Combustion Chemistry

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2011 Princeton-CEFRC Summer School on Combustion

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.

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

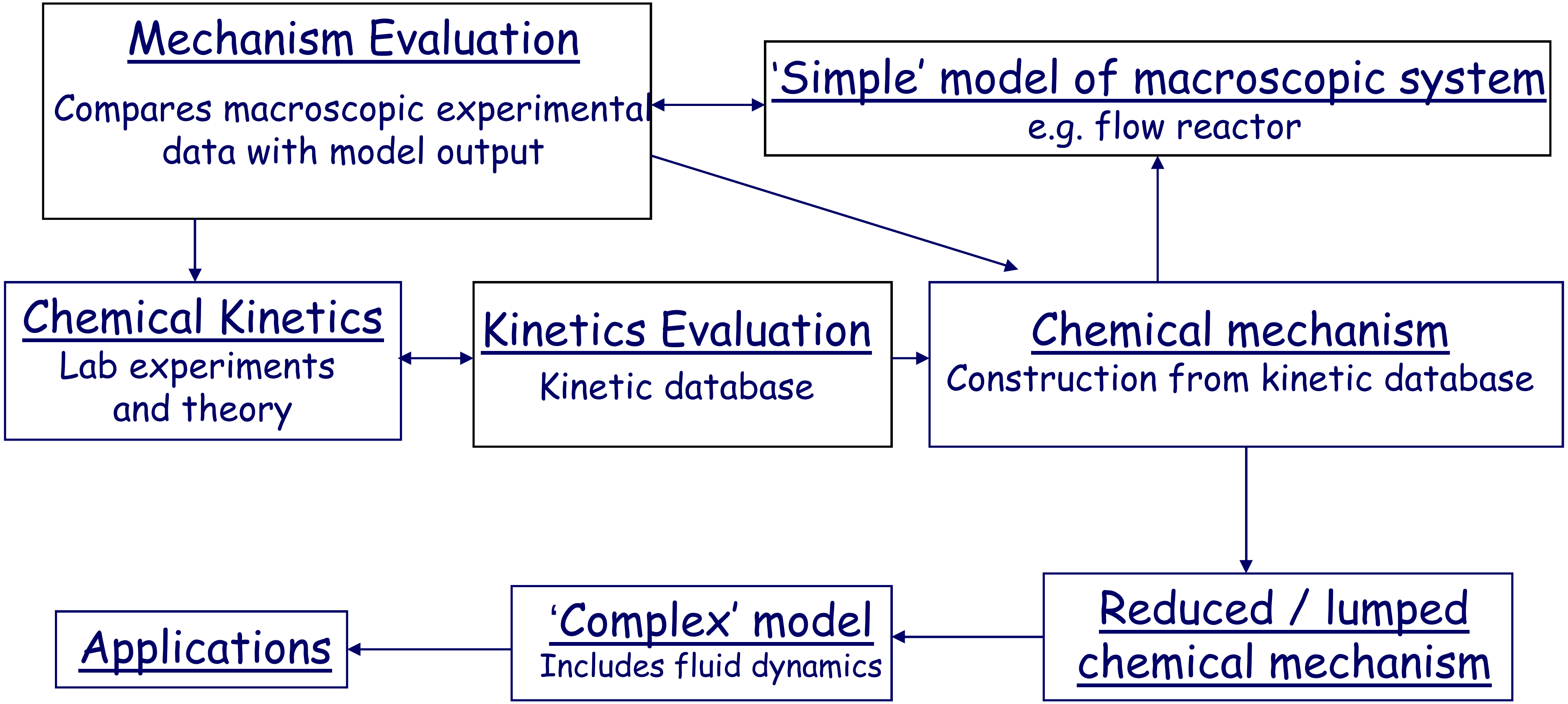
  does not describe the way in which the reaction occurs.

- 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.
- The course is linked to those given last year by Westbrook and Klippenstein, but has a different emphasis

Reaction kinetics contributions to combustion models



Mechanism Evaluation

Compares macroscopic experimental data with model output

'Simple' model of macroscopic system

e.g. flow reactor

Chemical Kinetics

Lab experiments and theory

Kinetics Evaluation

Kinetic database

Chemical mechanism

Construction from kinetic database

Applications

'Complex' model

Includes fluid dynamics

Reduced / lumped chemical mechanism

Understanding

Similar approaches in atmospheric chemistry, interstellar chemistry.

