

Topic 5

Chemical mechanisms

Examine ways in which mechanisms are constructed, their dependence on rate and thermodynamic data and their evaluation using experimental targets

Hierarchical approach

- Westbrook and Dryer, Proc. Combust. Inst. 18 (1981) 749-766, Prog. Energy Combust. Sci. 10 (1981) 1-57. Construction of comprehensive, hierarchical chemical mechanisms.
- Examples, H_2/O_2 :
 - Li et al. Int J Chem Kinet 36: 566-575, 2004, 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, 633-644, 2011

Li et al

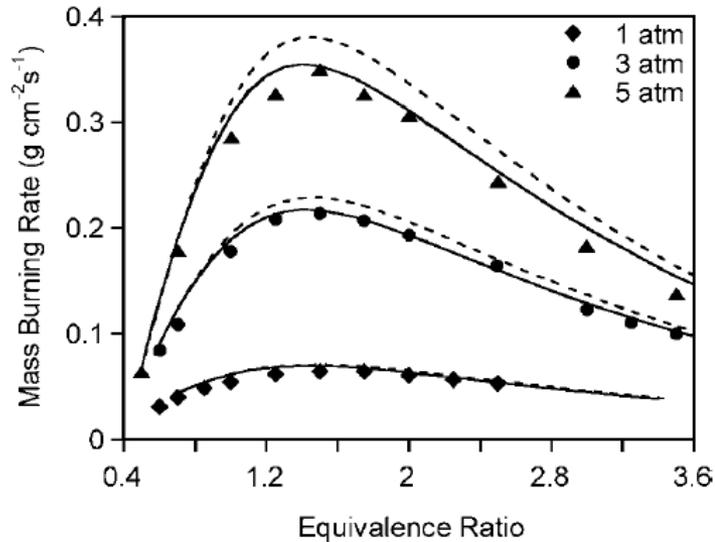


Figure 7 Laminar flame mass burning rate at 1, 3, and 5 atm for H₂/O₂/He mixture (O₂:He = 1:7). Symbols: experimental data [7]; solid lines: the present model; dashed lines: the model of Mueller et al. [1].

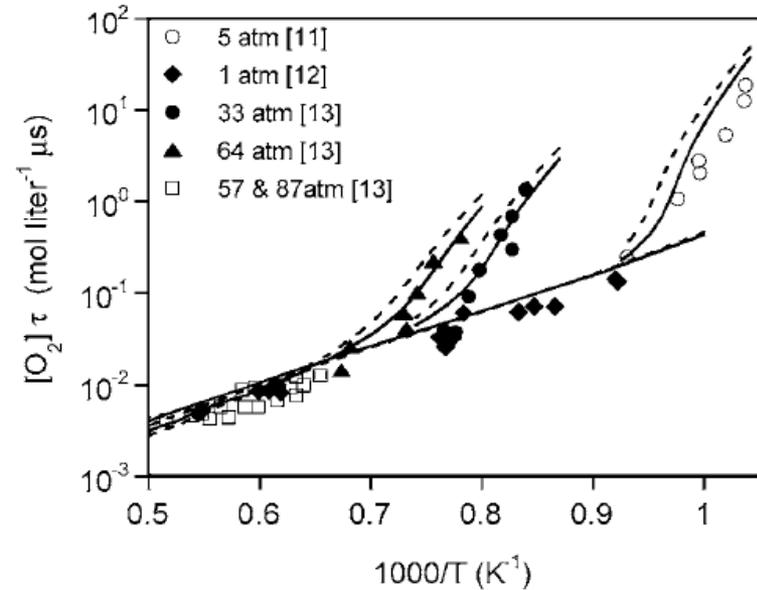
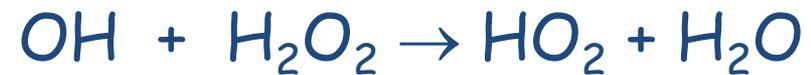
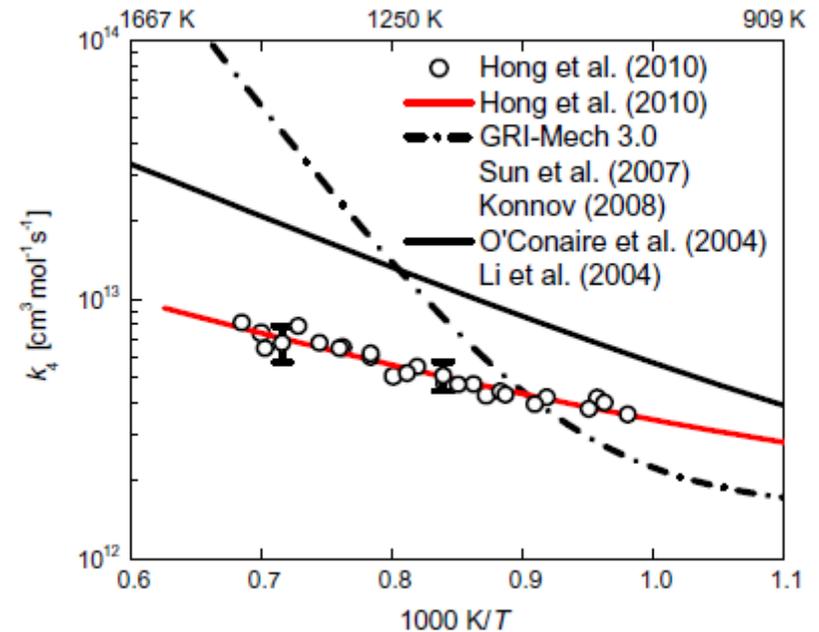
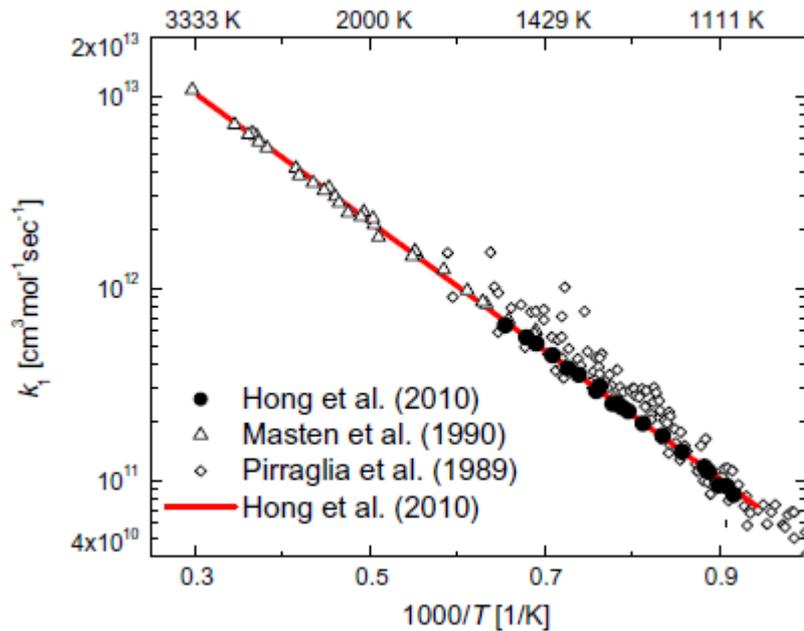
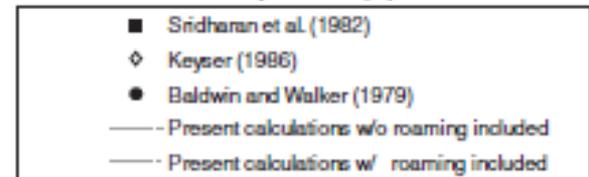
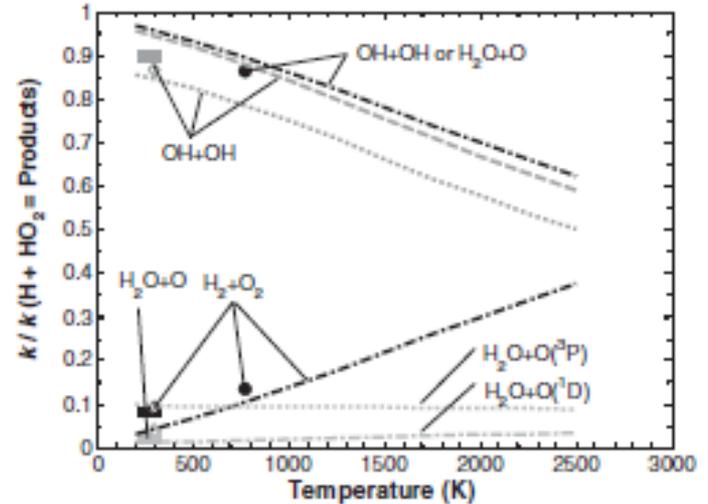
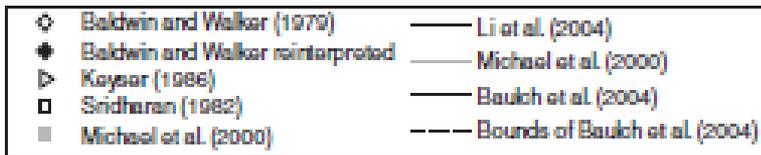
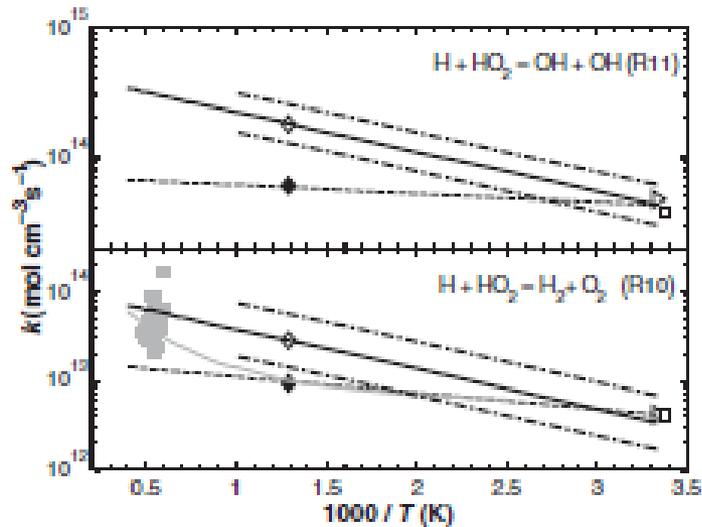


