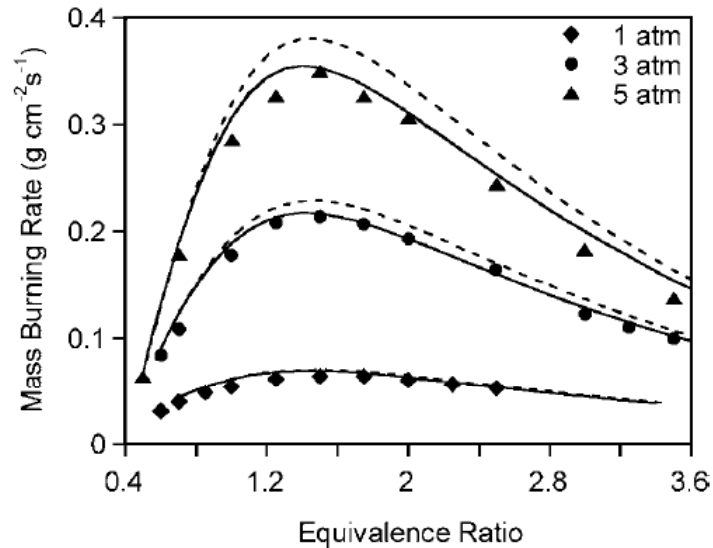


# Chemical mechanisms

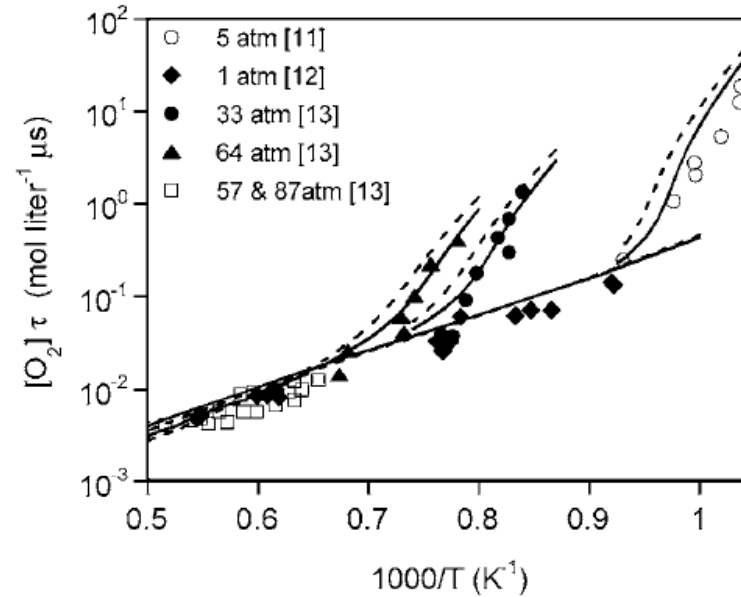
Examine (i) ways in which mechanisms are constructed, (ii) their dependence on rate and thermodynamic data and (iii) their evaluation using experimental targets

## 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. Current update in press in IJCK
  - Konnov, Combustion and Flame 152 (2008) 507-528. Examination of uncertainties in rate coefficients based on earlier (2004 )mechanism



**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  $1 \times 10^{-6}$  mol/L; and for Ref. [13], by the maximum of  $\frac{d[\text{OH}]}{dt}$ .

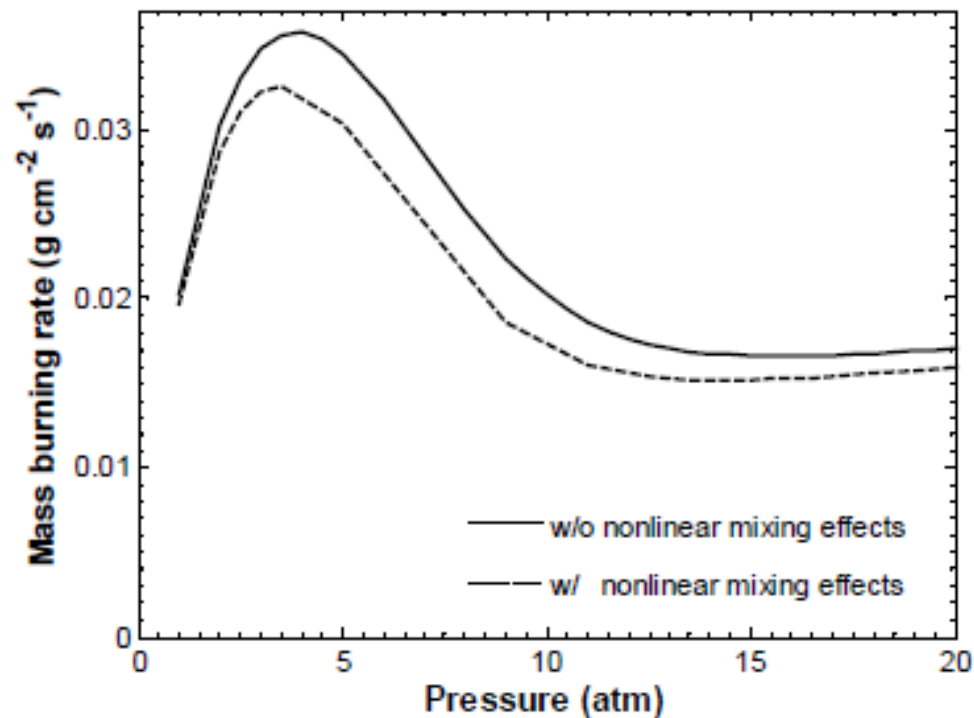
## Comprehensive H<sub>2</sub>/O<sub>2</sub> Kinetic Model for High-Pressure Combustion

Michael P. Burke, Marcos Chaos, Yiguang Ju,  
Frederick L. Dryer, Stephen J. Klippenstein

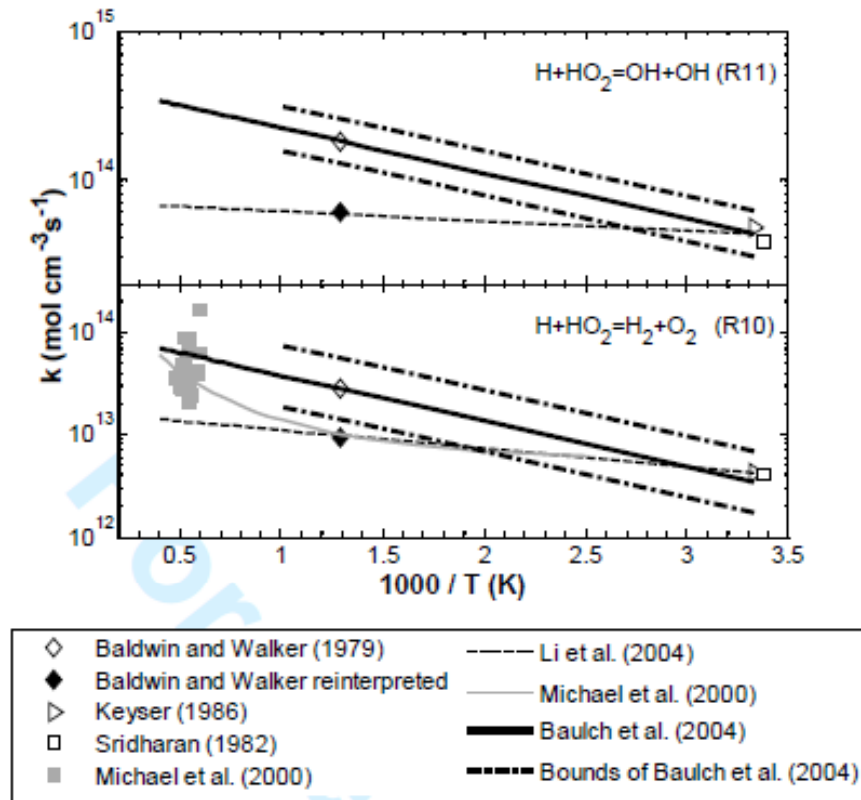
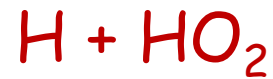
An updated H<sub>2</sub>/O<sub>2</sub> kinetic model based on that of Li et al. is presented and tested against a wide range of combustion targets. The primary motivations of the model revision are to incorporate recent improvements in rate constant treatment as well as resolve discrepancies between experimental data and predictions using recently published kinetic models in dilute, high-pressure flames.

