Combustion Chemistry
Part 4

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Today's Agenda

- Accuracy, Error Bars, Uncertainty Representation
    +"Evaluated" Numbers (e.g. k(T,P))
- Reaction Mechanisms
    - How they are constructed
    - Sensitivity Analysis & Uncertainty Propagation
    - Flux Analysis
    - What can be learned by comparing their predictions with experiment

Review of previous lectures

- Liquid Fuels are best energy carriers, but most come from fossil fuels, contribute to climate change
- We want predictive models for combustion chemistry
  - for design of better engine/fuel system
- Models need lots of thermochemistry & rate coefficients
- Can measure thermo and some rates very accurately
  - But we need more numbers than we can measure
- Can roughly estimate most thermo quickly
  - But accurate enough?
- Can calculate most thermo, rates with quantum chem
  - Accurate enough to be useful, but not perfect
  - Numerous approximations, so not perfectly accurate
  - Ongoing research to reduce these errors

Accuracy, Error Bars are Big Issue

- We want fuel models so we can make predictions
- What accuracy do we need in the predictions?
- What corresponding accuracy needed in k(T,P)?
  - k(T,P) are important inputs to combustion models
  - Garbage in, Garbage out

This topic is of great current interest, not resolved.

- Error bars often omitted from journal papers, or the error bars given are not accurate.
  - Subsequent re-measurements often disagree outside quoted error bar!
  - Work to build community consensus to report data, error bars in ways that make it easier for others to check
- sometimes Expert **Evaluation** Panels give recommended values with recommended Error Bars

Evaluated Kinetic Data for Combustion Modeling: Supplement II

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And ten co-authors

The next few slides show the structure of a typical data sheet

Example $O + OH \rightarrow O_2 + H$

1. Thermodynamic Data

$\Delta H^{\circ}_{298} = -68.29 \text{ kJ mol}^{-1}$

$\Delta S^{\circ}_{298} = -25.04 \text{ J K}^{-1} \text{ mol}^{-1}$

$K_c = 3.48 \cdot 10^{-3} \, T^{0.367} \exp(+8390/T)$

$$(300 \leq T/K \leq 5000)$$

2. Rate coefficient data

$k/\mathrm{cm^3\ molecule^{-1}\ s^{-1}}$	T/K	Reference	Comments
Rate Coefficient Measurements			
$2.0 \cdot 10^{-11} \exp(112/T)$	221—499	Lewis and Watson, 1980[1]	(a)
$3.8 \cdot 10^{-11}$	258	Howard and Smith, 1980[2]	(b)
$6.7 \cdot 10^{-10} \, T^{-0.5}$	250—515	Howard and Smith, 1981[3]	(b)
$3.1 \cdot 10^{-11}$	300	Brune, Schwab, and Anderson, 1983[4]	(c)
$3.5 \cdot 10^{-11}$	299	Keyser, 1983[5]	(d)
$4.2 \cdot 10^{-11}$	294	Smith and Stewart, 1994[6]	(e)
$4.5 \cdot 10^{-11}$	227		
$5.2 \cdot 10^{-11}$	190		
$6.1 \cdot 10^{-11}$	158		
Reviews and Evaluations			
$5.42 \cdot 10^{-13} \, T^{0.375} \exp(1112/T)$	1000—5300	Michael, 1992[7]	(f)
$2.0 \cdot 10^{-11} \exp(112/T)$	220—500	CEC, 1992; 1994[8]	(g)
$2.4 \cdot 10^{-11}$	1000—2000		
$2.2 \cdot 10^{-11} \exp(120/T)$	220—500	NASA, 1997[9]	(h)
$2.3 \cdot 10^{-11} \exp(110/T)$	220—500	IUPAC, 1997[10]	(i)

Provides data on recent measurements and evaluations, including
Rate coefficient
Temperature range
Reference
Link to comments

Comments (examples)

(e) Fast flow system in which OH radicals were created by pulsed laser photolysis at 266 nm of HNO_3 in the presence of a much higher concentration of O atoms previously produced upstream of the HNO_3 injection point by the N+NO reaction. [OH] was monitored by LIF, pumping at ~ 282.5 nm and observing at ~ 310 nm. The time delay between the pulse generating OH and the LIF probe pulse was varied. Results were also obtained at 103 K, 50 K, and 10 K but with large uncertainties.

(f) Calculated from thermodynamic data and $k(H+O_2)$.

(g) Expression of Lewis and Watson[1] adopted for low temperature range and high temperature expression derived from thermodynamic data and $k(H+O_2)$.

Preferred values

- $k = 2.00 \cdot 10^{-10} \ T^{-0.352} \exp(113/T) \ \text{cm}^3 \ \text{molecule}^{-1} \ \text{s}^{-1}$ over the range 250-3000 K.

- *Reliability*
- $\Delta \log k = \pm 0.2$ over the range 250-3000 K.

Comments on preferred values

- The only direct studies on this reaction have been carried out at low temperatures where there is excellent agreement among the more recent of them.

- Although there have been no direct measurements of k above 515 K the reverse reaction has been extensively investigated at temperatures in the range 800-3400 K. The preferred expression for k has been derived, therefore, by a fit to the data obtained by combining the expression for $k(H+O_2)$ from the present evaluation with the thermodynamic data at temperatures above 800 K together with the directly obtained experimental data at temperatures below 500 K. The reaction has been the subject of a number of theoretical studies; see Miller,[19-21] Troe,[22] Harding *et al.*[23] and Troe and Ushakov.[24]

O + OH Arrhenius Plot
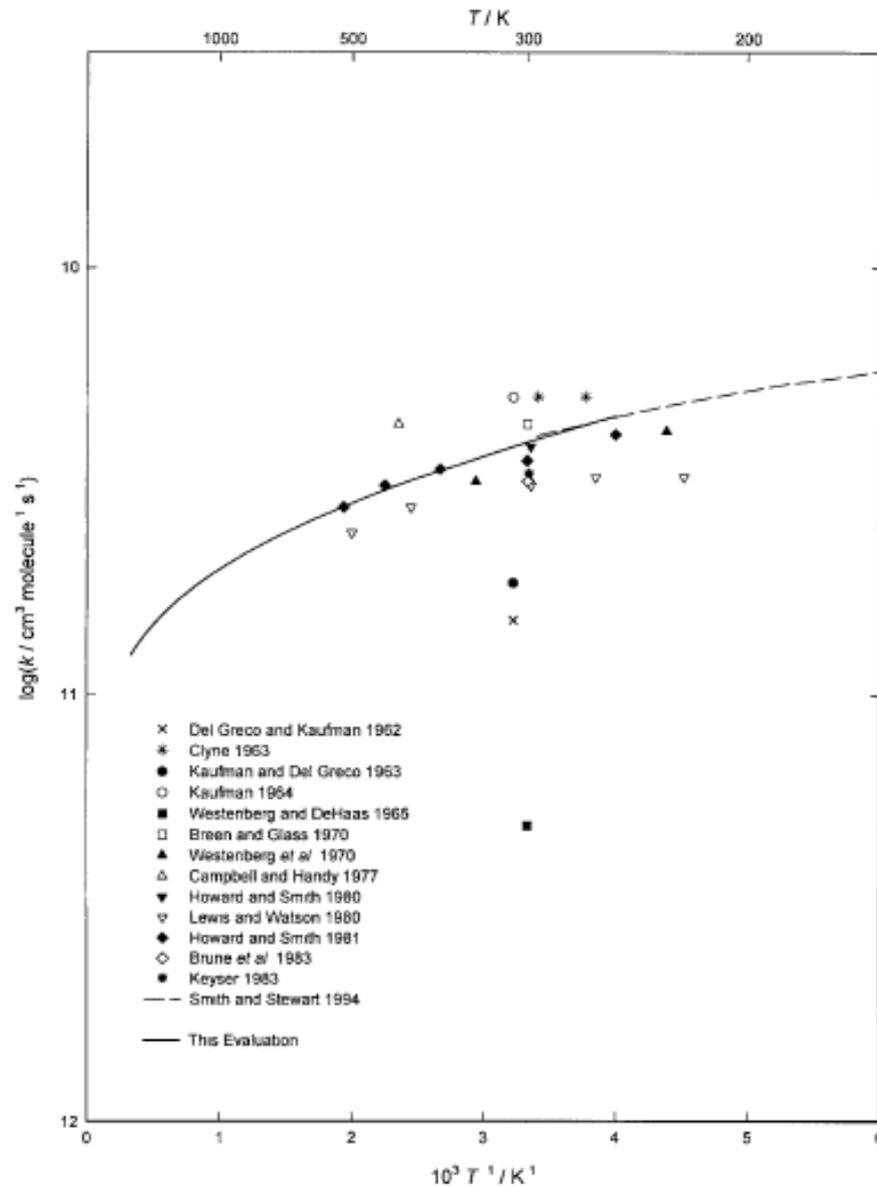
Reverse reaction: $H + O_2 \rightarrow O + OH$

- $k = 3.43 \cdot 10^{-10} \, T^{-0.097} \exp(-7560/T)$ cm^3 molecule^{-1} s^{-1} over the range 800-3500 K.

- $\Delta \log k = \pm 0.1$ at 800 K, rising to ± 0.2 at 3500 K.

- There are no direct measurements of k below 500 K and the recommended values are based on data obtained at temperatures above 800 K. The majority of the determinations of k have been made using shock tube techniques and, generally, are in good agreement.[1-10,15-25] There is a trend in the more recent studies[1-10] to give slightly lower values of E/R than most of the older determinations.[11,5-25] Our preferred expression for k is based on the more recent studies, which are cited in the Table. The expression derived gives values very similar to the expression used by Smith *et al.*[26] in modelling studies using the GRI mechanism.

