) 2765-2784.
- W.K. Metcalfe et al., " A hierarchical and comparative kinetic modeling study of C₁-C₂ hydrocarbon and oxygenated fuels", Int. J. Chem. Kinet. (2013) 45(10) 638-675.
- A. Kéromnès, et al. " An Experimental and Detailed Chemical Kinetic Modelling Study of Hydrogen and Syngas Mixtures at Elevated Pressures" Combustion and Flame (2013) 160 995-1011.
- **Web site:** <http://www.nuigalway.ie/c3/aramco2/frontmatter.html>

USC Mechanism:

http://ignis.usc.edu/Mechanisms/USC-Mech%20II/USC_Mech%20II.htm

- Incorporates the recent thermodynamic, kinetic, and species transport updates relevant to high-temperature oxidation of hydrogen, carbon monoxide, and C1-C4 hydrocarbons. This model was developed on the basis of:
 - Optimised H₂/CO combustion
 - GRI-Mech 1.2, 3.0
 - Comprehensive mechanism for ethene and ethyne combustion
 - Mechanism for C₃ and 1,3 butadiene combustion
- Validated with:
 - Ignition delays
 - Species profiles in shock tube oxidation studies
 - Laminar flame speeds
 - Flow reactor data
 - Burner stabilized flame data

Development of a tuned mechanism

GRI-Mech

- G.P. Smith, D.M. Golden, M. Frenklach, N.W.Moriarty, B. Eiteneer, M. Goldenberg, C.T. Bowman, R. Hanson, S. Song, W.C. Gardiner, Jr., V.Lissianski, Z. Qin, Available at: http://www.me.berkeley.edu/gri_mech/
- GRI-Mech is a list of elementary chemical reactions and associated rate constant expressions
- Sensitivity tests against target experimental data allow selection of rate parameters for tuning
- process of automatic simultaneous parameter optimization, to get the parameter set for each successive release of GRI-Mech. Strict constraints keep the rate parameters within predetermined bounds based on
 - evaluations of the uncertainties in measurements of the rates of elementary reactions
 - applications of conventional reaction rate theory

GRI-Mech contd

- GRI-Mech is optimized as a whole, substitutions, further selective tuning should not be done.
- All reactions treated as reversible; thermodynamic data (based on NASA, Technion) provided.
- to use the input files directly you need the Chemkin-II programs
- GRI-Mech 3.0 has 53 species, 325 reactions, with associated rate and thermodynamic data.
- Optimized for methane as a fuel. Includes C2 and propane chemistry.
- Optimized against chosen targets in ranges: $T = 1000$ to 2500 K, $p = 10$ Torr to 10 atm, $\phi = 0.1$ to 5 for premixed systems
- http://akrmys.com/public/chemkin/CKm_inp.html.en
- <http://www.reactiondesign.com/products/chemkin/>

http://www.me.berkeley.edu/gri_mech/data/frames.html - Internet Explorer provided by MaPS Faculty

http://www.me.berkeley.edu/gri_mech/data/frames.html

Leeds University Library H... Leeds University Library H... University of Leeds Web Slice Gallery

http://www.me.berkeley.edu/gri_mech/data/fra...

26	$\text{O} + \text{C}_2\text{H}_5 \rightarrow \text{CH}_3 + \text{CH}_2\text{O}$	2.24E+13			
27	$\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{OH} + \text{C}_2\text{H}_5$	8.98E+07	1.9	5690	3.0
28	$\text{O} + \text{HCCO} \rightarrow \text{H} + \text{CO} + \text{CO}$	1.00E+14			
29	$\text{O} + \text{CH}_2\text{CO} \rightarrow \text{OH} + \text{HCCO}$	1.00E+13		8000	
30	$\text{O} + \text{CH}_2\text{CO} \rightarrow \text{CH}_2 + \text{CO}_2$	1.75E+12		1350	
31	$\text{O}_2 + \text{CO} \rightarrow \text{O} + \text{CO}_2$	2.50E+12		47800	
32	$\text{O}_2 + \text{CH}_2\text{O} \rightarrow \text{HO}_2 + \text{HCO}$	1.00E+14		40000	1.2; 2.1; 3.0
33	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	2.80E+18	-0.9		2.1; 3.0
34	$\text{H} + \text{O}_2 + \text{O}_2 \rightarrow \text{HO}_2 + \text{O}_2$	2.08E+19	-1.2		3.0
35	$\text{H} + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	1.13E+19	-0.8		1.1; 1.2; 2.1; 3.0
36	$\text{H} + \text{O}_2 + \text{N}_2 \rightarrow \text{HO}_2 + \text{N}_2$	2.60E+19	-1.2		2.1; 3.0
37	$\text{H} + \text{O}_2 + \text{AR} \rightarrow \text{HO}_2 + \text{AR}$	7.00E+17	-0.8		1.2; 2.1; 3.0
38	$\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}$	2.65E+16	-0.7	17041	1.1; 1.2; 2.1; 3.0
39	$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	1.00E+18	-1.0		
40	$\text{H} + \text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}_2$	9.00E+16	-0.6		
41	$\text{H} + \text{H} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{H}_2\text{O}$	6.00E+19	-1.2		3.0
42	$\text{H} + \text{H} + \text{CO}_2 \rightarrow \text{H}_2 + \text{CO}_2$	5.50E+20	-2.0		
43	$\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	2.20E+22	-2.0		1.1; 1.2; 2.1; 3.0
44	$\text{H} + \text{HO}_2 \rightarrow \text{O} + \text{H}_2\text{O}$	3.97E+12		671	
45	$\text{H} + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2$	4.48E+13		1068	3.0
46	$\text{H} + \text{HO}_2 \rightarrow \text{OH} + \text{OH}$	8.40E+13		635	3.0

All and Find Reactions Instructions

Internet | Protected Mode: On 100%

http://www.me.ber... 5. mechanism cons... Inbox - Microsoft O... Kinetics Special Iss... Sticky Notes JPL_15 2006.pdf - A... Manuscript jp-2011... Windows Update Microsoft PowerPo... 10:00

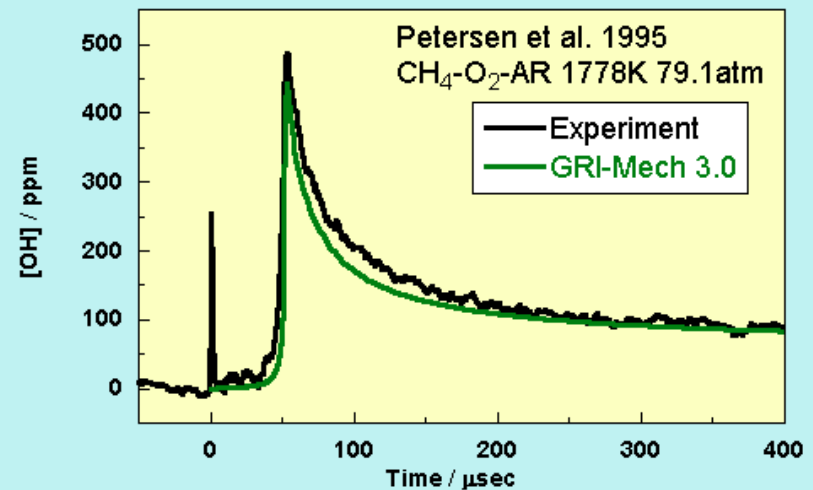
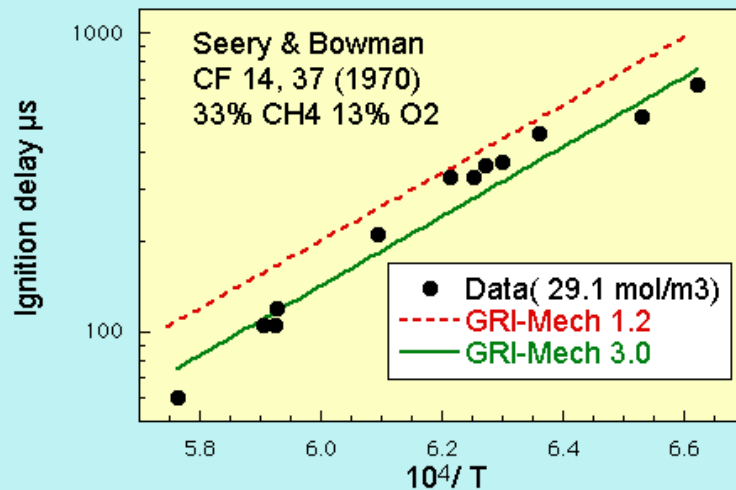
Example of reaction list from GRI-Mech
 Reaction in **bold** are those whose rate coefficients served as *active* parameters in model optimization, and those in red are active parameters whose values were changed as a result of optimization
 Click on reaction number for information
 e.g. Reaction 35: Served as an optimization variable in GRI-Mech 3.0 release and was changed by a factor of 1.2.