- [http://www.princeton.edu/mae/people/faculty/dryer/homepage/combustion\\_lab/](http://www.princeton.edu/mae/people/faculty/dryer/homepage/combustion_lab/)

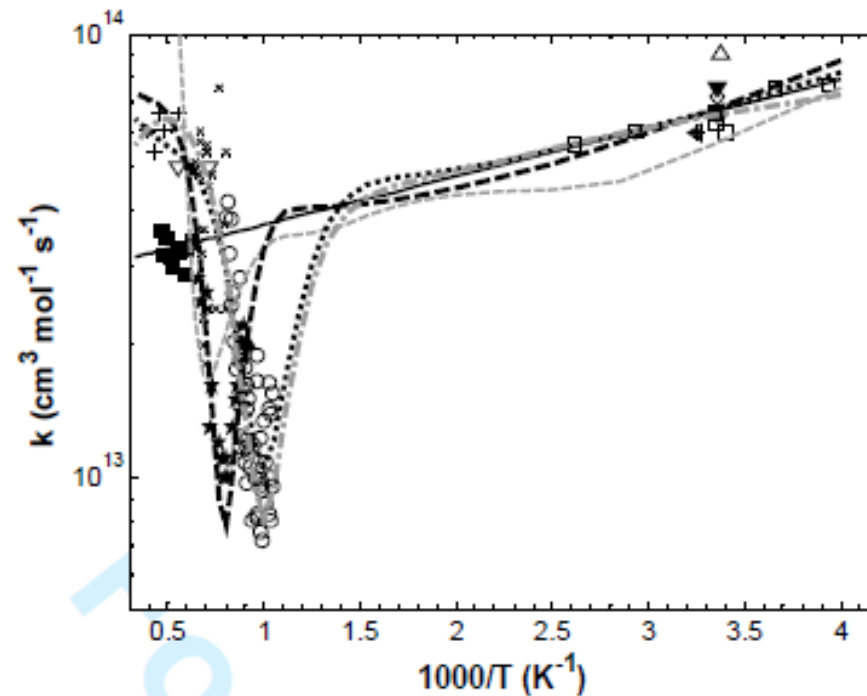
## Non linear mixture effects - H + O<sub>2</sub> + M



**Fig. 4.** Laminar flame mass burning rates in H<sub>2</sub>/O<sub>2</sub>/He mixtures of equivalence ratio 0.3 and He dilution such that the adiabatic flame temperature is near 1400 K. Solid lines represent the present model; dashed lines a modified version of the present model where  $k_0$  is adjusted to simulate nonlinear mixture behavior.

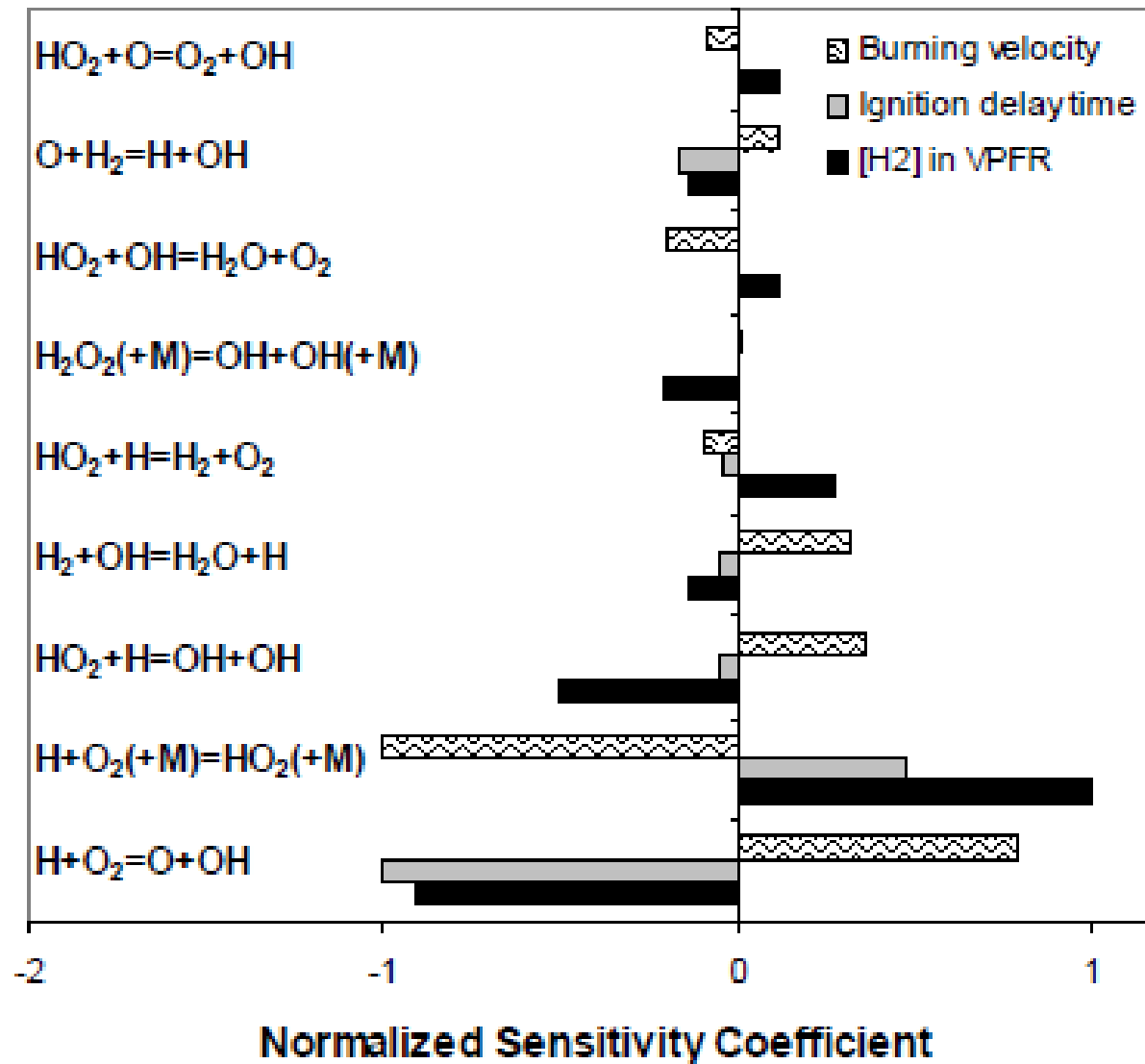


adopts the rate constant expression proposed by Michael et al. [51] for R10 while imposing a  $\sim 25\%$  reduction in the *A-factor* (within present uncertainties) in order to maintain agreement against the flow reactor speciation data from Mueller et al.