$H + O_2 \rightarrow O + OH$

Figure is too small to read but it shows the large number of Investigations and demonstrates how the results mainly cluster around the best fit line.
Illustrates the ideas of upper and lower bounds and of a probability distribution function (pdf)
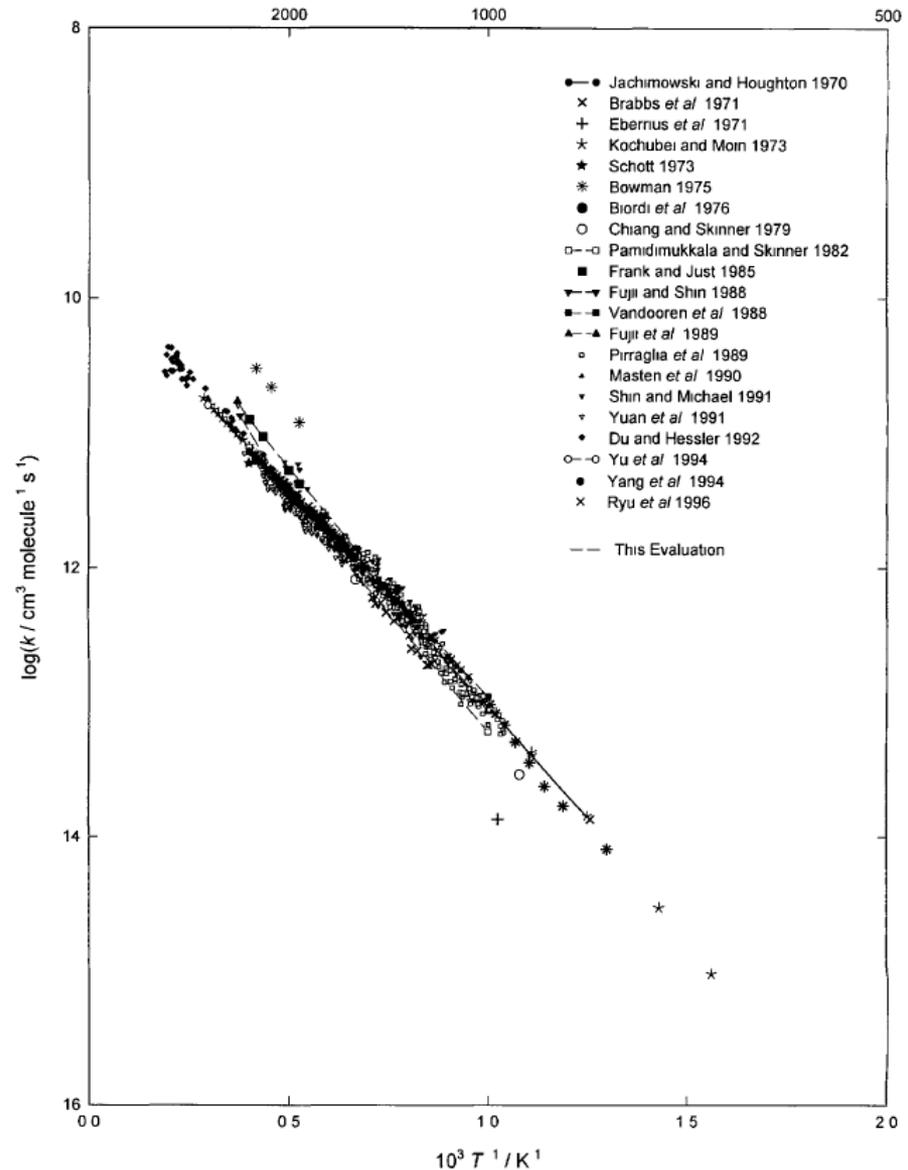
How to represent Uncertainty?

- Traditional approach is to quote a number and an error bar
- Many would assume this means Gaussian distribution of errors, with error bar = 1 sigma: OFTEN NOT TRUE!
- Some fields assume quoted error means 2 sigma, or 3 sigma, or "I am absolutely sure the value is not outside this error range".
- For kinetics, best to report error in (log k), not k.
  - $k(T,P)$ must be positive
  - Both experiments and calculations prone to multiplicative errors, not additive errors
- Sometimes true uncertainty is not Gaussian at all
  - Often experiment sets an upper bound on k, no lower bound
  - Sometimes there are two competing values, indicating some systematic problem, bimodal pdf might be best
  - Often uncertainty in k is correlated with uncertainty in K_c, or in another k (e.g. relative rates measurement)

More recently remeasured!
$H + O_2 \rightarrow OH + O$
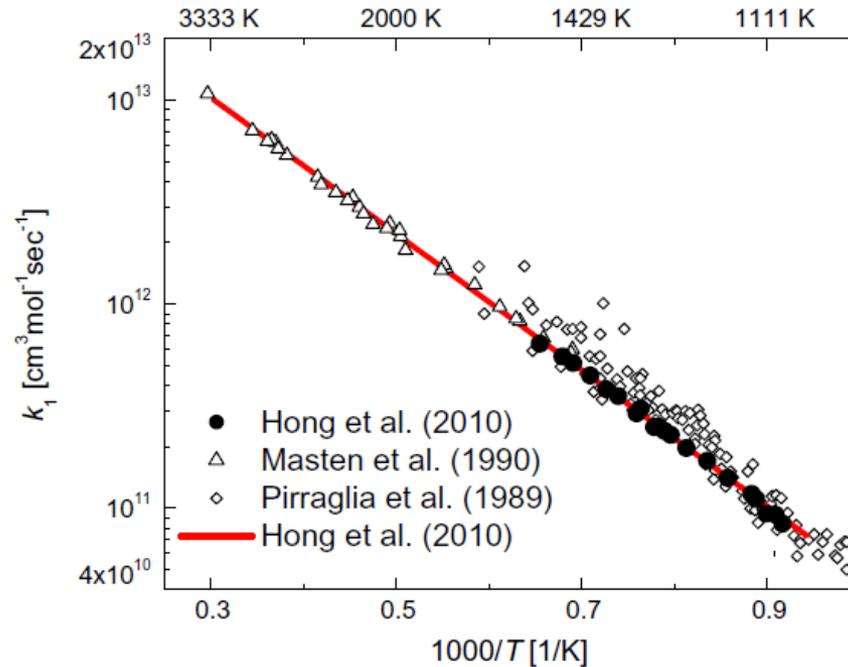
- From Hong et al., shock tube measurements. Comb Flame 2011, 158,633, $k = 1.7 \times 10^{-10} \exp(-7670/T)$ (1100 – 3370 K). Uncertainty ± 10%.
- See Burke et al. Int J Chem Kinet, 2012, 44, 444, who support the rate coefficient

$^3CH_2 + CH_3 \rightarrow C_2H_4 + H$ – an example with limited measurements

Rate Coefficient Data

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
Rate Coefficient Measurements			
$5 \cdot 10^{-11}$	298	Pilling and Robertson, 1975[1]	(a)
$1.0 \cdot 10^{-10}$	298	Laufer and Bass, 1975[2]	(b)
$3 \cdot 10^{-11}$	1800-2700	Olson and Gardiner, 1978[3]	(c)
$3 \cdot 10^{-11}$	1700-2200	Bhaskaran et al., 1979[4]	(d)
$(7-10) \cdot 10^{-11}$	1320-2300	Frank and Braun-Unkhoff, 1987[5]	(e)
$1.1 \cdot 10^{-10}$	298	Deters et al., 1998[6]	(f)
$1.7 \cdot 10^{-11}$	1350-2400	Hidaka et al., 2000[7]	(g)
$2.1 \cdot 10^{-10}$	298	Wang and Fockenberg, 2001[8]	(h)

7×10^{-11}, when most recent value for k(CH$_3$+CH$_3$) used

Shock tube measurements used mechanisms with several steps and literature rate data
Not possible to correct for more recent values – emphasises need to store raw data to allow accurate re-evaluation

$^3CH_2 + CH_3$ continued

- k = $1.2 \cdot 10^{-10}$ cm^3 molecule^{-1} s^{-1} over the range 298-3000 K.
- Δlog k = $\pm$ 0.3 at 298 K, rising to $\pm$ 0.7 at 3000 K.

Comments:

- Considerable scatter on the data at 298 K. The rate data of references 1 and 2, which were derived from very similar studies, need correction for the value of the rate constant for the methyl radical recombination used in the simulations.

- Reaction presumed to proceed via an ethyl radical adduct. A significant temperature dependence for k is therefore not expected, - supported by results from the shock tube studies. May suggest a very small negative temperature dependence, but scatter at high T large and, provisionally, a temperature independent k is recommended with substantial error limits.

Pressure dependent reactions - reminder

$$k = \frac{k_0 k_\infty [M]}{k_0[M] + k_\infty} F = k_0[M] \left(\frac{1}{1 + k_0[M]/k_\infty} \right) F$$

$$= k_\infty \left(\frac{k_0[M]/k_\infty}{1 + k_0[M]/k_\infty} \right) F.$$

$$\log F \cong \frac{\log F_c}{1 + \left[\dfrac{\log(k_0[M]/k_\infty)}{N} \right]^2}, \qquad N = 0.75 - 1.27 \log F_c$$

$$F_c = (1-a)\exp(-T/T^{***}) + a\exp(-T/T^{*})$$

$$+ \exp(-T^{**}/T),$$

Pressure dependent reaction: $H + C_2H_4$

- $k_o = 1.3 \cdot 10^{-29} \exp(-380/T)$ cm^6 molecule^{-2} s^{-1} for M = He over the range 300-800 K.
- $k_o = 1.3 \cdot 10^{-29} \exp(-380/T)$ cm^6 molecule^{-2} s^{-1} for M = N$_2$ over the range 300-800 K.
- $k_\infty = 6.6 \cdot 10^{-15} \ T^{1.28} \exp(-650/T)$ cm^3 molecule^{-1} s^{-1} over the range 200-1100 K.
- $F_c = 0.24 \exp(-T/40) + 0.76 \exp(-T/1025)$ for M = He and N$_2$ over the range 300-800 K.

Reliability

- $\Delta \log k_o = \pm 0.3$ for M = He, N$_2$ over the range 300-800 K.
- $\Delta \log k_\infty = \pm 0.3$ over the range 200-1100 K.
- $\Delta F_c = \pm 0.1$ for M = He, N$_2$ over the range 300-800 K.