Figure 11 Ignition delay of H₂/O₂/Ar mixtures in shock tubes. Initial conditions: H₂ = 8.0%, O₂ = 2.0% at 5 atm [11]; H₂ = 1.0%, O₂ = 2.0% at 1 atm [12]; H₂ = 2.0%, O₂ = 1.0% at 33, 57, 64, and 87 atm [13]. Symbols: experimental data [11–13]; solid lines: the present model; dashed lines: Mueller et al. [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 $\frac{d[OH]}{dt}$.

Hong et al.



Burke et al.



Branching ratios

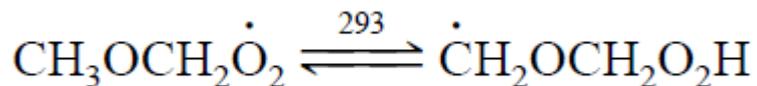
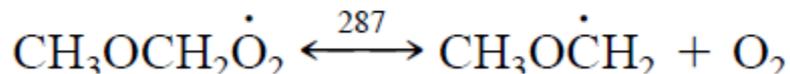
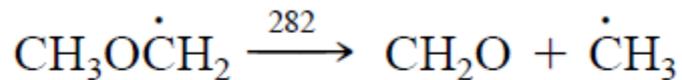
More complex mechanisms 1.

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>.

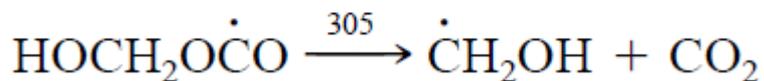
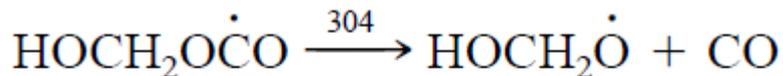
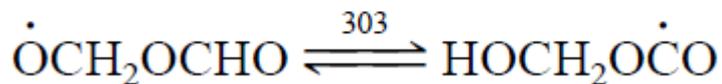
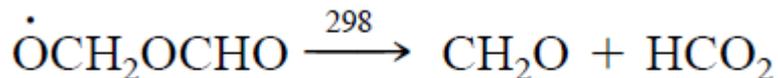
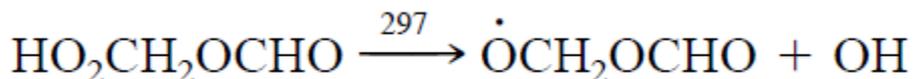
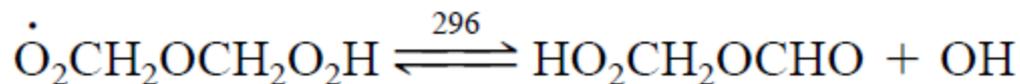
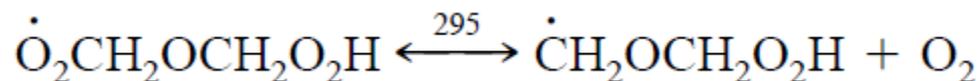
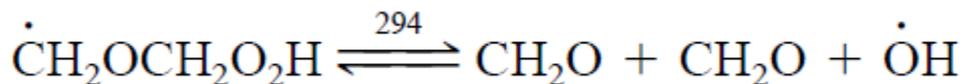
More complex mechanisms