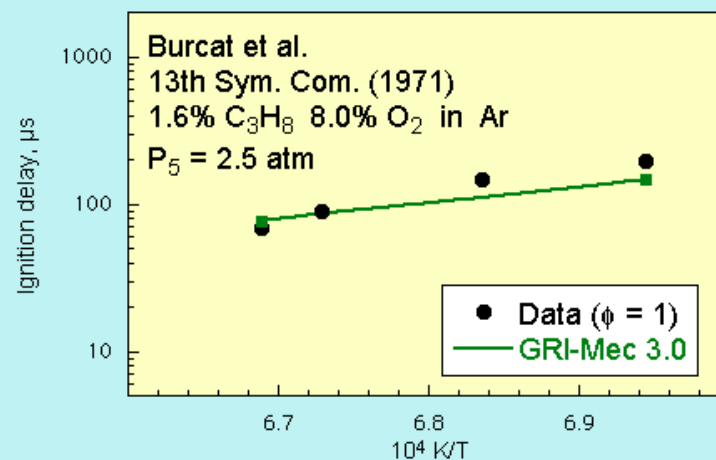
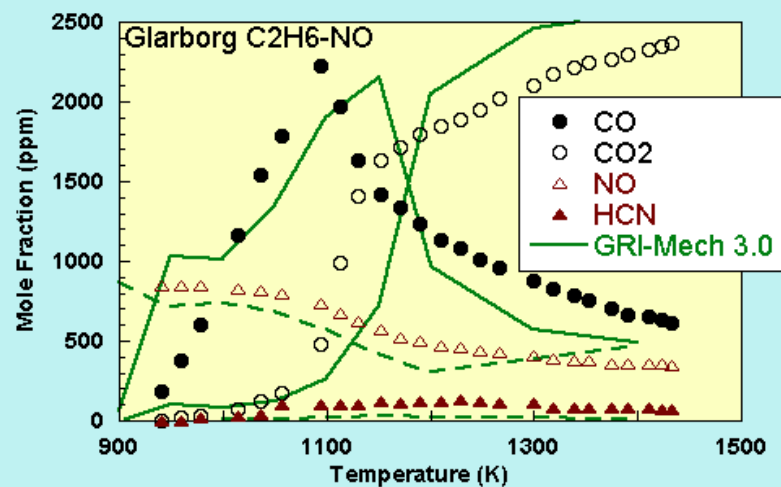
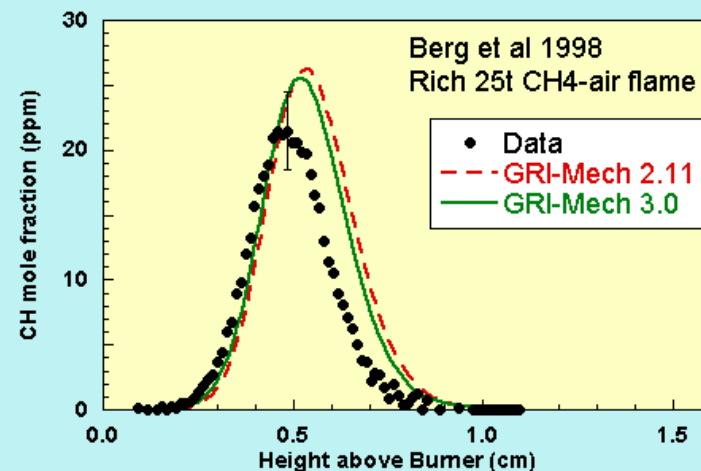
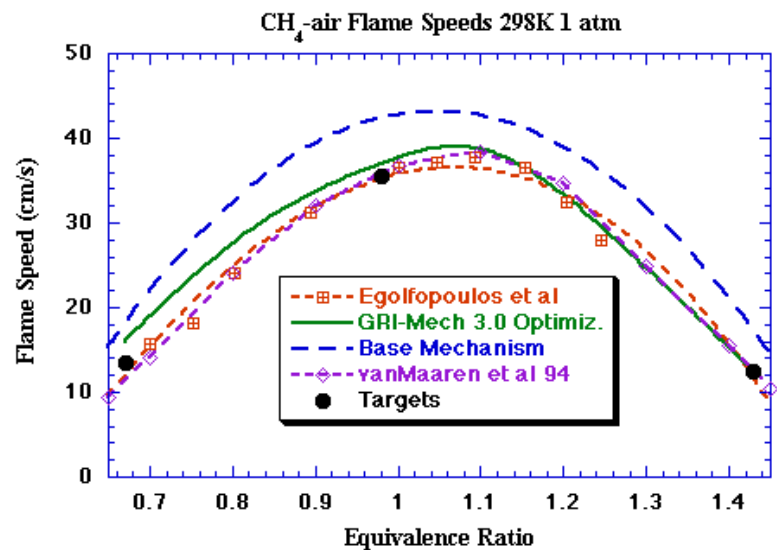
Thermodynamic and kinetic data for reaction 35

Temp (K)	delta-S (cal/mol K)	delta-H (kcal/mol)	kf ---- (mol, cm3, s) -----	kr -----	Keq (cm3/mol)
300	-21.7	-49.1	1.48E+17	5.59E-19	2.64E+35
500	-23.4	-49.8	1.00E+17	5.63E-05	1.78E+21
1000	-25.1	-51.0	5.90E+16	1.61E+06	3.68E+10
1500	-25.7	-51.7	4.34E+16	4.31E+09	1.01E+07
2000	-26.0	-52.2	3.49E+16	2.03E+11	1.72E+05
2500	-26.1	-52.4	2.94E+16	1.91E+12	1.55E+04
3000	-26.2	-52.6	2.57E+16	8.05E+12	3.19E+03

Optimisation against a wide list of targets

- Shock tube ignition delay and species profiles, reactors, laminar flame speed, prompt NO, HCN oxidation, reburning. Examples:





Engagement of the community in mechanism development PrIMe

Frenklach, Proc Comb Inst 31 (2007) 125-140

Discussed the future of predictive combustion models through what he termed Process Informatics which "relies on three major components: proper organization of scientific data, availability of scientific tools for analysis and processing of these data, and engagement of the entire scientific community in the data collection and analysis."

Current site: <https://prime.cki-know.org/>

- The PrIMe project started from informal discussions in 2001.
- **Depository and Library.** *PrIMe Data Warehouse* consists, conceptually, of two parts: *Depository* and *Library*. The *Depository* is a repository of data provided by the community. The only requirement for the acceptance of the data into the *Depository* is the data-record completeness, which is checked electronically with the use of data schemas. The *Library* is a set of data evaluated by the *PrIMe Work Groups* (PWG). A set of primekinetics [codes](#) is being developed to assist in both initial submission and PWG-evaluation of the data.

Current site: <https://prime.cki-know.org/PrIME>

Group directory 1

<u>Name</u>	Subscribers	<u>Description</u>
BioFuels	9	BioFuels
Burner-stabilized premixed flames	33	Burner-stabilized premixed flames H ₂ /O ₂ /CO + C ₁ /C ₂ hydrocarbon pyrolysis and oxidation
C0-C2	69	C ₃ -C ₄ hydrocarbon pyrolysis and oxidation
C3-C4	47	C ₅ -C ₁₆ hydrocarbon pyrolysis and oxidation
C5-C16	35	C ₆ + aromatic hydrocarbon pyrolysis and oxidation
C6 + aromatics	20	Cyber-numerics
Cyber-numerics	33	Diffusion flames
Diffusion flames	22	

PrIMe Group directory 2

Flow reactors	2	Flow reactors	Spectroscopy	7	Spectroscopy
Industrial	13	Industrial	Stirred reactors	9	Stirred reactors
Laminar premixed flames	32	Laminar premixed flames (global properties)	Test	1	For testing only
N	8	Nitrogen containing	Thermo	42	Thermodynamic data
P-dependence	15	Pressure dependence of reactions	Transport	11	Transport data
Quantum chemistry	2	Quantum chemistry	TST	25	Transition-State theory
ReactionDesign	24	ReactionDesign	Turbulent flames	1	Turbulent flames
Shock tubes	35	Shock tubes			
Soot	67	Soot			

Systematic provision of targets

- E.g. Davidson et al. Combustion and Flame 157 (2010) 1899-1905: Multi-species time-history measurements during n-heptane oxidation behind reflected shock waves
- 1300-1600 K, 2 atm (Ar) 300 ppm n-heptane, 3300 ppm oxygen ($\phi = 1$)
- Monitoring:
 - n-Heptane and ethylene, IR gas laser absorption, 3.39 and 10.53 μm , resp.
 - OH UV laser absorption at 306.5 nm
 - CO₂ and H₂O tunable IR diode laser absorption at 2.7 and 2.5 μm , resp.