H + C2H4
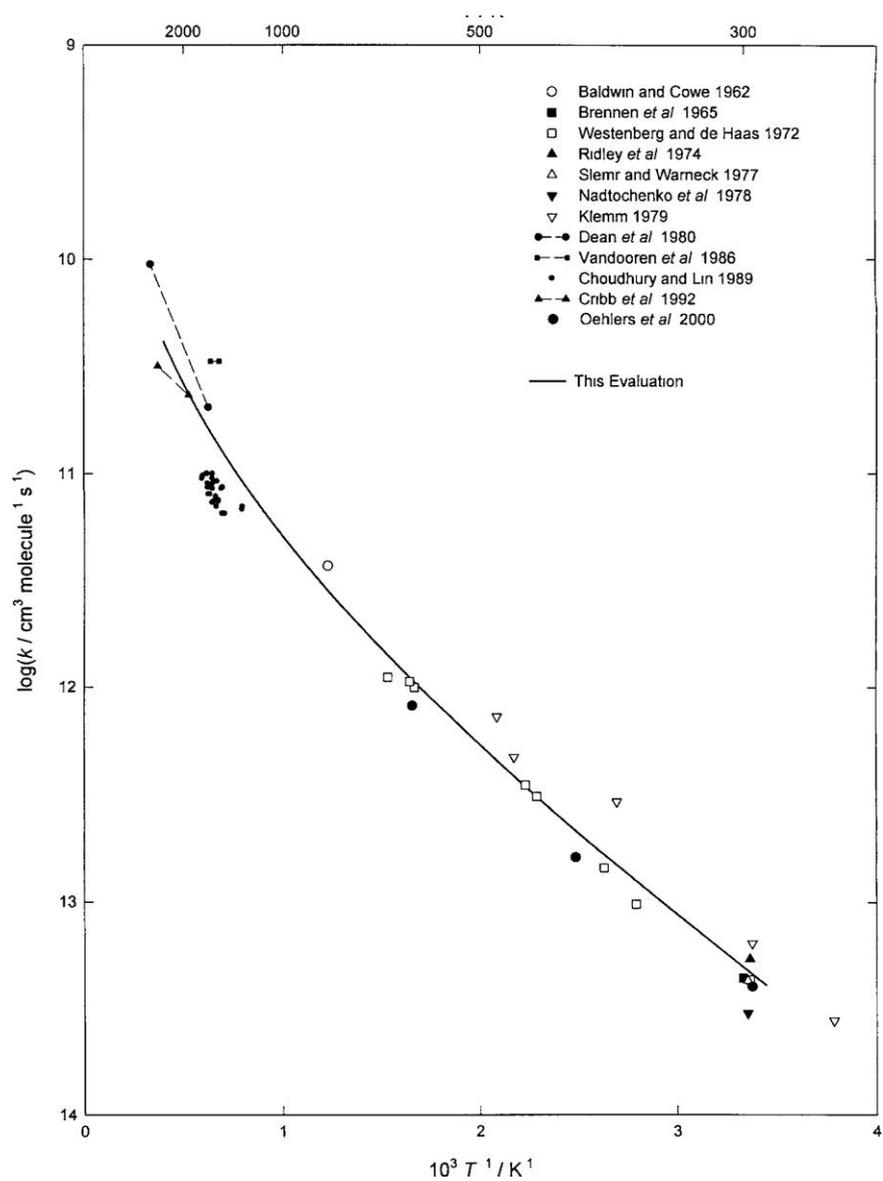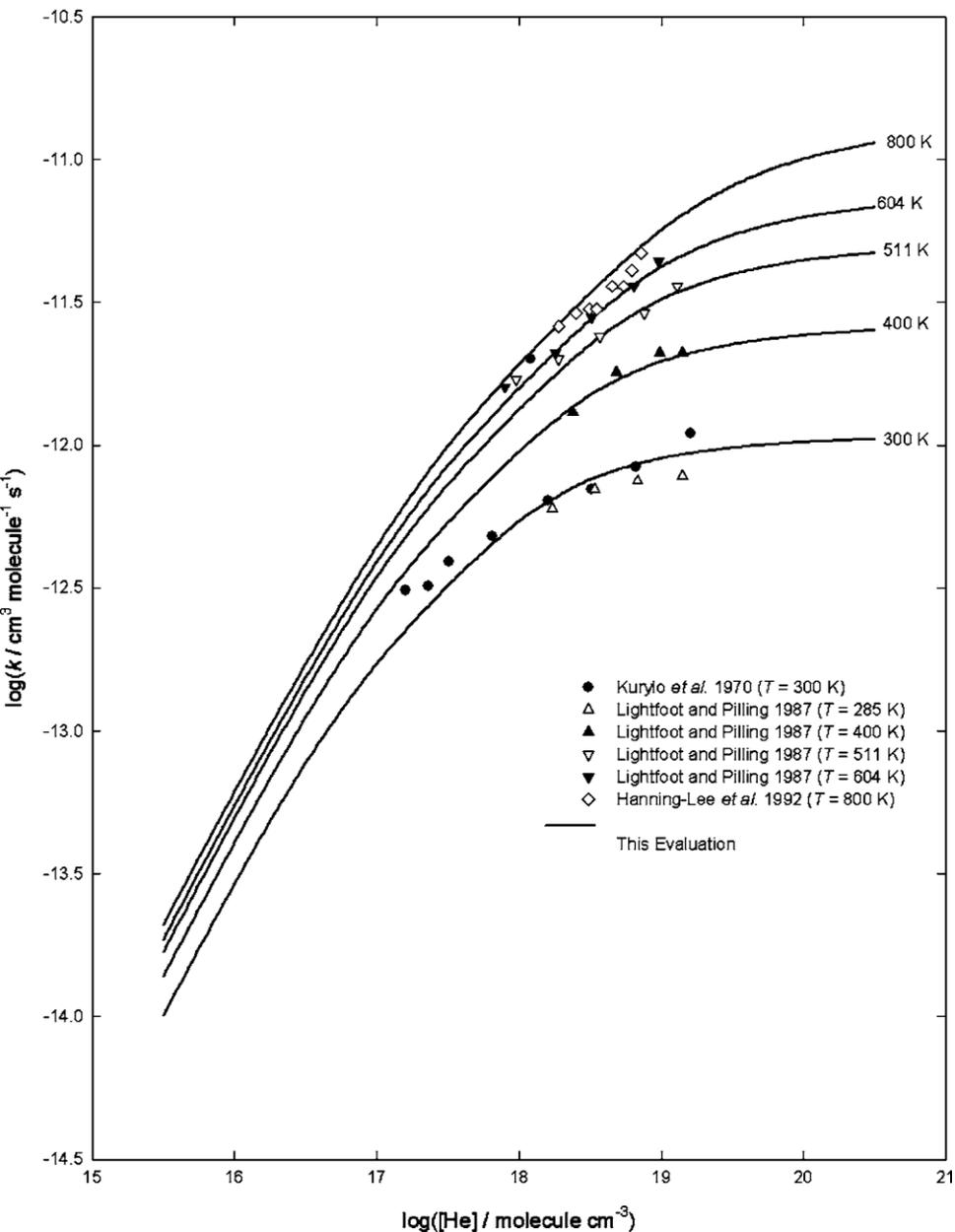
Nagy and Turanyi, Uncertainty of Arrhenius Parameters
Int J Chem Kinet 43: 359–378, 2011

- Analytical expression is derived that describes the temperature dependence of the uncertainty of k as a function of the elements of the covariance matrix of the Arrhenius parameters.

- Recommendations are given for an improved representation of the uncertainty information in future chemical kinetics databases using the covariance matrix of the Arrhenius parameters

- Method suggested for determination of covariance matrix and joint probability density function of Arrhenius parameters from the present uncertainty information given in the kinetics databases.

O + C$_2$H$_4$: evaluation

O + C$_2$H$_4$ → CH$_2$CHO + H   (1)
      → HCO + CH$_3$ (2)
      → HCHO + CH$_2$ (3)
      → CH$_2$CO + H$_2$ (4)

- $k = 2.25 \cdot 10^{-17}\ T^{1.88} \exp(-92/T)$ cm^3 molecule^{-1} s^{-1} over the range 220-2000 K.

- Reliability

  $\Delta \log k = \pm 0.1$ over the range 300-1000 K, rising to ± 0.3 at 220 K and 2000 K

$CH_3 + H \rightarrow {}^1CH_2 + H_2$
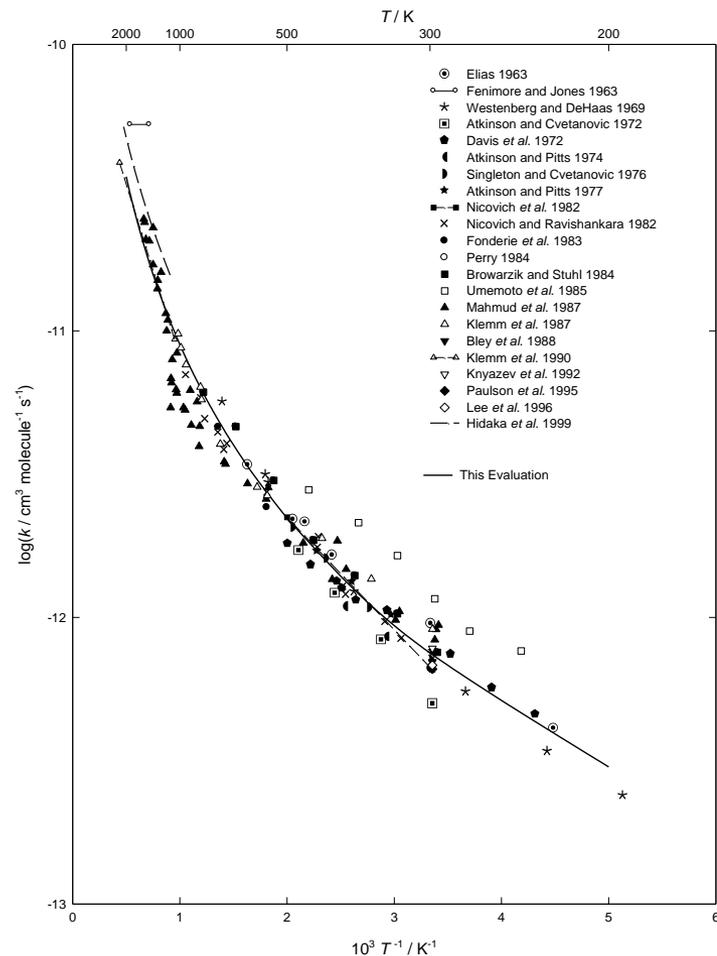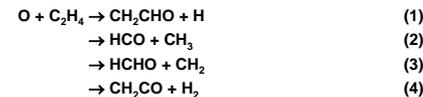
- $k = 2.1 \cdot 10^{-8} \, T^{-0.56} \exp(-8000/T) \, cm^3 \, molecule^{-1} \, s^{-1}$ over the range 300-2500 K.

- <u>Reliability</u>

  $\Delta \log k = \pm 0.15$ over the range 300-1000 K, ± 0.3 over the range 1000-1700 K, and ± 0.2 over the range 1700-2500 K.

- <u>Comments on Preferred Values</u>

  The values of k obtained in the <u>shock tube studies</u> of Bhaskaran *et al.*[1] and Davidson *et al.*[3] are in reasonable agreement and also agree to within a factor of ~ 3 with the rate constants predicted by <u>combining the thermodynamic data with the low temperature data on the reverse reaction</u>, whereas the value of k obtained in the flame study of Langley and Burgess[2] seems unacceptably high.