▽ Peeters and Mahnen (1973)	★ Hippler et al. (1995)
▼ DeMore (1979)	○ Kappel et al. (2002)
△ Lii et al. (1980)	× Srinivasan et al. (2006)
† Cox et al. (1981)	■ Hong et al. (2010)
△ Kurylo et al. (1981)	— Keyser (1988)
● Braun et al. (1982)	— Sivaramakarishnan et al. (2007)
◇ DeMore (1982)	—■— Chaos & Dryer (2008) - Hippler
+ Goodings & Hayhurst (1988)	—●●● Chaos & Dryer (2008) - Kappel
□ Keyser (1988)	—···· Rasmussen et al. (2008)
▲ Hippler & Troe (1992)	

# Normalized sensitivity coefficients of observables to A-factors of reactions for selected representative cases:





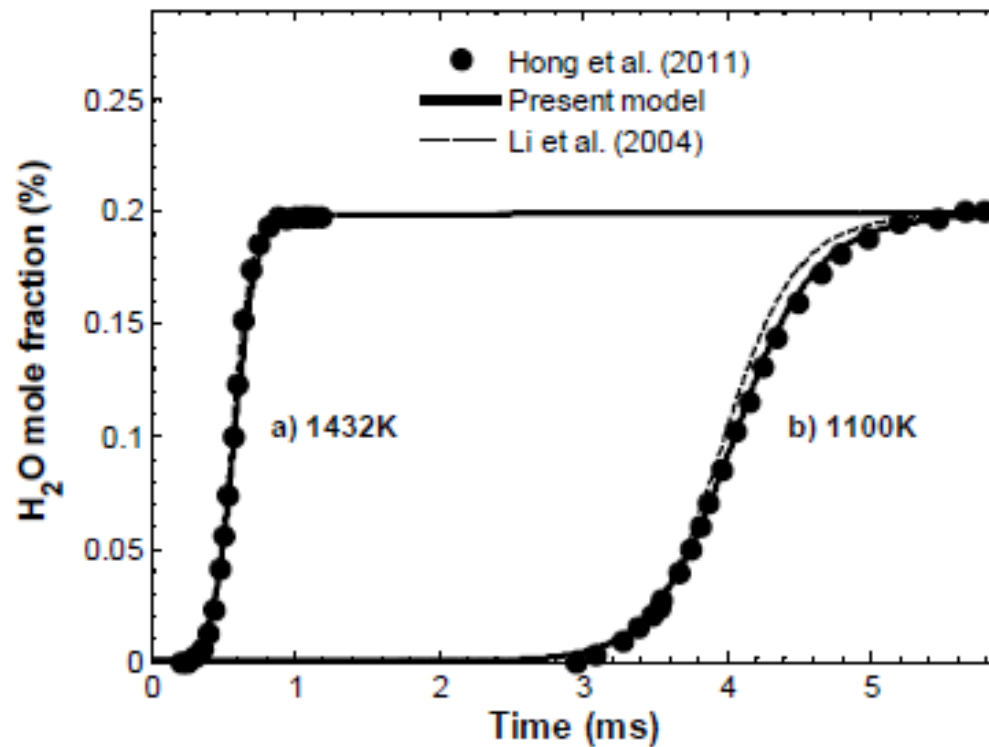


Fig. 11.  $\text{H}_2\text{O}$  time-histories behind shock waves in  $\text{H}_2/\text{O}_2/\text{Ar}$  mixtures composed of a)  $\text{H}_2 = 0.9\%$ ,  $\text{O}_2 = 0.1\%$ , and Ar balance at 1.83 atm and 1472 K; b)  $\text{H}_2 = 2.9\%$ ,  $\text{O}_2 = 0.1\%$ , and Ar balance at 1.95 atm at 1100 K. Symbols represent experimental data from Hong et al. [40]; solid lines the present model; dashed lines the model of Li et al. [12]. Simulations performed using constant  $u$ - $v$  and  $p$ - $h$  assumptions yield identical predictions.

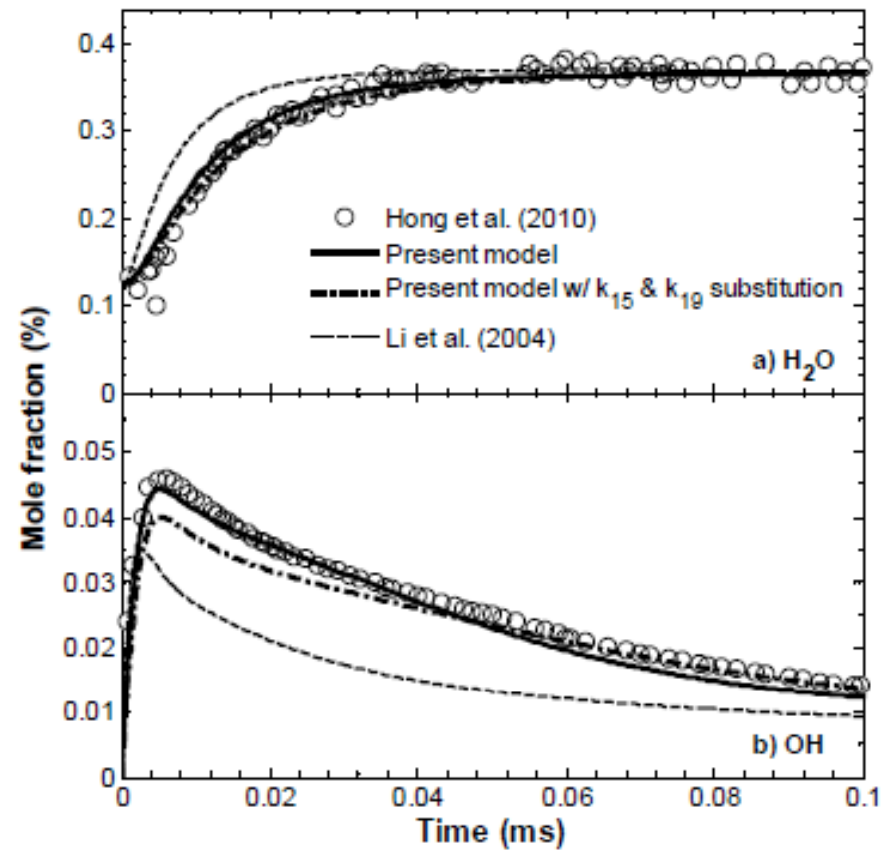
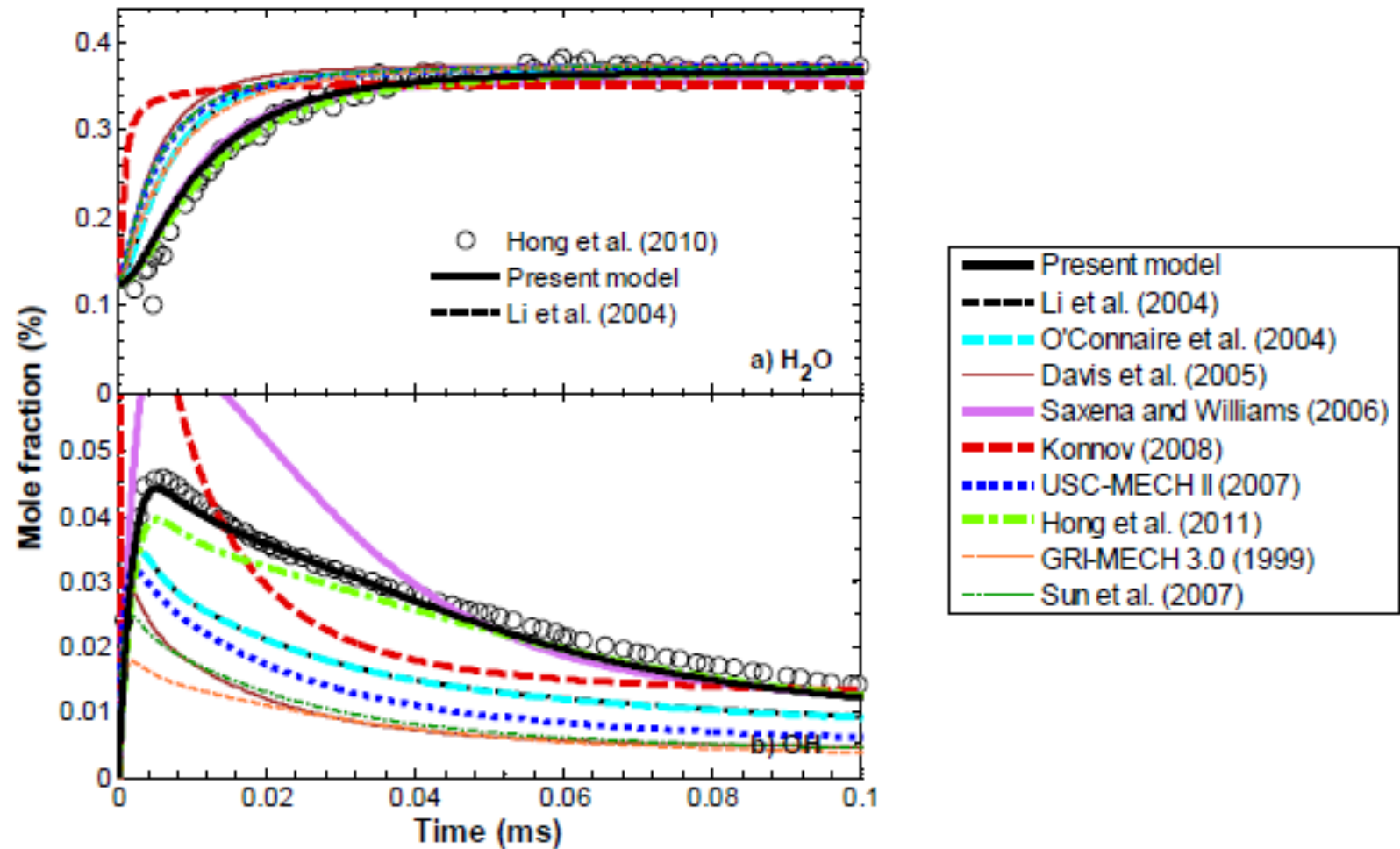


