Discussion

Mike Pilling

Emphasis of meeting – integration and interaction

- Meeting has covered
  - Studies of whole systems, importance of species measurement and definition of system parameters, major developments in mass spectrometry and resolution of isomers
  - Mechanisms – construction, validation
  - Elementary reactions – experiment and theory
  - Different environments – combustion, atmosphere, ISM
- Expertise usually demands these activities are conducted in different labs
- Understanding and integration of results, at all levels, is essential, as is interaction between different groups.

Possible discussion topics

- New experimental methods, including developments at NSRL
- Experiment / theory design. How do we decide on the systems / reactions to study, the developments that are needed and the conditions to use, the mechanism improvements needed and their implementation?
- Methods for analysing data and of combining theory and experiment. What about reanalysing data in the literature as new understanding, data, modelling methods become available.
- Chemical kinetic databases. What do we need in an ideal world? Does RESPECTH fulfil these requirements? Do we need competitive systems?
- Working across environmental boundaries:
  - Combustion
  - Atmospheric chemistry
  - Interstellar chemistry

Experimental methods

- New developments at NSRL

- Developments in
  - Diagnostics for combustion systems
  - Reactors
  - Measurements of rate constants for elementary reactions / links with theory

A PRIORI THEORETICAL CHEMICAL KINETICS

General Progress:

High Accuracy Energies; ANL0 ~ 0.2 kcal/mol; CCSDT(Q); CCSD(T)-F12; Core-Val. CBH (Conn. Based Hierarch.)

Better DFT; B2PLYPD3 ~ CCSD(T); WB97XD – cost effective

High Accuracy Partition Functions; Vib. Adia. Multidim. Tors., Anh., VTST, Tunneling

Better Master Equations; 2D with $k_{coll}(E,J;E',J')$; Nonlinear Collider Mixtures; with ISC, with Exit Channels

Combustion

- Progress
  - ❑ Automation
    - ✓ EStokTP; PACChem
  - ❑ Non-Thermal
    - ✓ $H_2CO + X \rightarrow H + CO + HX$;
    - ✓ $CH_3 + H + X \rightarrow CH_4^* + X \rightarrow CH_3 + HX$

- Forefront Challenges
  - ❑ Higher Accuracy for Larger Species
  - ❑ Whole Mechanisms
  - ❑ Collider Effects
  - ❑ Incorporate Non-Thermal Effects in Modeling

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UQ: OUR PERSPECTIVES & APPROACH

Challenges inferring parameters

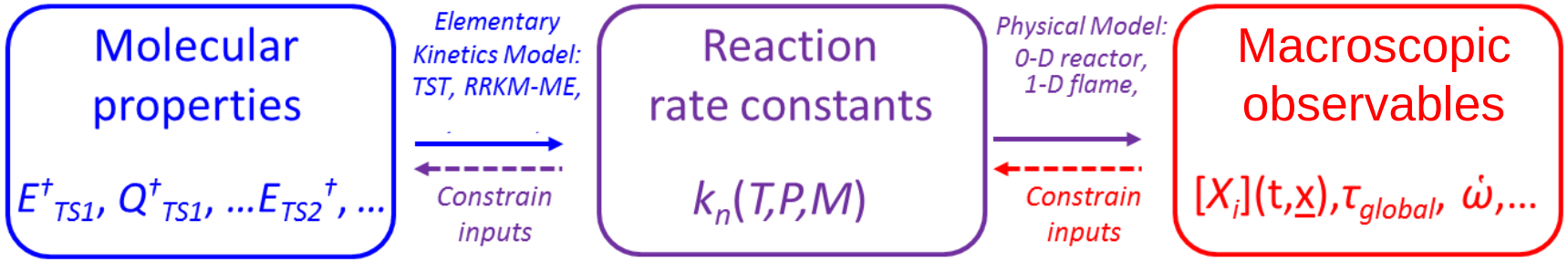
- When inferring rate parameters
  - Rarely enough experimental data to constrain $T/P/\underline{X}$ dependence
  - Extrapolations rely heavily on functional forms (e.g. Arrhenius, Troe)
- Rate constant determinations often depend on secondary reactions and physical models
- Structural uncertainties comparable to parametric uncertainties for combustion targets
  - Chemically termolecular reactions, mixture rules, prompt dissociation,…