T dependent uncertainty parameter, $k = AT^n \exp(-E/RT)$

- Covariance matrix:

$$\Sigma_{\mathbf{p}} = \overline{(\mathbf{p} - \bar{\mathbf{p}})\,(\mathbf{p} - \bar{\mathbf{p}})^{\mathrm{T}}}$$

$$= \begin{bmatrix} \sigma_{\alpha}^2 & r_{\alpha n}\,\sigma_{\alpha}\,\sigma_n & r_{\alpha\varepsilon}\,\sigma_{\alpha}\,\sigma_{\varepsilon} \\ r_{\alpha n}\,\sigma_{\alpha}\,\sigma_n & \sigma_n^2 & r_{n\varepsilon}\,\sigma_n\,\sigma_{\varepsilon} \\ r_{\alpha\varepsilon}\,\sigma_{\alpha}\,\sigma_{\varepsilon} & r_{n\varepsilon}\,\sigma_n\,\sigma_{\varepsilon} & \sigma_{\varepsilon}^2 \end{bmatrix}$$

- Uncertainty parameter (M = 3/ln10 or 2/ln10) depending on definition of reliability in evaluation

$$F(T) = M\sqrt{\sigma_{\alpha}^2 + \sigma_n^2 \ln^2 T + \sigma_{\varepsilon}^2 T^{-2} + 2r_{\alpha n}\sigma_{\alpha}\sigma_n \ln T - 2r_{\alpha\varepsilon}\sigma_{\alpha}\sigma_{\varepsilon}T^{-1} - 2r_{n\varepsilon}\sigma_n\sigma_{\varepsilon}T^{-1}\ln T}$$

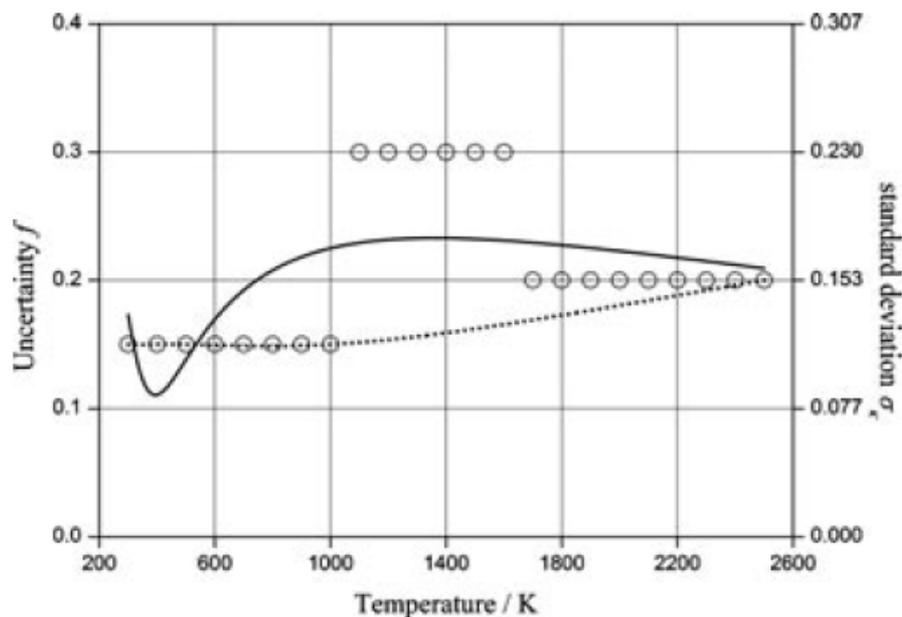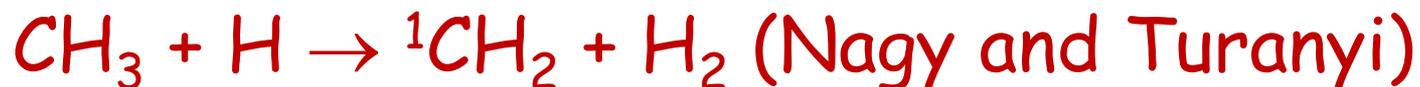# CH$_3$ + H → ^{1}CH$_2$ + H$_2$ (Nagy and Turanyi)

Figure 7 Uncertainties of reaction R5 are defined [14] in three temperature intervals and the uncertainty–temperature function was fitted to the values represented by the circles. The best least squares fit (solid line; see row **R5** in Table IV) does not approach these points well, because the recommended uncertainties were not consistent. The alternatively proposed $f(T)$ curve (dotted line) remains below all uncertainty points and has the highest average value of $\sigma_\kappa^2(T)$ in the inverse temperature interval of $[1/T_2, 1/T_1]$ (see text and row **R5m** in Table IV).

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

(R1): H + O2 = OH + O

(R2): H + O2 + M = HO2 + M (low-pressure limit, M = N2 or Ar)

- 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.

- the optimal Arrhenius parameters are then sought within this domain to reproduce the selected direct and indirect measurements

- 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
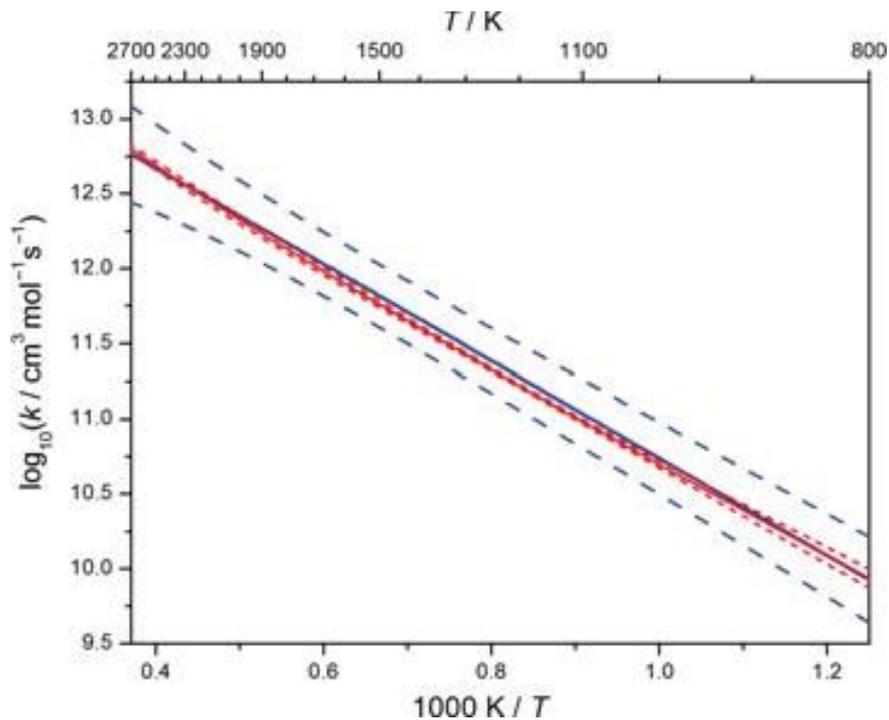
Arrhenius plots of the initial and optimized main values and uncertainty limits for reaction (R1): H + O_2 = OH + O. Thin solid blue line: initial value, recommended by Baulch et al.; blue dashed lines: initial uncertainty limits; red line: optimized rate coefficient; red dashed lines: optimized uncertainty limits.
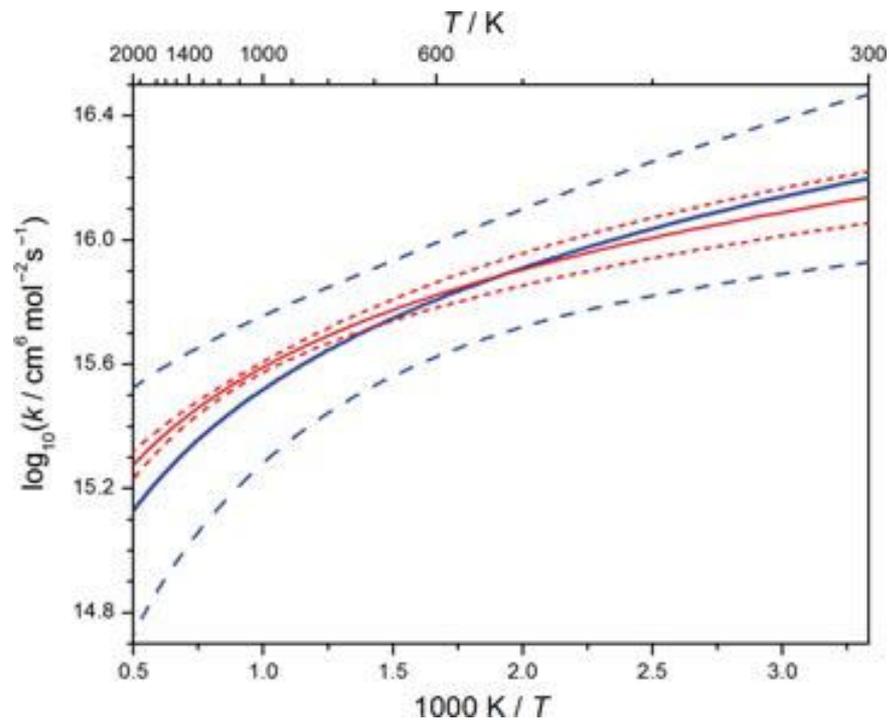
Arrhenius plots of the initial and optimized main values and uncertainty limits for reaction (R2): H + O_2 + N_2 = HO_2 + N_2 (low-pressure limit). Thin solid blue line: initial value, recommended by Baulch et al.; blue dashed lines: initial uncertainty limits; red line: optimized rate coefficient; red dashed lines: optimized uncertainty limits.

