Combustion Chemistry

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CEFRC Combustion Summer School

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UNIVERSITY OF LEEDS

Background 1

- Combustion involves the oxidation of a fuel, ideally leading, for an organic fuel such as octane or ethanol, to the formation of carbon dioxide and water, with the release of heat.

- The overall chemical equation, e.g.

$$C_2H_5OH + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$$

  does not describe the way in which the reaction occurs.

- Instead the reaction involves a sequence of elementary, or single step reactions, many of which involve atoms or radicals, which are short-lived species with high reaction rates.

Background 2

This series of lectures examines how the rates of these elementary reactions can be determined experimentally and understood theoretically; how chemical mechanisms describing the overall sequence of reactions can be constructed and then used to model the chemistry of combustion systems.

An example – $H_2 + O_2$

The overall reaction is: $2H_2 + O_2 \rightarrow 2H_2O$

A minimal set of the component elementary reactions is:

1. $H_2 + O_2 \rightarrow H + HO_2$
2. $H + O_2 \rightarrow OH + O$
3. $O + H_2 \rightarrow OH + H$
4. $OH + H_2 \rightarrow H + H_2O$
5. $H + O_2 + M \rightarrow HO_2 + M$
6. $H, O, OH \rightarrow$ wall
7. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

Rates of elementary reactions

- The rate of each elementary reaction is determined by the reactant concentrations and the rate coefficient, k. k depends on T and, in some cases p.
  We also need to know the products of the reaction, which in some cases isn't clear.

- Example: reaction 2: $H + O_2 \rightarrow OH + O$; k_2

Rate of this reaction = $-d[H]/dt = k_2[H][O2] = d[OH]/dt = d[O]/dt$

- k_2 depends on temperature and this is usually expressed in Arrhenius form:

$$k_2 = A\exp(-E_a/RT)$$

or modified Arrhenius form:

$$k_2 = AT^n\exp(-E_a/RT)$$

A is the A factor, E_a the activation energy, n the temperature exponent and R the gas constant.

- One aim of experimental and theoretical studies of elementary reactions is to determine A, E_a, n

- Definitions: order of reaction; units of rate coefficients

Relationship between forward and reverse rate coefficients (e.g. $H_2 + O_2 \rightarrow H + HO_2$ and the reverse)

$$K = \frac{\prod_{products}(a_i^{\nu_i})}{\prod_{reactants}(a_i^{\nu_i})}$$

a is the *activity*. For ideal systems, $a = p/p^\circ = c/c^\circ$ so that *K* is dimensionless. Other definitions of equilibrium constants are:

$$K_c = \frac{\prod_{products}(c_i^{\nu_i})}{\prod_{reactants}(c_i^{\nu_i})} \qquad K_p = \frac{\prod_{products}(p_i^{\nu_i})}{\prod_{reactants}(p_i^{\nu_i})}$$

These have dimensions if $(\Sigma\nu_i)_{reactants} \neq (\Sigma\nu_{i)products}$

At equilibrium, forward rate = reverse rate:

$$k_f \prod_{products} (c_i^{\nu_i}) = k_r \prod_{reactants} (c_i^{\nu_i}) \qquad \frac{k_f}{k_r} = K_c$$

Detailed balance
Use of thermodynamic databases

Thermodynamic relations (more detail on Wednesday)

At constant T, the Gibbs energy, G is given by:

$$\Delta G = \Delta H - T\Delta S$$

and the equilibrium constant is related to ΔG by:

$$RT\ln K = -\Delta G$$

The equilibrium constant, K, can be calculated from tabulated values of the enthalpy H and entropy S, and hence the reverse rate coefficient(say) determined from the forward rate coefficient and K.

Constructing coupled differential (rate) equations from chemical mechanisms

1. $H_2 + O_2 \rightarrow H + HO_2$
2. $H + O_2 \rightarrow OH + O$
3. $O + H_2 \rightarrow OH + H$
4. $OH + H_2 \rightarrow H + H_2O$
5. $H + O_2 + M \rightarrow HO_2 + M$
6. H, O, OH $\rightarrow$ wall
7. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

The chemical mechanism is set up together with the associated rate coefficients

The coupled rate equations are then written down for each species

d[X]/dt = Total rate of forming X -Total rate of removing X:

$$\frac{d[\mathrm{H}]}{dt} = k_1[\mathrm{H_2}][\mathrm{O_2}] - k_2[\mathrm{H}][\mathrm{O_2}] + k_3[\mathrm{O}][\mathrm{H_2}] + k_4[\mathrm{OH}][\mathrm{H_2}] - k_5[\mathrm{H}][\mathrm{O_2}][\mathrm{M}] - k_6[\mathrm{H}]$$

$$\frac{d[\mathrm{O}]}{dt} = k_2[\mathrm{H}][\mathrm{O_2}] - k_3[\mathrm{O}][\mathrm{H_2}] - k_6[\mathrm{O}]$$

etc .....

Solve the set of coupled differential equations numerically, subject to initial conditions.

The quasi steady state approximation, QSSA

- The QSSA is sometimes used to simplify kinetic problems
- Consider the scheme:

  $A \rightarrow B \rightarrow C$, with rate coefficients k_1 and k_2

  Set up the rate equations, with a = [A], etc.

$$\frac{da}{dt} = -k_1 a; \frac{db}{dt} = k_1 a - k_2 b$$

$$a = a_0 \exp(-k_1 t)$$

$$b = \frac{a_0 k_1}{(k_2 - k_1)} \{\exp(-k_1 t) - \exp(-k_2 t)\}$$

$$c = a_0 - a - b$$

QSSA continued

Figure (a): $k_1 > k_2$ $\quad b = \dfrac{a_0 k_1}{(k_1 - k_2)}\{\exp(-k_2 t) - \exp(-k_1 t)\}$

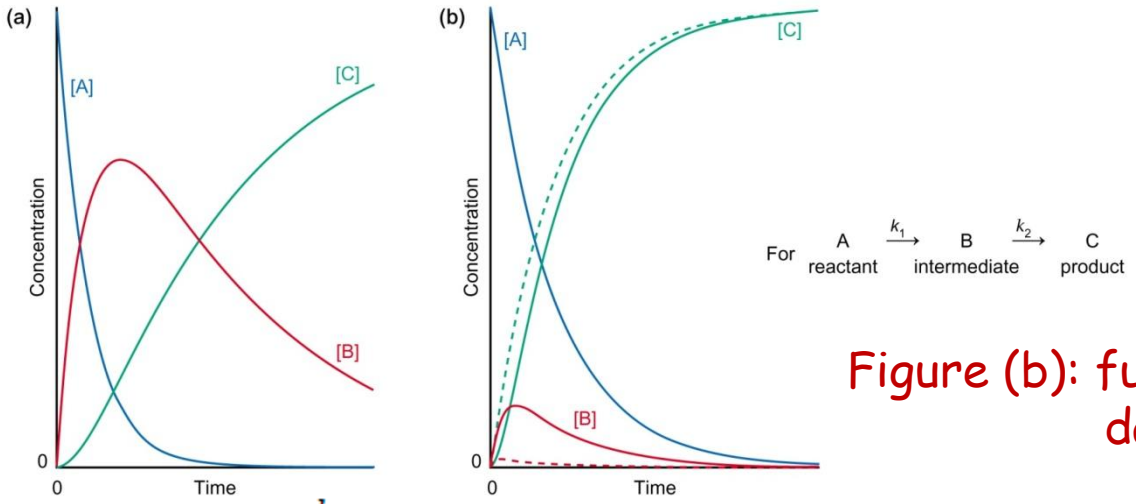


Figure (b): full, $k_2 = 5k_1$
dashed, $k_2 = 50k_1$

Figure (b): $k_1 < k_2$ $\quad b = \dfrac{a_0 k_1}{(k_2 - k_1)}\{\exp(-k_1 t) - \exp(-k_2 t)\}$

For $k_1 \ll k_2$ and for times long compared with $(k_2)^{-1}$

$$b = \frac{a_0 k_1}{(k_2 - k_1)}\{\exp(-k_1 t)\} \approx \frac{a_0 k_1}{k_2}\{\exp(-k_1 t)\} = \frac{a k_1}{k_2}$$

$$\therefore b \ll a \text{ and } \frac{db}{dt} \ll \frac{da}{dt}$$

- QSSA: $db/dt \approx 0$: rate of forming of B ≈ rate of removing B

Pressure dependent association reaction

An association reaction involves collisional stabilisation of the adduct:

$$A + B \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} AB^* \xrightarrow{k_s[M]} AB.$$

Examples include

$CH_3 + CH_3 \rightarrow C_2H_6$

$OH + C_2H_4 \rightarrow C_2H_4OH$

Apply QSSA:

$$k = \frac{k_a k_s[M]}{k_{-a} + k_s[M]}$$

$$\text{As } [M] \rightarrow \infty, k \rightarrow k_a = k^{\infty}$$

$$\text{As } [M] \rightarrow 0, k \rightarrow \frac{k_a k_s[M]}{k_{-a}} = k_0[M]$$

Substituting in first equation

$$k = \frac{k_0[M]k^{\infty}}{k^{\infty} + k_0[M]}$$

Similar treatment for dissociation reactions

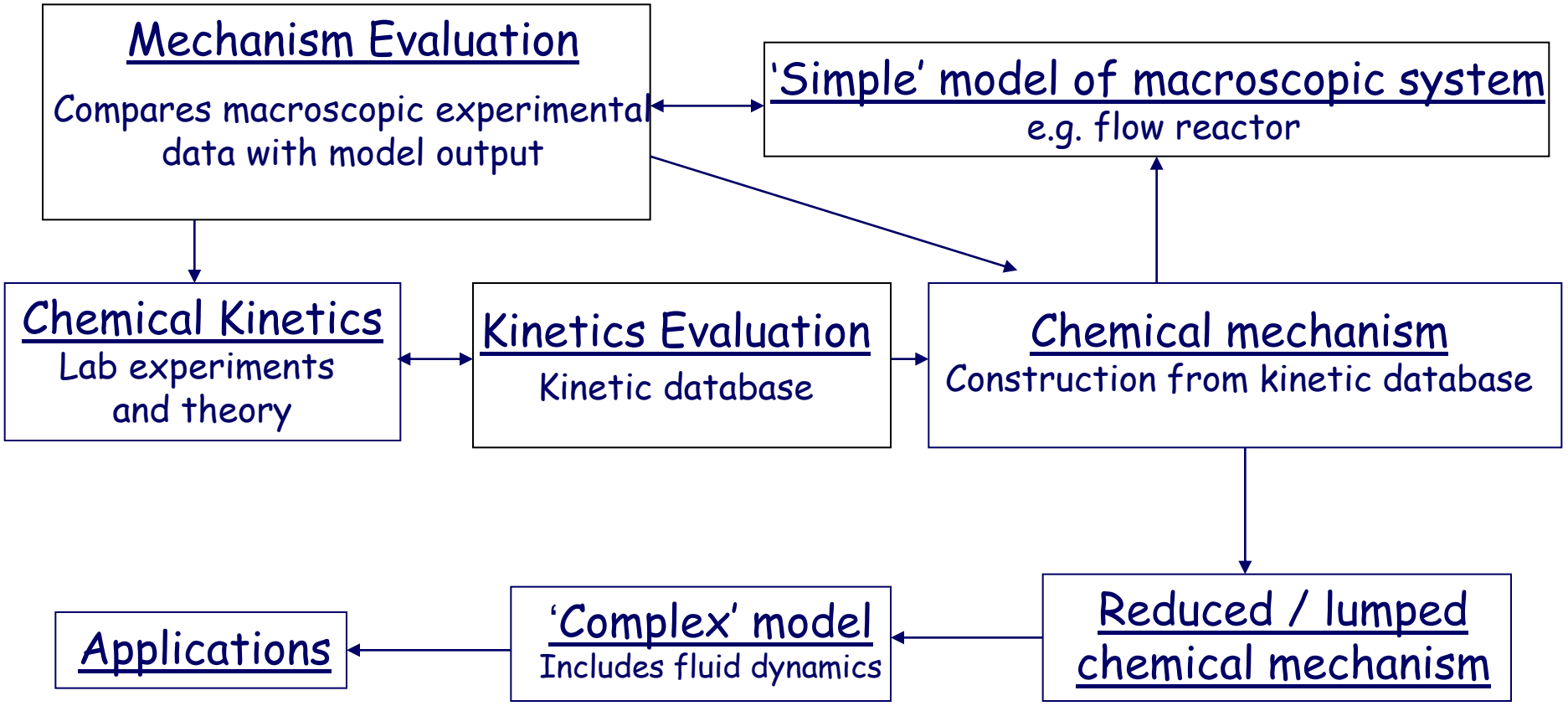
Types of elementary reaction in combustion

A minimal set of the component elementary reactions is:

1. $H_2 + O_2$	$\rightarrow$	$H + HO_2$	I
2. $H + O_2$	$\rightarrow$	$OH + O$	B
3. $O + H_2$	$\rightarrow$	$OH + H$	B
4. $OH + H_2$	$\rightarrow$	$H + H_2O$	P
5. $H + O_2 + M$	$\rightarrow$	$HO_2 + M$	T
6. H, O, OH	$\rightarrow$	wall	T
7. $HO_2 + HO_2$	$\rightarrow$	$H_2O_2 + O_2$	T

- Types of reaction: I = initiation; B = branching; P = propagation, T = termination

Reaction kinetics contributions to combustion models



Understanding
Similar approaches in atmospheric chemistry, interstellar chemistry.

Synopsis

- Topic 1: Experimental measurements of rate coefficients and product yields for elementary reactions.
- Topic 2: Linking experiment and theory.
- Topic 3:Thermodynamics.
- Topic 4: Rate coefficient evaluation
- Topic 5: Mechanism construction and evaluation.
- Topic 6: NOx chemistry.
- Topic 7: Combustion emissions, climate change and air quality.

Measurement of rates of elementary reactions 1

- Concentrate on reactions of atoms and radicals; say something briefly about reactions that don't involve radicals and are involved in initiation steps
- Need to cover a range of T from 1000 to 3000 K for reactions involved in high temperature combustion reactions; 600 – 1000 K for low T oxidation in the autoignition regime; 200 – 300 K for reactions of combustion generated pollutants in the lower atmosphere (the troposphere)

Measurement of rates of elementary reactions 2

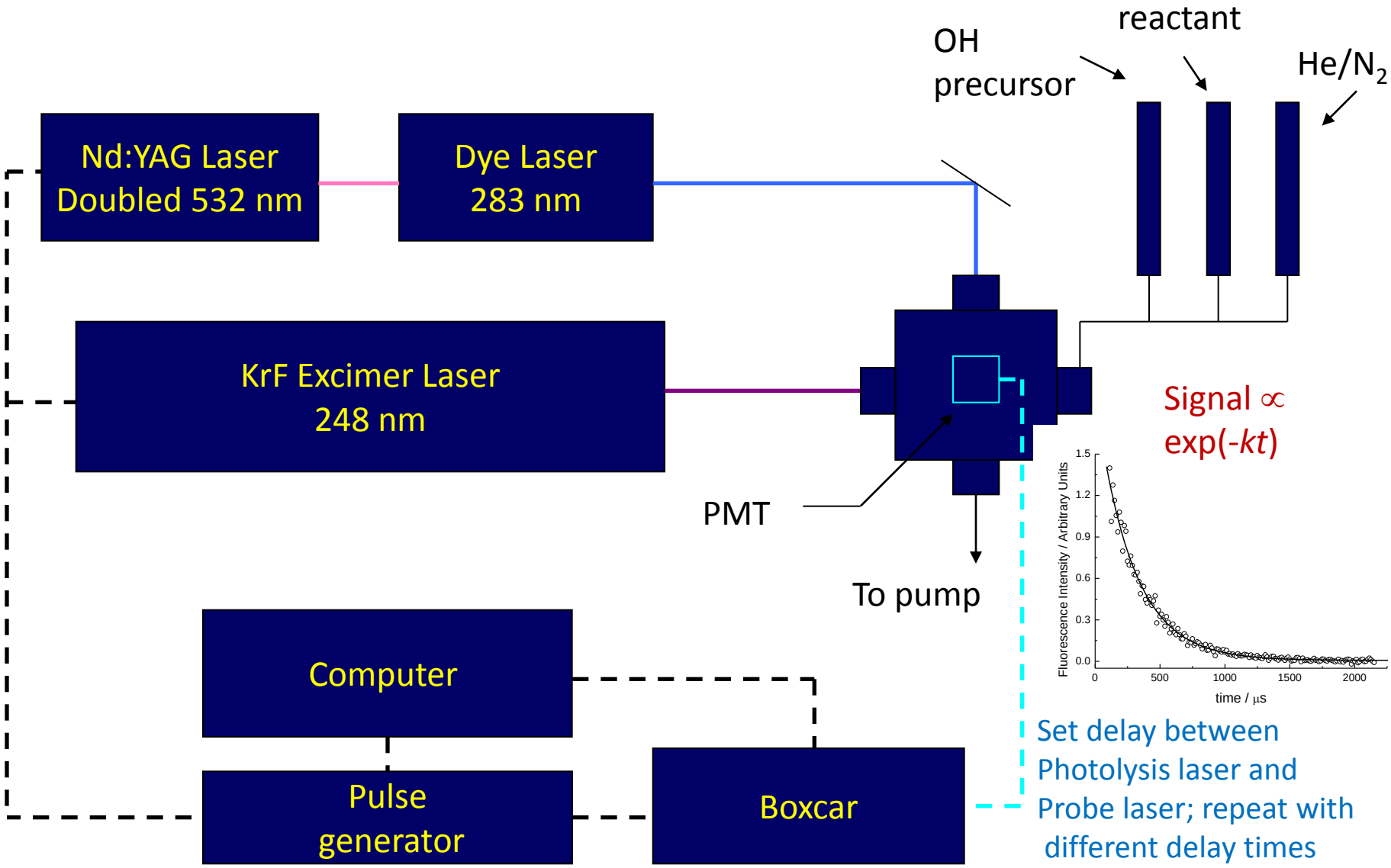
- Ideally, isolate the individual reaction and study it at the appropriate combustion conditions.
- Not always possible:
  - May have to model the system to extract *k*s of interest
  - May need to extrapolate to appropriate *T*, *p*. Ideally achieve this with the help of theory.