Fig. 13.  $\text{H}_2\text{O}$  and OH time-histories behind reflected shock waves in  $\text{H}_2\text{O}_2/\text{H}_2\text{O}/\text{O}_2/\text{Ar}$  mixtures composed of  $\text{H}_2\text{O}_2 = 0.25\%$ ,  $\text{H}_2\text{O} = 0.062\%$ ,  $\text{O}_2 = 0.031\%$ , and Ar balance at 1398 K and 1.91 atm. Symbols represent experimental data from Hong et al. [79]; solid lines the present model; dashed-dotted lines the present model with  $k_{15}$  and  $k_{19}$  substituted from Hong et al. [79]; dashed lines the model of Li et al. [12]. Simulations were performed using a constant  $p$ - $h$  assumption as used in Hong et al. [79].

K15:  $\text{H}_2\text{O}_2 + \text{M}$ ; k19:  $\text{OH} + \text{H}_2\text{O}_2$



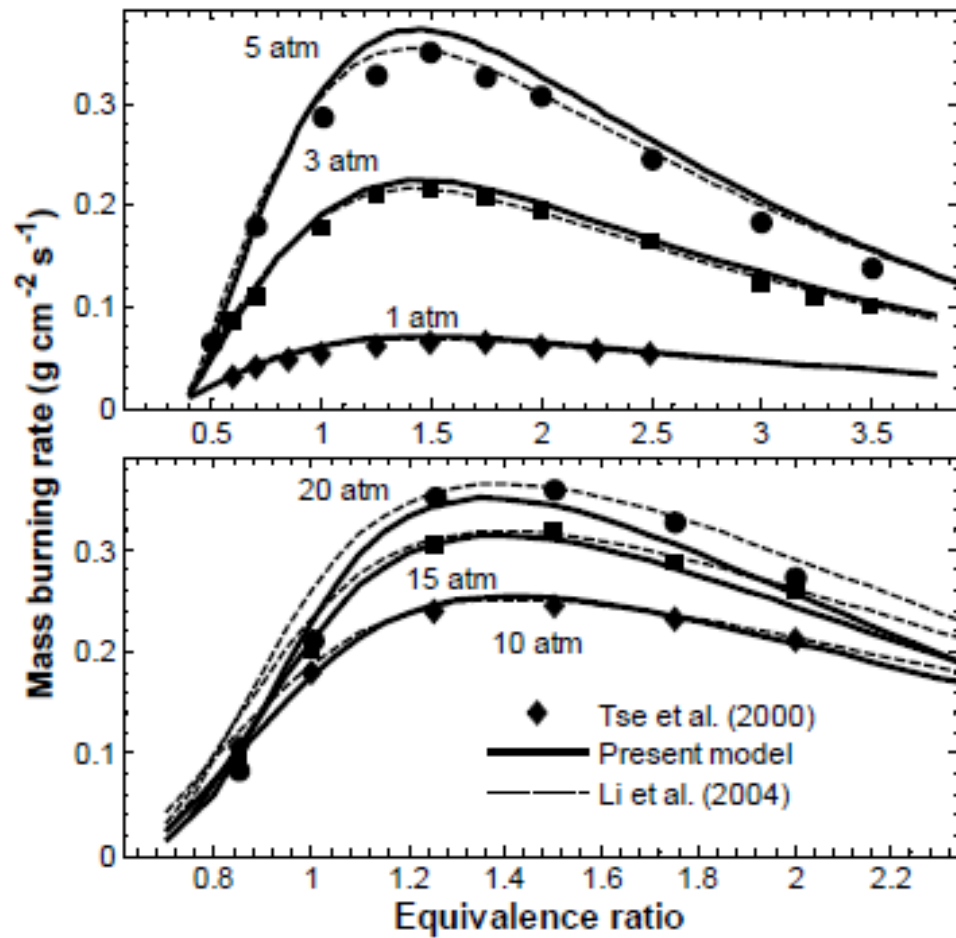
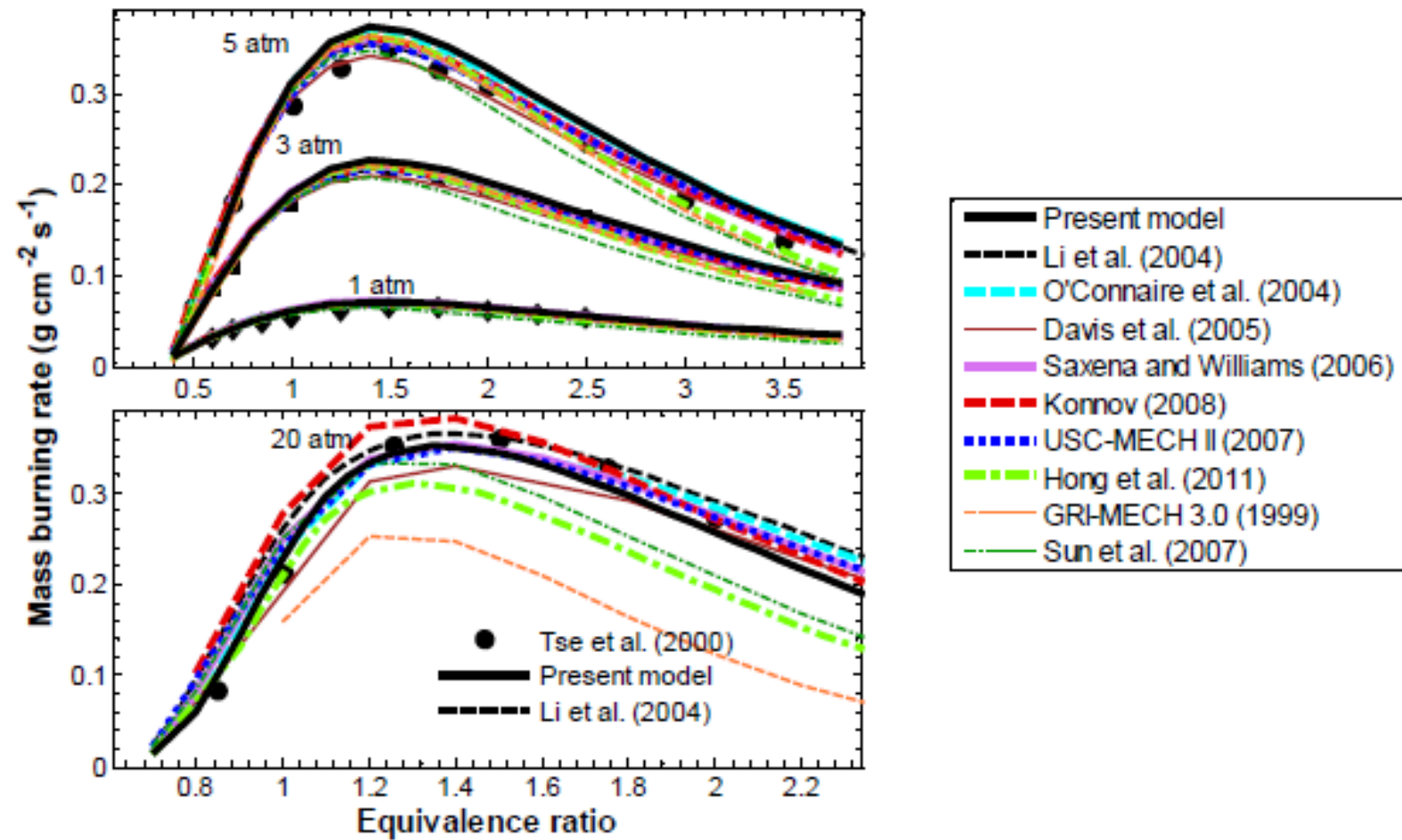


Fig. 21. Laminar flame mass burning rate a) at 1, 3, and 5 atm for  $H_2/O_2/He$  mixture with dilution ratio  $O_2:He = 1:7$  and b) at 10, 15, and 20 atm for  $H_2/O_2/He$  mixture with dilution ratio  $O_2:He = 1:11.5$ . Symbols represent experimental data from Tse et al. [4]; solid lines the present model; dashed lines the model of Li et al. [12].