Uncertainty parameters for reactions R1 and R2.
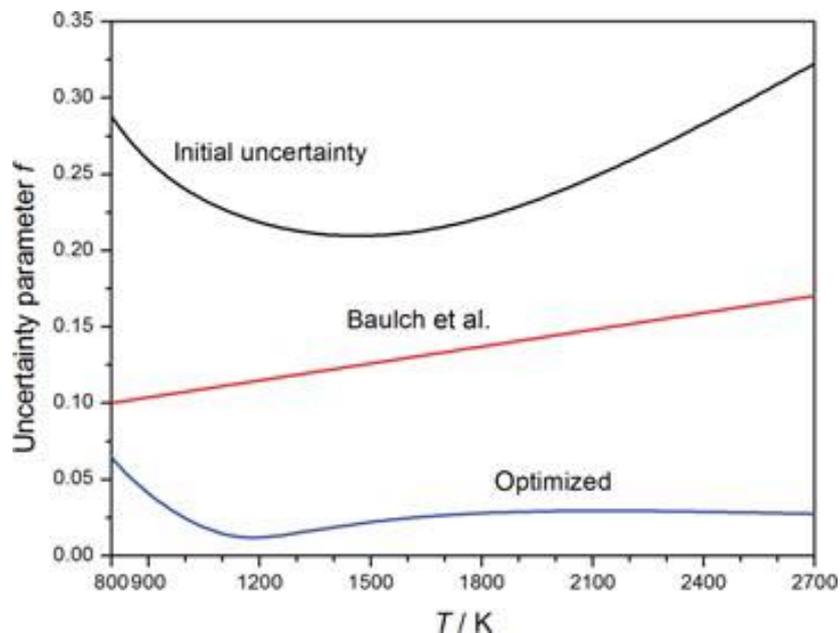
Uncertainty parameter (*f*) *as a function of temperature* for reaction (R1): H + O2 = OH + O, according to the evaluation of Baulch et al. [3] (red line), and *f calculated* from the covariance matrix of the Arrhenius parameters in two different ways: The "initial uncertainty" belongs to the *kmin(T) and kmax(T) functions (black line), and the "optimized"* belongs to the optimized rate parameters (blue line).
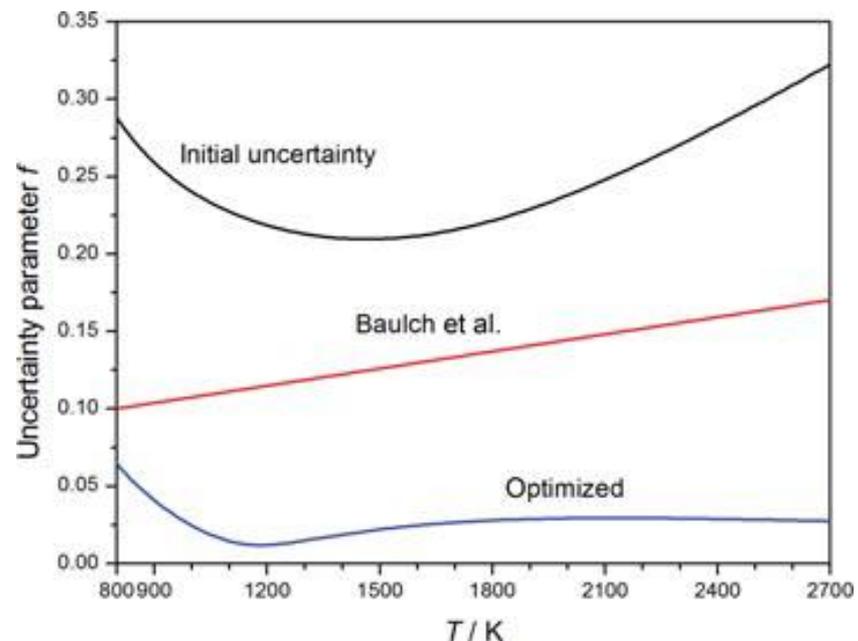
Uncertainty parameter (*f*) *as a function of temperature* for reaction (R2): H + O2 + N2 = HO2 + N2 (low-pressure limit) according to the evaluation of Baulch et al. (red line), and *f calculated from the covariance* matrix of the Arrhenius parameters in two different ways: The "initial uncertainty" belongs to the *kmin(T) and kmax(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 (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 (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 (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 (Ar)						1

Table I Evaluated and Optimized Rate Parameters for Reaction $H + O_2 = OH + O$ (R1)

Reference	A (cm^3 mol^{-1} 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 $H + O_2 + M = HO_2 + M$ (R2)

Reference	Bath Gas	A (cm^6 mol^{-2} 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

Current Challenge: How to Combine Experimental Data with Quantum Chemistry

- Most error bars in kinetics are estimates, not rigorously determined
  - Usually systematic errors are larger than noise
  - A lot of judgment involved in thinking of all the possible systematic problems, and estimating how much they could affect the results
- This is particularly true for Quantum Chemistry
  - Most computed A factors and S, Cp, zero-point energies derived from DFT with a non-rigorous energy functional $E[\rho(x,y,z)]$
  - Many approximations in V(R) and Q calcs, most are not error-controlled
  - Basis-set convergence sometimes checked

Combining Quantum + Expt Error Bars

- Important, since an increasing fraction of what is known about k(T,P) and thermo is coming from quantum chemistry.
- See recent works from Argonne National Lab
  - Michael Burke
  - Alison Tomlin (of Leeds)

Today's Agenda

- Accuracy, Error Bars, Uncertainty Representation
  +"Evaluated" Numbers (e.g. k(T,P))
- Reaction Mechanisms
  - How they are constructed
  - Sensitivity Analysis & Uncertainty Propagation
  - Flux Analysis
  - What can be learned by comparing their predictions with experiment

How to construct Reaction Mechanisms

- "Hierarchical Approach"
  - Issues with this Approach
- GRI-Mech and PrIMe
- What is being done currently for most fuels
  - "Adjusted to Fit" vs. "Predictive Approach"
  - "By-Hand" vs. "Automatic"
  - Issues with these approaches

The Popular "Hierarchical Approach"

- – Concept is to be Comprehensive. Start with small reaction set, nail down k(T,P) for those reactions, then add more
- – Start with H2/O2 (no carbon atoms)
- – Add some small carbon-containing molecules, work under conditions where molecular-weight-growth is negligible.
- – Add bigger carbon-containing molecules
- – Add small molecules containing heteroatoms
- – Ideally, can firmly determining all the k(T,P) at each stage with very tight error bars, then you can treat them as fixed, and only vary k(T,P) for the new reactions added in the next stage.

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

Issues with the Hierarchical Approach

- Has been found to be challenging to firmly nail down H2/O2…
    - Even 20 k(T,P) can be hard to determine with tight error bars. (With N parameters you can overfit an elephant)
    - Best H2/O2 models use some information from quantum chemistry…but unknown error bars
    - If H2/O2 k(T,P) not really nailed down, do we have to re-adjust them at every stage? Or freeze them?
- At each stage, need to add many additional k(T,P), so number of adjustable parameters growing faster than number of independent data to constrain them.
- Restricted to conditions where no molecular weight growth occurs (otherwise adding many new molecules and many new reactions). So k(T,P) are being determined over limited T,P range
- Number of isomers grows rapidly, so hard to be comprehensive.

GRI-Mech (CH4 model)

- 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

- This important project wrote down a limited set of reactions (similar to hierarchical approach)
- But then tried to adjust *all* thermo and k(T,P) to try to find fit consistent with **all** experimental data
  - Did not hold previously-determined parameters fixed.
- Resulting model was a huge step forward for methane chemistry, very widely used for natural gas problems.
- This philosophy (vary all the uncertain parameters within their error bars, use all the available data to constrain the fits) continues in the PrIMe project.
- Highlights the need to maintain access to raw data, so one can refit parameters to that data later (when one discovers that some of the assumptions in the original paper are not accurate).

GRI-Mech contd

- GRI-Mech is optimized <u>as a whole</u>, substitutions, further selective tuning should not be done.

- All reactions treated as reversible; thermodynamic data (based on NASA, Technion) provided.

- 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, ϕ = 0.1 to 5 for premixed systems

26	O + C2H5 -> CH3 + CH2O	2.24E+13			
27	**O + C2H6 -> OH + C2H5**	8.98E+07	1.9	5690	3.0
28	O + HCCO -> H + CO + CO	1.00E+14			
29	O + CH2CO -> OH + HCCO	1.00E+13		8000	
30	O + CH2CO -> CH2 + CO2	1.75E+12		1350	
31	O2 + CO -> O + CO2	2.50E+12		47800	
32	**O2 + CH2O -> HO2 + HCO**	1.00E+14		40000	1.2; 2.1; 3.0
33	**H + O2 + M -> HO2 + M**	2.80E+18	-0.9		2.1; 3.0
34	**H + O2 + O2 -> HO2 + O2**	2.08E+19	-1.2		3.0
35	H + O2 + H2O -> HO2 + H2O	1.13E+19	-0.8		1.1; 1.2; 2.1; 3.0
36	**H + O2 + N2 -> HO2 + N2**	2.60E+19	-1.2		2.1; 3.0
37	**H + O2 + AR -> HO2 + AR**	7.00E+17	-0.8		1.2; 2.1; 3.0
38	**H + O2 -> O + OH**	2.65E+16	-0.7	17041	1.1; 1.2; 2.1; 3.0
39	H + H + M -> H2 + M	1.00E+18	-1.0		
40	H + H + H2 -> H2 + H2	9.00E+16	-0.6		
41	**H + H + H2O -> H2 + H2O**	6.00E+19	-1.2		3.0
42	H + H + CO2 -> H2 + CO2	5.50E+20	-2.0		
43	**H + OH + M -> H2O + M**	2.20E+22	-2.0		1.1;1.2;2.1; 3.0
44	H + HO2 -> O + H2O	3.97E+12		671	
45	H + HO2 -> O2 + H2	4.48E+13		1068	3.0
46	H + HO2 -> OH + OH	8.40E+13		635	3.0