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

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

Example of reaction list from GRI-Mech

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

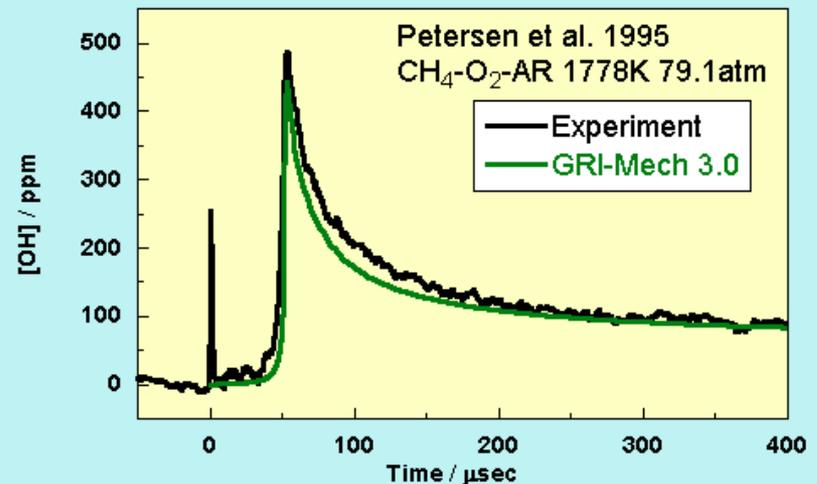
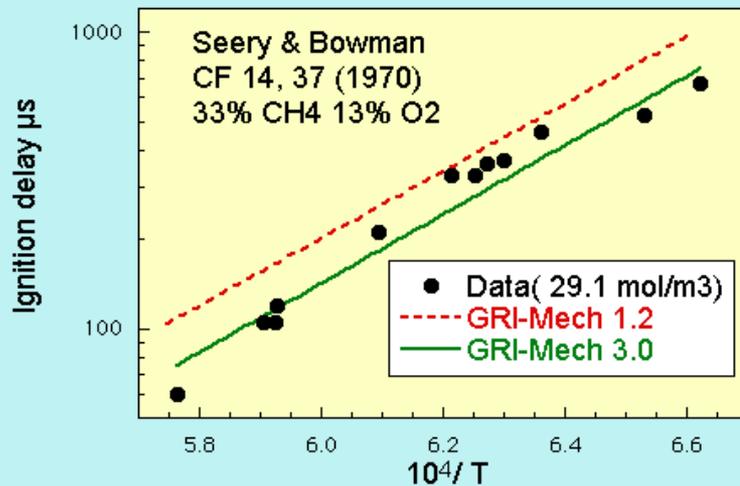
Click on reaction number for information e.g. Reaction 35: Served as an optimization variable in GRI-Mech 3.0 release and was changed by a factor of 1.2.

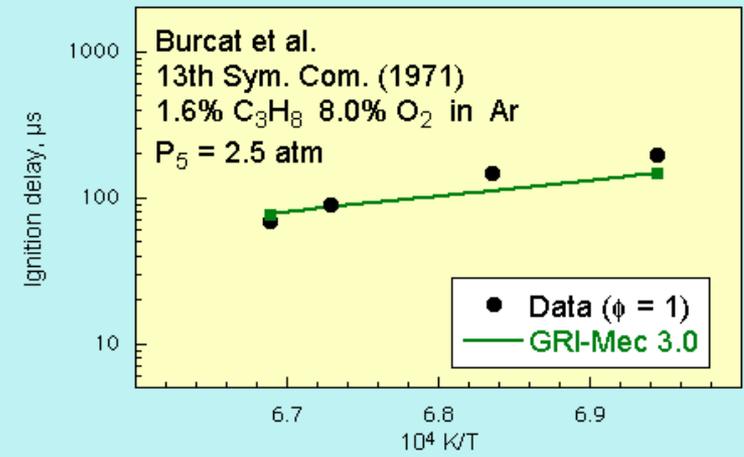
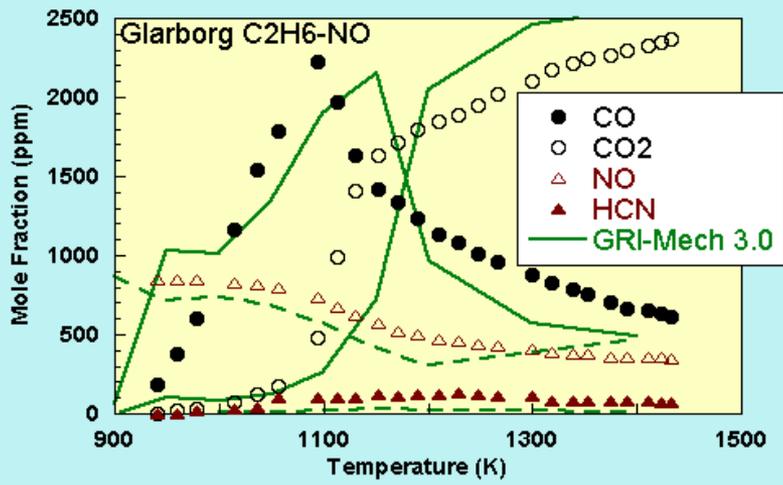
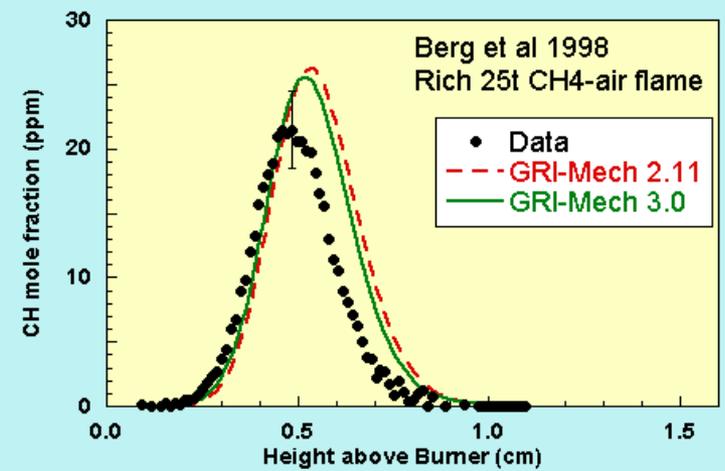
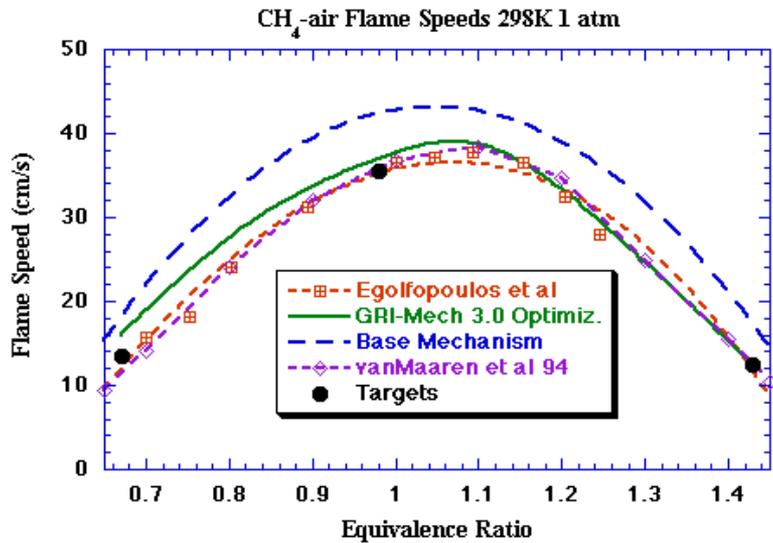
Thermodynamic and kinetic data for reaction 35