Example of experimental measurements and comparison with existing mechanism

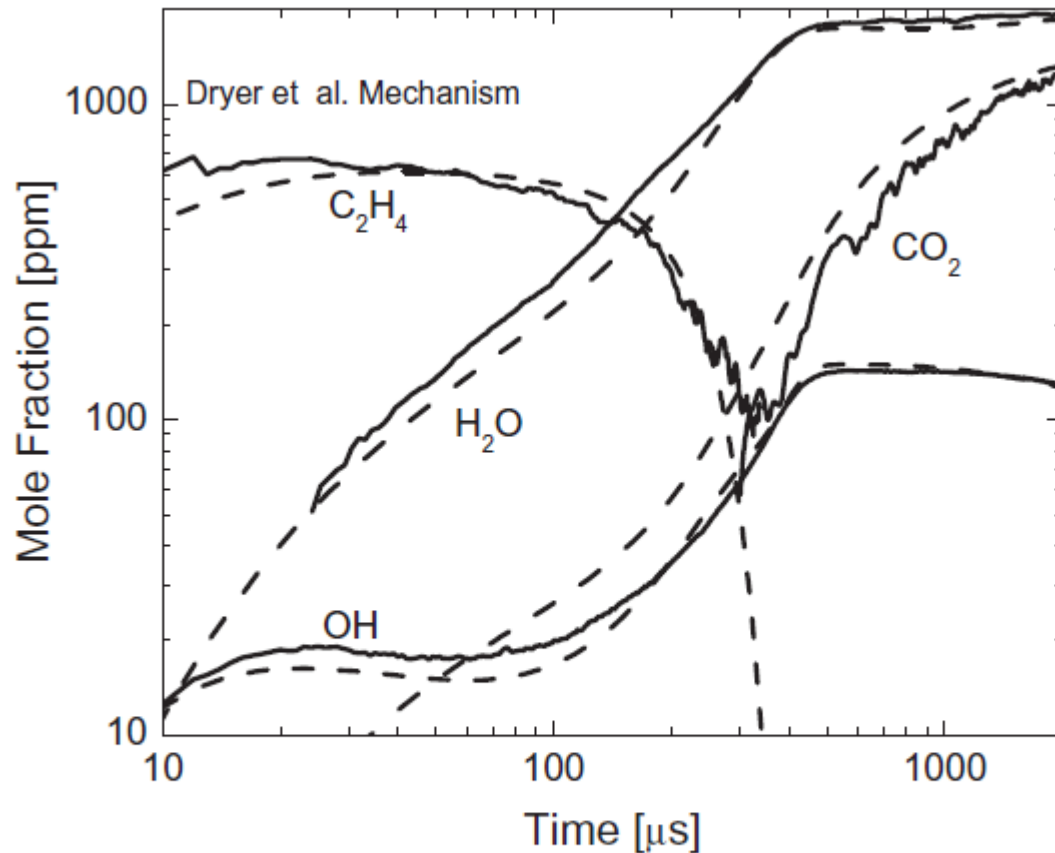


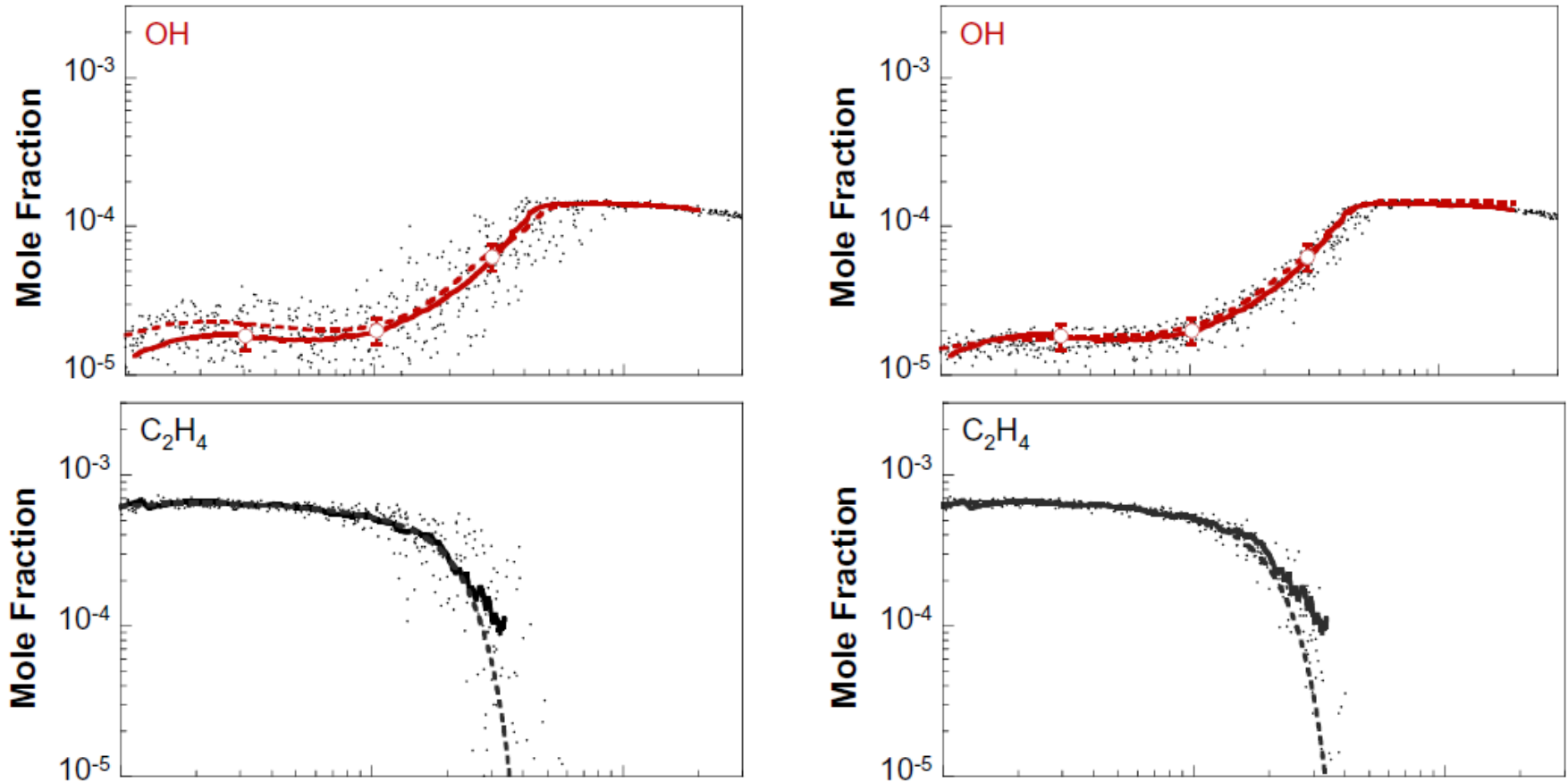
Fig. 7. Comparison of laser-absorption measurements with the Dryer et al. model [4]. Reflected shock wave conditions: 1494 K, 2.15 atm, 300 ppm *n*-heptane/O₂/argon, $\phi = 1$.

Use of target data from Davidson et al.
Sheen and Wang, Combustion and Flame 158 (2011)
645-656 (quotes from abstract)

Combustion kinetic modeling using multispecies time histories in shock-tube oxidation of heptane

- Precise nature of measurements of Davidson et al. impose critical constraints on chemical kinetic models of hydrocarbon combustion.
- while an as-compiled, prior reaction model of n-alkane combustion can be accurate in its prediction of the detailed species profiles, the kinetic parameter uncertainty in the model remains too large to obtain a precise prediction of the data.
- Constraining the prior model against the species time histories within the measurement uncertainties led to notable improvements in the precision of model predictions against the species data as well as the global combustion properties considered.
- accurate data of global combustion properties are still necessary to predict fuel combustion.

Model measurement comparisons



- Experimental (solid lines) and computed (dashed lines: nominal prediction; dots: uncertainty scatter). The open circles and the corresponding error bars designate data used as Series 1 targets and 2 σ standard deviations, respectively. Left panel: prior model (Model I). Right panel: posterior model (Model II).

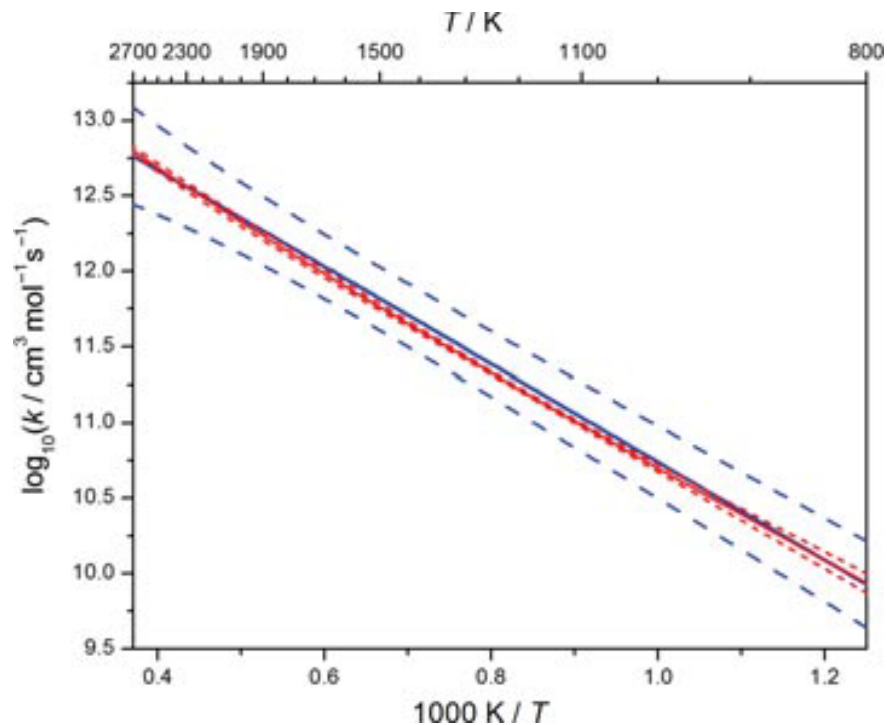
Turanyi et al. Determination of Rate Parameters Based on Both Direct and Indirect Measurements