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.
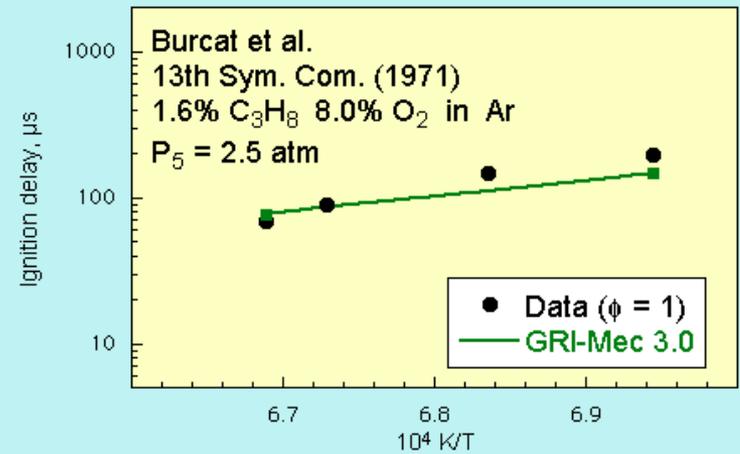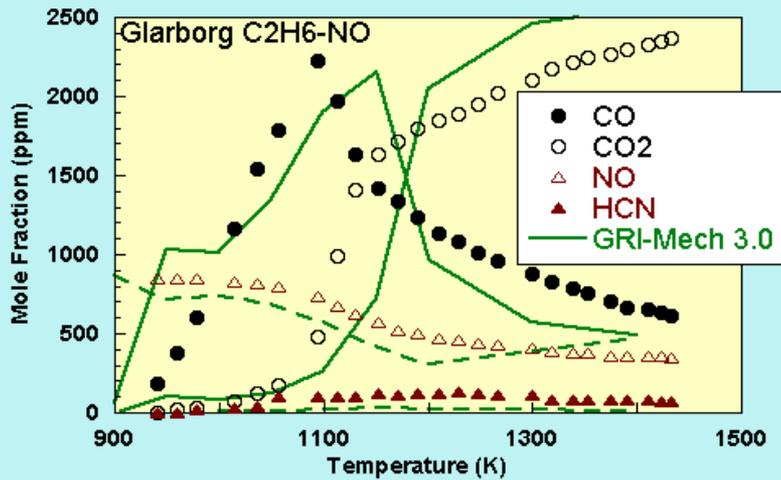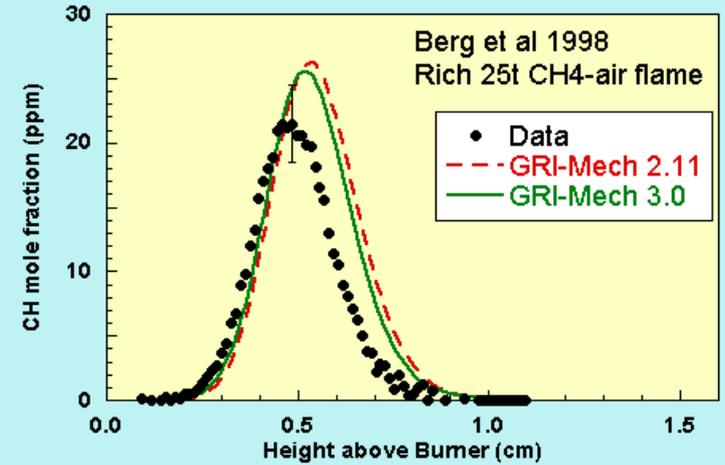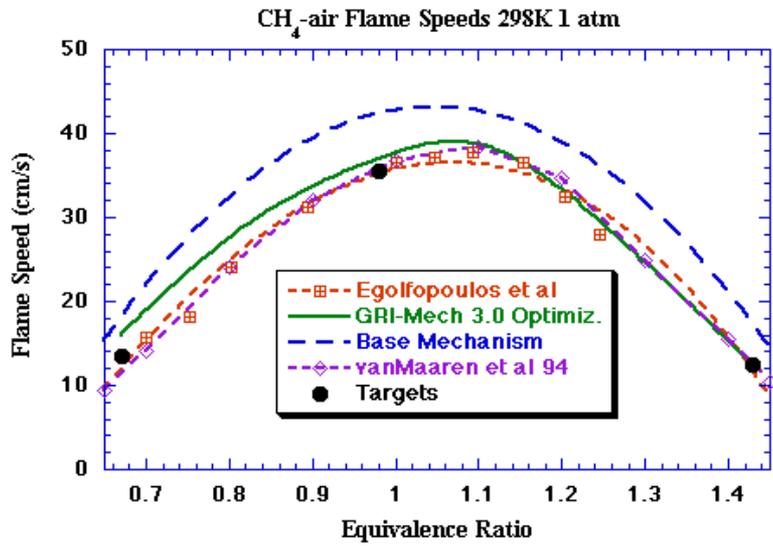
Thermodynamic and kinetic data for reaction 35

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:

CH₄-air Flame Speeds 298K 1 atm

Berg et al 1998
Rich 25t CH4-air flame

Glarborg C2H6-NO

Burcat et al.
13th Sym. Com. (1971)
1.6% C₃H₈ 8.0% O₂ in Ar
P₅ = 2.5 atm
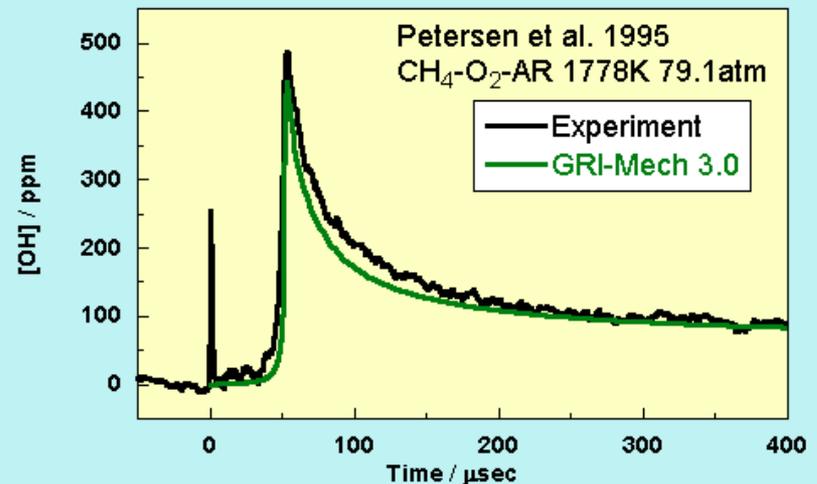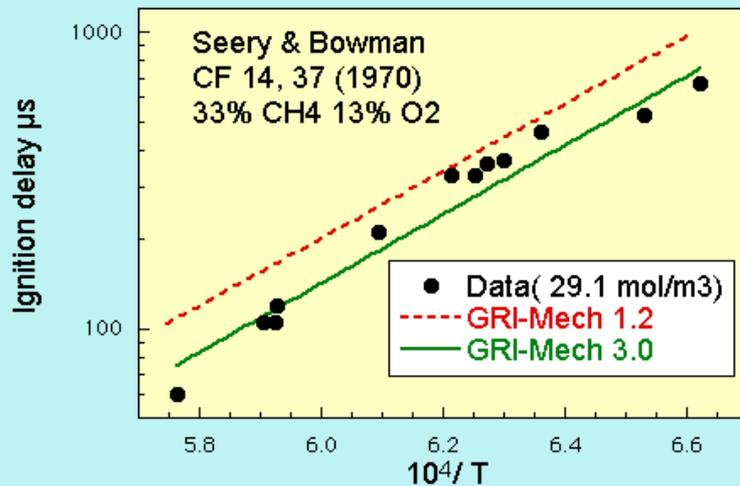
PrIMe
Frenklach, Proc Comb Inst 31 (2007) 125–140

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 ofthe entire scientific community in the data collectionand analysis."

PrIMe Group directory 1

Name	Subscribers	Description
BioFuels	3	BioFuels
Burner-stabilized premixed flames	24	Burner-stabilized premixed flames
C0-C2	52	H2/O2/C0 + C1/C2 hydrocarbon pyrolysis and oxidation
C3-C4	40	C3-C4 hydrocarbon pyrolysis and oxidation
C5-C16	35	C5-C16 hydrocarbon pyrolysis and oxidation
C6 + aromatics	20	C6 + 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

CH2O+OH = HCO + H2O

Stanford shock tube

Prime Recommendation
k (cm^3mol^-1s^-1) = 3.3E7 T^1.75 exp(1250/1.987/T)

upper bound

M.C.Lin (TST)

GRI-Mech

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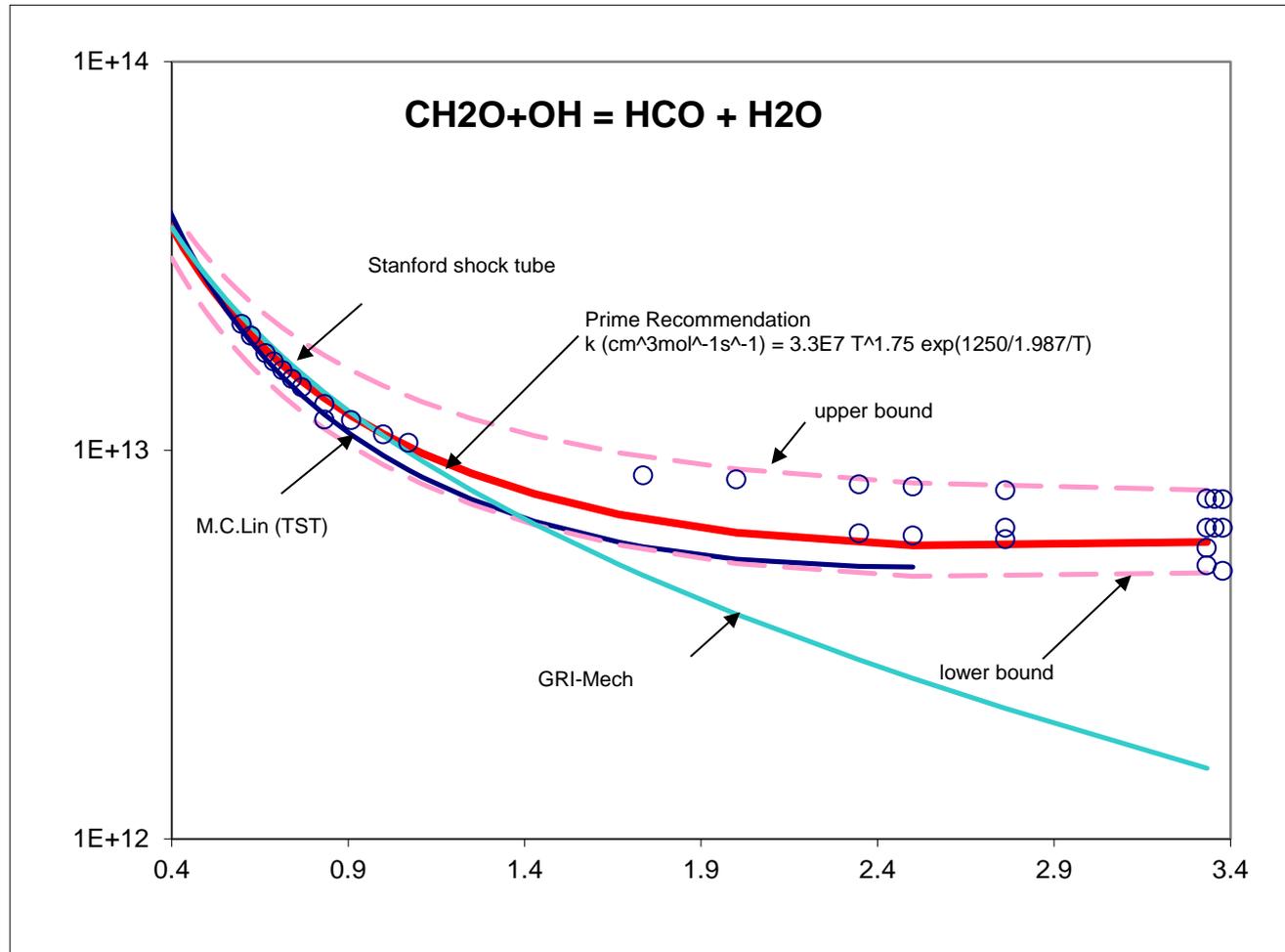
The best fit uses the Stanford shock tube data, as well as some of the room temperature experiments and Lin's TST results.