Temp (K)	delta-S (cal/mol K)	delta-H (kcal/mol)	kf ---- (mol, cm ³ , s) -----	kr -----	Keq (cm ³ /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:





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."

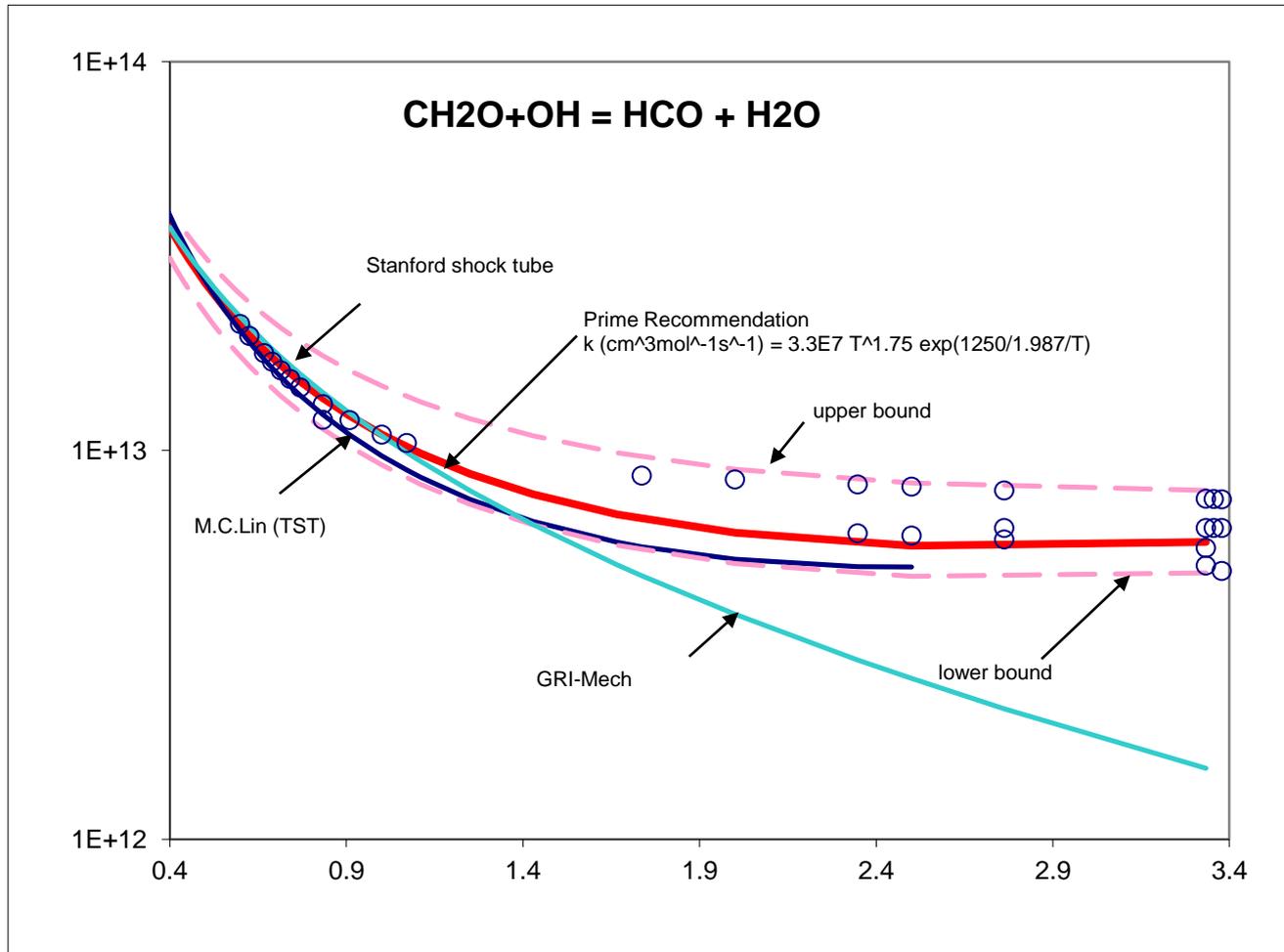
PrIMe Group directory 1

<u>Name</u>	<u>Subscribers</u>	<u>Description</u>
BioFuels	3	BioFuels
Burner-stabilized premixed flames	24	Burner-stabilized premixed flames
C0-C2	52	H ₂ /O ₂ /C ₀ + C ₁ /C ₂ hydrocarbon pyrolysis and oxidation
C3-C4	40	C ₃ -C ₄ hydrocarbon pyrolysis and oxidation
C5-C16	35	C ₅ -C ₁₆ hydrocarbon pyrolysis and oxidation
C6 + aromatics	20	C ₆ + aromatic hydrocarbon pyrolysis and oxidation
Cyber-numerics	26	Cyber-numerics
Diffusion flames	22	Diffusion flames
Flow reactors	2	Flow reactors
Industrial	8	Industrial
Laminar premixed flames	32	Laminar premixed flames (global properties)

PrIMe Group directory 2

N	7	Nitrogen containing
P-dependence	15	Pressure dependence of reactions
Quantum chemistry	2	Quantum chemistry
ReactionDesign	22	ReactionDesign
Shock tubes	32	Shock tubes
Soot	54	Soot
Spectroscopy	5	Spectroscopy
Stirred reactors	7	Stirred reactors
Thermo	36	Thermodynamic data
Transport	11	Transport data
TST	9	Transition-State theory
Turbulent flames	1	Turbulent flames

OH + CH₂O - PrIME recommendation



The best fit uses the Stanford shock tube data, as well as some of the room temperature experiments and Lin's TST results.