Techniques

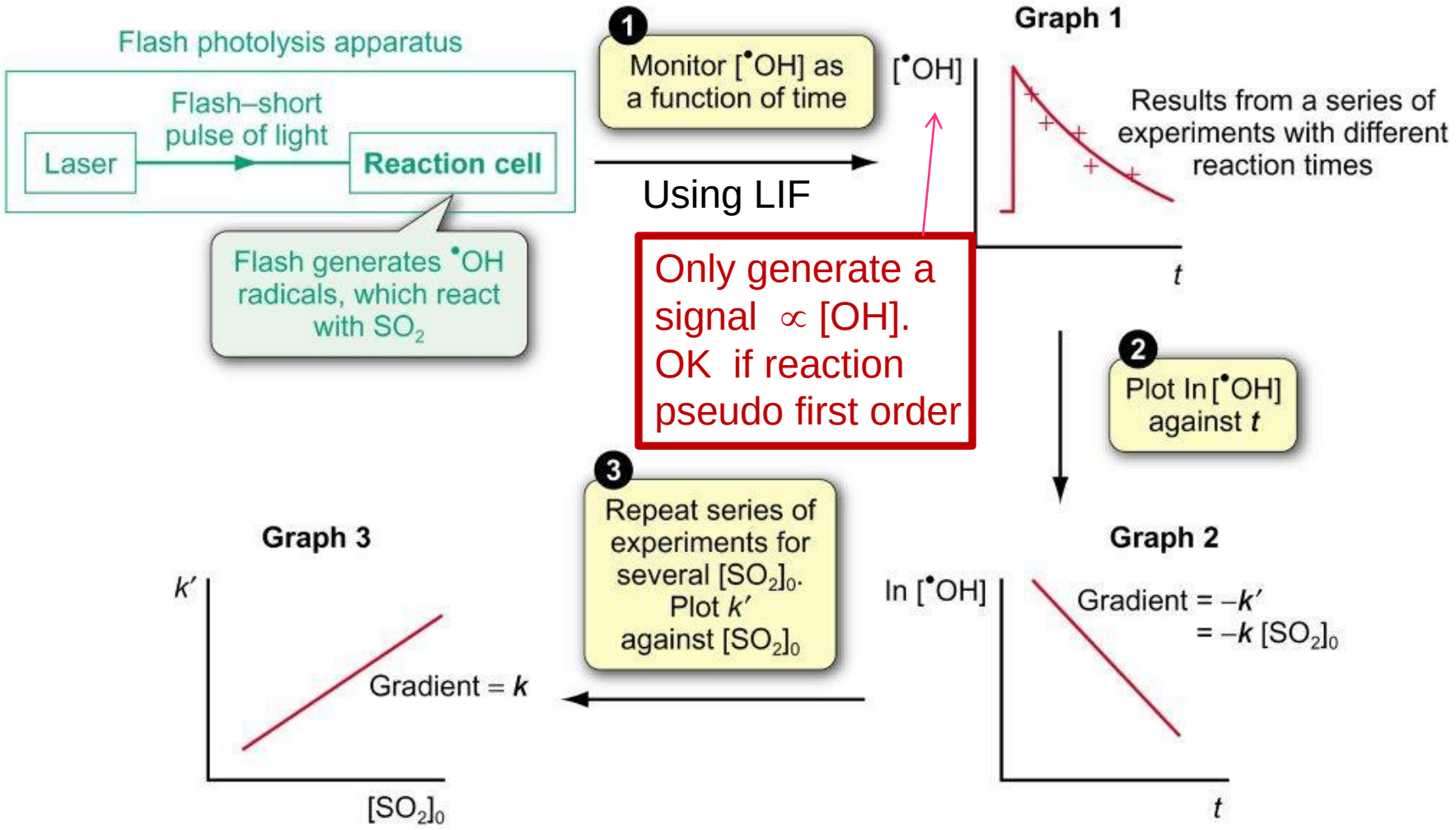
- Pulsed laser photolysis (laser flash photolysis)
- Shock tubes
- Flow tubes for elementary reactions and whole systems
- Static studies of whole systems

Pulsed laser photolysis

Laser flash photolysis (LFP) / laser induced fluorescence (LIF) for the study of OH + reactant

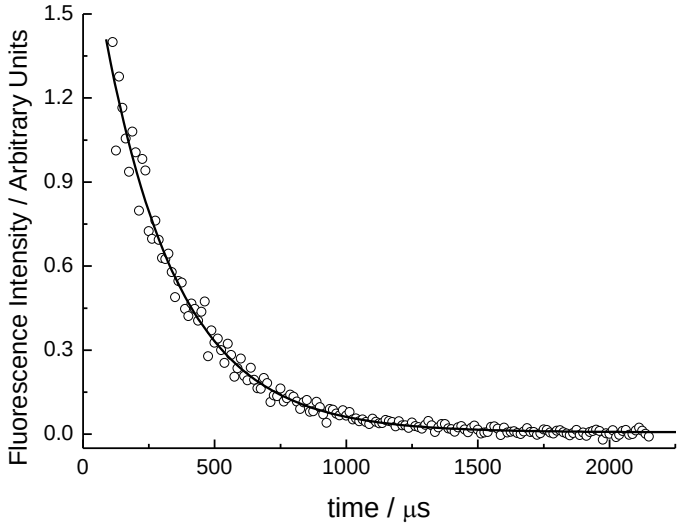


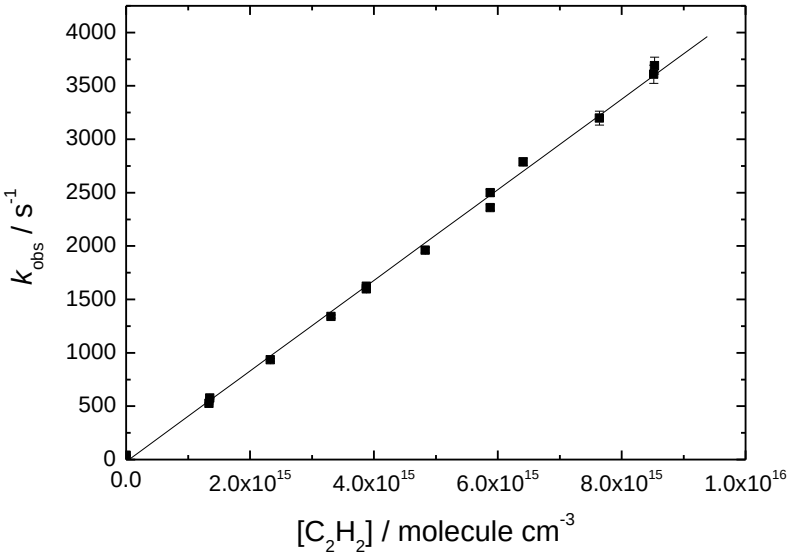
Procedure for determining rate coefficients for pseudo first order reactions using LFP for OH + SO_2

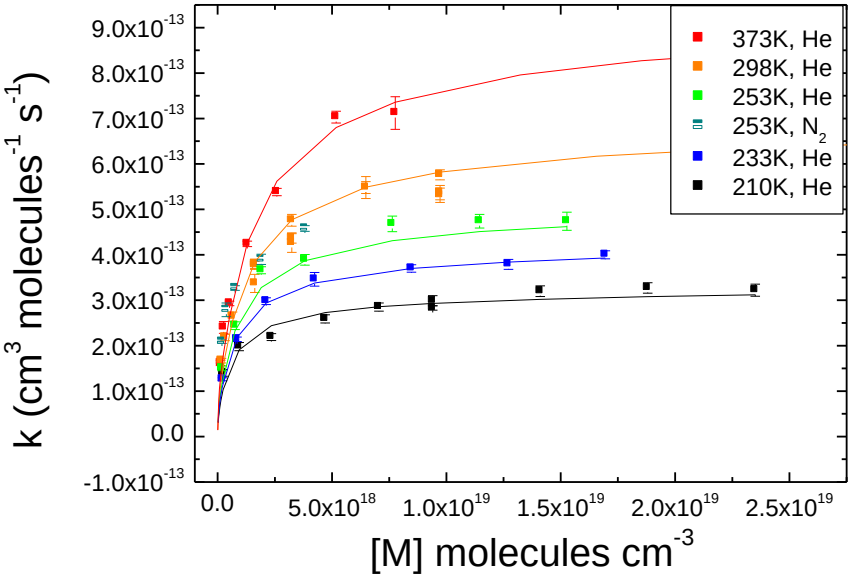


$OH + C_2H_2 + M \rightarrow C_2H_2OH + M$
Cleary et al. J. Phys. Chem., 2007, 111, 4043-4055

- Pressure dependent (association) reaction.
- Study as a function of temperature and pressure

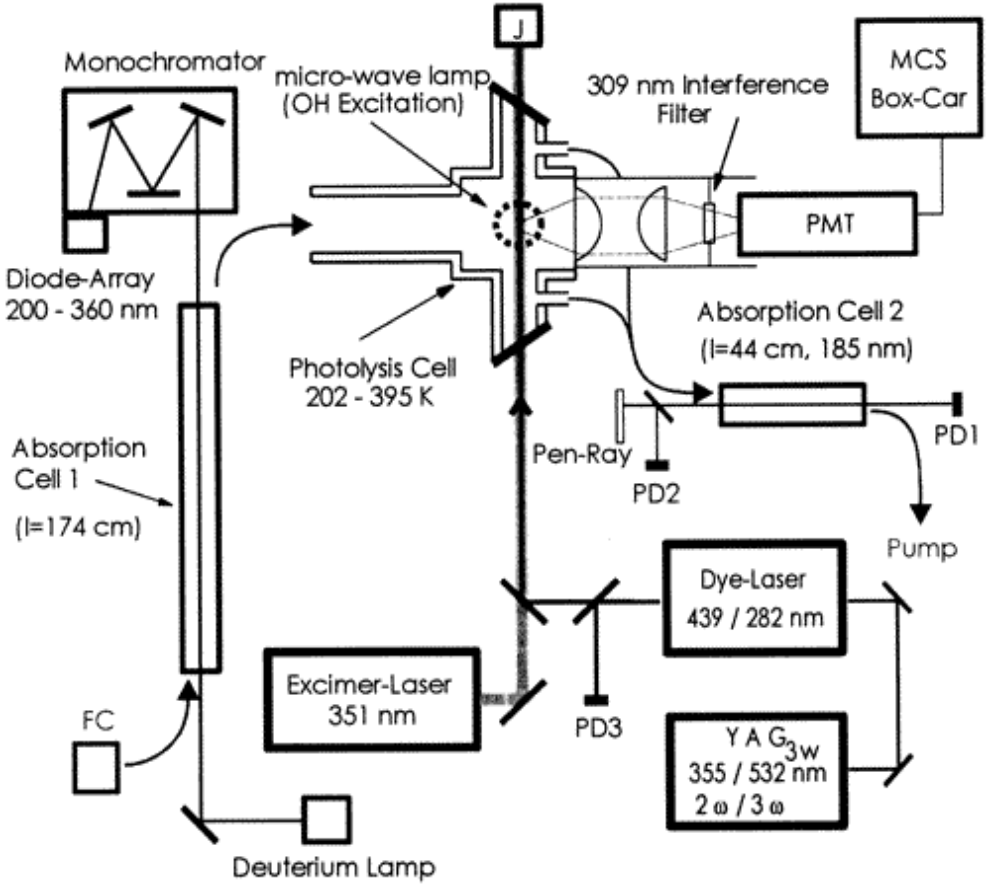


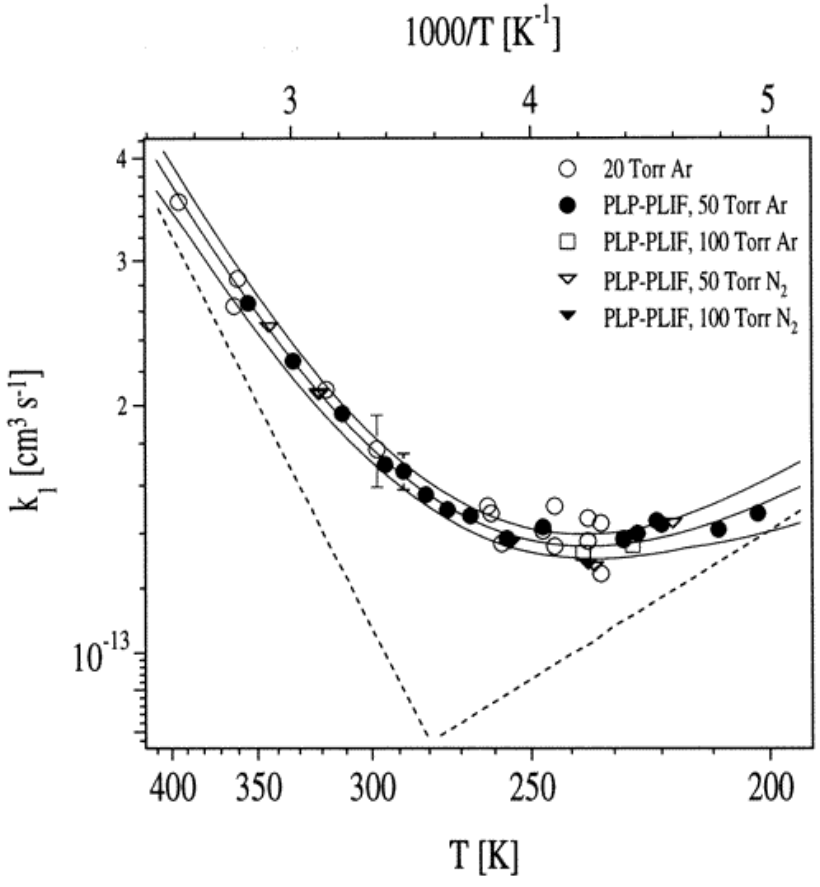




OH + acetone, J N Crowley, JPCA, 2000, **104**,2695

laser flash photolysis, resonance fluorescence/laser induced fluorescence to measure [OH] (relative). Optical measurement of [acetone] before and after reactor.





Detection using time of flight mass spectrometry

Blitz et al. Rev. Sci. Inst. 2007, 78, 034103

ToFMS

Turbo Pump 300 l/s

VUV-Photoionisation

Flight Tube ~5*10^{-6} Torr

248 nm
Excimer
Laser Beam

1 mm

d= 1.27 cm, l = 70 cm

Metal/ Quartz Flow Reactor

Quartz window

Pump 28 l/h

Diffusion Pump 3000 l/h

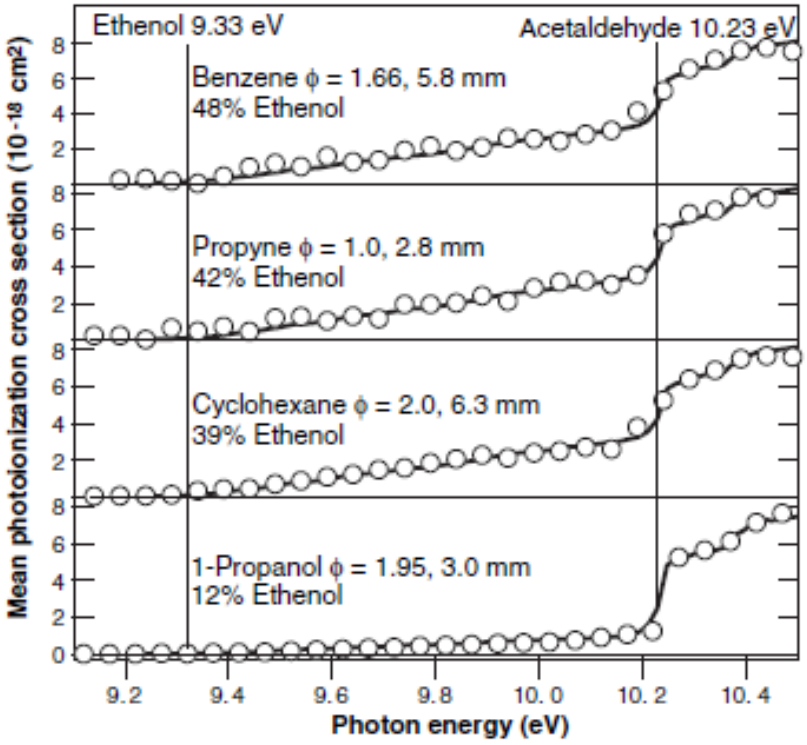
Main Vacuum
Chamber 10^{-3}-10^{-4}
Torr

Application of synchrotron radiation for photoionization (SVUV-PIMS) to distinguish isomers in flames
1. ALS, USA