International Journal of Chemical Kinetics 2012 DOI 10.1002/kin.20717

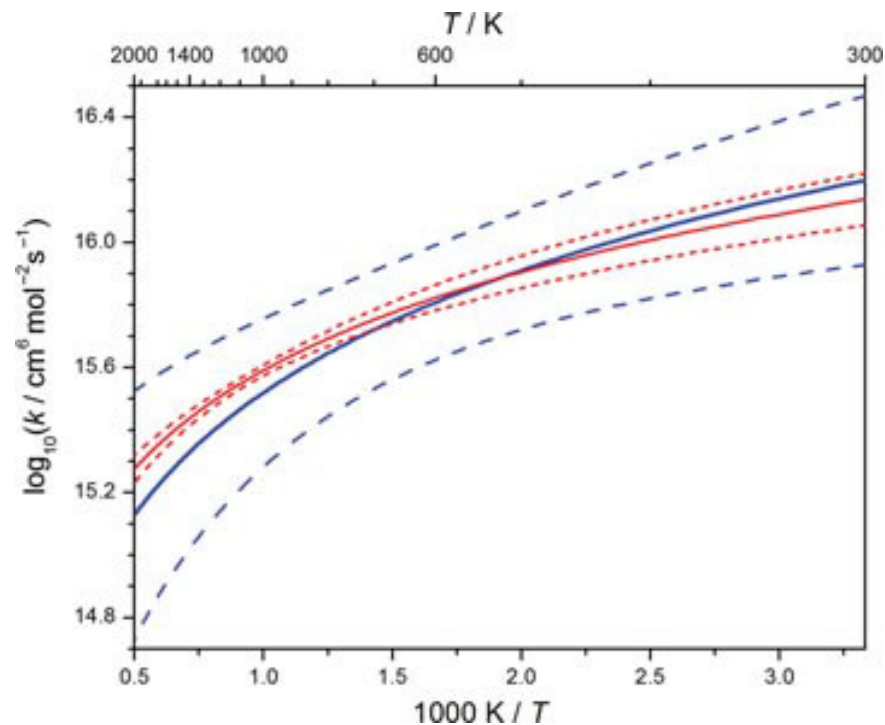


- new approach that takes into account both direct and indirect measurements and optimizes all influential rate parameters
- First, the domain of feasibility of the Arrhenius parameters is determined from all of the available direct measurements (see topic 5).
- the optimal Arrhenius parameters are then sought within this domain to reproduce the selected direct and indirect measurements
- 9 direct measurements for reaction (R1) (745 data points)
- 10 direct measurements for reaction (R2) (258 data points)
- 11 ignition time measurements (79 data points) were taken into account.
- A new fitting algorithm and a new method for error calculation were developed to determine the optimal mean values and the covariance matrix of all parameters

Arrhenius plots and uncertainties

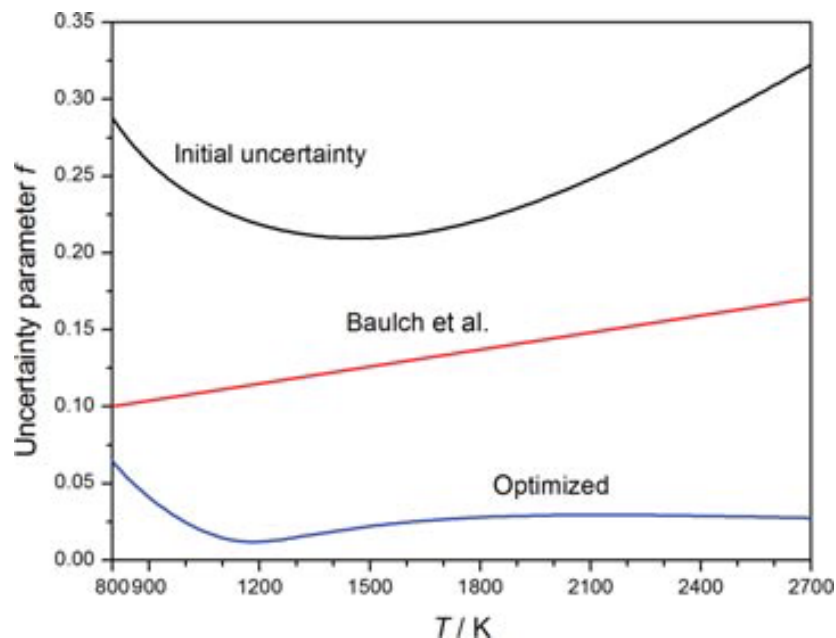


Arrhenius plots of the initial and optimized main values and uncertainty limits for reaction (R1): $\text{H} + \text{O}_2 = \text{OH} + \text{O}$. Thin solid blue line: initial value, recommended by Baulch et al.; blue dashed lines: initial uncertainty limits; red line: optimized rate coefficient; red dashed lines: optimized uncertainty limits.

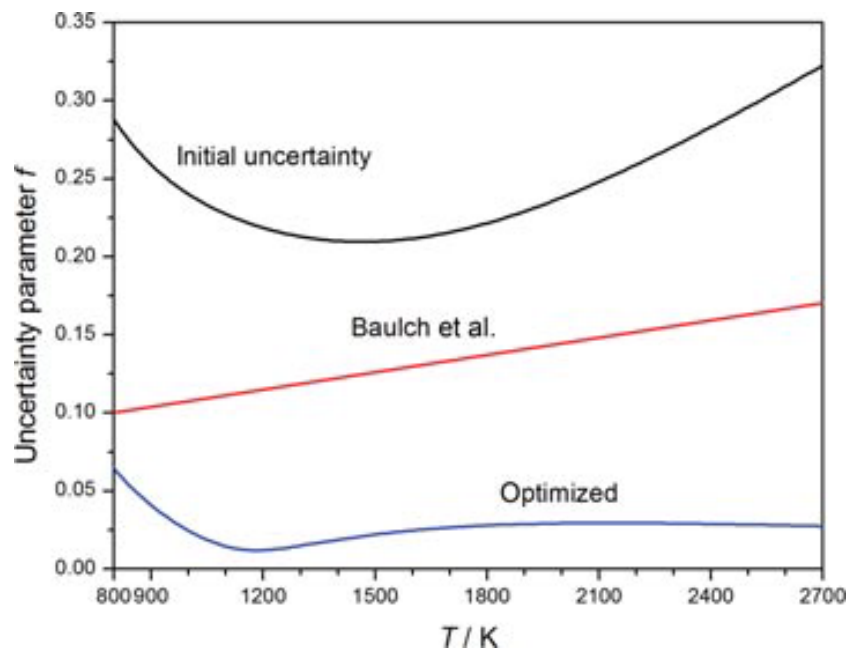


Arrhenius plots of the initial and optimized main values and uncertainty limits for reaction (R2): $\text{H} + \text{O}_2 + \text{N}_2 = \text{HO}_2 + \text{N}_2$ (low-pressure limit). Thin solid blue line: initial value, recommended by Baulch et al.; blue dashed lines: initial uncertainty limits; red line: optimized rate coefficient; red dashed lines: optimized uncertainty limits.

Uncertainty parameters for reactions R1 and R2.



Uncertainty parameter (f) as a function of temperature for reaction (R1): $\text{H} + \text{O}_2 = \text{OH} + \text{O}$, according to the evaluation of Baulch et al. [3] (red line), and f calculated from the covariance matrix of the Arrhenius parameters in two different ways: The "initial uncertainty" belongs to the $k_{\min}(T)$ and $k_{\max}(T)$ functions (black line), and the "optimized" belongs to the optimized rate parameters (blue line).



Uncertainty parameter (f) as a function of temperature for reaction (R2): $\text{H} + \text{O}_2 + \text{N}_2 = \text{HO}_2 + \text{N}_2$ (low-pressure limit) according to the evaluation of Baulch et al. (red line), and f calculated from the covariance matrix of the Arrhenius parameters in two different ways: The "initial uncertainty" belongs to the $k_{\min}(T)$ and $k_{\max}(T)$ functions (black line), and the "optimized" belongs to the optimized rate parameters (blue line).