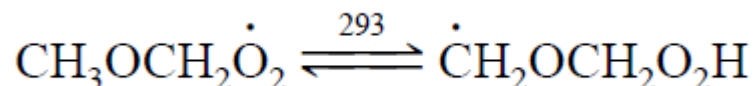
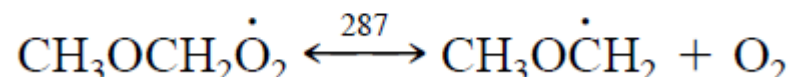
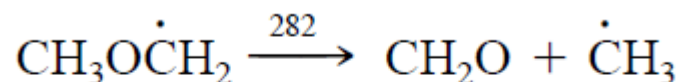


## Selective optimisation

- Turanyi et al.
- R1:  $\text{H} + \text{O}_2 = \text{OH} + \text{O}$  and R2:  $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$ .  
In total, 8 direct measurements for reaction R1 (725 data points), 5 direct measurements for reaction R2 (93 data points), 11 ignition time measurements (77 data points) and 6  $\text{H}_2\text{O}$  concentration–time curves (20500 data points) were taken into account.  
Covariance matrices provided for rate parameters

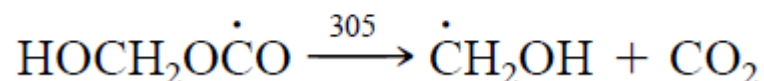
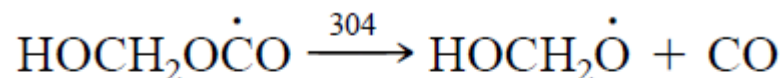
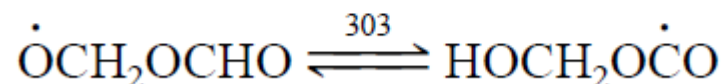
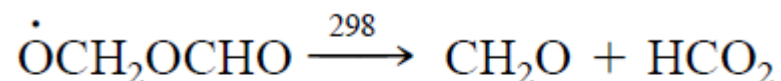
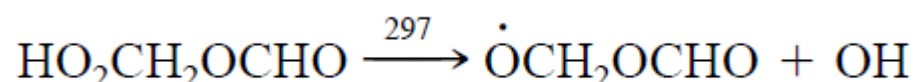
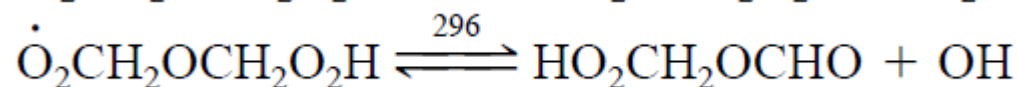
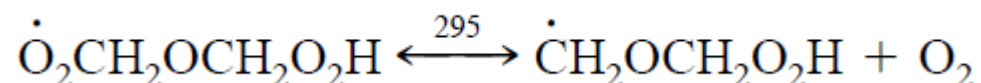
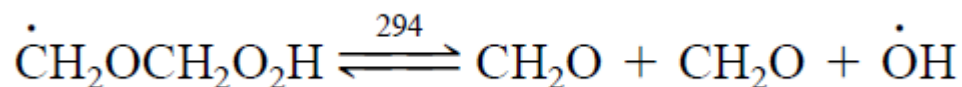
## More complex mechanisms

### 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/](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://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