- ALS is tuneable and so it is feasible to distinguish isomers, which have the same mass, through their differing photoionization efficiency curves.
- Traces show m/z=44 for different flames:

  acetaldehyde: CH_3CHO

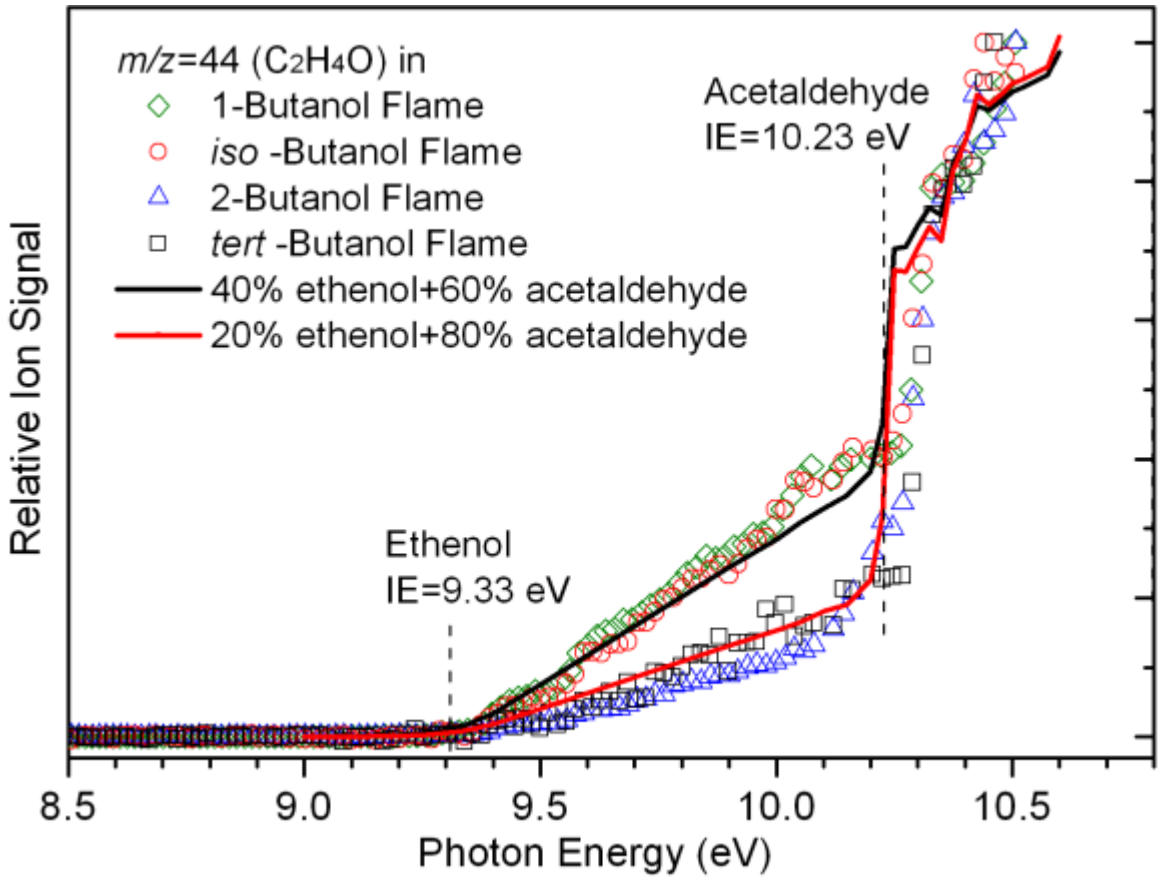
  ethenol: CH_2=CHOH

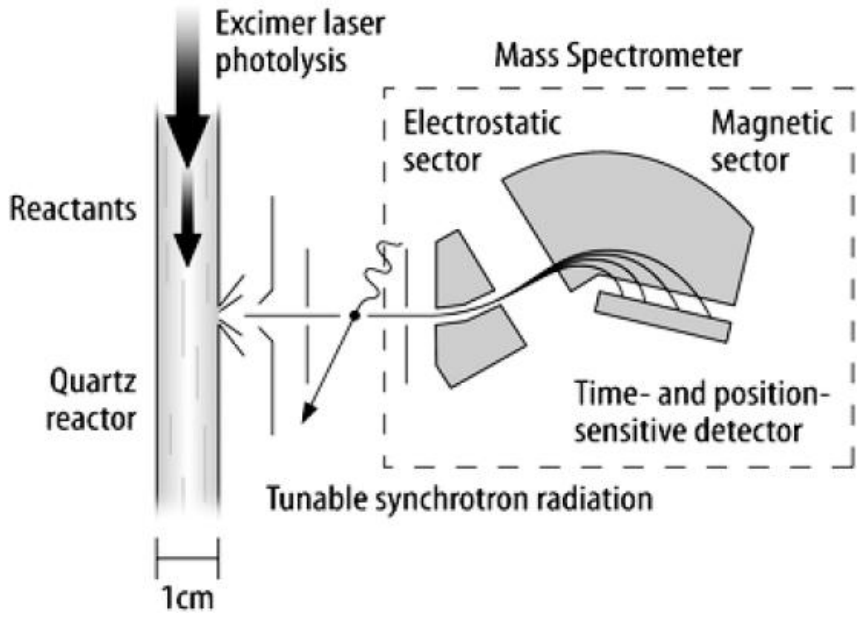


Taatjes et al. *Science* 2005, **308**, 1887

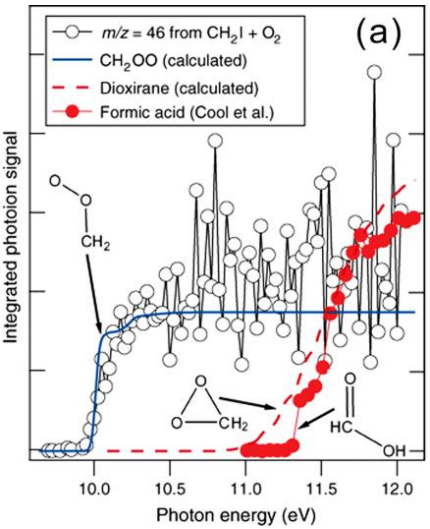
2. NSRL China
Various butanol flames,

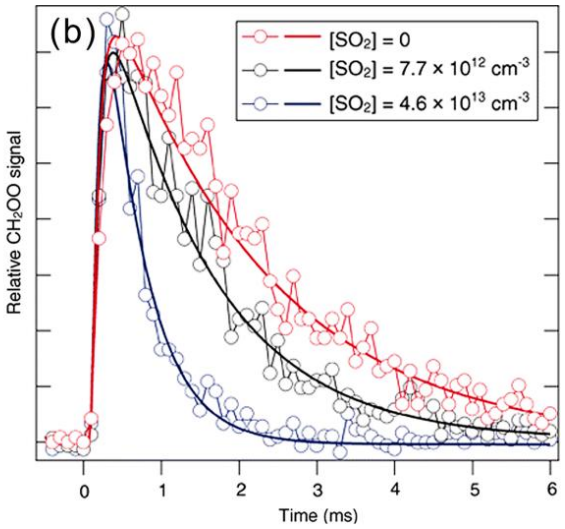
- Yang et al.Combust. Flame 148 (2007) 198-209.





SVUV-PIMS for kinetics Taatjes et al., PCCP, 2008, 10, 20 – 34

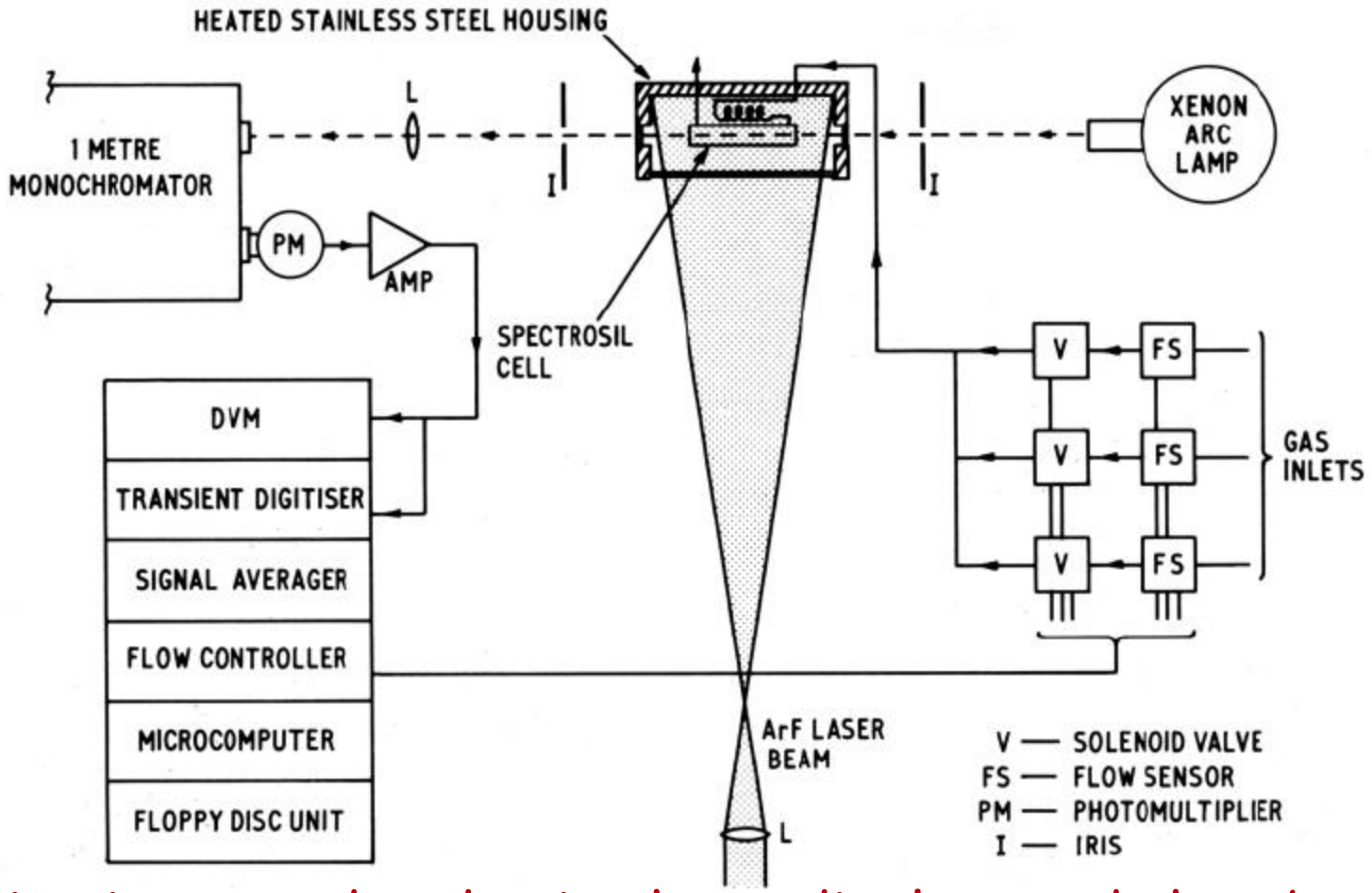




(a) The calculated photoionization spectra of the Criegee intermediate CH_2OO and dioxirane, the experimental photoionization spectrum for formic acid, as well as schematic chemical structures, are shown.

(b) Time-dependent CH_2OO signals for various concentrations of SO_2. Solid lines represent fits to the data traces, including convolution with a measured instrument response function, from which pseudo-first order decay constants are derived Welz et al. Science 335, 204-207

Radical detection using absorption spectroscopy: $C_3H_5 + C_3H_5$

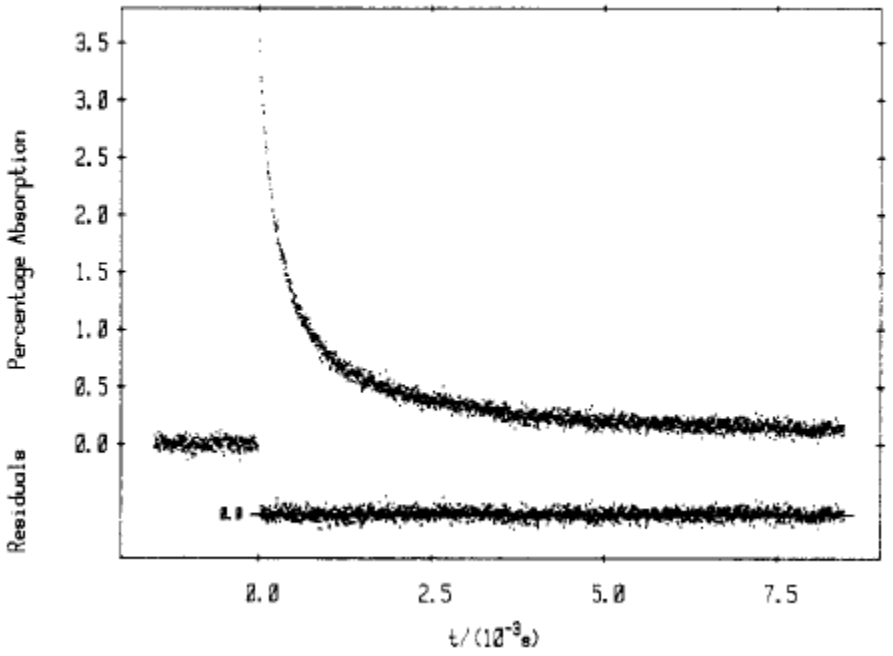


Reaction is second order in the radical – need the absolute concentration to determine *k*.

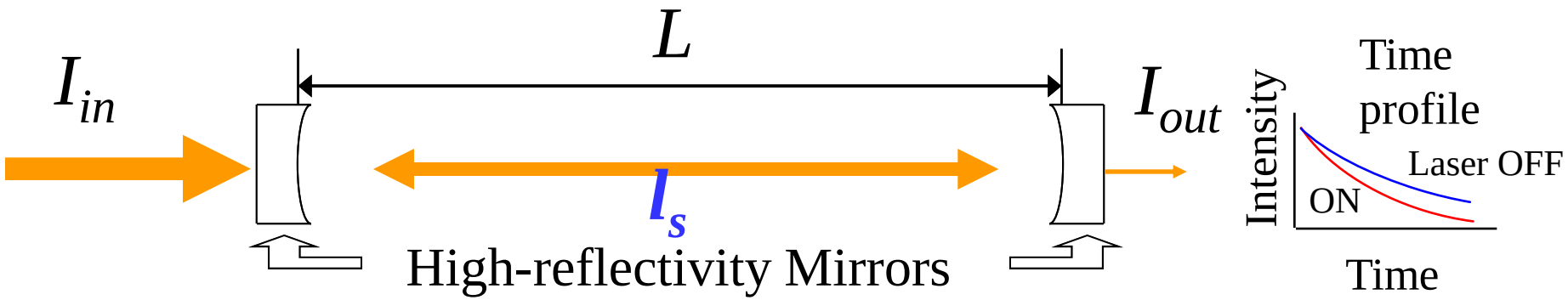
Tulloch et al. *J. Phys. Chem.* l982, *86*, 3812-3819

$C_3H_5 + C_3H_5$:Absorption spectroscopy 2

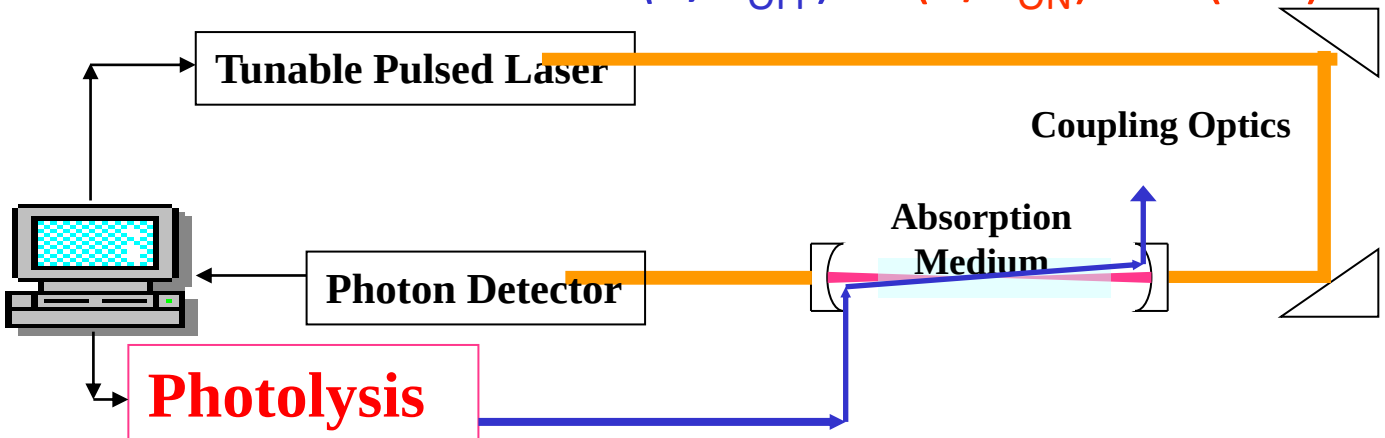
- Reaction is second order in C_3H_5
- Need to know absolute concentration of radical – absorption spectroscopy provides a good route to this. (see J. Phys. Chem. 1985, 89, 2268-2274 for discussion for CH_3)
- $I/I_0 = \exp(-\sigma[C_3H_5]L)$ where I_0 is the incident and I the transmitted light intensity, σ is the absorption cross section and L is the path length.