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
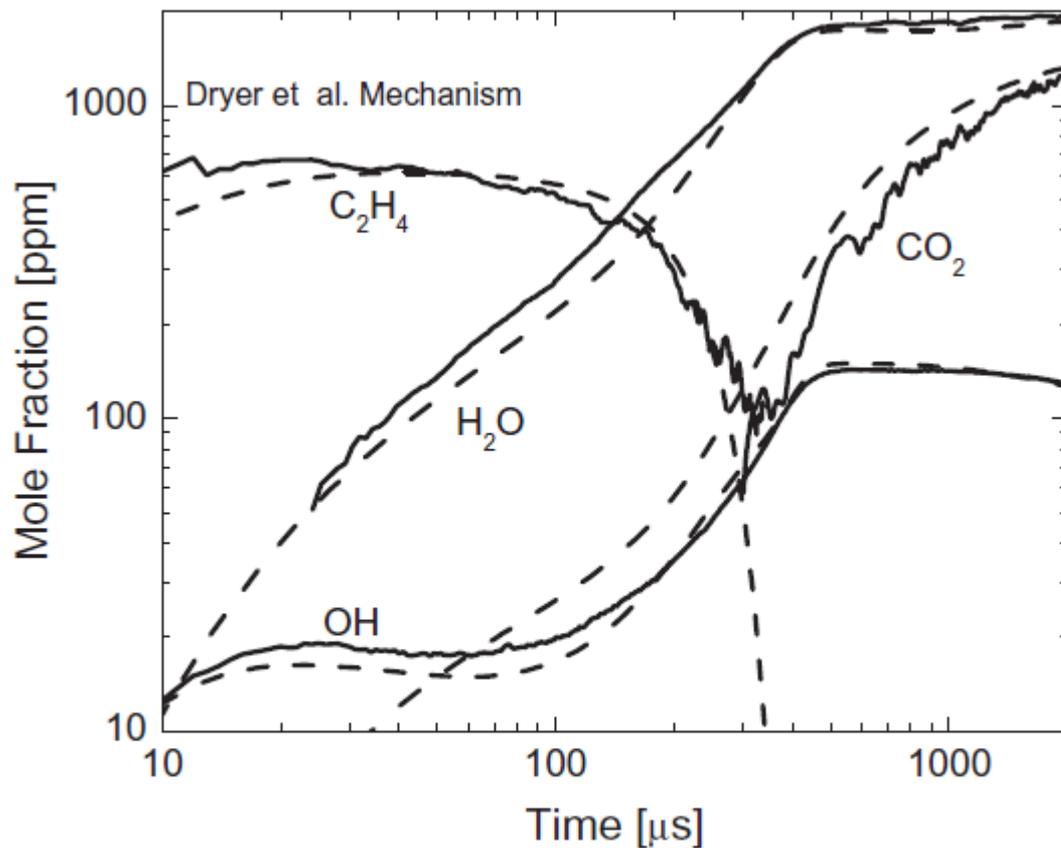
Fig. 7. Comparison of laser-absorption measurements with the Dryer et al. model [4]. Reflected shock wave conditions: 1494 K, 2.15 atm, 300 ppm n-heptane/O_2/argon, $\phi = 1$.

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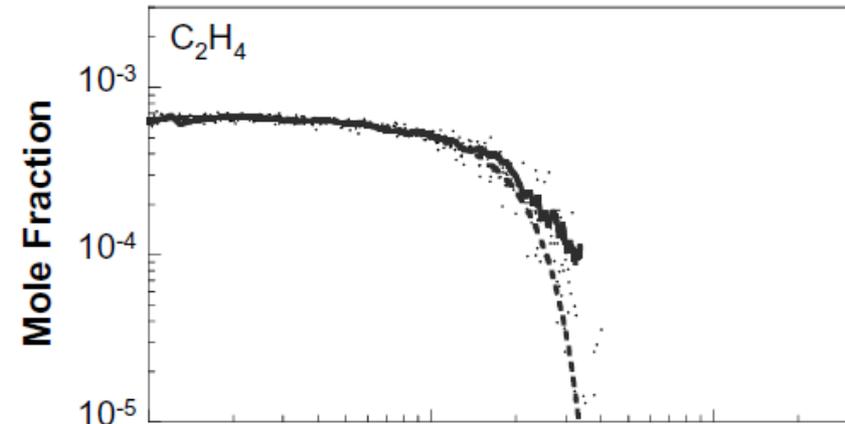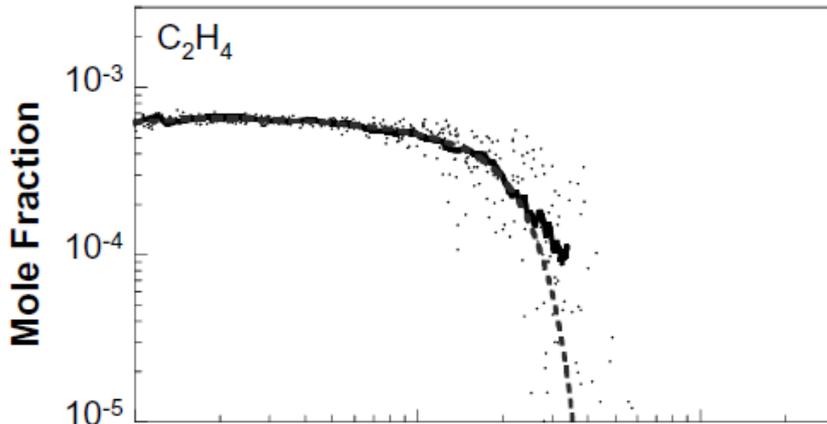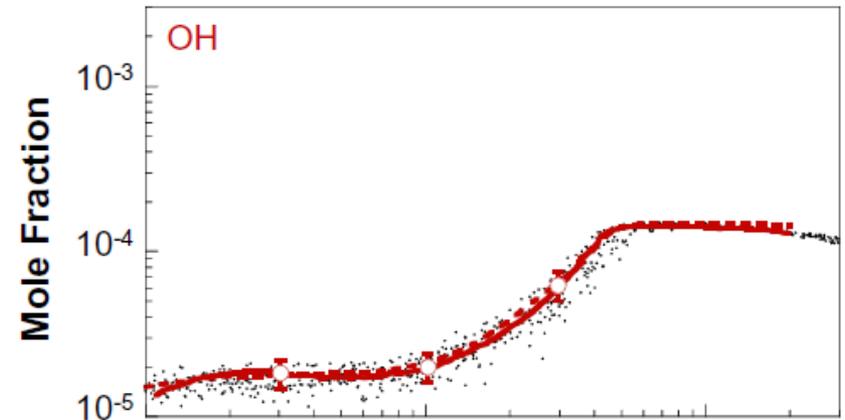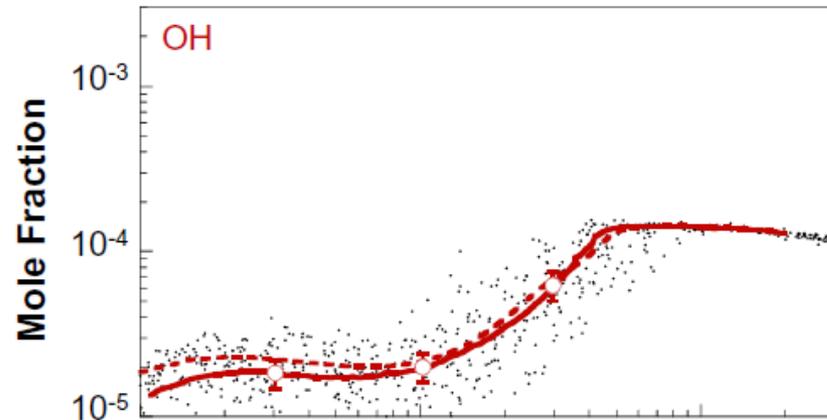
- Experimental (solid lines) and computed (dashed lines: nominal prediction; dots: uncertainty scatter). The open circles and the corresponding error bars designate data used as Series 1 targets and 2σ standard deviations,
- respectively. Left panel: prior model (Model I). Right panel: posterior model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

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

- the domain of feasibility of the Arrhenius parameters is determined from all of the available <u>direct</u> measurements
- optimal Arrhenius parameters are sought within this domain to reproduce the selected direct and indirect measurements.

R1): H + O2 = OH + O

(R2): H + O2 + M = HO2 + M (low-pressure limit, M = N2 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.

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

$$H + O_2 \rightarrow O + OH \qquad (R1)$$
Branching
$$H + O_2 + M \rightarrow HO_2 + M \quad (R2)$$
Terminating
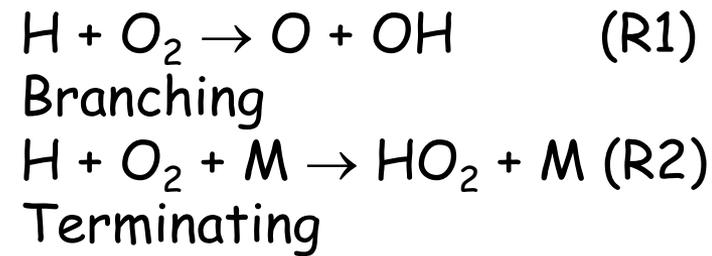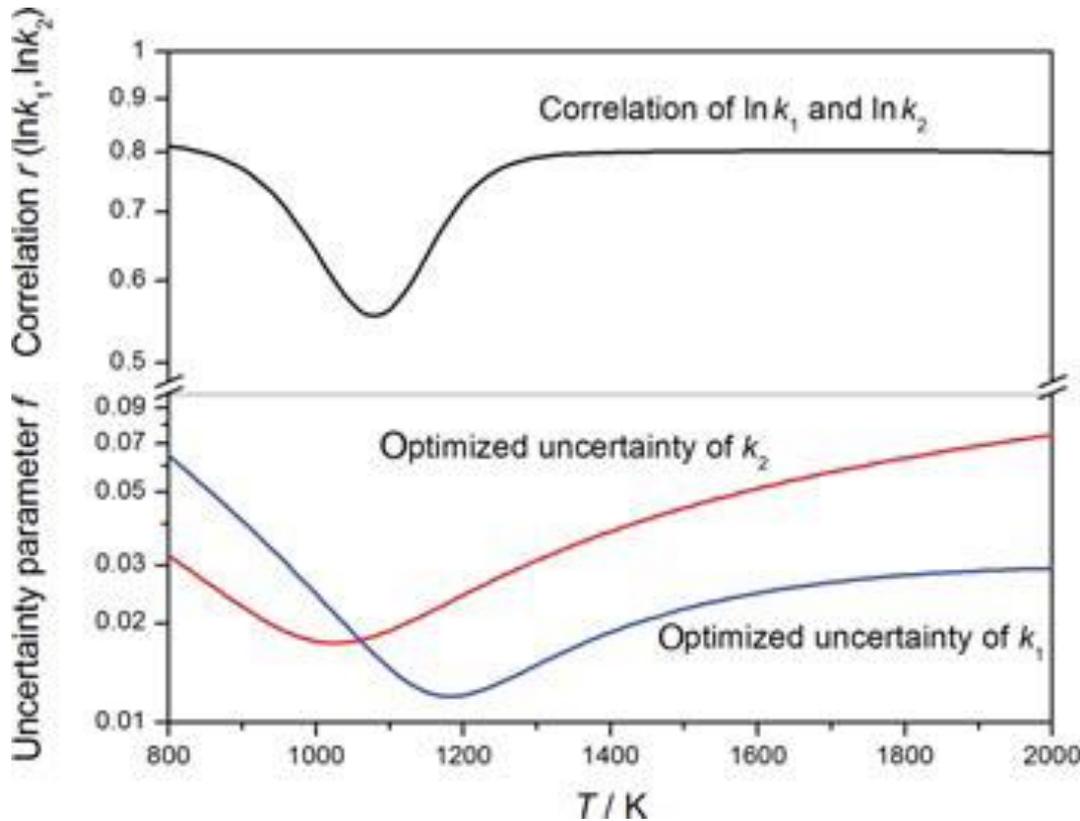
- increasing the rate coefficients of reactions (R1) and (R2), the calculated ignition delay time decreases and increases respectively. Simultaneous increase of both rate coefficients may keep the ignition delay time constant.: positive correlation coefficient.