Table VII The Determined Covariances of the Rate Parameters

	$\ln A_1$	n_1	E_1/R	$\ln A_2$	n_2	$m \text{ (Ar)}$
$\ln A_1$	1.0609×10^0	-1.2149×10^{-1}	2.3661×10^2	-4.4080×10^{-1}	6.3586×10^{-2}	-3.0367×10^{-3}
n_1		1.3924×10^{-2}	-2.6989×10^1	4.9745×10^{-2}	-7.1782×10^{-3}	3.5276×10^{-4}
E_1/R			5.3824×10^4	-1.0438×10^2	1.5020×10^1	-6.0886×10^{-1}
$\ln A_2$				3.3293×10^{-1}	-4.7993×10^{-2}	7.4402×10^{-4}
n_2					6.9222×10^{-3}	-1.1576×10^{-4}
$m \text{ (Ar)}$						9.2352×10^{-5}

Table VIII The Determined Correlations of the Rate Parameters

	$\ln A_1$	n_1	E_1/R	$\ln A_2$	n_2	$m \text{ (Ar)}$
$\ln A_1$	1	-0.99957	0.99015	-0.74170	0.74199	-0.30679
n_1		1	-0.98586	0.73062	-0.73116	0.31108
E_1/R			1	-0.77976	0.77814	-0.27309
$\ln A_2$				1	-0.99973	0.13418
n_2					1	-0.14478
$m \text{ (Ar)}$						1

Table I Evaluated and Optimized Rate Parameters for Reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ (R1)

Reference	A ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	n	E/R (K)	f	T Range (K)
Baulch et al. [3]	2.07×10^{14}	-0.097	7560	0.1 at 800 K, 0.2 at 3500 K	800–3500
Li et al. [41]	3.55×10^{15}	-0.41	8359	—	—
Ó Conaire et al. [42]	1.91×10^{14}	0	8278	—	—
Konnov [43]	2.06×10^{14}	-0.097	7564	0.176	800–3500
Hong et al. [44]	1.04×10^{14}		7705		1100–3370
This work	3.003×10^{10}	0.965	6158	0.025 at 1000 K, 0.022 at 1500 K, 0.029 at 2000 K	950–3550

Table II Evaluated Rate Parameters for Low-Pressure Limit Reaction $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ (R2)

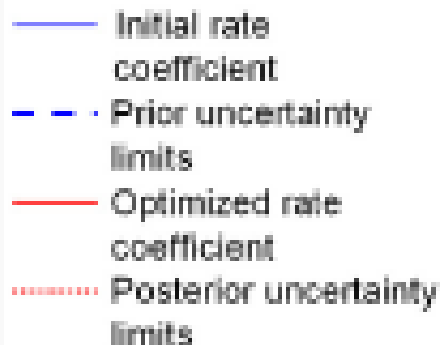
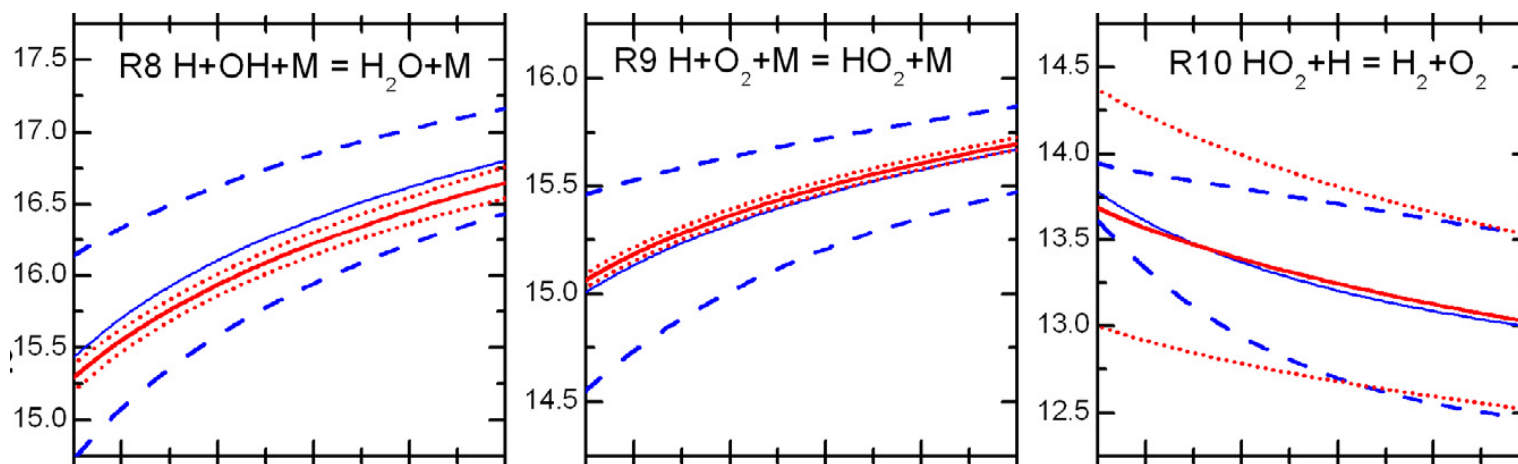
Reference	Bath Gas	A ($\text{cm}^6 \text{ mol}^{-2} \text{ s}^{-1}$)	n	E/R (K)	f	T Range (K)
Baulch et al. [3]	N_2	2.65×10^{19}	-1.3	0	0.1 at 298 K, 0.2 at 2000 K	298–2000
Baulch et al. [3]	Ar	6.9×10^{18}	-1.2	0	0.1 at 298 K, 0.2 at 2000 K	298–2000
Li et al. [41]	N_2	6.37×10^{20}	-1.72	261.8	—	—
Li et al. [41]	Ar	9.04×10^{19}	-1.50	246.7	—	—
Ó Conaire et al. [42]	N_2	3.482×10^{16}	-0.41	-561.5	—	—
Konnov [43]	N_2	5.70×10^{19}	-1.4	0	0.079	300–2000
Konnov [43]	Ar	7.43×10^{18}	-1.2	0	0.079	300–2000
Hong et al. [44]	N_2	2.65×10^{19}	-1.3	0	—	—
Hong et al. [44]	Ar	6.81×10^{18}	-1.2	0	—	—
This work	N_2	7.856×10^{18}	-1.100	0	0.032 at 800 K, 0.018 at 1000 K, 0.045 at 1500 K	300–1850

Optimization of a hydrogen combustion mechanism using both direct and indirect measurements

Varga et al, Proc Comb Inst 35 (2015) 589-596

- Optimisation of Keromnes mechanism using ignition measurements from shock tubes (566 datapoints, 43 datasets) and rapid compression machines (219/19) + flame velocities (364/59)
- Sensitivity analysis showed that parameters for 11 elementary reactions could be optimised. Also utilized 1749 direct k measurements from 56 datasets, with prior uncertainty ranges
- Analysis provides new mechanism including new $k(T)$ s, with covariance matrix and T dependent posterior uncertainty ranges
- Demonstrate much reduced overall error function compared with 13 earlier mechanisms

Examples of results for rate constants



- Global parameter optimization from Int J Chem Kinet, 44 (2012) 284 - 302
- Based on minimization of objective function:

$$E(p) = \frac{1}{N} \sum_{i=1}^N \frac{1}{N_i} \sum_{j=1}^{N_i} \left(\frac{Y_{ij}^{mod} - Y_{ij}^{exp}}{\sigma(Y_{ij}^{exp})} \right)^2$$

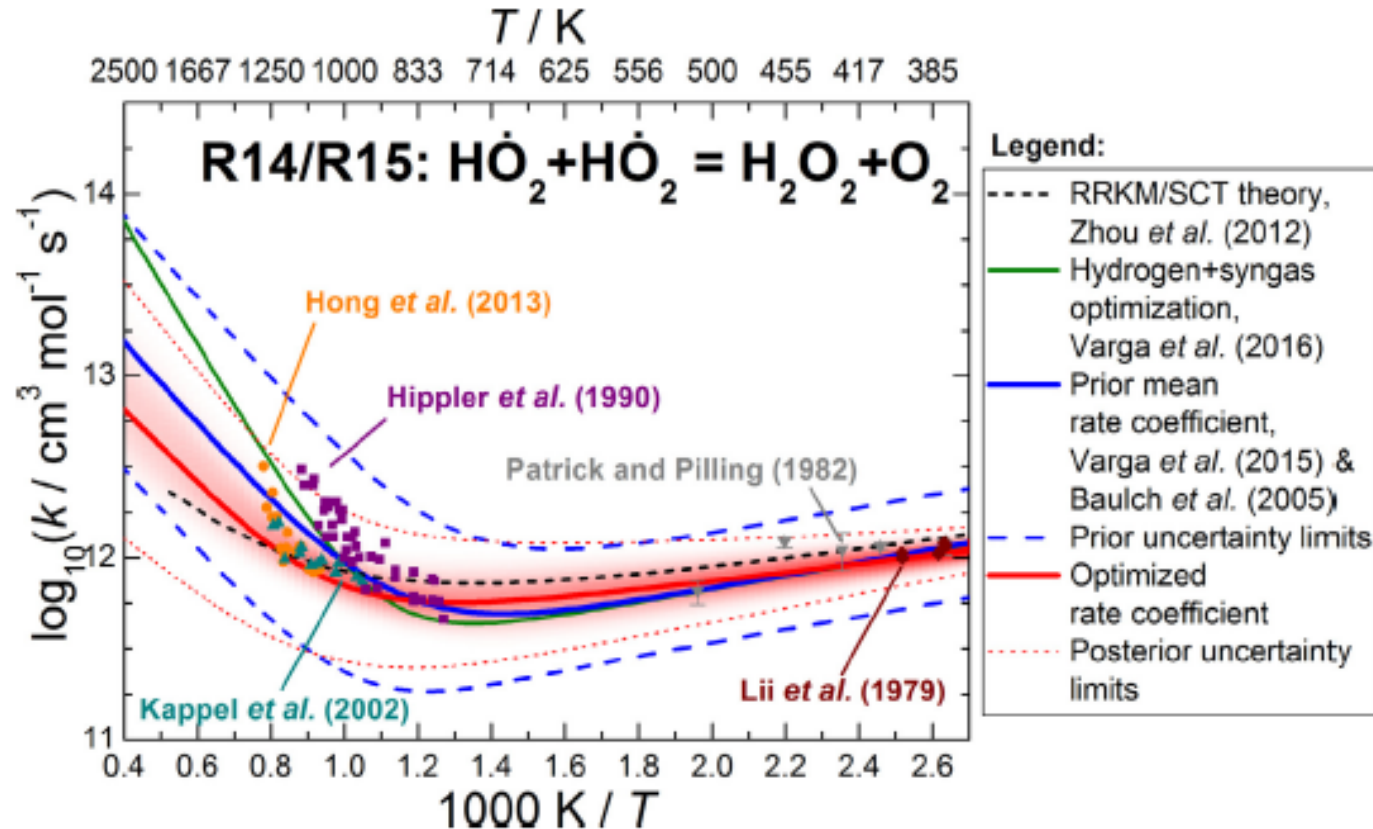
where N is the total number of datasets and N_i is the number of datapoints in the i th dataset. $\sigma(Y_{ij}^{exp})$ is the experimental std deviation in the j th datapoint, i th dataset