Our approach

- Constrain molecular parameters
  - Use theory to constrain full $T/P/\underline{X}$ dependence
  - Use elementary kinetics theories for extrapolation
- Interpret raw experimental data to account for secondary reaction and physical model uncertainties
- Choose targets for specific purpose
  - Dilute experiments
    → infer parameters
  - Non-dilute (combustion) experiments
    → test model structure

MULTI-SCALE INFORMATICS (MSI)

Optimize and quantify uncertainties for set of molecular parameters informed by data across all scales



Active Parameters

- Molecular parameters:
  - $E^{\dagger}$'s, $v^{\dagger}$'s, $v^{\dagger}_{imag}$'s, f_{VRC}'s, …
- Rate parameters:
  - A's, n's, E_a's,…
- *Physical model parameters:*
  - T_0's, P_0's, $\underline{X}_0$'s, …
  - $\underline{\sigma}_{\lambda}$''s, …

Targets

- Electronic structure calc's
  - $E^{\dagger}$'s, $v^{\dagger}$'s, $v^{\dagger}_{imag}$'s, f_{VRC}'s, …
- Rate constant determinations:
  - k's
- *Macroscopic observables:*
  - T_0's, P_0's, $\underline{X}_0$'s, …
  - $\underline{X}(t)$'s, $absorbance_{\lambda}$'s, …

Mathematical Implementation

- Local surrogate model
- Least squares error minimization
- Iterated until converged

→ $\underline{x}_{opt}$, C_x

1. M.P. Burke, *Int. J. Chem. Kinet.* 48 (2016) 212-235.
2. M.P. Burke, S.J. Klippenstein, L.B. Harding, *PCI* 34 (2013) 547-555.
3. M.P. Burke, C.F. Goldsmith, S.J. Klippenstein, O. Welz, H. Huang, I.O. Antonov, J.D. Savee, D.L. Osborn, J. Zádor, C.A. Taatjes, L. Sheps, *J. Phys. Chem A* (2015)

Experiment / theory design. How do we decide on the systems / reactions to study, the developments that are needed and the conditions to use, the mechanism improvements needed and their implementation?

Using sensitivity entropy in experimental design for uncertainty minimization of combustion kinetic models

Shuang Li [a,b], Tao Tao [b,c], Jiaxing Wang [b,c], Bin Yang [b,c,*], Chung K. Law [a,e], Fei Qi [a,d]

Proc Combust Inst 2017, 36, 709-716

Global Uncertainty Propagation and Sensitivity Analysis in the $CH_3OCH_2 + O_2$ System: Combining Experiment and Theory To Constrain Key Rate Coefficients in DME Combustion

R. J. Shannon,[†] A. S. Tomlin,*[,‡] S. H. Robertson,[§] M. A. Blitz,[†] M. J. Pilling,[†] and P. W. Seakins[†]

J Phys Chem A 2015, 119 7430

- Which experiment (direct / indirect) / calculations should we do and under which conditions? Best approaches to experimental design.

Chemical kinetic databases / websites. What do we need in an ideal world? Does RESPECTH fulfil these requirements? Do we need competitive systems?

Storage of raw experimental data.

Should it be a requirement for publication?

How raw is raw?