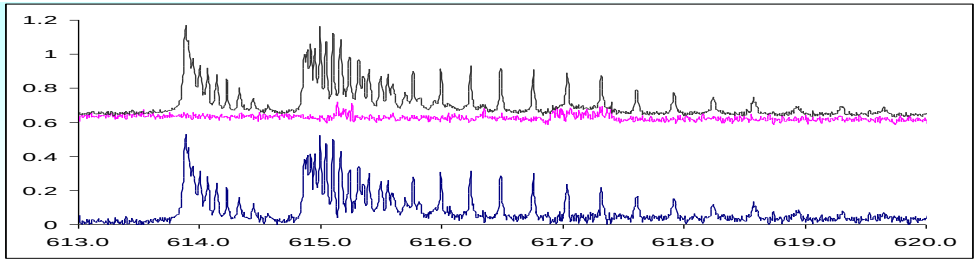


Detection of HCO using cavity ring down spectroscopy (CRDS)



$(1/k_{OFF}) - (1/k_{ON}) = A\,(\sigma c l)$



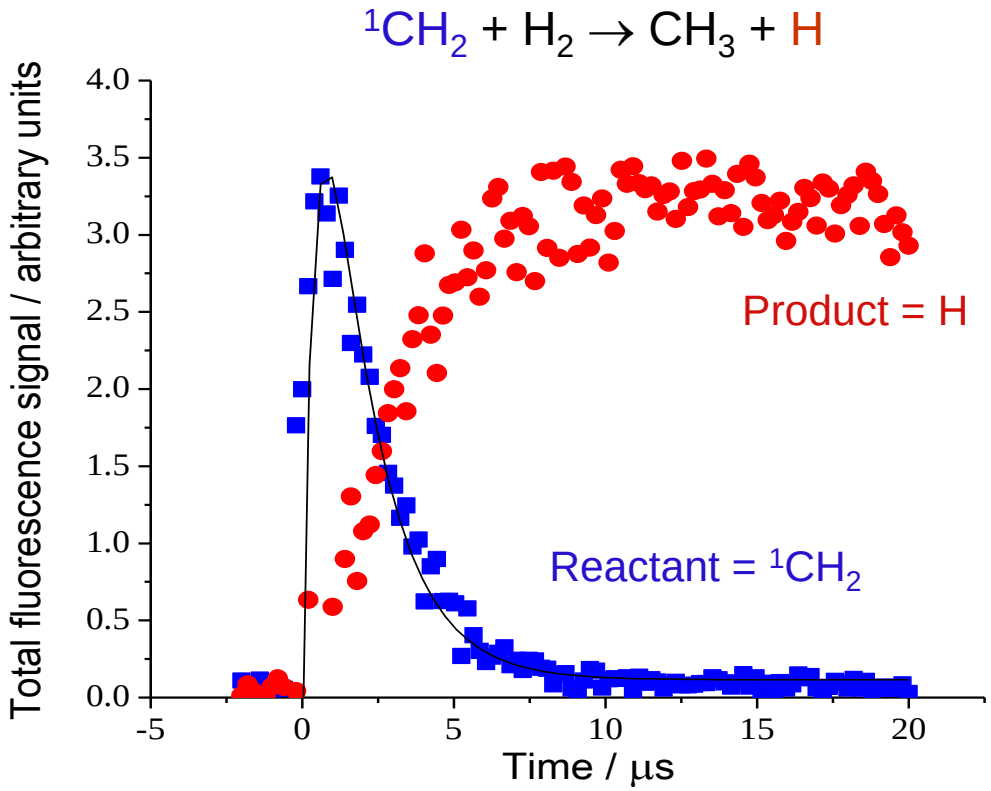


Determination of product yields by Laser Flash Photolysis 1

- Use laser pulse to generate radical on short timescale (~10 ns)
- Observe radical concentration vs time. Obtain kinetics from decay time constant
- Also observe product - calibration gives channel yield for a multi channel reaction:

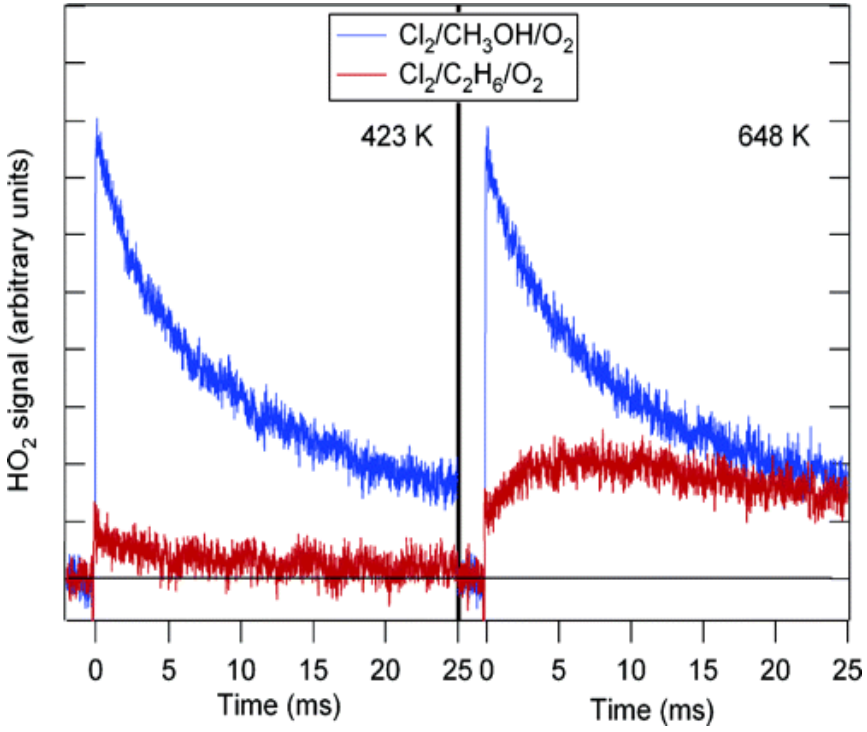
$$A + B \rightarrow C + D$$
$$\rightarrow E + F$$

Detection technique : laser induced fluorescence for CH_2 and H



Determination of product yields by Laser Flash Photolysis 2: $C_2H_5 + O_2$

- Taatjes et al. (J. Phys. Chem. A 104 (2000) 11549 – 11560) observed the formation of OH and HO_2, determining the fractional yields. Used 100% yield of HO_2 from $CH_2OH + O_2$ to calibrate the system.
- HO_2 yield↑ as T↑ and p↓
- Two timescales at higher T
- OH yield is small.
- Theoretical interpretation and relevance to autoignition chemistry will be discussed later



$C_2H_5 + O_2 \rightarrow C_2H_5O_2^*$

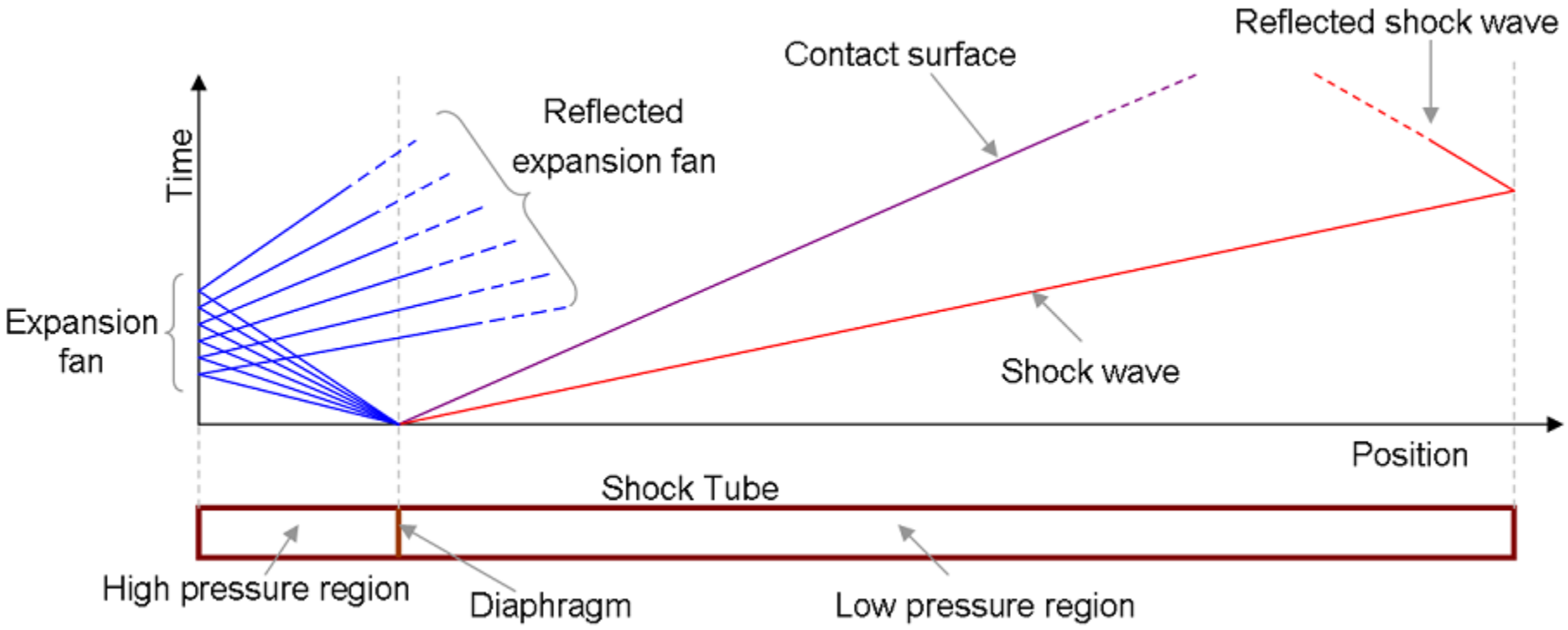
$C_2H_5O_2^* + M \rightarrow C_2H_5O_2 + M$

$C_2H_5O_2^* \rightarrow C_2H_4 + HO_2$

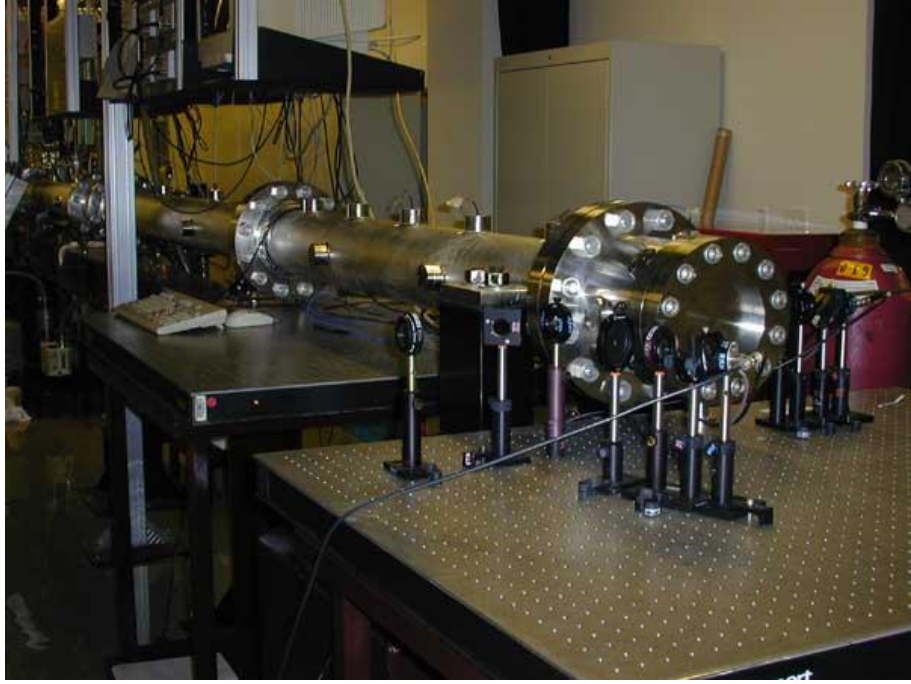
$C_2H_5O_2 + M \rightarrow C_2H_4 + HO_2$

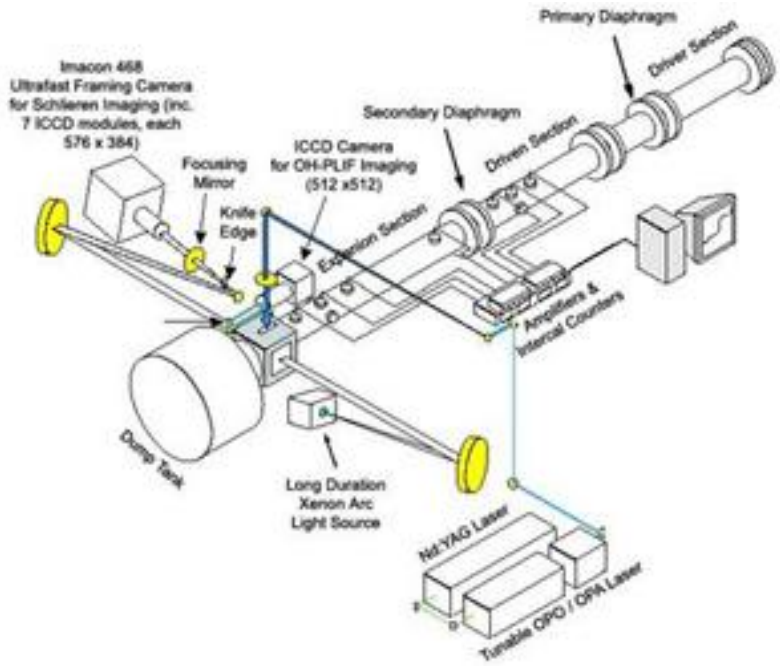
Shock tubes

Shock tube - basics



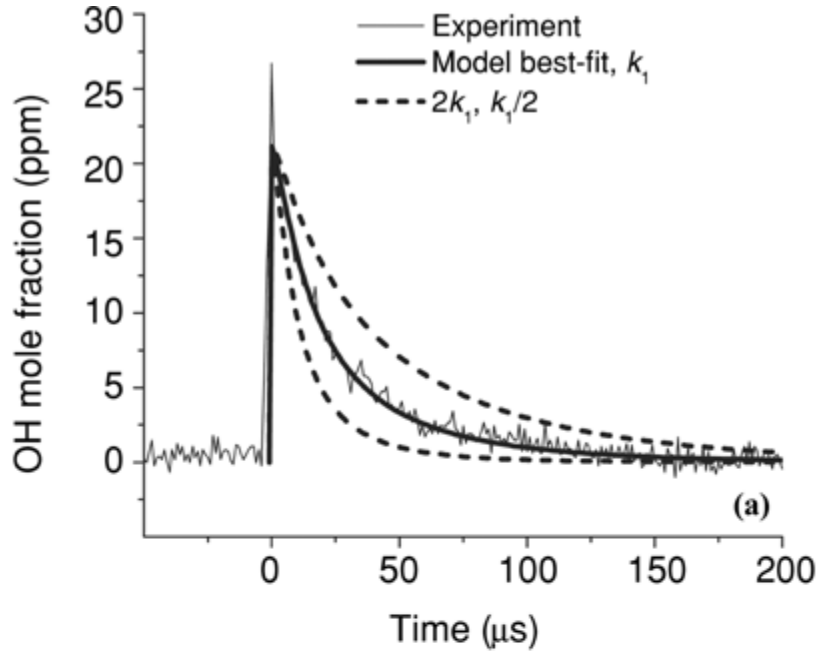
Shock tube:
Hanson lab at Stanford

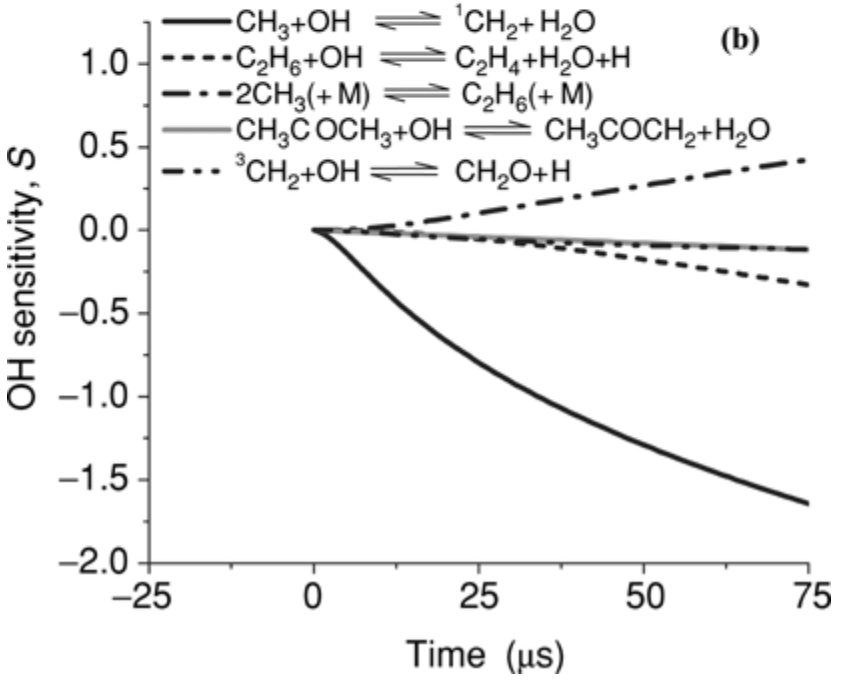




Shock tubes

- Compressive heating of reaction mixture
- Radicals generally formed from thermal dissociation of precursor
- Single shot, so no signal averaging, but impressive optimisation of signal
- Generally need to assess secondary reactions and use numerical chemical model with sensitivity analysis to show viability of measurements.
- Example: Measurement of CH_3 + OH by the Hanson group





Vasudevan et al, International Journal of Chemical Kinetics (2008), 40(8), 488-495.

OH + HCHO, 934 K to 1670 K, 1.6 atm
Int J Chem Kinet 37: 98–109, 2005

- Behind reflected shock waves. OH radicals shock-heating tert-butyl hydroperoxide
- OH concentration time-histories were inferred from laser absorption using the R1(5) line of the OH A-X (0, 0) band near 306.7 nm.
- Other reactions contribute to the OH time profile, especially CH_3 + OH.
- Rate coefficient determined by fitting to detailed model (GRI-Mech – see Wednesday), with addition of acetone chemistry, deriving from dissociation of OH precursor (t-butylhydroperoxide). Detailed uncertainty analysis

Determination of *k* and uncertainty analysis

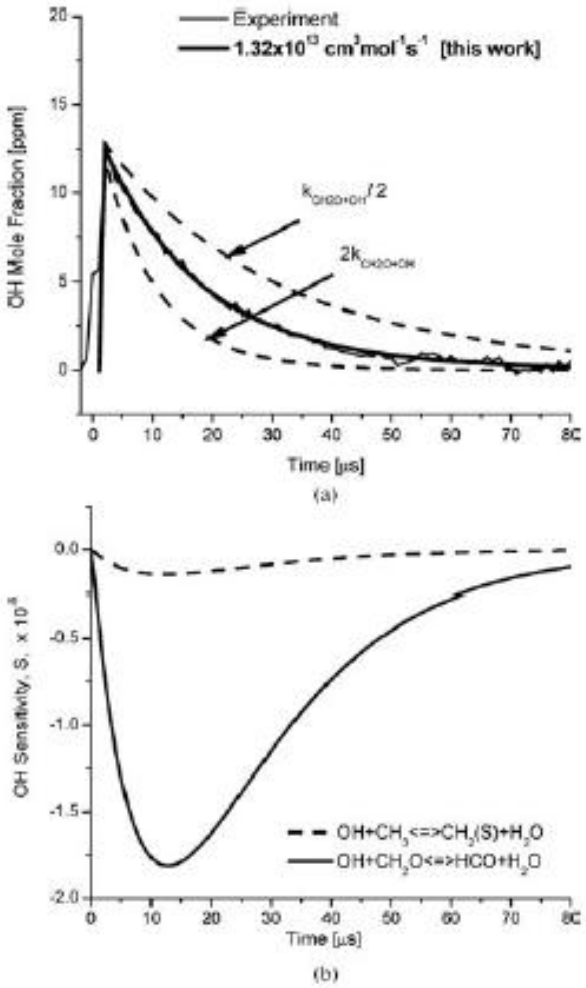


Figure 2 (a) OH concentration time history. 13.25 ppm TBHP, 80 ppm $(CH_2O)_3$, Ar; initial reflected shock conditions: 1229 K, 1.64 atm. (b) Sensitivity analysis. 13.25 ppm TBHP, 80 ppm $(CH_2O)_3$, Ar; initial reflected shock conditions: 1229 K, 1.64 atm. $S = (dX_{OH}/dk_i)(k_i)$, where k_i is the rate constant for reaction i.