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
 - CO_2 and H_2O tunable IR diode laser absorption at 2.7 and 2.5 μm , resp.

Example of experimental measurements and comparison with existing mechanism

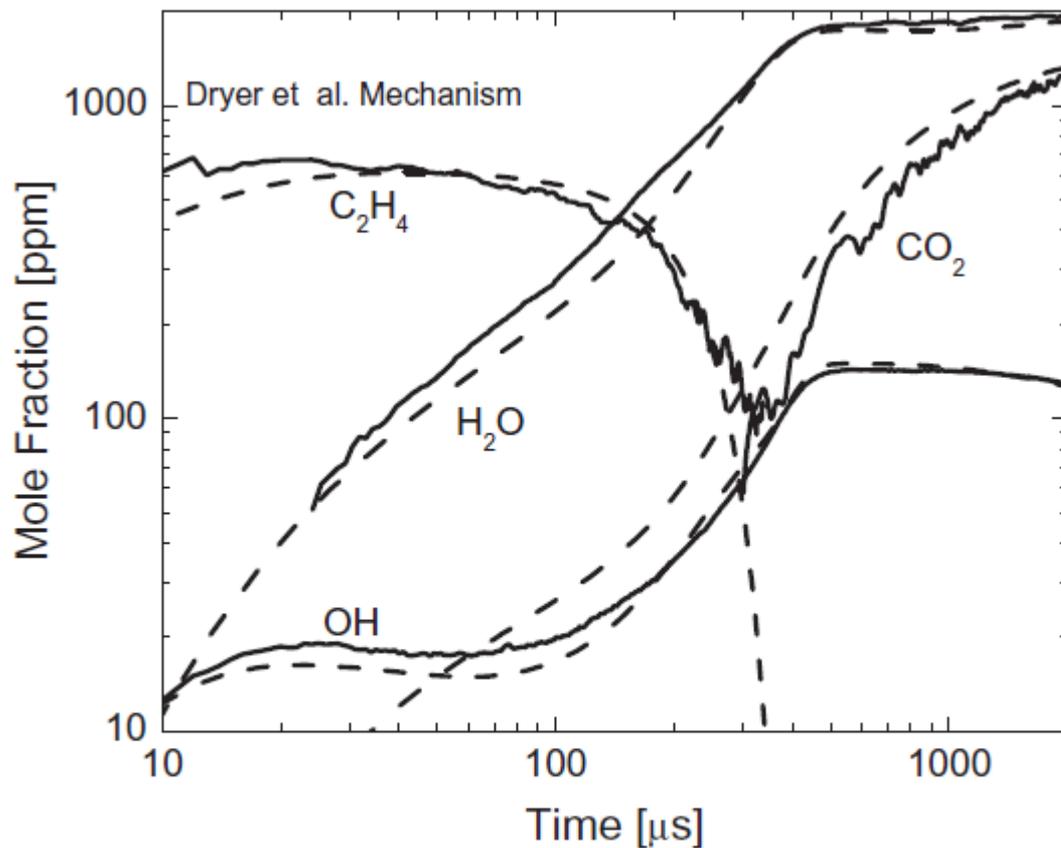


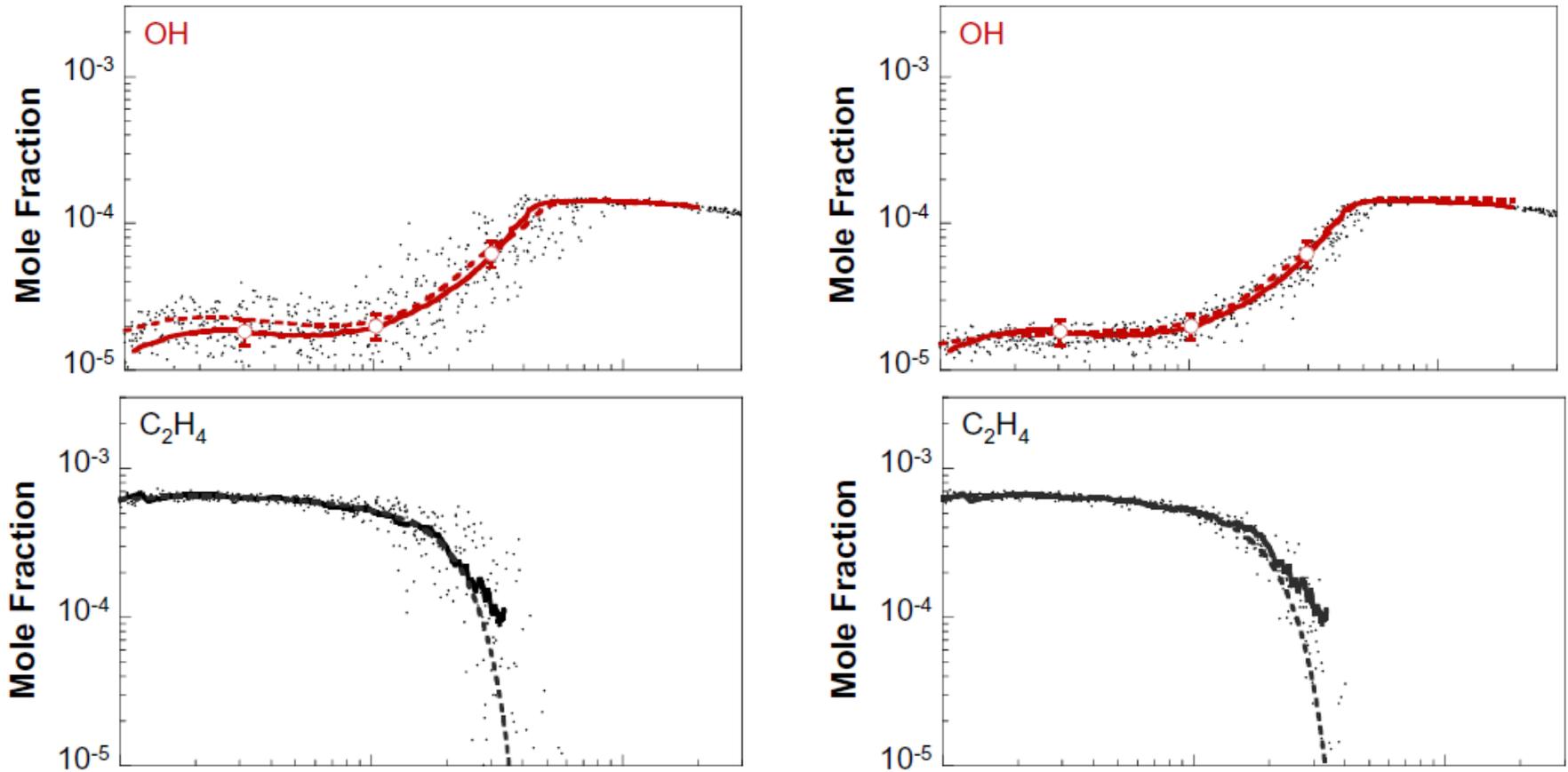
Fig. 7. Comparison of laser-absorption measurements with the Dryer et al. model [4]. Reflected shock wave conditions: 1494 K, 2.15 atm, 300 ppm *n*-heptane/O₂/argon, $\phi = 1$.