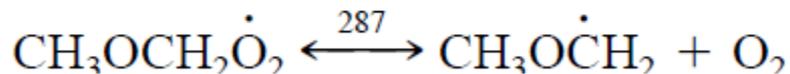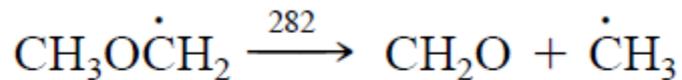# What is being done currently for most fuels

- Start from the best small-molecule model you can find (maybe from Hierarchical or PrIMe approaches)
- Add in additional reactions and species you think are important for your fuel / conditions of interest.
- Estimate all the new parameters (usually by group-additivity and analogy, sometimes by quantum chemistry).
- Either adjust some of the parameters to force a fit with the (limited) experimental data you have access to…
- ….or don't adjust anything, and just compare the new model predictions with some experiments as a validation test

Example of most-common approach:
Oxidation of C1-C5 Alkane Quinternary Natural Gas Mixtures at High Pressures

- Rapid compression machine and shock tube
- detailed chemical kinetic mechanism
- . Mixtures of $CH_4/C_2H_6/C_3H_8/n$-C_4H_{10}/n-C_5H_{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

$$CH_3O\dot{C}H_2 \xrightarrow{282} CH_2O + \dot{C}H_3$$

$$CH_3OCH_2\dot{O}_2 \xleftrightarrow{287} CH_3O\dot{C}H_2 + O_2$$

$$CH_3OCH_2\dot{O}_2 \underset{}{\overset{293}{\rightleftharpoons}} \dot{C}H_2OCH_2O_2H$$

$$\dot{C}H_2OCH_2O_2H \underset{}{\overset{294}{\rightleftharpoons}} CH_2O + CH_2O + \dot{O}H$$

$$\dot{O}_2CH_2OCH_2O_2H \xleftrightarrow{295} \dot{C}H_2OCH_2O_2H + O_2$$

$$\dot{O}_2CH_2OCH_2O_2H \underset{}{\overset{296}{\rightleftharpoons}} HO_2CH_2OCHO + OH$$

$$HO_2CH_2OCHO \xrightarrow{297} \dot{O}CH_2OCHO + OH$$

$$\dot{O}CH_2OCHO \xrightarrow{298} CH_2O + HCO_2$$

$$\dot{O}CH_2OCHO \underset{}{\overset{303}{\rightleftharpoons}} HOCH_2O\dot{C}O$$

$$HOCH_2O\dot{C}O \xrightarrow{304} HOCH_2\dot{O} + CO$$

$$HOCH_2O\dot{C}O \xrightarrow{305} \dot{C}H_2OH + CO_2$$
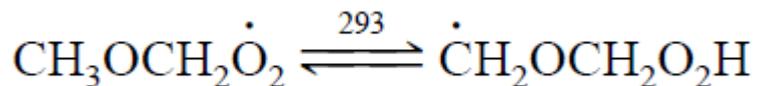
$$\varepsilon_a = \Delta H_{rxn} + \text{ring strain} + E_{abst}$$

$$E_{abst} = 12.7 + (\Delta H_{rxn} \times 0.37)$$
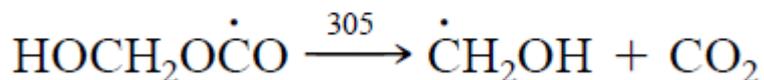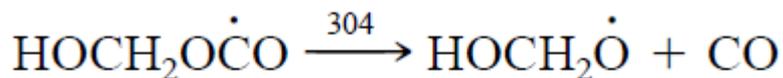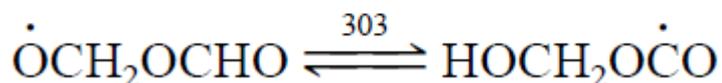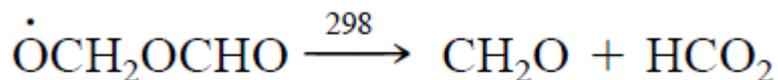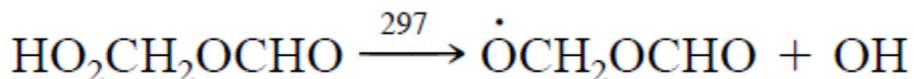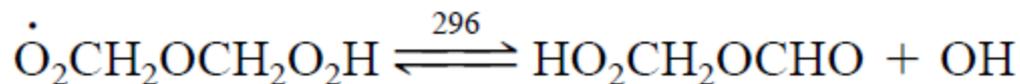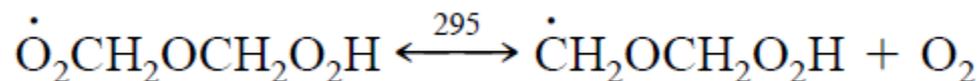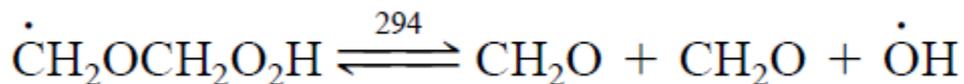
Most of rate coefficients have not been measured and were estimated – e.g. through relations with thermodynamic data.

Int J Chem Kinet, 2000, 32, 741

Important Issues

- Which species, reactions included in model?
  - Question of "Mechanism Completeness"
  - We don't care about all the species, so should be able to reduce level of detail in model: "Mechanism Reduction"
  - Current CFD algorithms cannot handle many species, stiffness
- How are thermo, k(T,P) estimated?
  - Numerous issues
  - Sequential refinement: focus effort on most important parameters: "Sensitivity Analysis"
  - Uncertainty Propagation into model predictions
- When the model predictions do not match experiment, should anything be adjusted?
  - Almost never is there enough data to determine any of the many parameters unambiguously.

A Quantitative Explanation for the Apparent Anomalous Temperature Dependence of OH + HO$_2$ = H$_2$O + 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 behavior (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
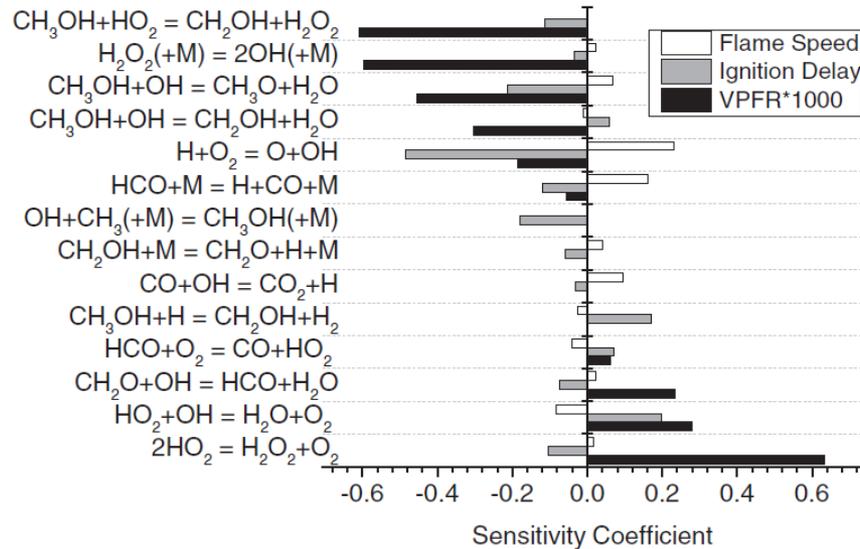
Sensitivity coefficients for flow reactor, shock tube and laminar premixed flame studies of methanol combustion
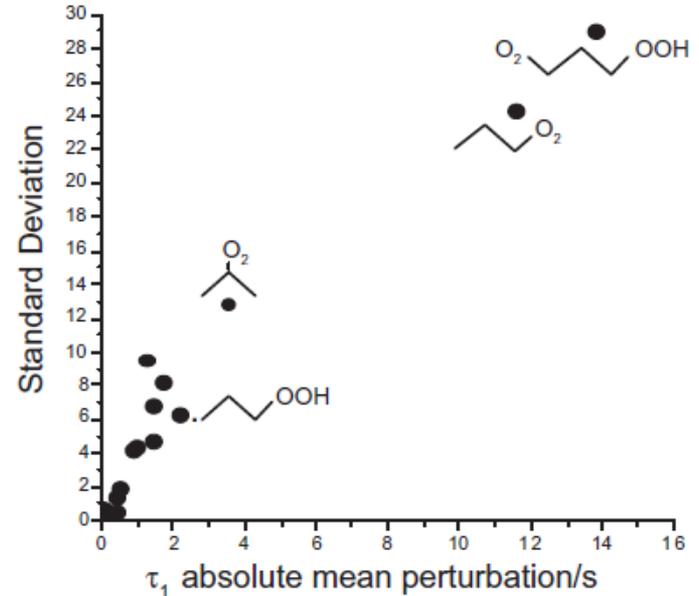
Global screening methods: Morris analysis for enthalpies of formation with respect to time to cool flame for propane oxidation

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.