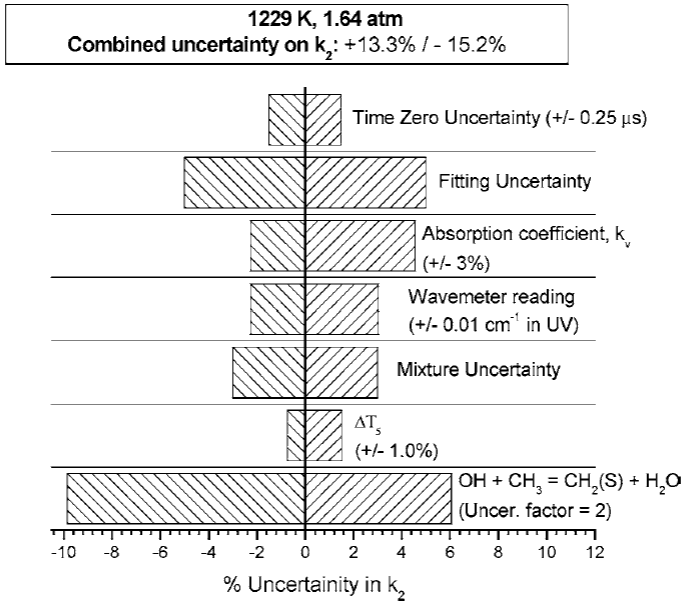


Figure 3 Uncertainty analysis for rate coefficient of $CH_2O + OH = HCO + H_2O$. Initial reflected shock conditions: 1229 K, 1.64 atm; individual error sources were applied separately and their effect on the rate of reaction (2) was determined. Uncertainties were combined to yield an overall uncertainty estimate for k_2.

Arrhenius plot for OH + HCHO

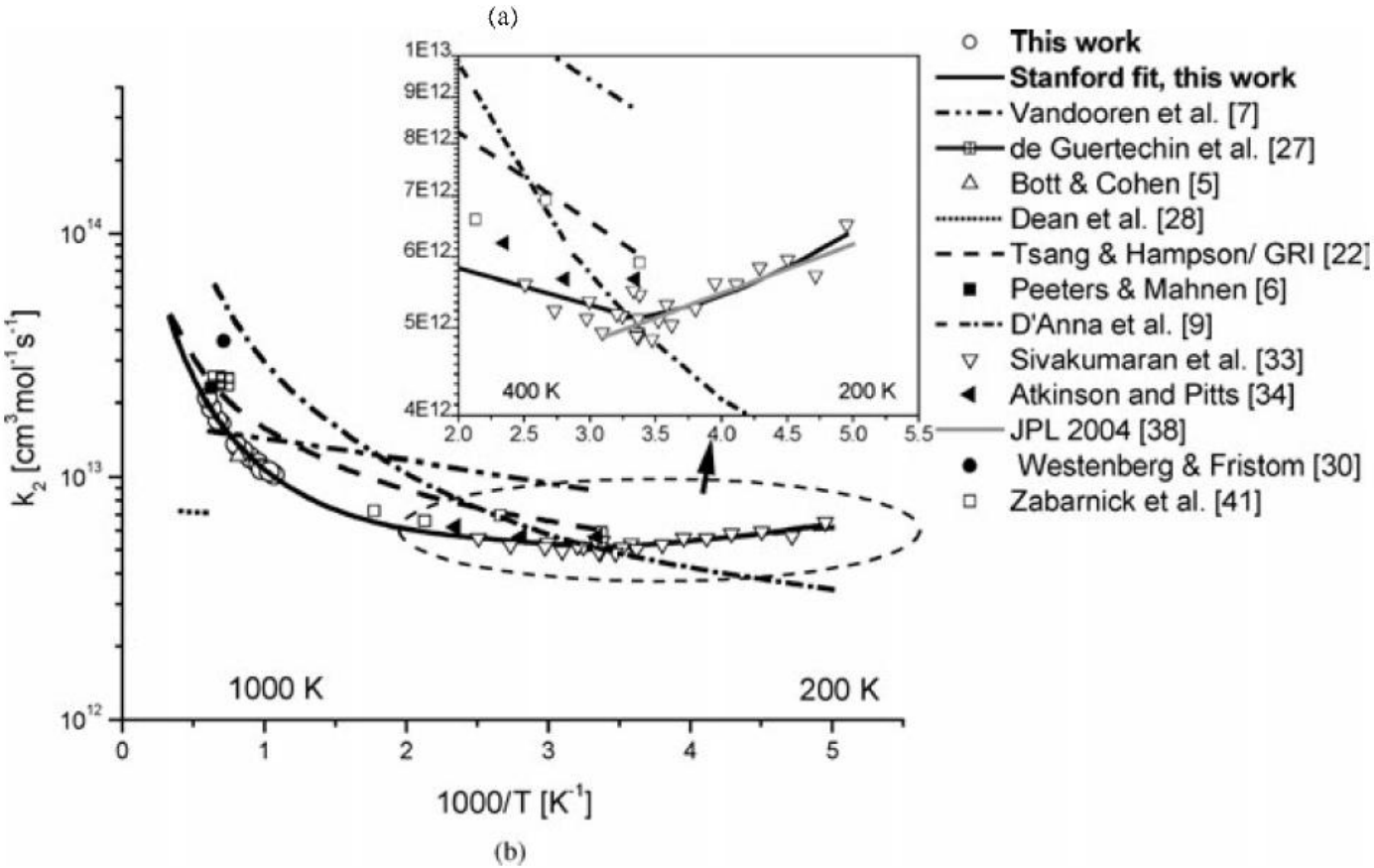


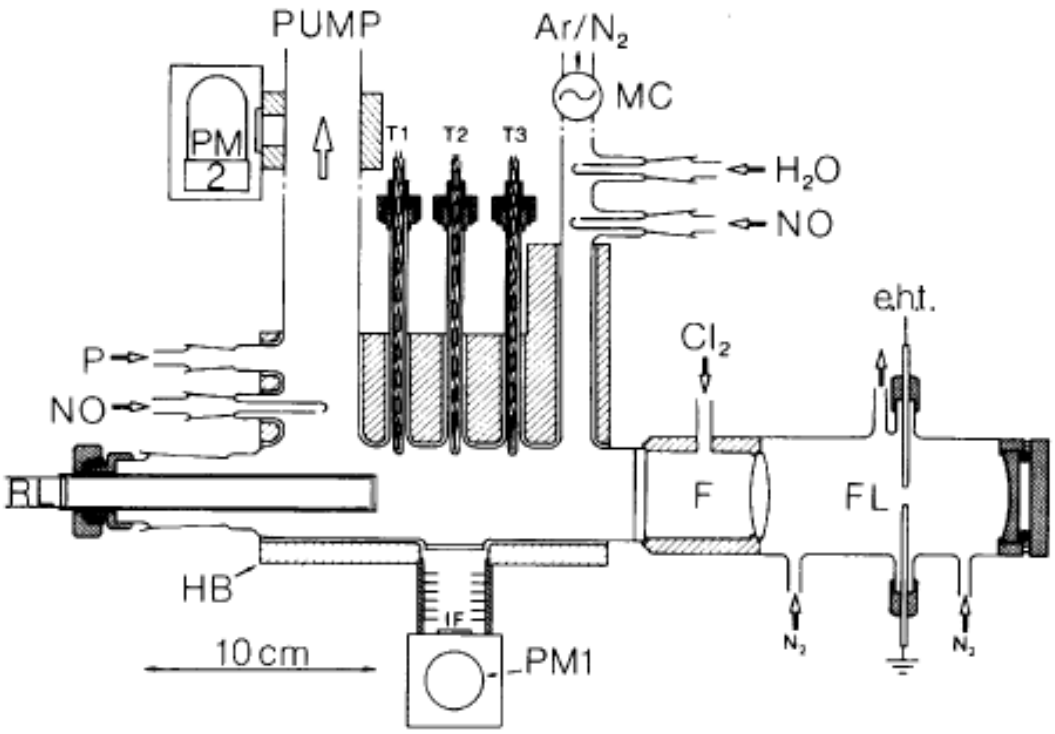
Figure 7 (a) Arrhenius plot for $CH_2O + OH = HCO + H_2O$ at high temperatures (800–2500 K). (b) Arrhenius plot for $CH_2O + OH = HCO + H_2O$ at all temperatures (200–2500 K) and low (200–500 K) temperatures.

- $k_2 = 7.82 \times 10^7\ T^{1.63} \exp(531/T)$ / cm^3 mol^{-1} s^{-1}

Flow tubes for elementary reactions and whole systems

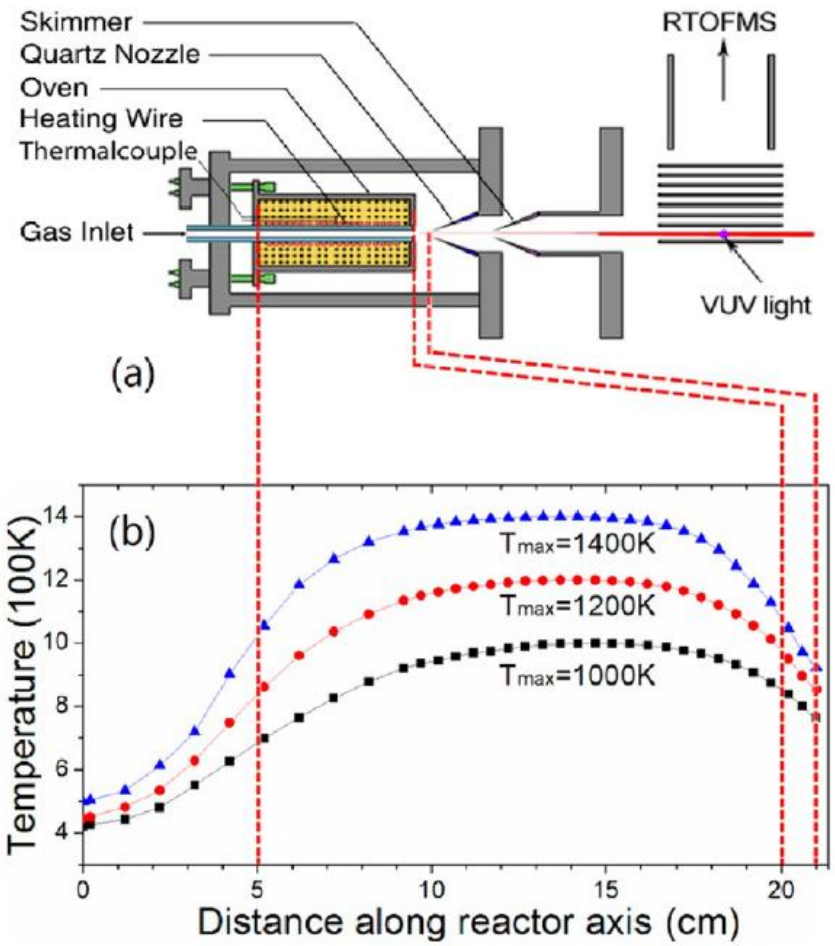
Combined flow tube and pulsed photolysis: O + OH

Howard and Smith, J. Chem. Soc FaradayTrans. 2, 1981,77,997-1008

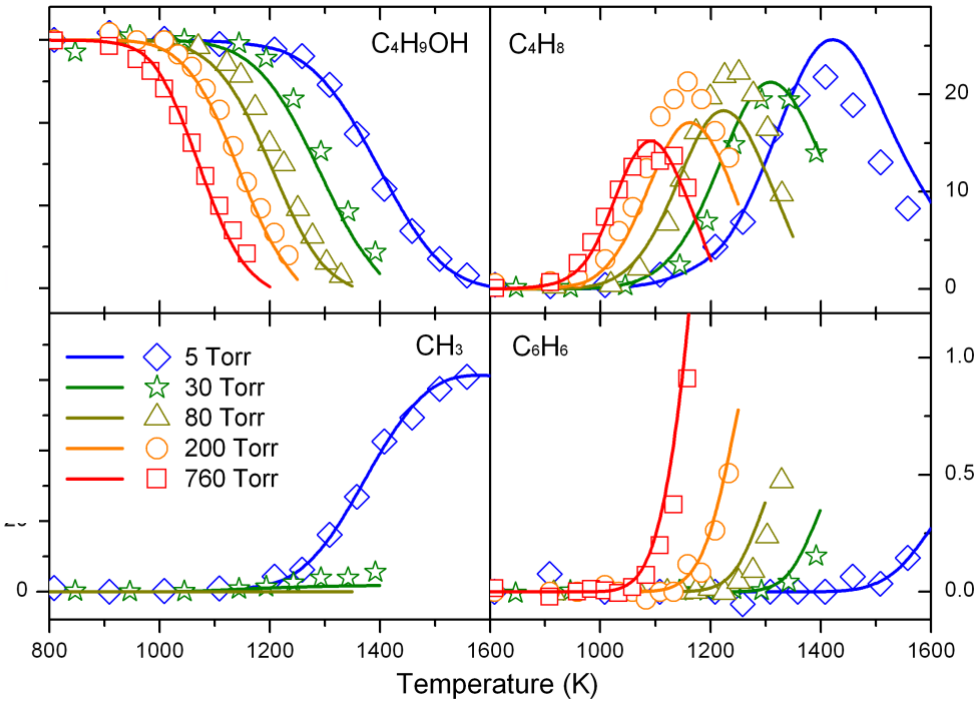


- O generated in discharge, OH by pulsed photolysis, with [O]>> [OH]. [O] generated from N + NO and concentration determined by titration.

Pyrolysis of butanol using molecular beam sampling from a plug flow reactor

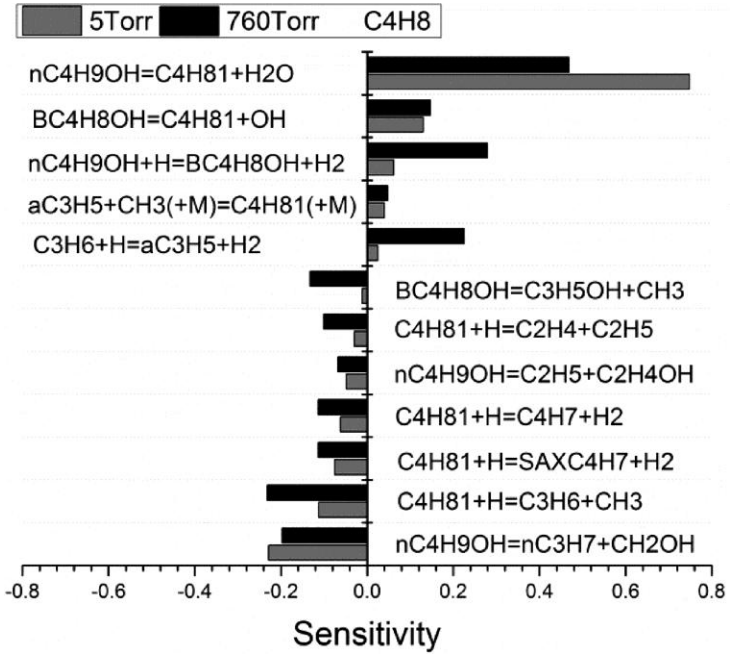


Cai et al. (Energy & Fuels, 26, 5550-5568 (2012))

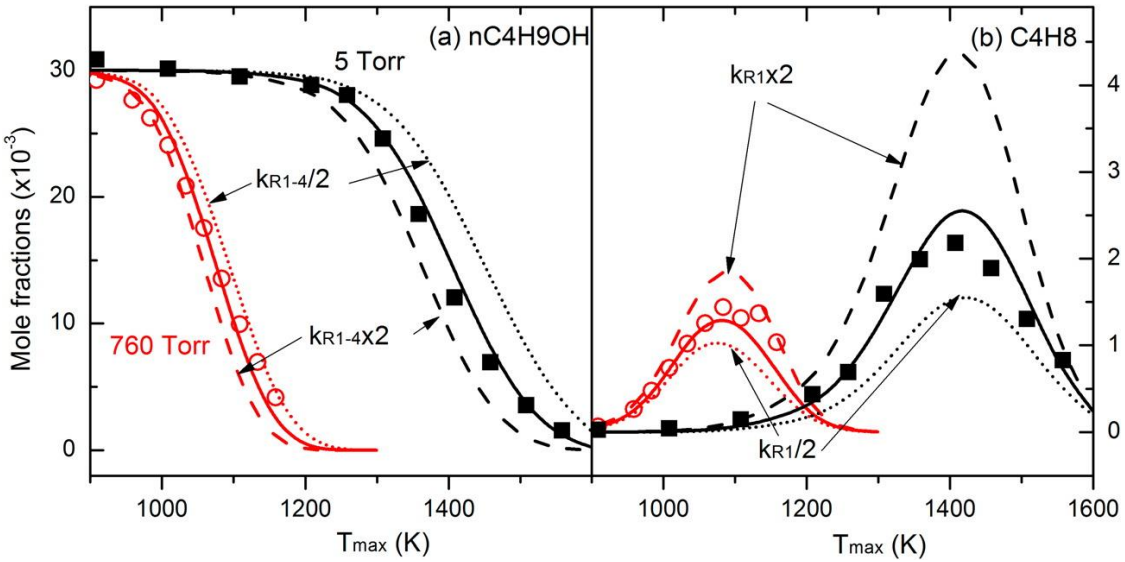


Use of species concentrations in flow reactor to determine rate coefficients: butanol dissociation