Recent 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



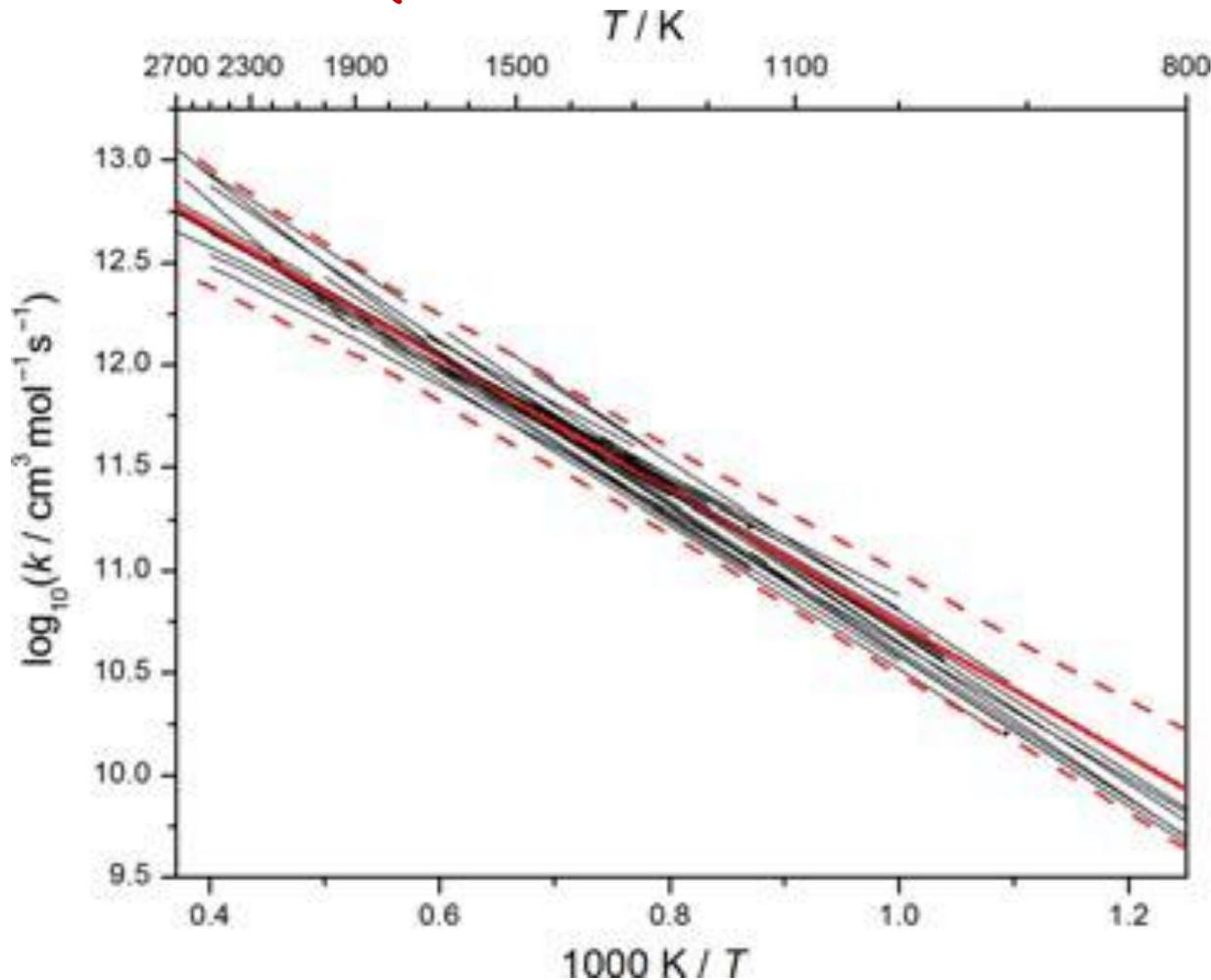
- Experimental (solid lines) and computed (dashed lines: nominal prediction; dots: uncertainty scatter). The open circles and the corresponding error bars designate data used as Series 1 targets and 2σ standard deviations, respectively. Left panel: prior model (Model I). Right panel: posterior model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

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

International Journal of Chemical Kinetics DOI 10.1002/kin.20717

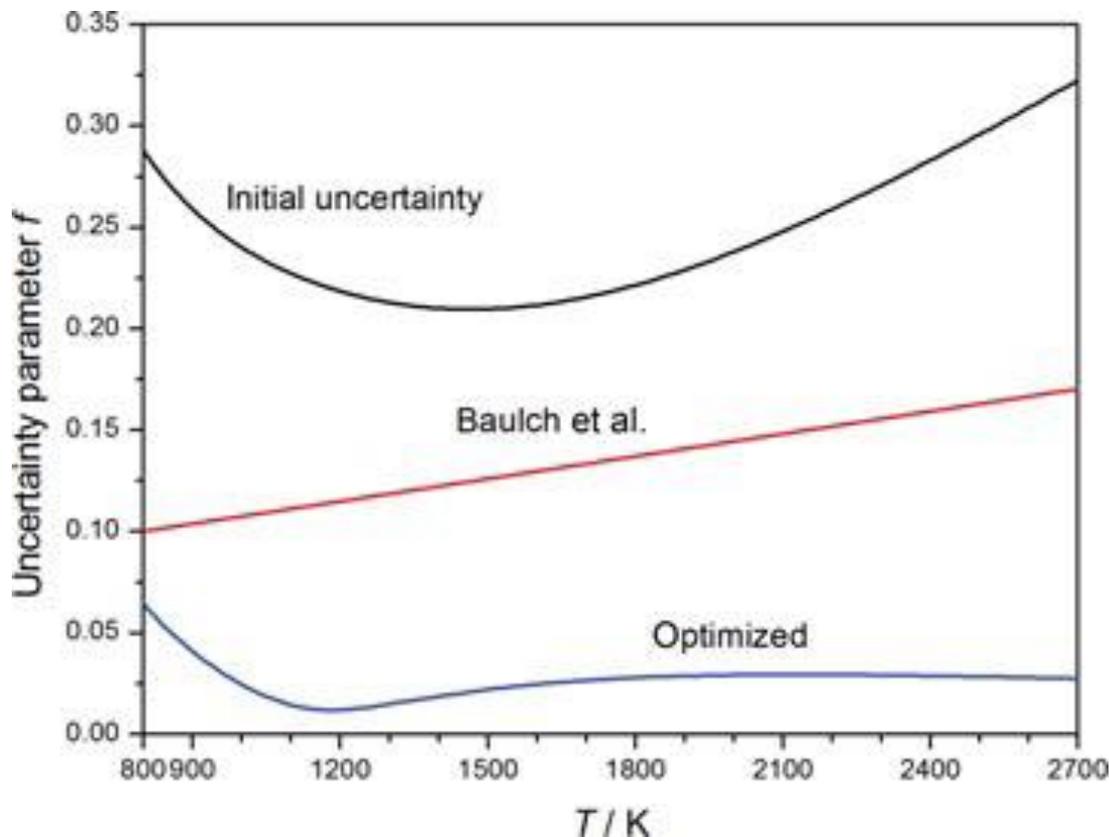
- the domain of feasibility of the Arrhenius parameters is determined from all of the available direct measurements
- optimal Arrhenius parameters are sought within this domain to reproduce the selected direct and indirect measurements.
(R1): $H + O_2 = OH + O$
(R2): $H + O_2 + M = HO_2 + M$ (low-pressure limit, $M = N_2$ or Ar).
- 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.