Comparison of the performance of several recent syngas combustion mechanisms

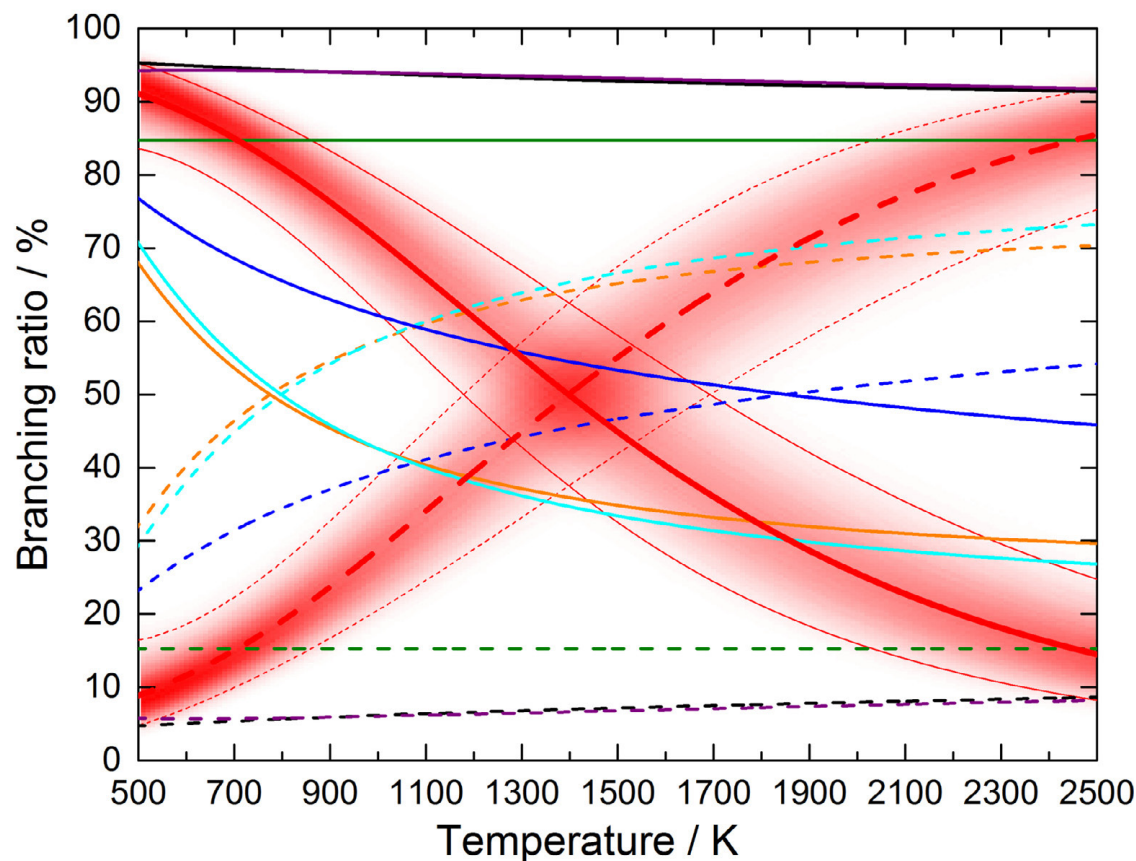
Olm et al Comb and Flame 162 (2015) 1793-1812

- Used same objective function approach to compare performance of 16 syngas (wet CO) mechanisms ignition studies in shock tubes and rapid compression machines, flame velocities and species concentration measurements from flow reactors, shock tubes and jet-stirred reactors. 4970 data points in 408 datasets from 52 publications.
- Some observations not well modelled.
- Five mechanisms performed better than others.
- influence of poorly reproduced experiments and weighting on the performance of the mechanisms investigated
- analysis of local sensitivity coefficients showed the influence of selected reactions and helped identify those reactions that require more attention

Uncertainty quantification optimized methanol, formaldehyde combustion mechanism (Olm et al, Comb & Flame 2017, 186, 45)



- The prior uncertainty limits are large especially at high T , reflecting substantial disagreements between direct experimental datasets (see Topic 2). Also theory gives lower values.
- The extensive set of indirect measurements (24900 points from 265 datasets) change the optimized k and substantially narrow the uncertainty limits



Channel Yields

$\text{CH}_3\text{OH} + \text{OH} \rightarrow$
 $\text{CH}_2\text{OH} + \text{H}_2\text{O}$ (R84)
 $\text{CH}_3\text{O} + \text{H}_2\text{O}$ (R83)

Reaction channel

Theoretical calculations: Xu and Lin (2007)
 Jodkowski *et al.* (1999)
 Bott and Cohen (1991)

Mechanism predictions: Marinov (1999)
 Leplat *et al.* (2011)
 Li *et al.* (2007)
 Rasmussen *et al.* (2008)

Optimized mechanism
 95% confidence interval

R84

— (VTST)
 — (TST/Eckart)
 — (TST, not used as target)
 —
 —
 —
 —
 —

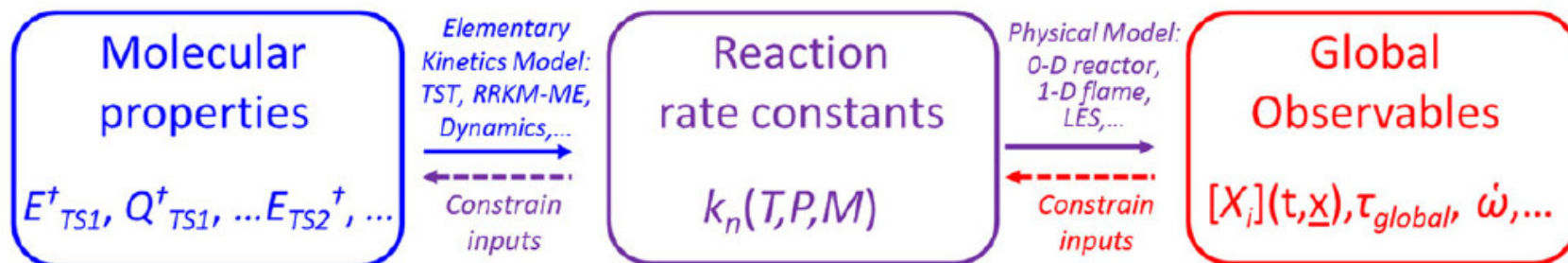
R83

- - (VTST)
 - - (TST/Eckart)
 - - (TST, not used as target)
 - -
 - -
 - -
 - -
 - -

Products of the
 $\text{CH}_3\text{OH} + \text{OH}$ reaction:
 R84: $\dot{\text{C}}\text{H}_2\text{OH} + \text{H}_2\text{O}$
 R83: $\text{CH}_3\dot{\text{O}} + \text{H}_2\text{O}$

Harnessing the Combined Power of Theoretical and Experimental Data through Multiscale Informatics