Cai et al. (Energy & Fuels, 5550-5568 (2012))

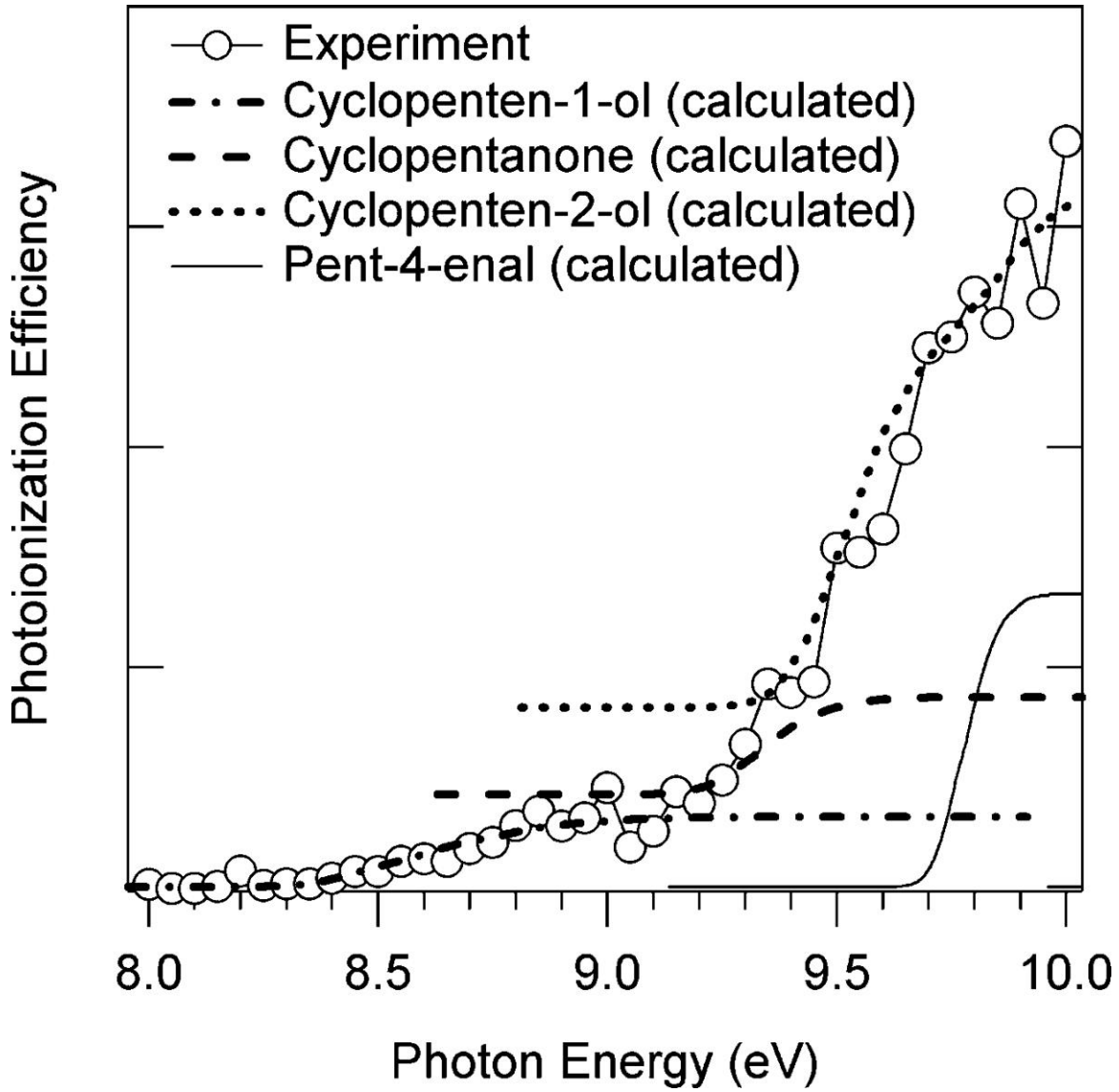


C_4H_8 sensitivity
T_{max} = 1450 K under 5 Torr (gray) and
T_{max} = 1100 K under 760 Torr (black)



Experimental mole fraction profiles (symbols) and modeling results (lines) of nC_4H_9OH pyrolysis at 5 and 760 Torr.

Decomposition of photoionization curves in a flow tube study of cyclopentene oxidation *J. Phys. Chem. A* 2008, *112,* 13444–13451



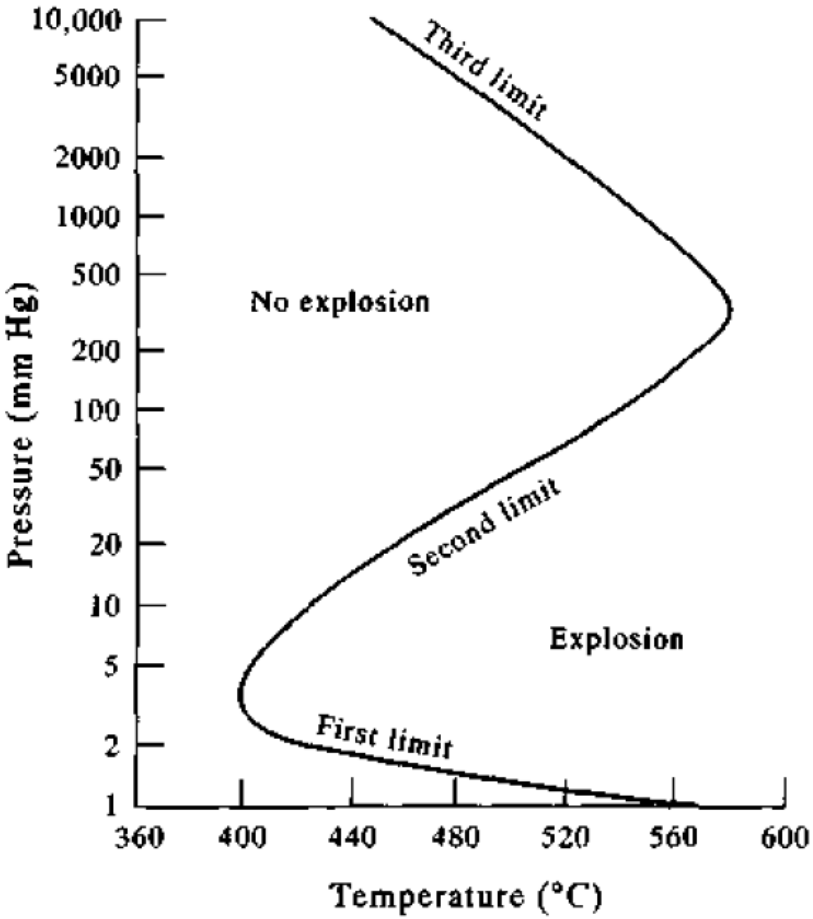
Schematic decomposition of the best fit to the experimental photoionization efficiency spectrum into the substituent calculated photoionization efficiency curves of the three isomers: 1-*c*-C_5H_7OH, *c*-C_5H_8O, and 2-*c*-C_5H_7OH. The isomeric photoionization efficiency curves are scaled by their weighting in the fit to the overall spectrum and vertically displaced for clarity.

Static reactors: Early studies of alkane oxidation kinetics and mechanism by Baldwin, Walker and co-workers

- The techniques rely on end product analysis using gas chromatography. Three techniques were used:
  - Addition of small amounts of alkane, RH, to a slowly reacting H_2 + O_2 mixture at ~ 750 K allowed measurements of, e.g. OH, H, HO_2 + RH. H_2 + O_2 provides a well-controlled environment containing the radicals. (JCS Faraday Trans 1., 1975, 71, 736)
  - Oxidation of aldehydes (550 – 800 K). Aldehydes act as a source of alkyl radicals, e.g. 2-C_3H_7 from 2-C_3H_7CHO (JCS Faraday Trans 2., 1987, 83, 1509)
  - Decomposition of tetramethylbutane (TMB) in the prsence of O_2. System acts as a source of HO_2. (JCS Faraday Trans 1., 1986, 82, 89)

Interaction of elementary reactions in $H_2 + O_2$

- There are three ignition (explosion) limits. In each case, there is a competition between a termination reaction (removing radicals, decelerating the rate) and a branching reaction (accelerating the rate)
- First limit – competition between termination at the wall e.g. $H \rightarrow$ wall (rate $\uparrow$as pressure $\downarrow$) and $H + O_2 \rightarrow OH + O$.
- Second limit – competition between $H + O_2 + M \rightarrow HO_2 + M$ (rate $\uparrow$as pressure $\uparrow$) and $H + O_2 \rightarrow OH + O$. HO_2 is an unreactive radical and reacts mainly by $HO_2 + HO_2 + M \rightarrow H_2O_2 + M$.
- Third limit – H_2O_2 dissociates generating OH radicals ($H_2O_2 + M \rightarrow 2OH$) and propagation and branching recommence



An analysis of the explosion limits of hydrogen-oxygen mixtures

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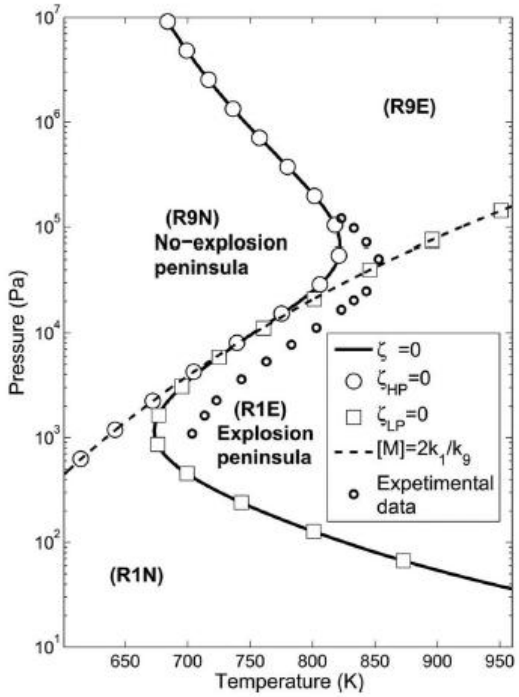
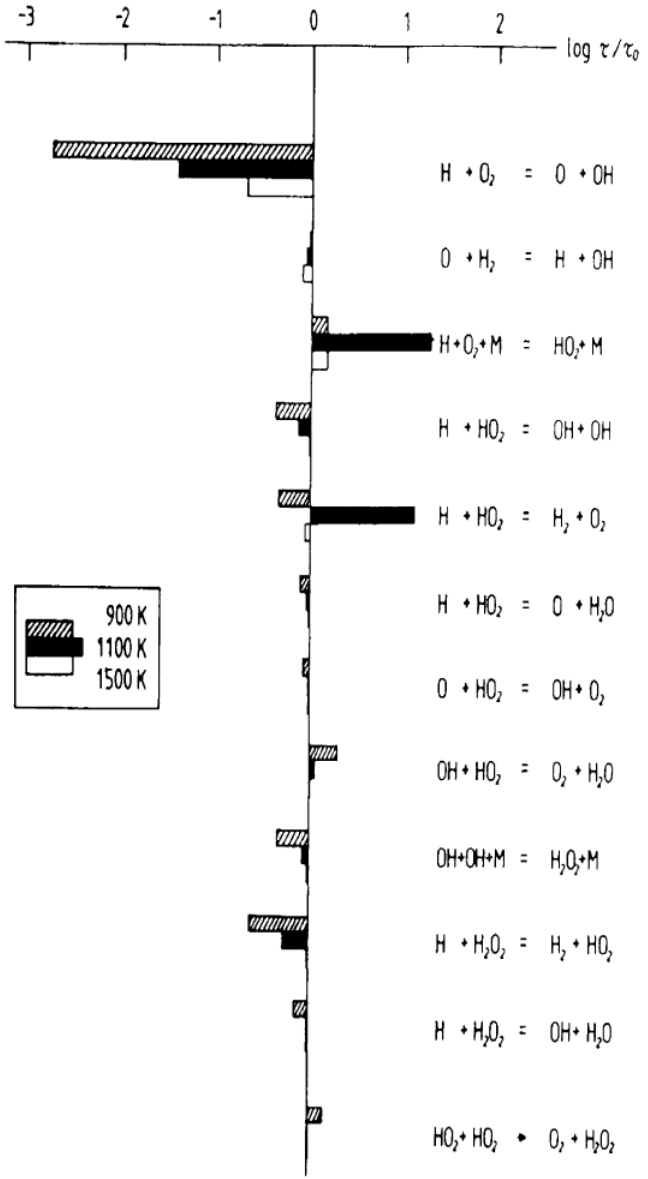
In this study, the essential factors governing the Z-shaped explosion limits of hydrogen-oxygen mixtures are studied using eigenvalue analysis. In particular, it is demonstrated that the wall destruction of H and HO_2 is essential for the occurrence of the first and third limits, while that of O, OH, and H_2O_2 play secondary, quantitative roles for such limits. By performing quasi-steady-state analysis, an approximate, cubic equation for the explosion limits is obtained, from which explicit expressions governing the various explosion limits including the state of the loss of non-monotonicity are derived and discussed. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4798459]



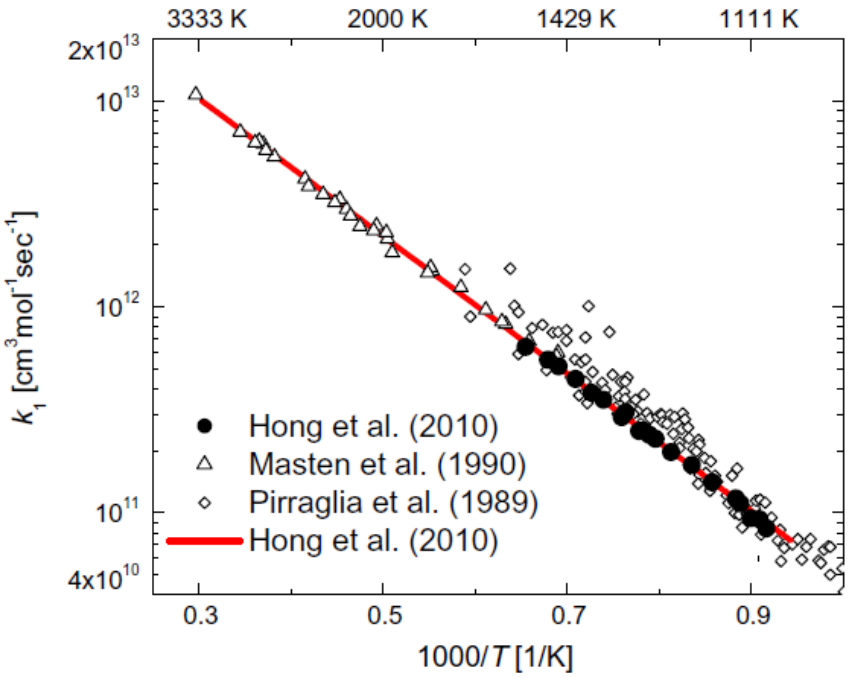
A recent paper discussing the explosion limits for H2/O2

Hydrogen oxygen system

- Review by Miller et al. (Proc Comb. Inst., 2005, 30, 45-88)
- Slide shows sensitivities for ignition delay times (8% H_2, 2% O_2, 90% Ar, 1 bar).
- Note the significance of the H + O_2 branching step, the termination step H + O_2 + M and the H + HO_2 steps



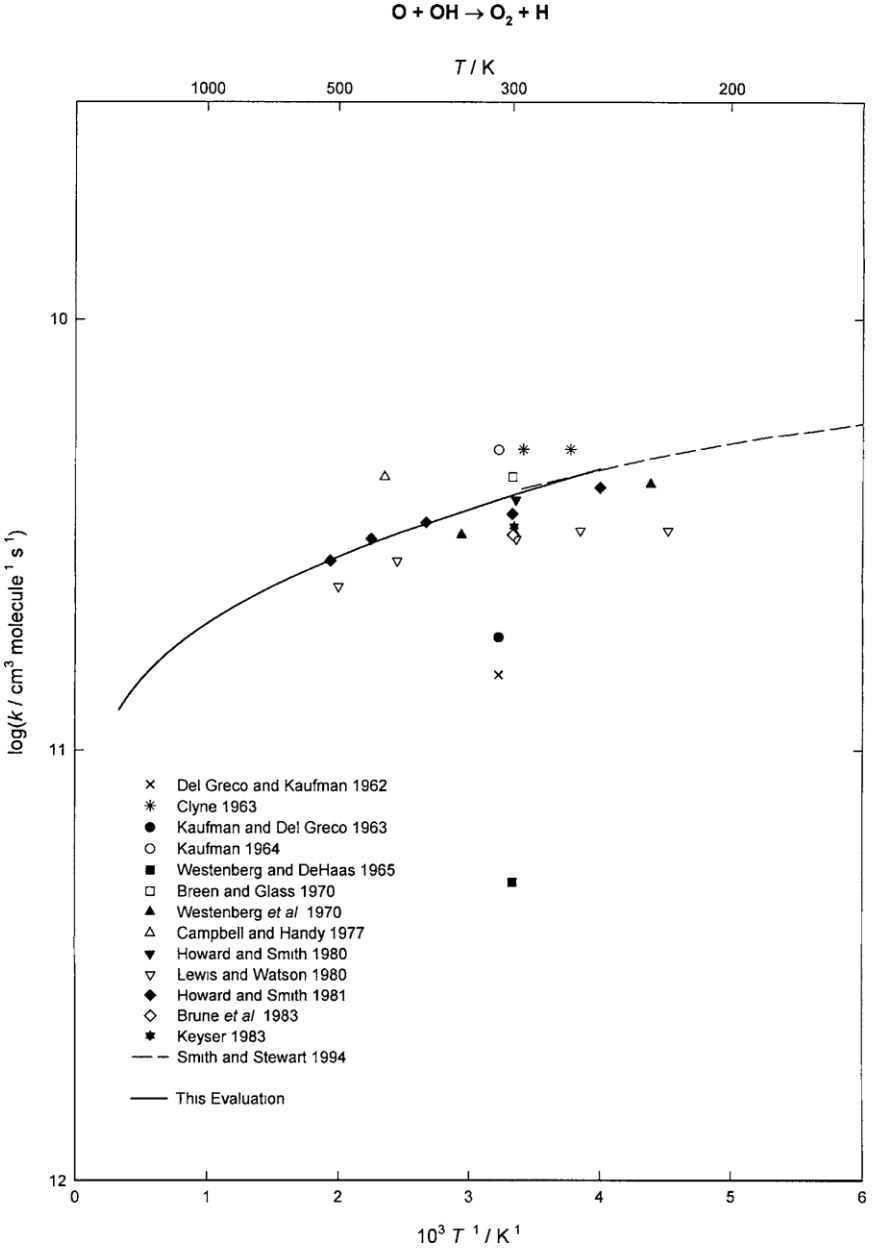
$H + O_2 \rightarrow OH + O$



- 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%.
- SeeBurke et al. Int J Chem Kinet, 2012, 44, 444, who support the rate coefficient
- See discussions on evaluation in later lectures.