<a href="#">26</a>	O + C2H5 -> CH3 + CH2O	2.24E+13			
<a href="#">27</a>	<b>O + C2H6 -&gt; OH + C2H5</b>	8.98E+07	1.9	5690	3.0
<a href="#">28</a>	O + HCCO -> H + CO + CO	1.00E+14			
<a href="#">29</a>	O + CH2CO -> OH + HCCO	1.00E+13		8000	
<a href="#">30</a>	O + CH2CO -> CH2 + CO2	1.75E+12		1350	
<a href="#">31</a>	O2 + CO -> O + CO2	2.50E+12		47800	
<a href="#">32</a>	<b>O2 + CH2O -&gt; HO2 + HCO</b>	1.00E+14		40000	1.2; 2.1; 3.0
<a href="#">33</a>	<b>H + O2 + M -&gt; HO2 + M</b>	2.80E+18	-0.9		2.1; 3.0
<a href="#">34</a>	<b>H + O2 + O2 -&gt; HO2 + O2</b>	2.08E+19	-1.2		3.0
<a href="#">35</a>	<b>H + O2 + H2O -&gt; HO2 + H2O</b>	1.13E+19	-0.8		1.1; 1.2; 2.1; 3.0
<a href="#">36</a>	<b>H + O2 + N2 -&gt; HO2 + N2</b>	2.60E+19	-1.2		2.1; 3.0
<a href="#">37</a>	<b>H + O2 + AR -&gt; HO2 + AR</b>	7.00E+17	-0.8		1.2; 2.1; 3.0
<a href="#">38</a>	<b>H + O2 -&gt; O + OH</b>	2.65E+16	-0.7	17041	1.1; 1.2; 2.1; 3.0
<a href="#">39</a>	H + H + M -> H2 + M	1.00E+18	-1.0		
<a href="#">40</a>	H + H + H2 -> H2 + H2	9.00E+16	-0.6		
<a href="#">41</a>	<b>H + H + H2O -&gt; H2 + H2O</b>	6.00E+19	-1.2		3.0
<a href="#">42</a>	H + H + CO2 -> H2 + CO2	5.50E+20	-2.0		
<a href="#">43</a>	<b>H + OH + M -&gt; H2O + M</b>	2.20E+22	-2.0		1.1; 1.2; 2.1; 3.0
<a href="#">44</a>	H + HO2 -> O + H2O	3.97E+12		671	
<a href="#">45</a>	<b>H + HO2 -&gt; O2 + H2</b>	4.48E+13		1068	3.0
<a href="#">46</a>	<b>H + HO2 -&gt; OH + OH</b>	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

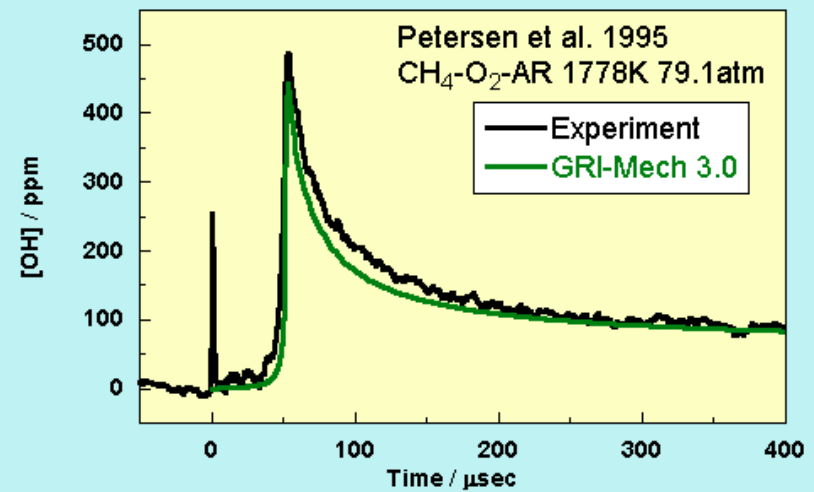
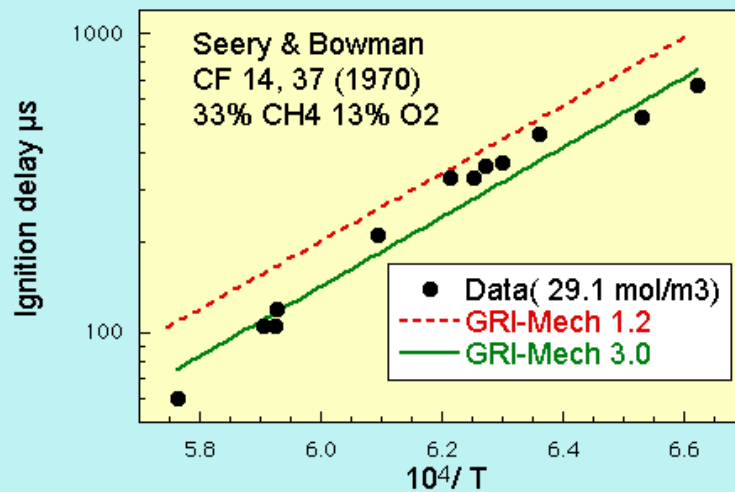
Example of reaction list from GRI-Mech  
 Reaction in **bold** are those whose rate coefficients served as *active* parameters in model optimization, and those in red are active parameters whose values were changed as a result of optimization  
 Click on reaction number for information  
 e.g. Reaction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