Arrhenius plot of all direct measurements of reaction (R1):
 $\text{H} + \text{O}_2 = \text{OH} + \text{O}$ (reminder from evaluation lectures)



- mean value (thick red line) is identical to the Baulch et al. evaluation. The upper and lower limits ($k_{\text{min}}(T)$ and $k_{\text{max}}(T)$) are indicated by red dashed lines.

Uncertainty parameter (f) as a function of temperature for reaction (R1): $\text{H} + \text{O}_2 = \text{OH} + \text{O}$,

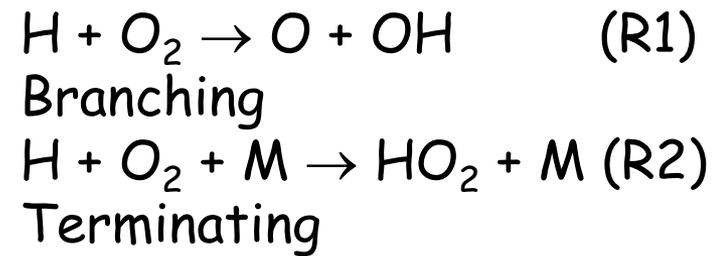
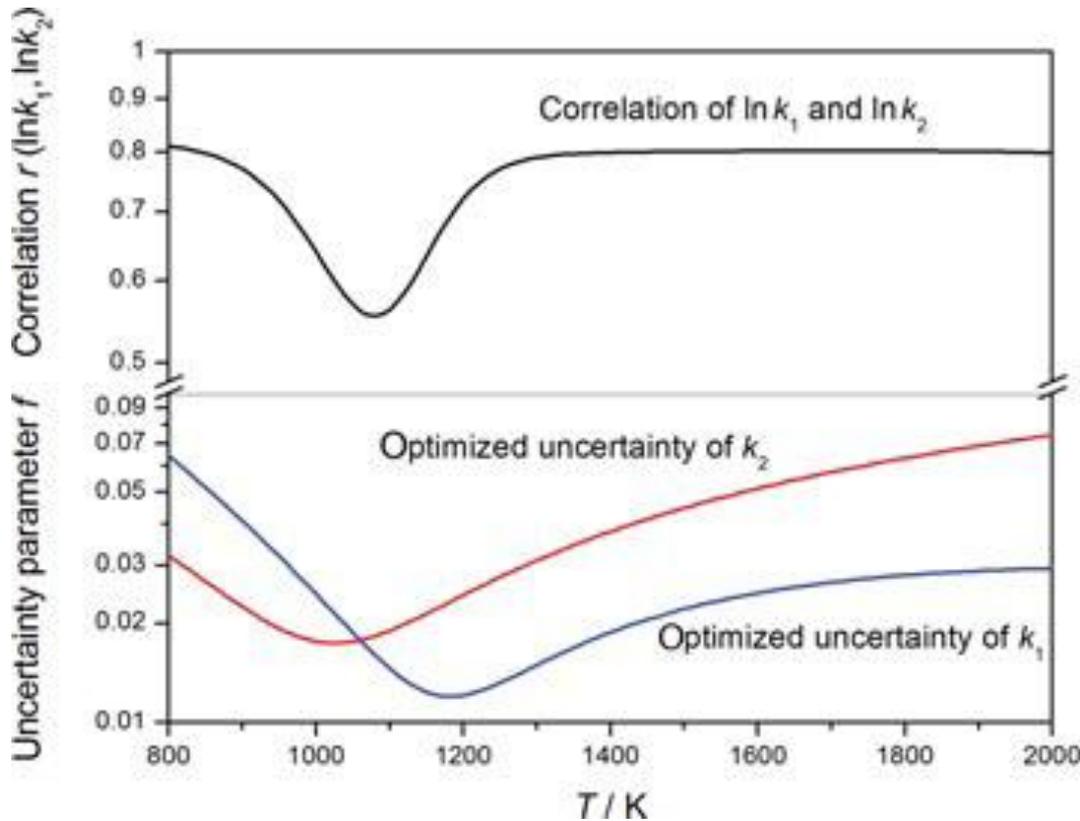


$$f(T) = \log_{10}(k^0(T)/k^{\min}(T)) \\ = \log_{10}(k^{\max}(T)/k^0(T))$$

can also link $f(T)$ to the standard deviation

- 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).

Correlation coefficient (r) between the logarithm of the rate coefficients of reactions (R1) and (R2) as a function of temperature.



- increasing the rate coefficients of reactions (R1) and (R2), the calculated ignition delay time decreases and increases respectively. Simultaneous increase of both rate coefficients may keep the ignition delay time constant.: positive correlation coefficient.