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

- Studied 150 – 500 K, mainly by discharge flow / laser flash photolysis.
- Not of great importance in combustion, but provides additional information on reverse reaction through thermodynamics
- $k = 2.00 \times 10^{-10}\ T^{-0.352}\ \exp(113/T)\ cm^3\ molecule^{-1}\ s^{-1}$ over the range 250–3000 K.
- $\Delta \log k = \pm 0.2$ over the range 250–3000 K.



Second branching step
$O + H_2 \rightarrow OH + H$

- Sutherland et al. (21st Symp(Int) Comb, 1986, 929). Used flash photolysis, monitoring O by resonance fluorescence, and shock tube, generating O by flash photolysis of NO and monitoring by ARAS. ()
- Davidson and Hanson (Comb and Flame, 1990, 82, 445) used shock tube, generating O by laser flash photolysis of NO and by pyrolysis of N_2O. O monitored by ARAS

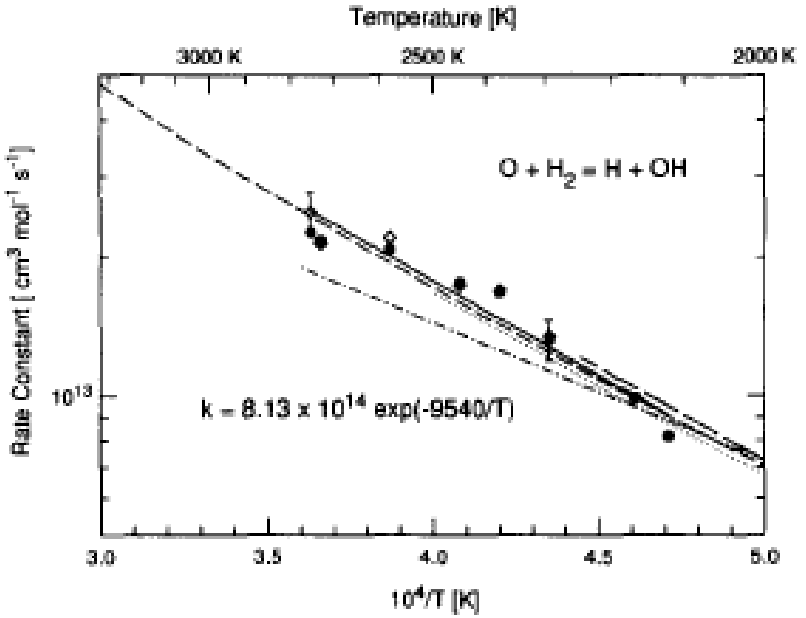
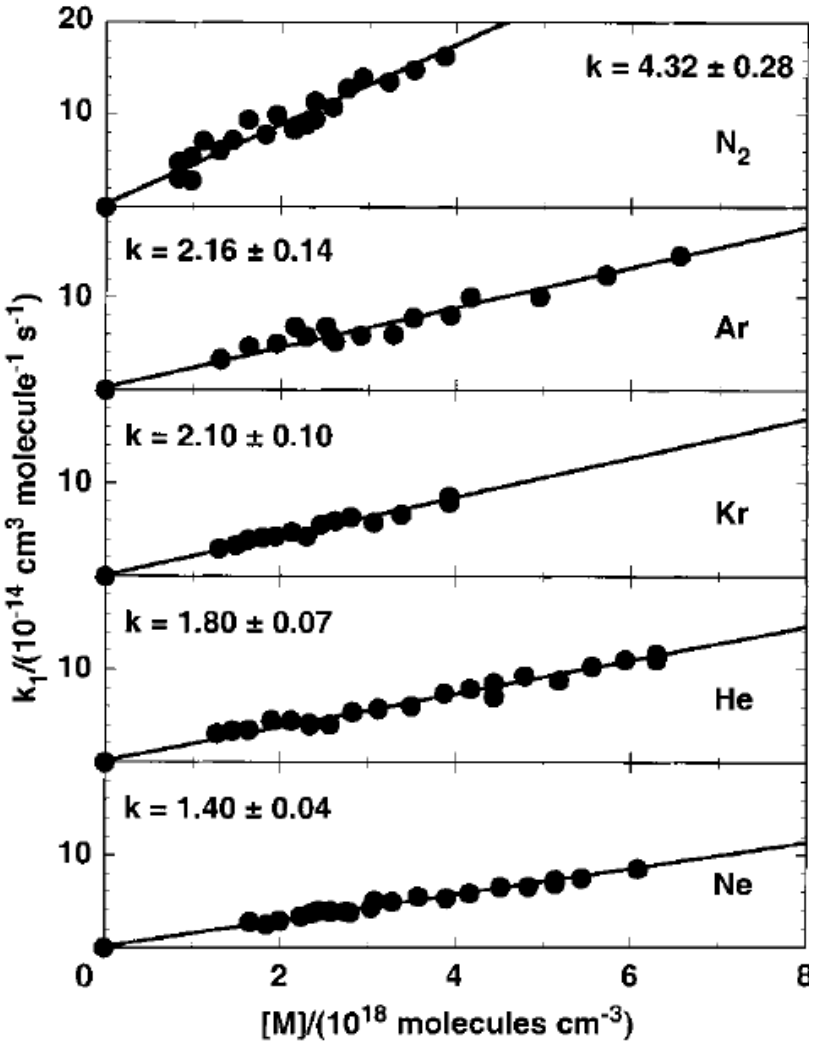


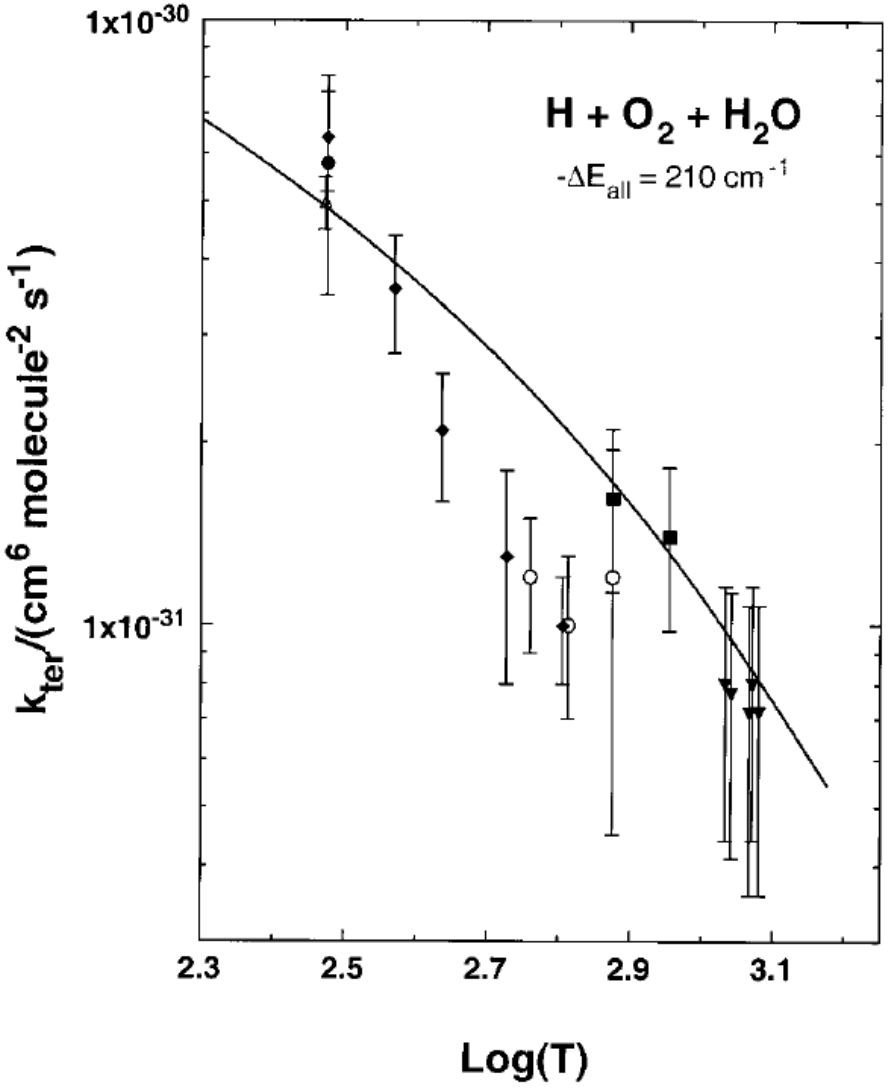
Fig. 2. Arrhenius diagram: $O + H_2 \rightarrow OH + H$. Filled circles—data derived from photolysis method. Open diamonds—data derived from pyrolysis method. Error bars represent ±10%. Solid line—best fit to present data. Dotted line—Sutherland et al. [8]. Dashed line—Nataranjan and Roth [9]. Dot-dashed line—Pamidimukkala and Skinner [10]. Long-dashed line—Shin et al. [11].

$H + O_2 + M \rightarrow HO_2 + M$

- Termination step at lower T, converting reactive H into less reactive HO_2. Acts as a route to branching through formation of H_2O_2 through $HO_2 + HO_2$ (and HO2 + RH in hydrocarbon combustion)
- Reaction is at the third order limit except at higher pressures.
- Michael et al. J. Phys. Chem. A 2002, 106, 5297-5313 used flash photolysis at room T for a wide range of third bodies, and a shock tube at higher T for Ar,. O_2 and N_2. Showed that H_2O is an unusually effective third body.
- Detailed analysis of collision frequencies and energy transfer parameters.

$H + O_2 + M \rightarrow HO_2 + M$

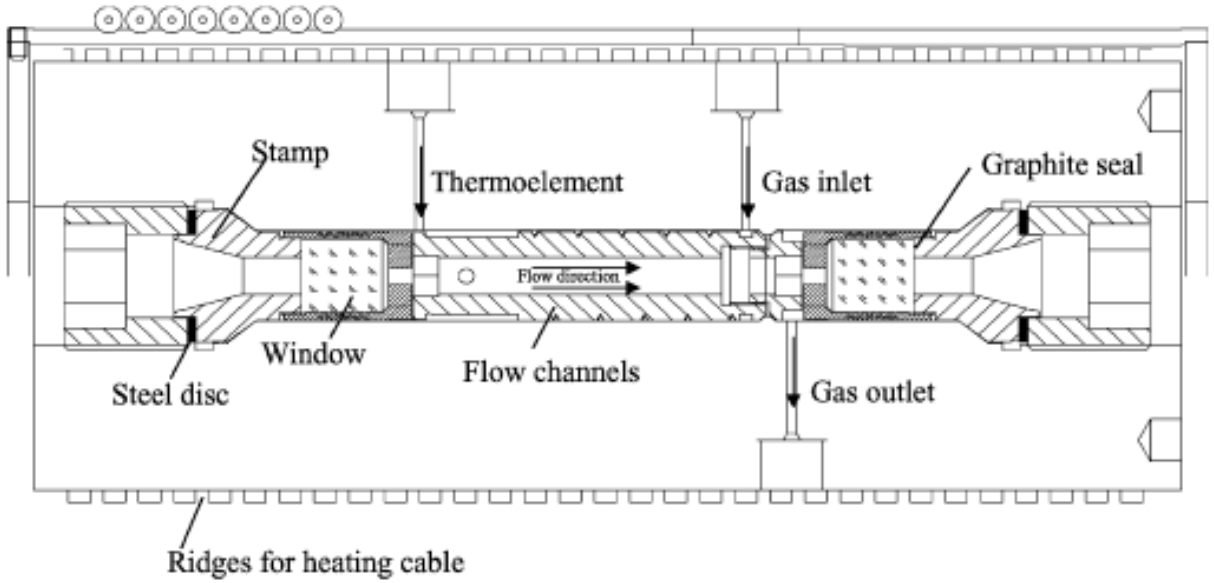




Units of k: 10^{-32} cm^6 $molecule^{-2}$ s^{-1}

High pressure pulsed photolysis / flow reactor

Fernandes et al. Phys. Chem. Chem. Phys., 2008, 10, 4313–4321



- $H + O_2 + M \rightarrow HO_2 + M$, 300 – 900 K, 1.5 – 950 bar
- H from photolysis NH_3 at 193 nm
- HO_2 detected by absorption spectroscopy at 230 nm.
- At these higher pressures, the reaction moves into the fall-off region

$H + O_2 + M \rightarrow HO_2 + M$

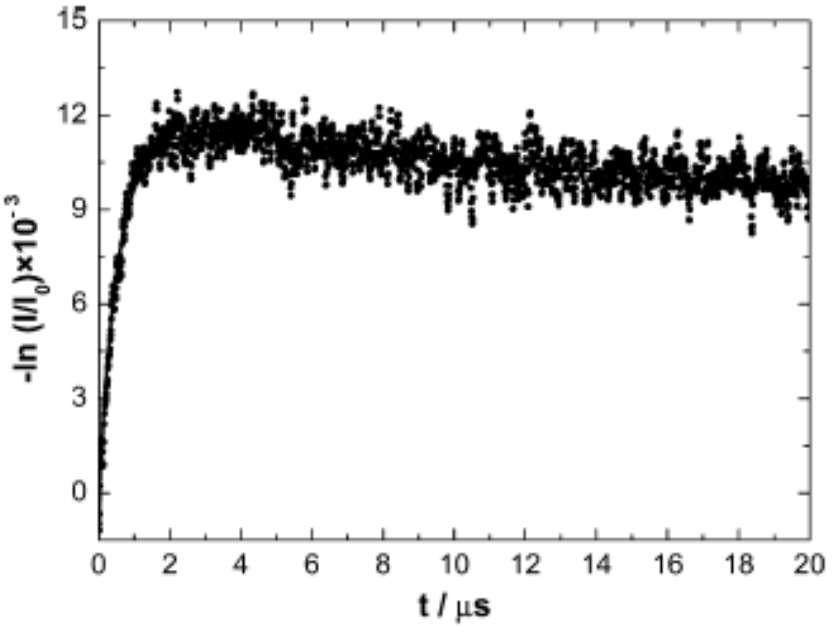


Fig. 2 Absorption–time profile of HO_2 (λ = 230 nm, T = 600 K, p = 300 bar, M = N_2).

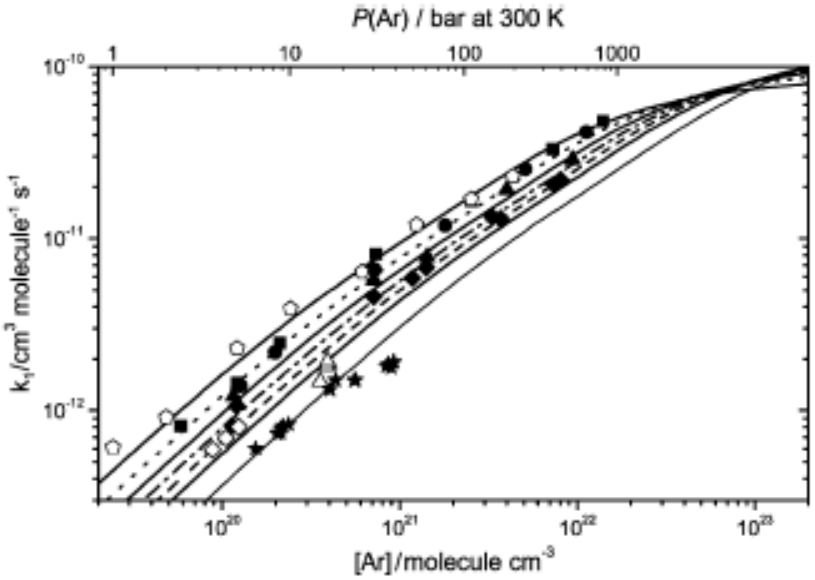


Fig. 5 Falloff curves for the recombination H + O_2 (+Ar) → HO_2 (+Ar) (representative upper pressure scale for 300 K; T/K = 300 (■), 400 (●), 500 (▲), and 600 (♦) from this work; 300 (⬠, ref. 19), 820 (◇, ref. 20), 1200 (★, ref. 22), and 1325 (△, ref. 21); the fitted curves at left from top to bottom are for T/K = 300, 400, 500, 600, 700, 820, and 1200, resp.).