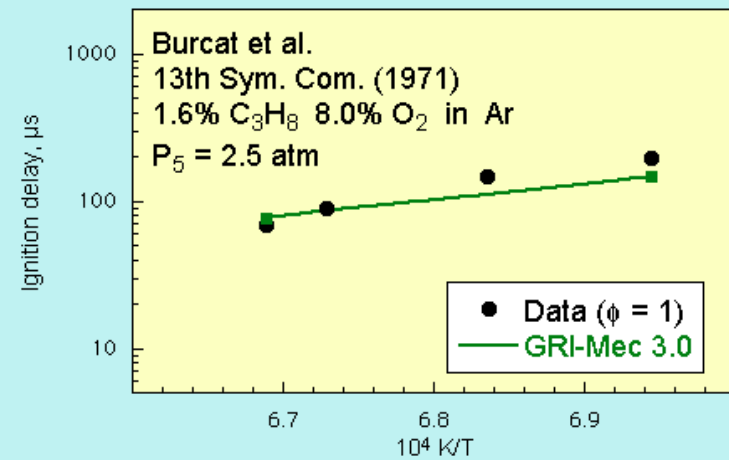
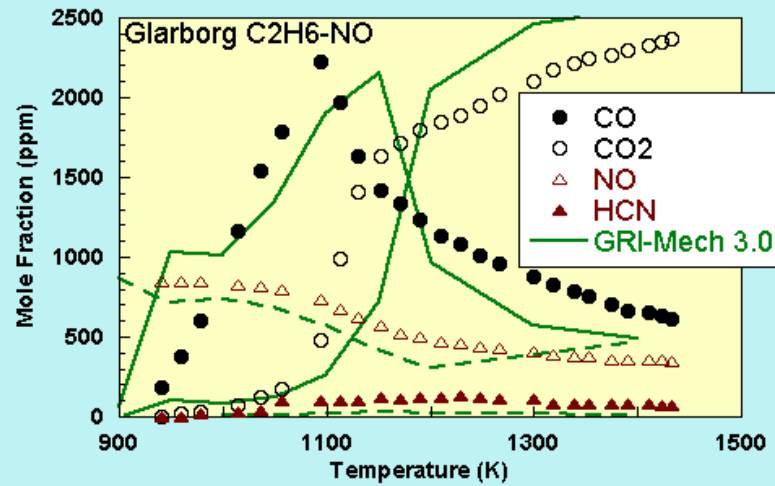
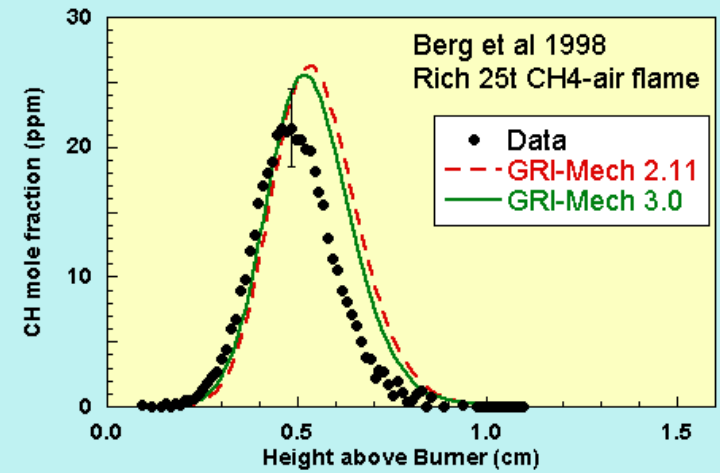
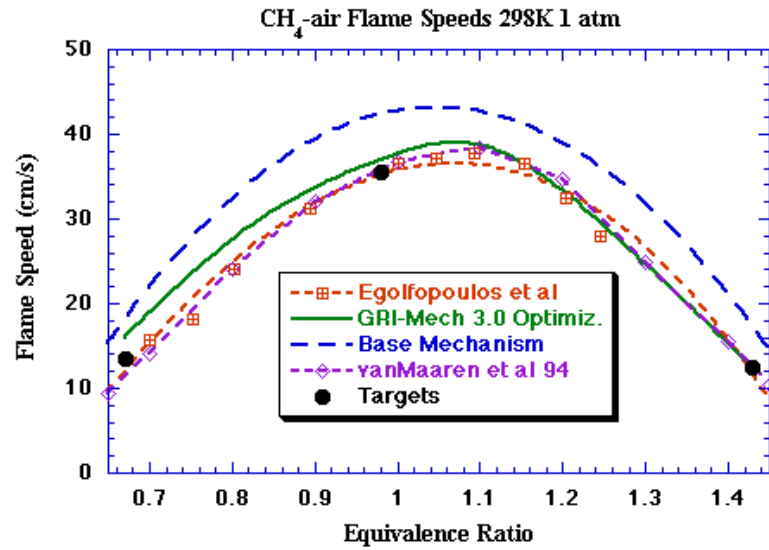
# Thermodynamic and kinetic data for reaction 35

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:





## 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

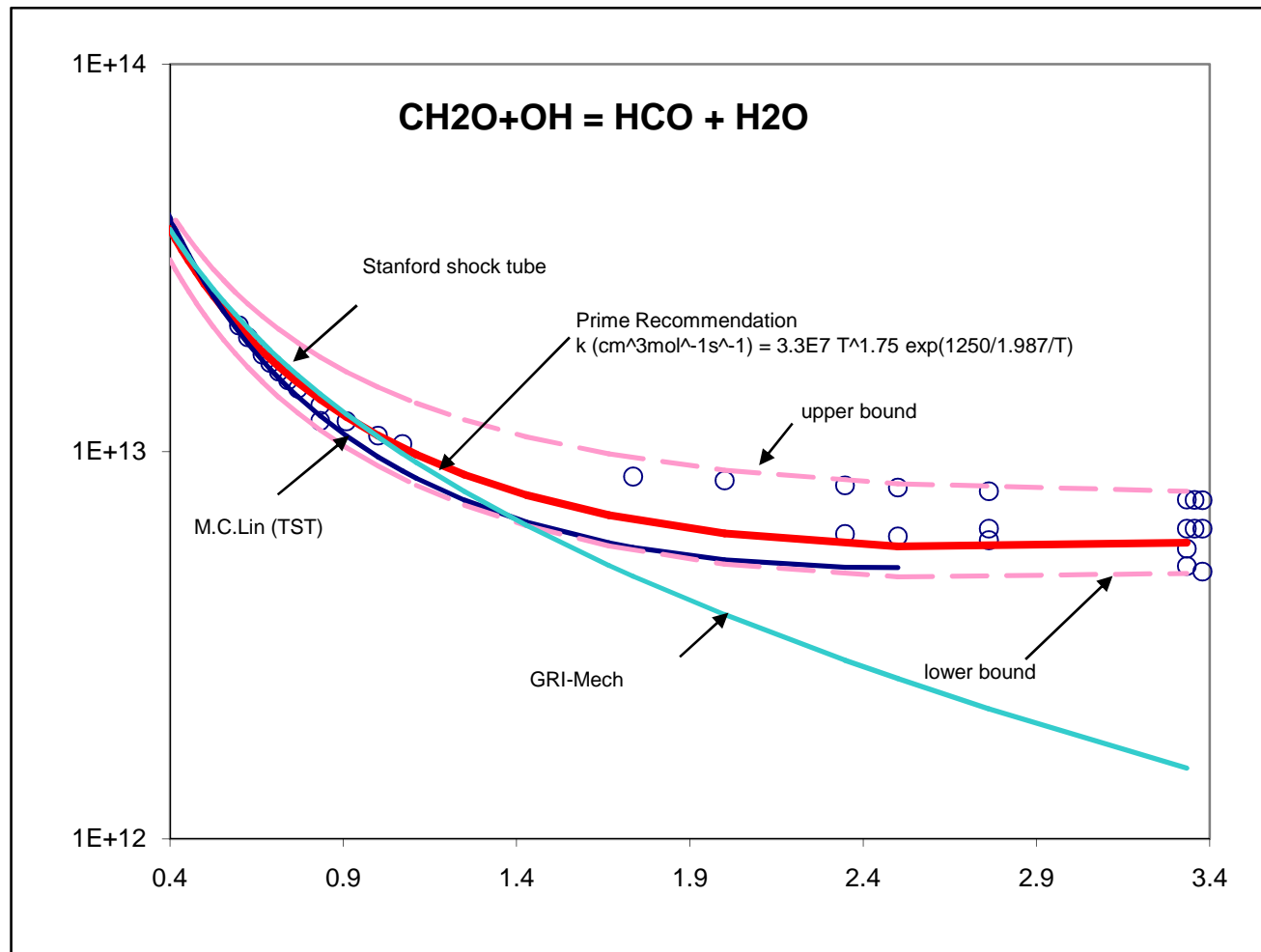
<u>Name</u>	Subscribers	<u>Description</u>
<a href="#">BioFuels</a>	3	BioFuels
<a href="#">Burner-stabilized premixed flames</a>	24	Burner-stabilized premixed flames
<a href="#">C0-C2</a>	52	H <sub>2</sub> /O <sub>2</sub> /C <sub>0</sub> + C <sub>1</sub> /C <sub>2</sub> hydrocarbon pyrolysis and oxidation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