M P Burke, Int J Chem Kinet 2016, 48,

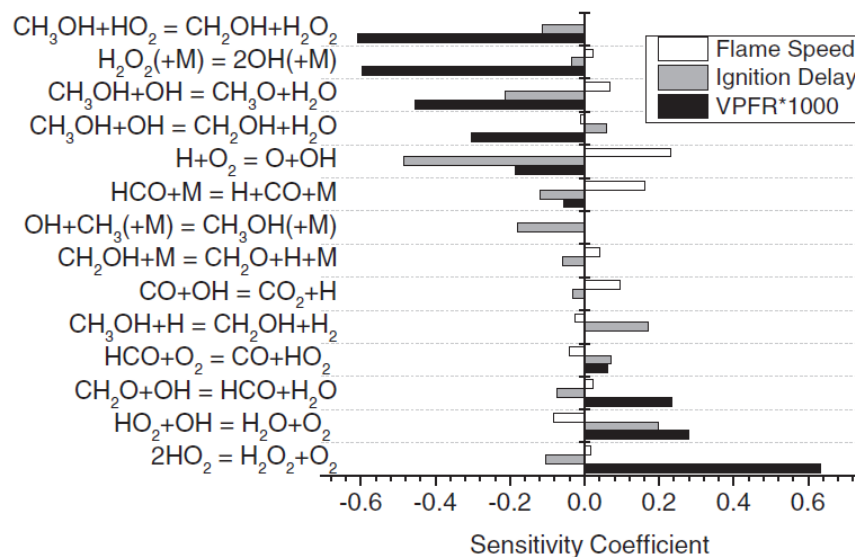


- Approach integrates information from a wide variety of sources and scales:
 - Theoretical parameters, e.g. TS energies, with constrained uncertainties
 - Through elementary kinetics models to rate constants, with propagated uncertainties
 - Through physical models to global observables, such as ignition delay times, with propagated uncertainties

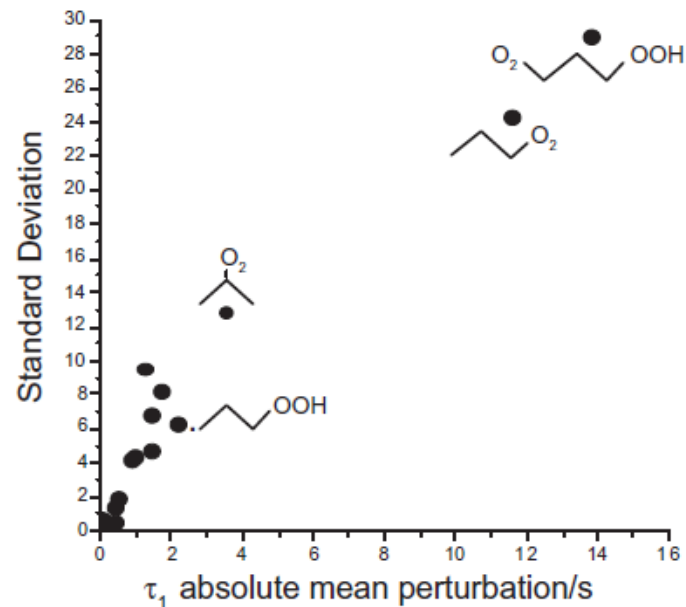
The role of sensitivity and uncertainty analysis in combustion modelling (A S Tomlin, Proc Comb Inst 34 (2013) 159-176)

- significant uncertainties in the data used to parameterise combustion models still exist.
- input uncertainties propagate through models of combustion devices leading to uncertainties in the prediction of key combustion properties.
- focus efforts on those parameters which drive predictive uncertainty, which may be identified through sensitivity analysis.
- Paper discusses how sensitivity and uncertainty analysis can be incorporated into strategies for model improvement

Local and global sensitivities



Sensitivity coefficients for flow reactor, shock tube and laminar premixed flame studies of methanol combustion



Global screening methods: Morris analysis for enthalpies of formation with respect to time to cool flame for propane oxidation

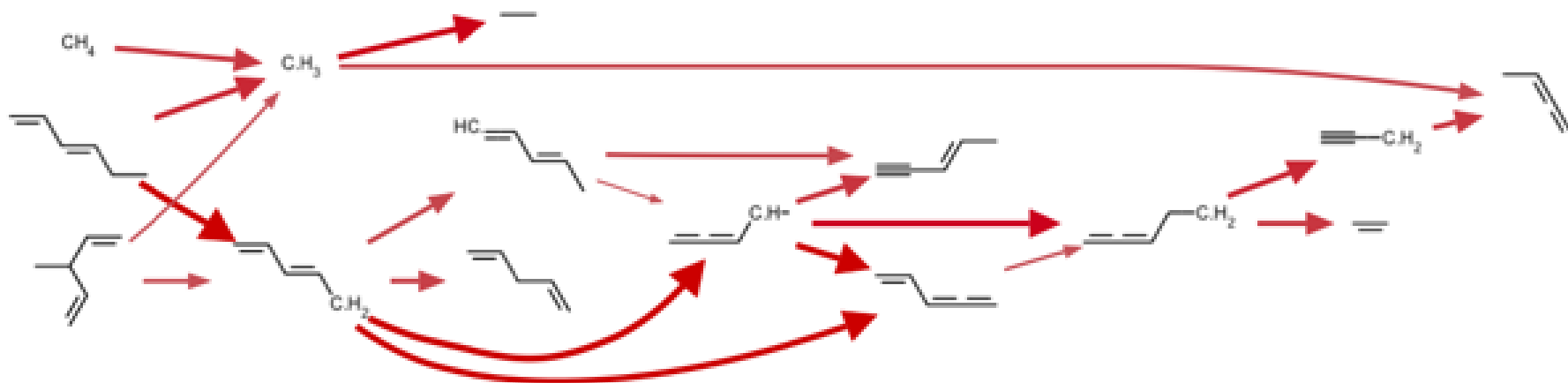
Investigation of the effect of correlated uncertain rate parameters via the calculation of global and local sensitivity indices
Valko et al, J Math Chem (2018) 56:864-889

- Applied to mechanism used to model ignition delay times in syngas / air (15 species, 48 reactions)
- Most of the parameters have large correlated sensitivity indices and the correlation between the parameters has a high influence on the results.
- The parameters belonging to five elementary reactions only, have significant final marginal sensitivity indices.
- Results of the global sensitivity analysis were compared with the corresponding results of local sensitivity analysis for the syngas-air combustion system. The same set of reactions was indicated to be important by both approaches

Automatic mechanism generation

W H Green et al <http://ReactionMechanismGenerator.github.io>

- Open source software, **Reaction Mechanism Generator (RMG)** is an automatic chemical reaction mechanism generator that constructs kinetic models composed of elementary chemical reaction steps using a general understanding of how molecules react.
- Latest version RMG-Py, written in Python
- **CanTherm**, developed and distributed as part of RMG-Py, can be used as a stand-alone application for Thermochemistry, Transition State Theory, and Master Equation chemical kinetics calculations
- Website includes a guide to the theory used in RMG
- Flux diagram for the pyrolysis of 1,3-hexadiene, an example model generated with RMG, showing the net carbon flux at an instant near the end of the simulation



RMG - an example

- Harper et al. Comprehensive reaction mechanism for n-butanol pyrolysis and combustion, Combustion and Flame 158 (2011) 16-41
- 263 species and 3381 reactions. Constructed using Reaction Mechanism Generator
- tested against recently published data - jet-stirred reactor mole fraction profiles, opposed-flow diffusion flame mole fraction profiles, autoignition delay times, and doped methane diffusion flame mole fraction profiles - and newly acquired n-butanol pyrolysis experiments.

Approach

- Base mechanism - GRI 3.0 with N chemistry removed.
- Where possible use published data for rate coefficients
- For some important p dependent reactions, calculate high pressure limit using canonical TST using electronic structure calculations.
- Methods available for calculating p dependence.
- Mechanism contains reaction rate constants for 147 different pressure-dependent networks, e.g. C_4H_9
- Extensive testing against experiments, and sensitivity analysis