$H + O_2 + M \rightarrow HO_2 + M$

- Data for different third bodies and temperatures can be rationalised and placed on the same plot using reduced falloff curves. Requires calculation of high pressure limiting rate coefficient (that isn't accessible to experiment for this reaction.)

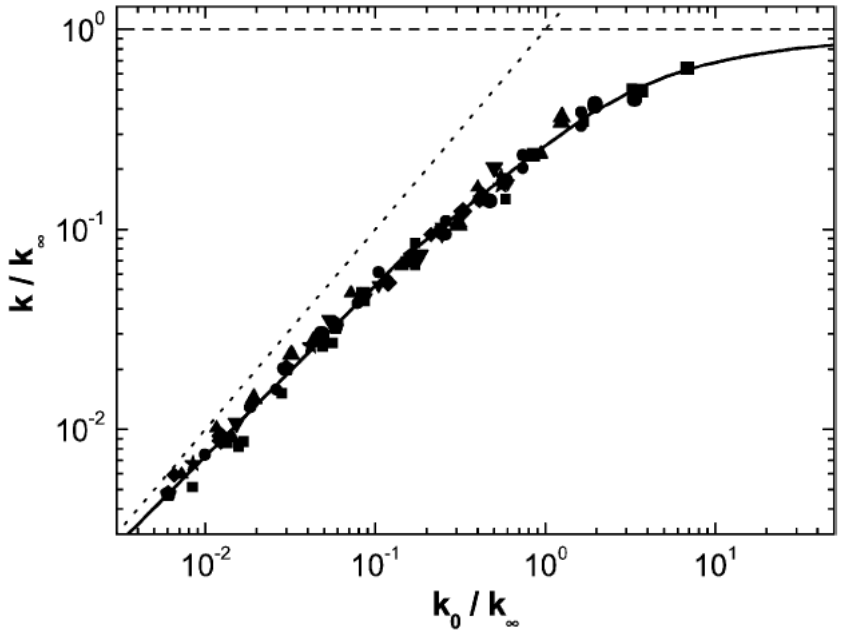
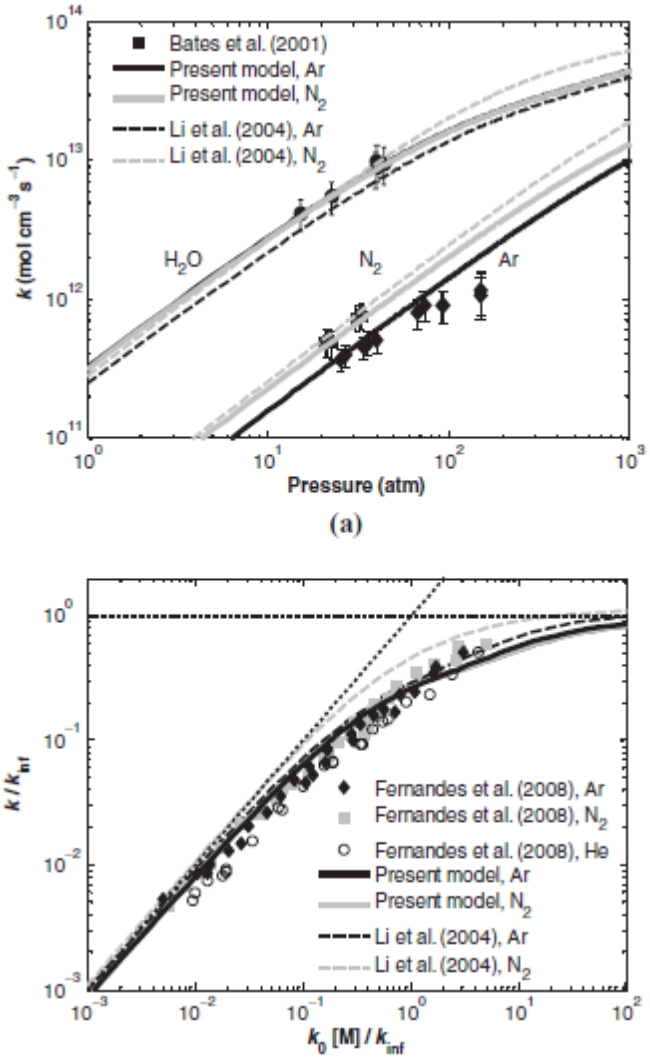


Fig. 7 Doubly reduced falloff curves for the recombination H + O_2 (+M) → HO_2 (+M) in the bath gases M = He, Ar, and N_2 (experimental points from this work from Tables 1–3; T/K = 300 (■), 400 (●), 500 (▲), 600 (▼), 700 (♦), 800 (★), and 900 (⬟), see text).

Most recent evaluation: Burke et al, Int J Chem Kinet 2012, 44, 444



- See paper for detailed discussion of Troe parameters (next slide), uncertainties etc.

Recall earlier slide: Pressure dependent association reactions

$$A + B \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} AB^* \xrightarrow{k_s[M]} AB.$$

$$k = \frac{k_a\, k_s[\mathrm{M}]}{k_{-a} + k_s[\mathrm{M}]}$$

$$k = \frac{k_0[\mathrm{M}]k^{\infty}}{k^{\infty} + k_0[\mathrm{M}]}$$

$$\text{As } [\mathrm{M}] \to \infty, k \to k_a = k^{\infty}$$

$$\text{As } [\mathrm{M}] \to 0, k \to \frac{k_a k_s[M]}{k_{-a}} = k_0[\mathrm{M}]$$

Similar treatment for dissociation reactions

- This is the Lindemann-Hinshelwood model of pressure dependent unimolecular reactions.
- The treatment is an approximation because (i) k_{-a} depends on the energy of AB* (ii) deactivation of AB* takes place in a number of steps.
- These have the effect of *broadening* the fall-off curve (k vs [M]). These effects have been incorporated in a fitting procedure developed by Troe that is widely used in parameterising rate coefficients for use in combustion modelling

Troe Fitting

Need to represent k(T,P) for Global Models

Standard is Troe Fitting

$$k(T,p) = \frac{k_0[M]k^{\infty}}{k^{\infty} + k_0[M]} F \qquad \log_{10} F = \frac{\log_{10} F_{cent}}{1 + \left[\frac{\log_{10}(p^*) + c}{N - d\left(\log_{10}(p^*) + c\right)}\right]^2}$$

$$p^* = k_0[M]/k^{\infty} \qquad d = 0.14$$

$$c = -0.4 - 0.67 \log_{10} F_{cent} \qquad N = 0.75 - 1.27 \log_{10} F_{cent}$$

Fit k_0 & k^{∞} to modified Arrhenius $k_0 = A_0 T^{n_0} \exp(-E_0/T)$

Fit F_{cent} to:

$$F_{cent} = (1-a)\exp\left(-T/T^{***}\right) + a\exp\left(-T/T^{*}\right) + \exp\left(-T^{**}/T\right)$$

$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$

- < 800 K. Flash photolysis, absorption spectroscopy
- Open circles: shock tube, absorption spectroscopy (Kappel et al, Phys Chem Chem Phys, 2002, 4, 4392)
- Reference 5: Hippler et al. J Chem Phys 1990, 93, 1755
- Signific ant disagreement > 1000 K
- Burke etal. 'Difficult to discern which, if any, (of the high T) determinations is reliable.' More measurements needed under combustion conditions.

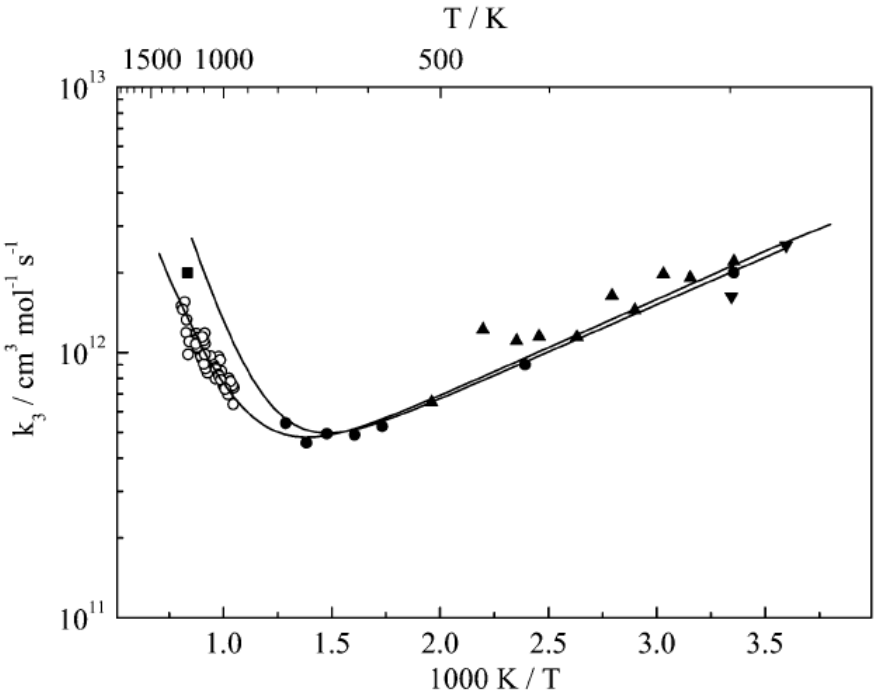


Fig. 10 Rate constants k_3 (■: ref. 2, ▲: ref. 35, ▼: ref. 36, ●: ref. 37, ○ and lower line: this work, upper line: ref. 5).

$H_2O_2 + M \rightarrow 2OH + M$

- Troe, Combustion and Flame 2011, 158, 594-601 The thermal dissociation/recombination reaction of hydrogen peroxide $H_2O_2 \rightleftharpoons 2OH$Analysis and representation of the temperature and pressure dependence over wide ranges.
- Reaction is far from the high pressure limit. To obtain a representation of k(T,p), Troe used the statistical adiabatic channel model to calculate k_∞, using an ab initio surface (Phys. Chem. Chem. Phys. 10 (2008) 3915; J. Chem. Phys. 111 (1999) 2565.
- An important aspect of this work was the use of thermodynamics to relate forward and reverse reactions, using the revised enthalpy of formation of OH – see Wednesday lecture on thermodynamics

Association reaction

- Flash photolysis coupled with saturated LIF.
- Use pressure dependence to separate from $O + H_2O$ channel
- Also problems with secondary reactions (see paper)

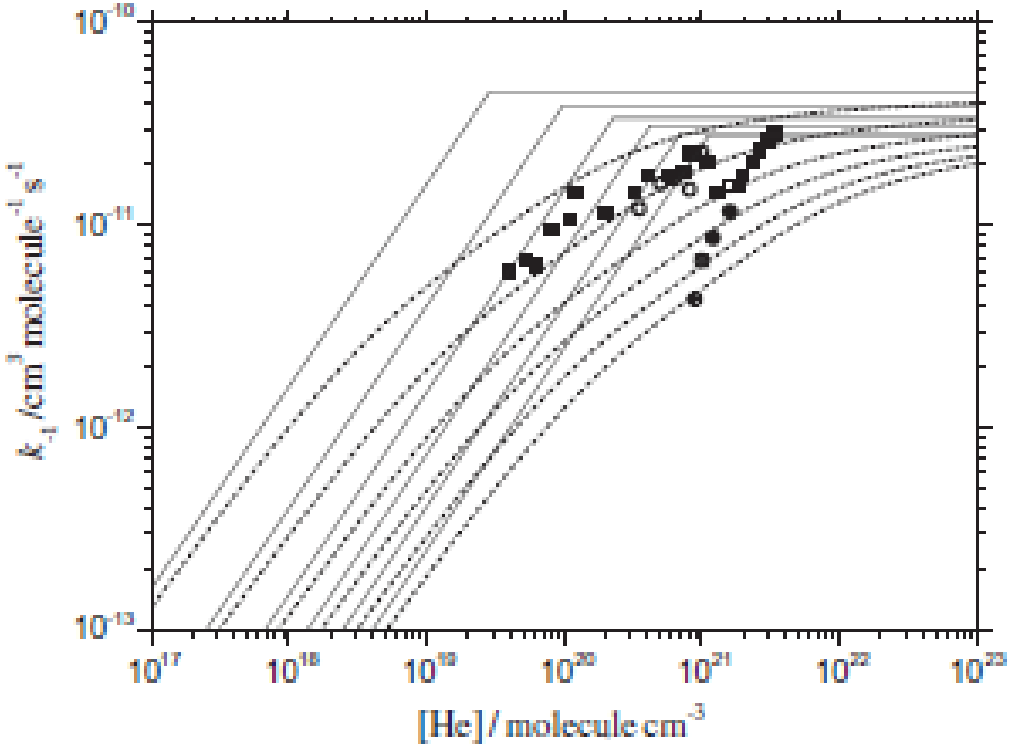
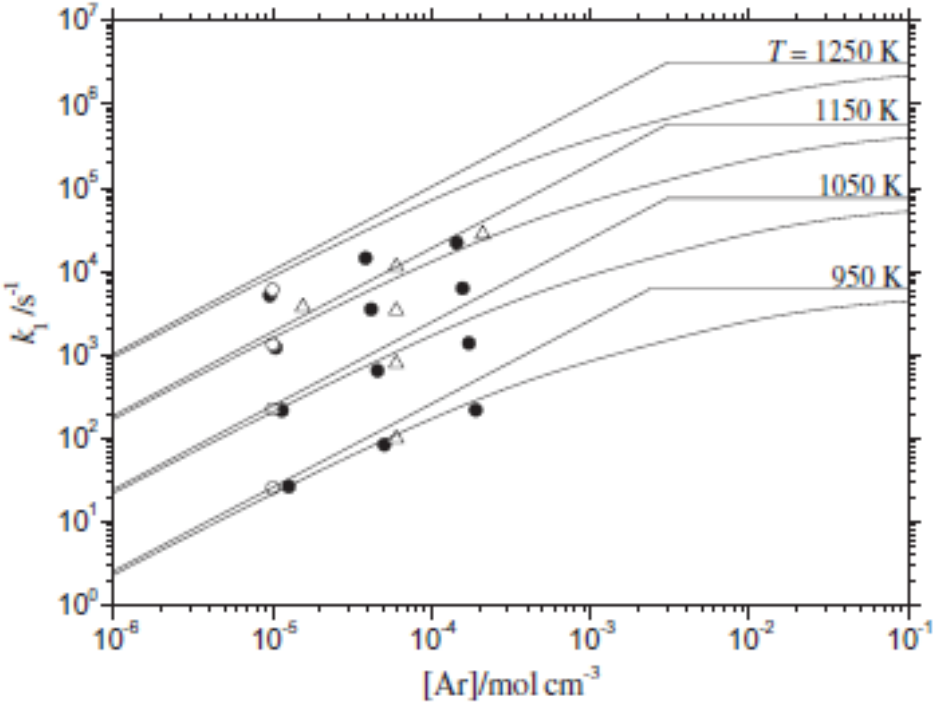


Fig. 3. Experimental recombination rate coefficients k_{-1} and their modelled falloff representation (M = He, experimental points from Refs. [30,31] at T/K = 210 (○), 298 (■), 406 (□), 510 (●), 614 (⊗), and 694 (⊕); full lines = modelled limiting low and high pressure rate coefficients from Section 5 of this work; dashed lines = falloff representation by Eq. (3.3) with F_c = 0.37 and N = 1.32).

Reaction is second order in radical, so absolute concentration is needed

Dissociation reaction

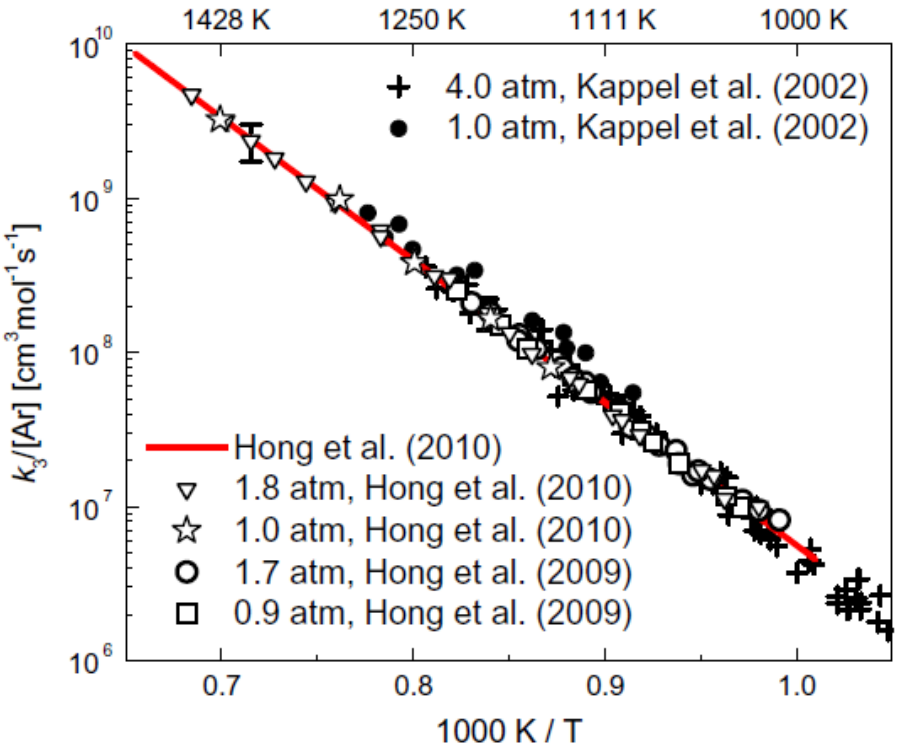
- Flow reactor and static studies at lower T and shock tube measurements above 950 K (see below)



Overall reaction

- Dissociation and association data fitted to Troe expression (see earlier) using theoretical high pressure limit and equilibrium constant

H_2O_2 dissociation
Hong et al. Comb Flame 2011, 158, 633



- Data refer to low pressure limit. Used shock tube with laser absorption detection of H_2O and OH