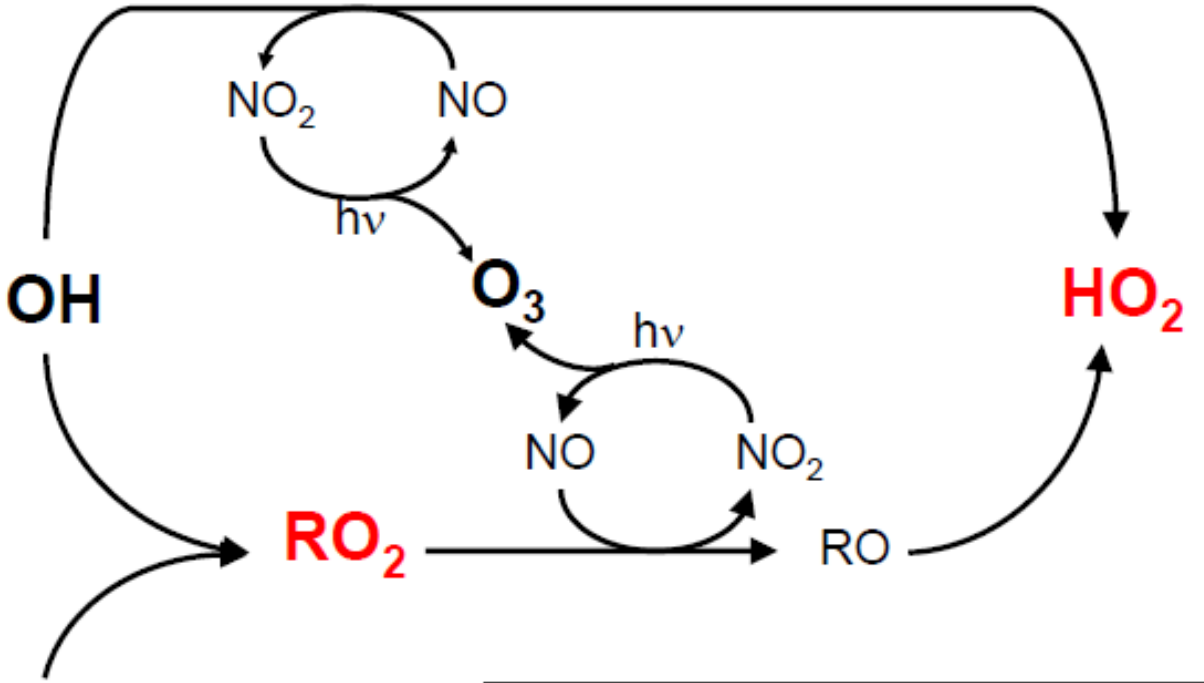
Working across environmental boundaries

- Understanding and modelling systems in combustion, atmospheric chemistry – what can we learn from one another?

- Highly oxidised molecules, autoxidation chemistry and formation of secondary organic aerosols.

RO_2 radicals in polluted atmosphere

Competing isomerisation of RO_2 to form QOOH and subsequent additions of O_2, with isomerisation to increase O:C ratio in a single chain cycle



Net formation of 2 molecules O_3

Working across environmental boundaries

- Understanding and modelling systems in combustion, atmospheric chemistry – what can we learn from one another?
- Highly oxidised molecules, autoxidation chemistry and formation of secondary organic aerosols.
- International consortium led by Bill Carter to develop atmospheric chemical mechanisms – future developments of Master Chemical Mechanism (MCM) and GECKO
- The role of theory in atmospheric and interstellar chemistry.

A PRIORI THEORETICAL CHEMICAL KINETICS

Atmospheric

- Progress
  - ❑ Multidimensional Vib. Adiabatic Partition Functions
  - ❑ Non-Thermal from Traj. + ME
  - ❑ Better Energies
- Forefront Challenges
  - ❑ van der Waals Stabilization
  - ❑ Are Different Torsional States one Species or Multiple Species
  - ❑ High Accuracy for Large Species

Interstellar

- Focus is on Barrierless Reactions
- Any Barrier => Too Slow
- Progress
  - ❑ Multiple Transition States
  - ❑ High Accuracy Energies to Delineate Presence or Absence of Barrier
- Forefront Challenges
  - ❑ Quantitative Prediction of Low Temperature Rise Due to Tunneling
  - ❑ Collider Effects at Low Temperature

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OH + acetone. Rate constant vs T