## PrIMe Group directory 2

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



# OH + CH2O - PrIME recommendation

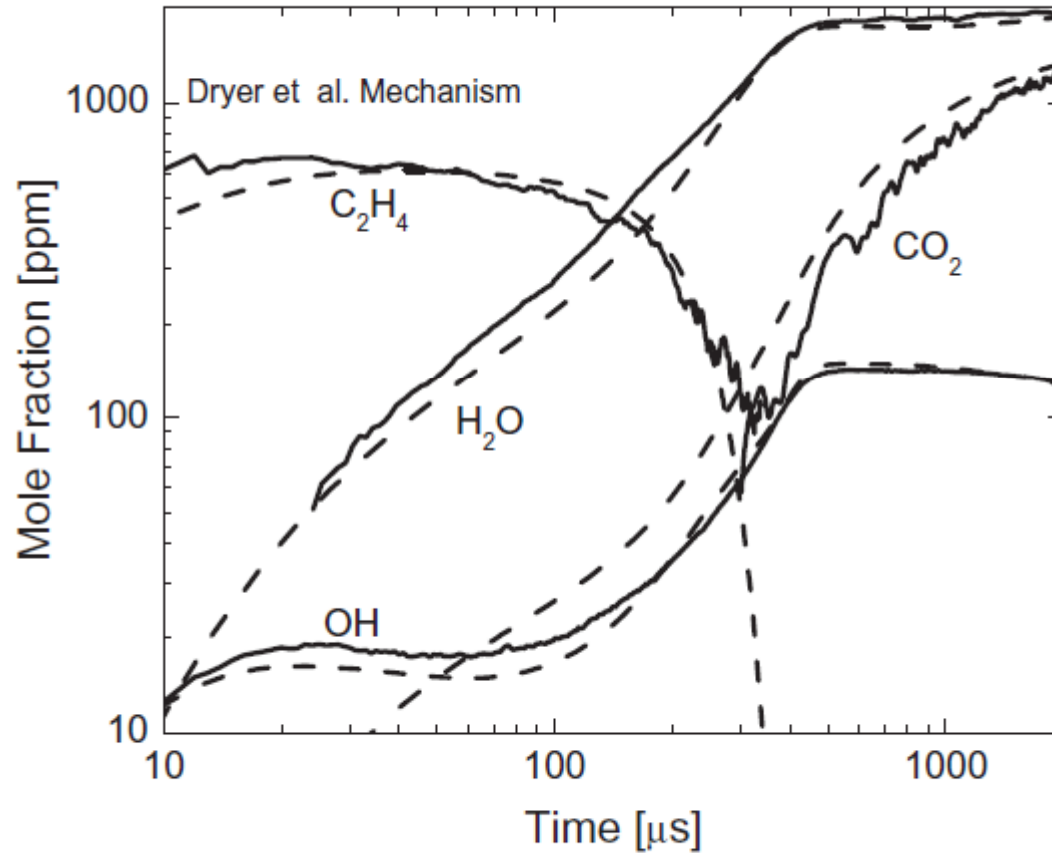


The best fit uses the Stanford shock tube data, as well as some of the room temperature experiments and Lin's TST results.

## 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  $\mu\text{m}$ , resp.
  - OH UV laser absorption at 306.5 nm
  - $\text{CO}_2$  and  $\text{H}_2\text{O}$  tunable IR diode laser absorption at 2.7 and 2.5  $\mu\text{m}$ , resp.

## Example of experimental measurements and comparison with existing mechanism



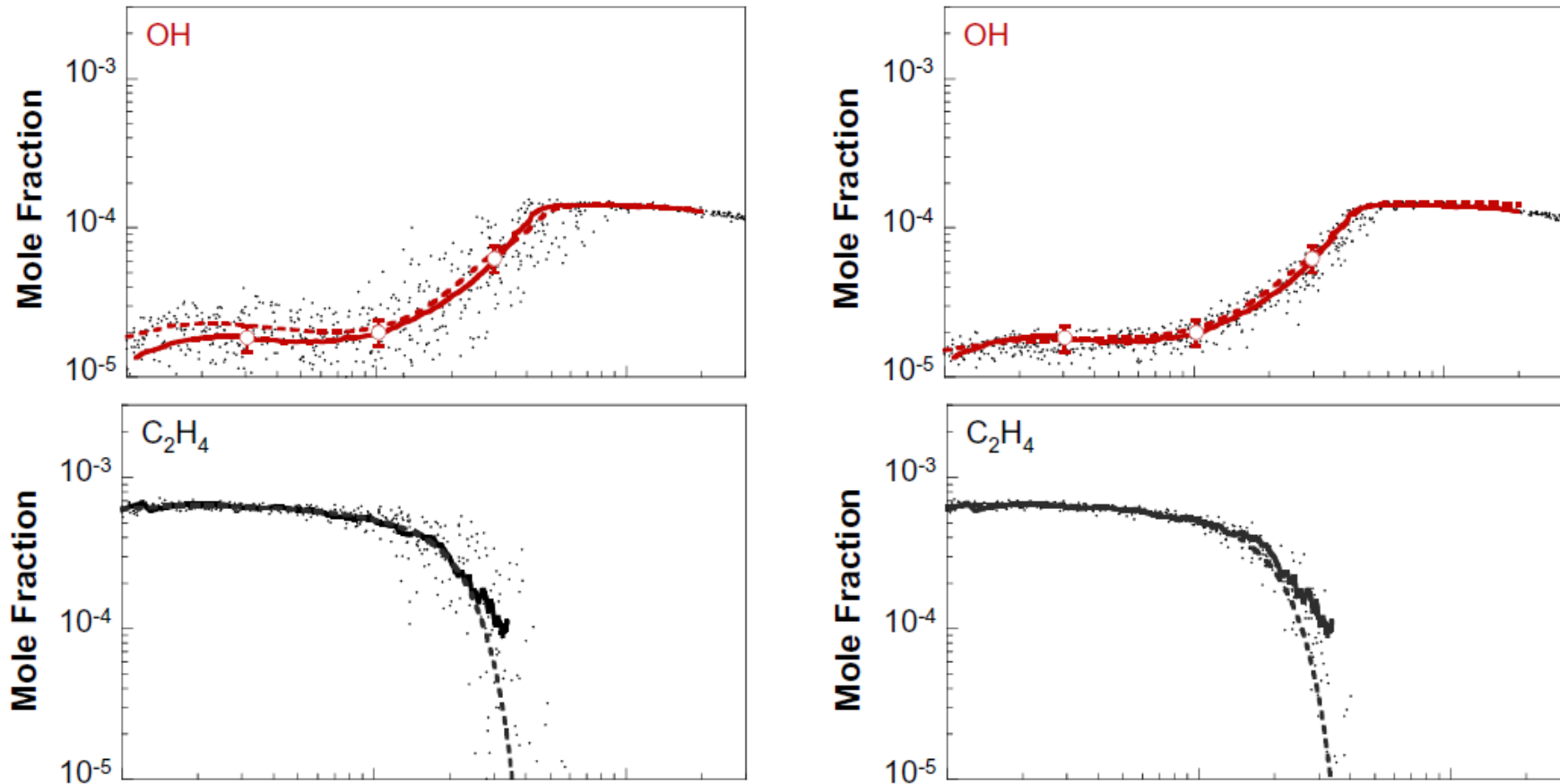
**Fig. 7.** Comparison of laser-absorption measurements with the Dryer et al. model [4]. Reflected shock wave conditions: 1494 K, 2.15 atm, 300 ppm *n*-heptane/O<sub>2</sub>/argon,  $\phi = 1$ .

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  $2\sigma$  standard deviations,
- respectively. Left panel: prior model (Model I). Right panel: posterior model (Model II).

## Automatic generation - a recent 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<sub>4</sub>H<sub>9</sub>
- 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