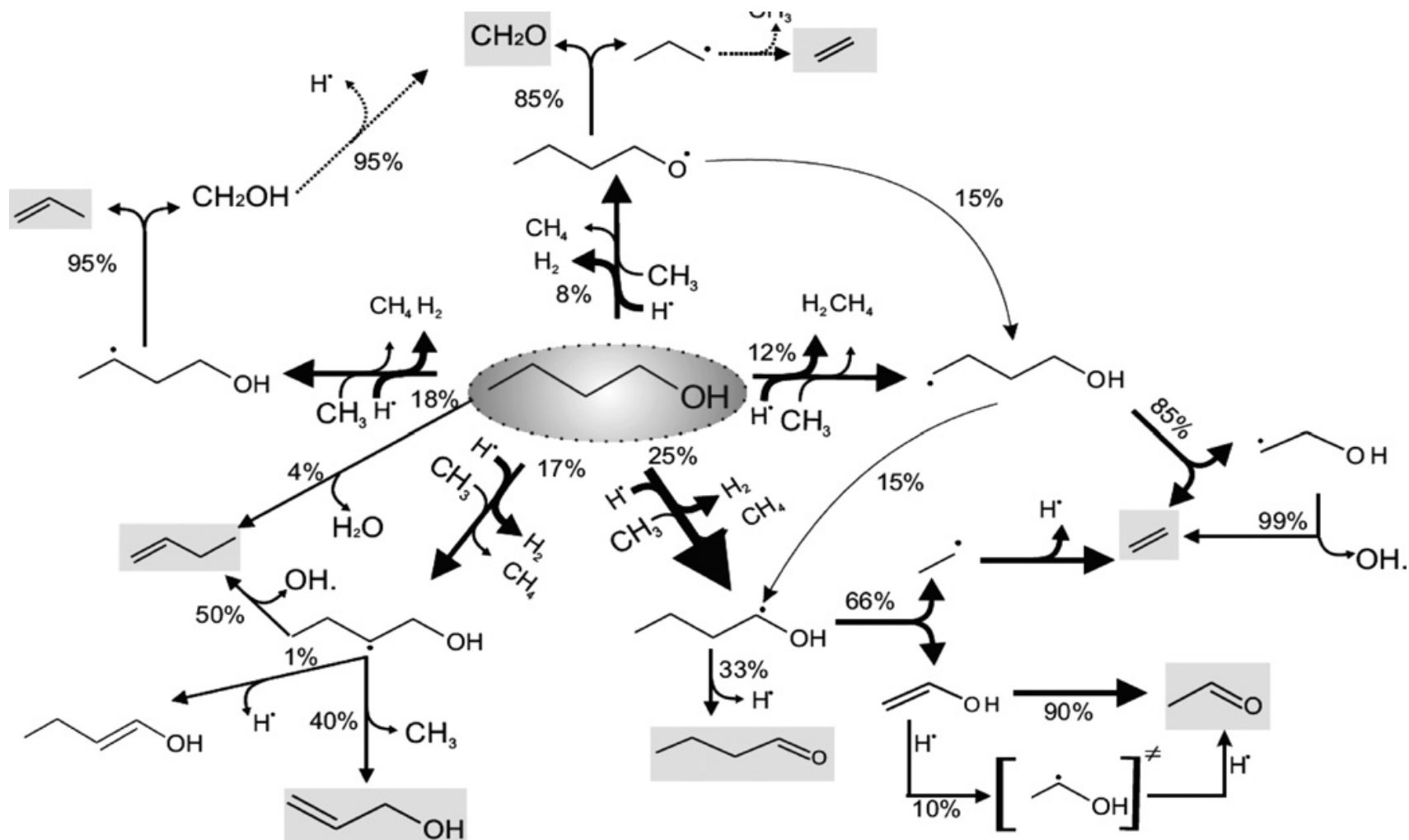
Example of reaction network: butyl

1-butyl isomerization to 2-butyl (via three- and four-member ring transition states)

the two beta-scission reactions of 1-butyl radical forming H atom + 1-butene and ethane + ethyl radical

the three beta-scission reactions of 2-butyl radical, forming H atom + 1-butene, H atom + 2-butene, and propene + methyl radical.

Example of reaction pathway analysis



Automatic estimation of pressure-dependent rate coefficients within RMG

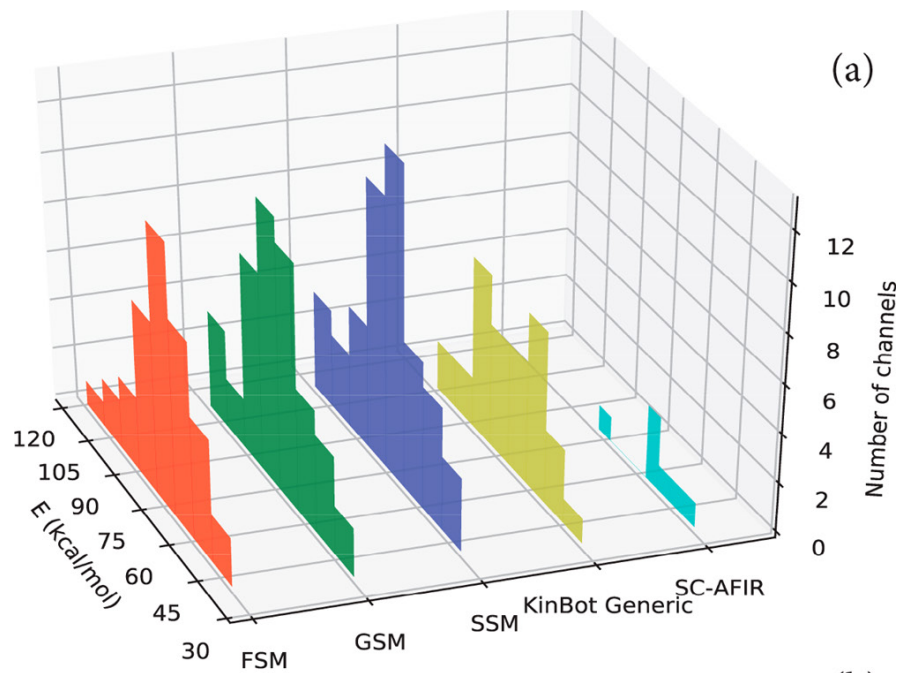
Allen et al. Phys. Chem. Chem. Phys., 2012, 14, 1131-1155

- A general framework for accurately and efficiently estimating the phenomenological pressure-dependent rate coefficients for reaction networks of arbitrary size and complexity using only high-pressure-limit information. Method includes:
- two methods of estimating the density of states of the species in the network, including a new method based on characteristic functional group frequencies.
- three methods of simplifying the full master equation model of the network to a single set of phenomenological rates.

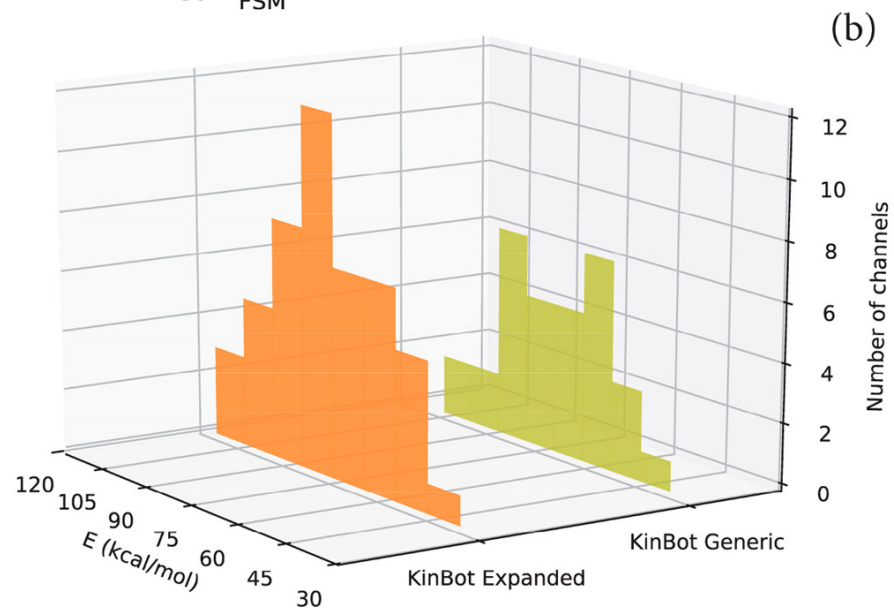
Unimolecular Reaction Pathways of a γ -Ketohydroperoxide from Combined Application of Automated Reaction Discovery Methods

Grambow et al, J Am Chem Soc, 2018, 140, 1035

- Combination of density functional theory with automated transition state search algorithms
- Applied to unimolecular reactions of 3-hydroperoxypropanal ($\text{CH}(\text{O})\text{CH}_2\text{CH}_2\text{OOH}$) using several different approaches
- 75 elementary unimolecular reactions were found, 68 of these were previously unknown and completely unexpected.
- Several of these involve low barrier reactions that may be relevant in combustion and atmospheric chemistry

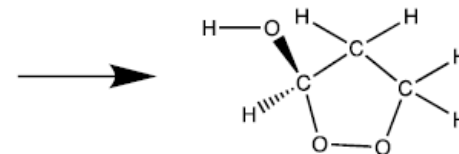
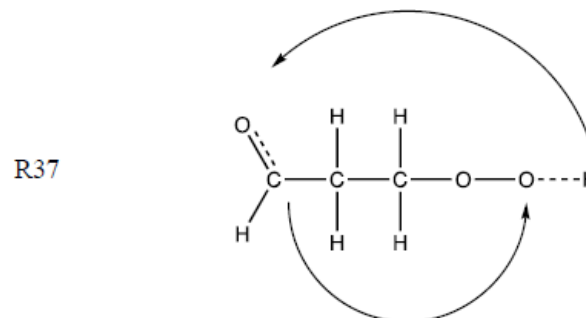


Histogram of energy barriers
using different methods





Energy barriers of 25 reactions with energy barriers below 40 kcal/mol



Korcek reaction

Some additional references on RMG

- ComputerPhysicsCommunications 203 (2016) 212-225 Reaction Mechanism Generator: Automatic construction of chemical kinetic mechanisms
- Combustion and Flame 160 (2013) 2343-2351 Hansen et al. The predictive capability of an automatically generated combustion chemistry mechanism: Chemical structures of premixed iso-butanol flames
- Computers and Chemical Engineering 52, (2013), 35-45 Magoon and Green Design and implementation of a next-generation software interface for on-the-fly quantum and force field calculations in automated reaction mechanism generation