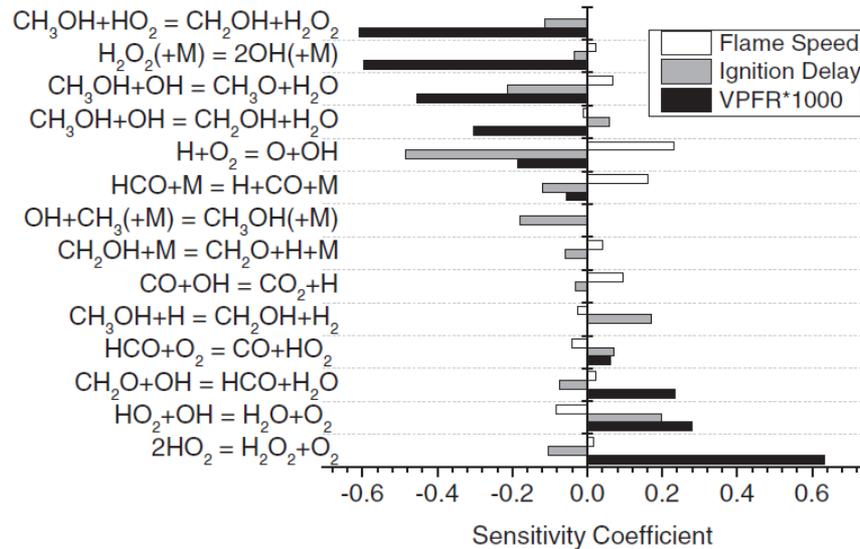
A Quantitative Explanation for the Apparent
Anomalous Temperature Dependence of $\text{OH} + \text{HO}_2 =$
 $\text{H}_2\text{O} + \text{O}_2$ through Multi-Scale Modeling
Burke et al. Comb Symp 2012

- kinetic model: theoretical kinetics parameters (with constrained uncertainties), related through kinetics calculations to T/P/M-dependent rate constants (with propagated uncertainties), and then through physical models to combustion behaviour (with propagated uncertainties).
- yields more reliable extrapolation of limited data to conditions outside the validation set.

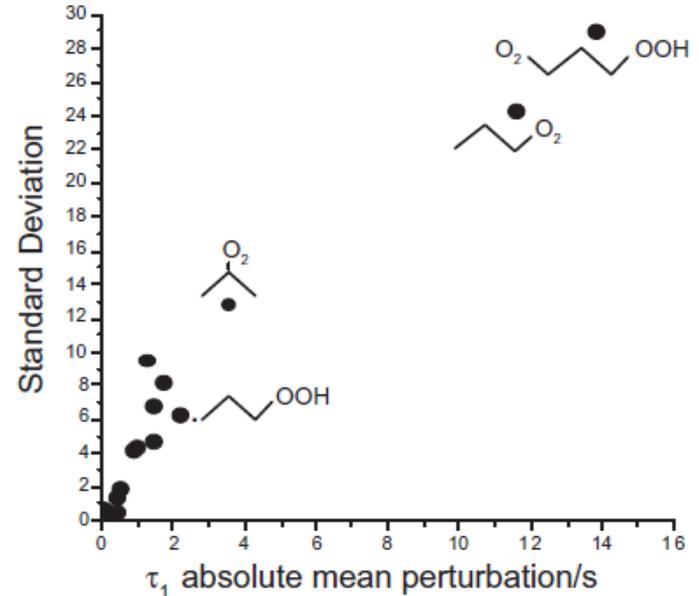
The role of sensitivity and uncertainty analysis in combustion modelling (A S Tomlin, Proc Comb Inst 34 (2013) 159-176)

- 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

Automatic generation - 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 (Green et al. "RMG - Reaction Mechanism Generator v3.1", 2009, <<http://rmg.sourceforge.net/>>).
- 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

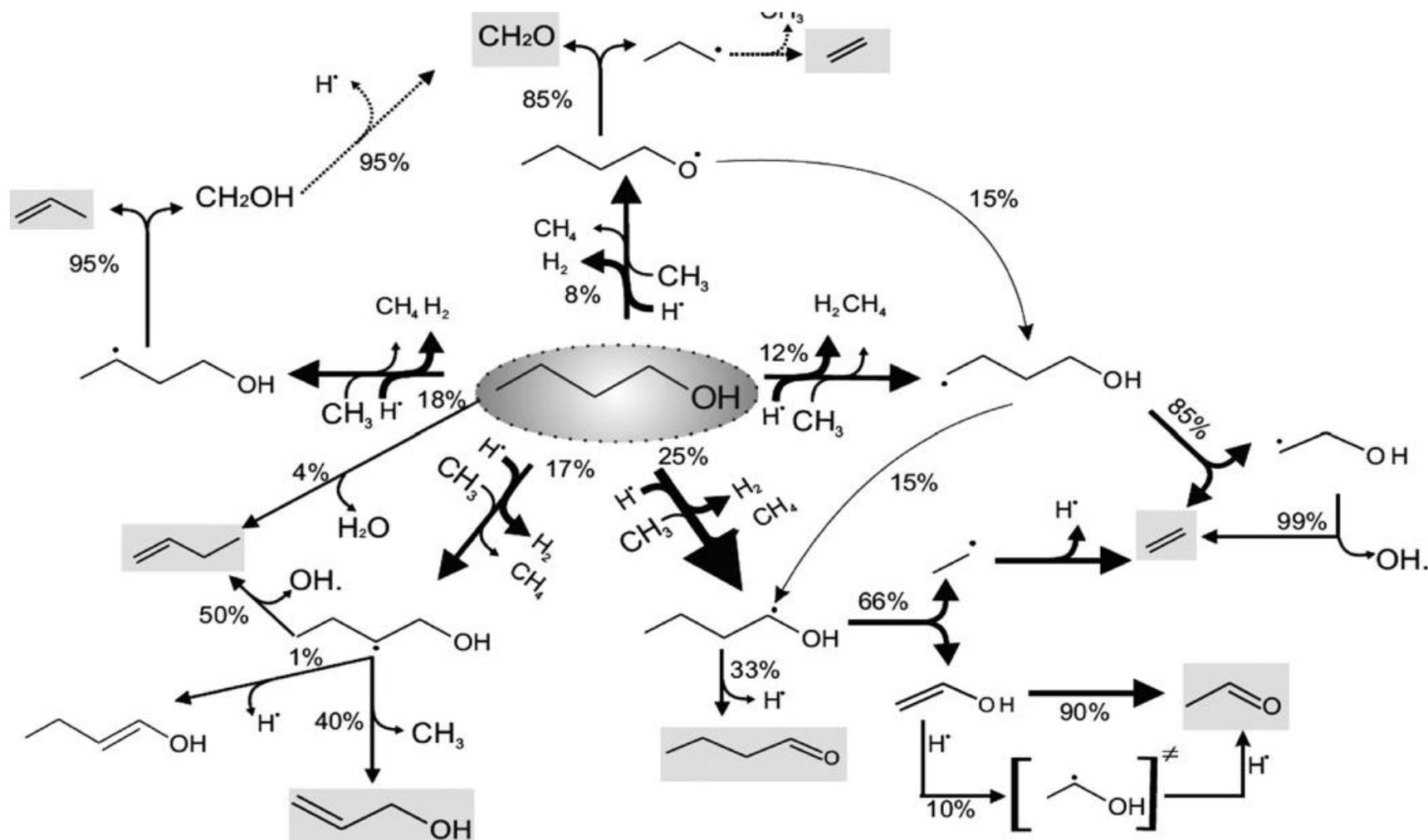
Example of reaction network: butyl

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.