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. $H_2 + O_2 \rightarrow H + HO_2$ 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 → wall T
7. $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$ T

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

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, $a = p/p^{\ominus} = c/c^{\ominus}$ so that *K* is dimensionless. *K* is linked to thermodynamic quantities. 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

Pressure dependent association reaction

An association reaction involves collisional stabilisation of the adduct:

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

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

Examples include
$CH_3 + CH_3 \rightarrow C_2H_6$
$OH + C_2H_4 \rightarrow C_2H_4OH$

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

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

Substituting in first equation

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

Similar treatment for dissociation reactions

Synopsis

- Experimental measurements of rate coefficients and product yields for elementary reactions.
- Links with theory.
- Thermodynamics.
- Rate coefficient evaluation
- Mechanism construction and evaluation.
- NOx chemistry.
- 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)

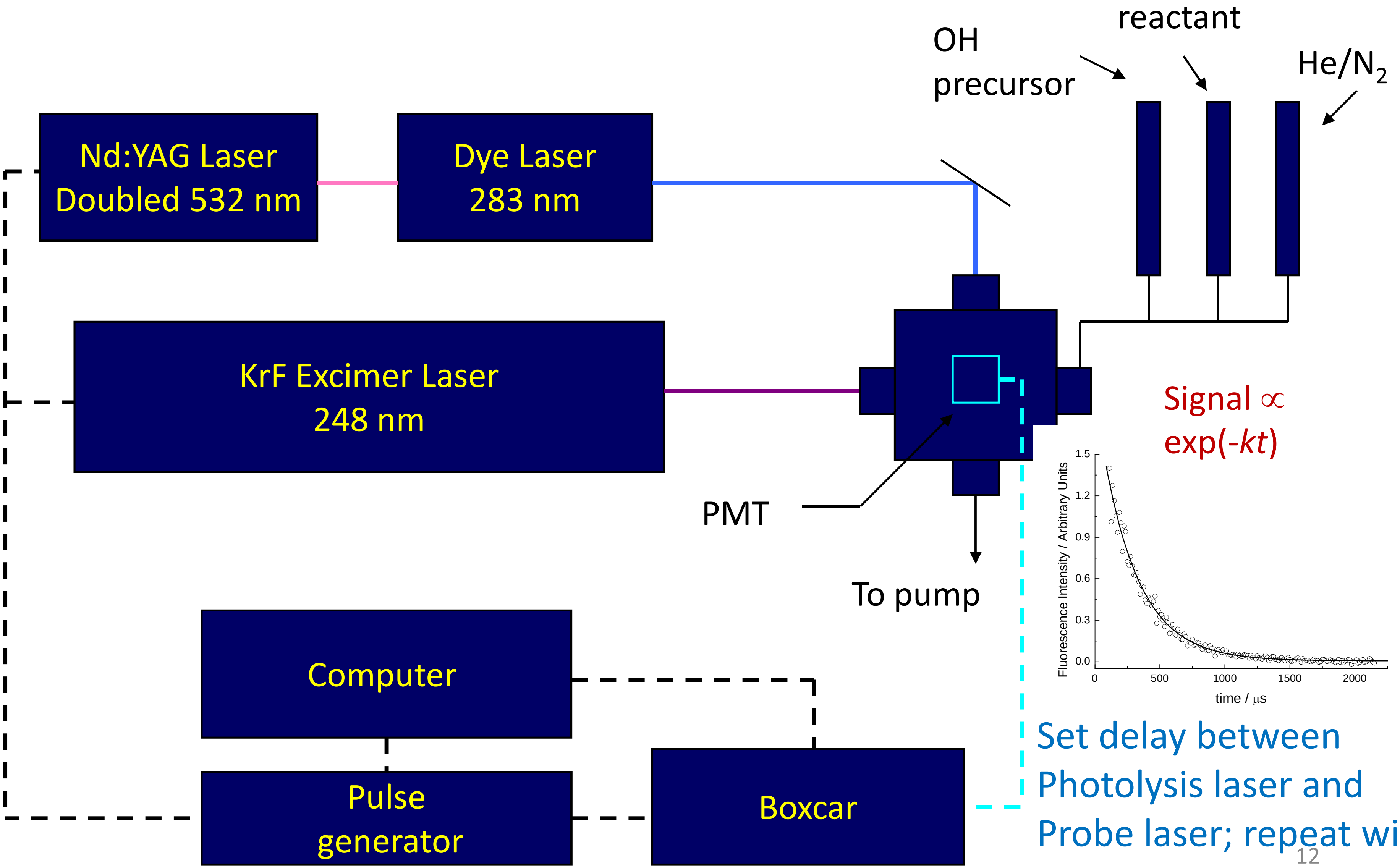
Measurement of rates of elementary reactions 2

- 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

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



OH precursor

reactant

He/N_2

Nd:YAG Laser
Doubled 532 nm

Dye Laser
283 nm

KrF Excimer Laser
248 nm

PMT

To pump

Computer

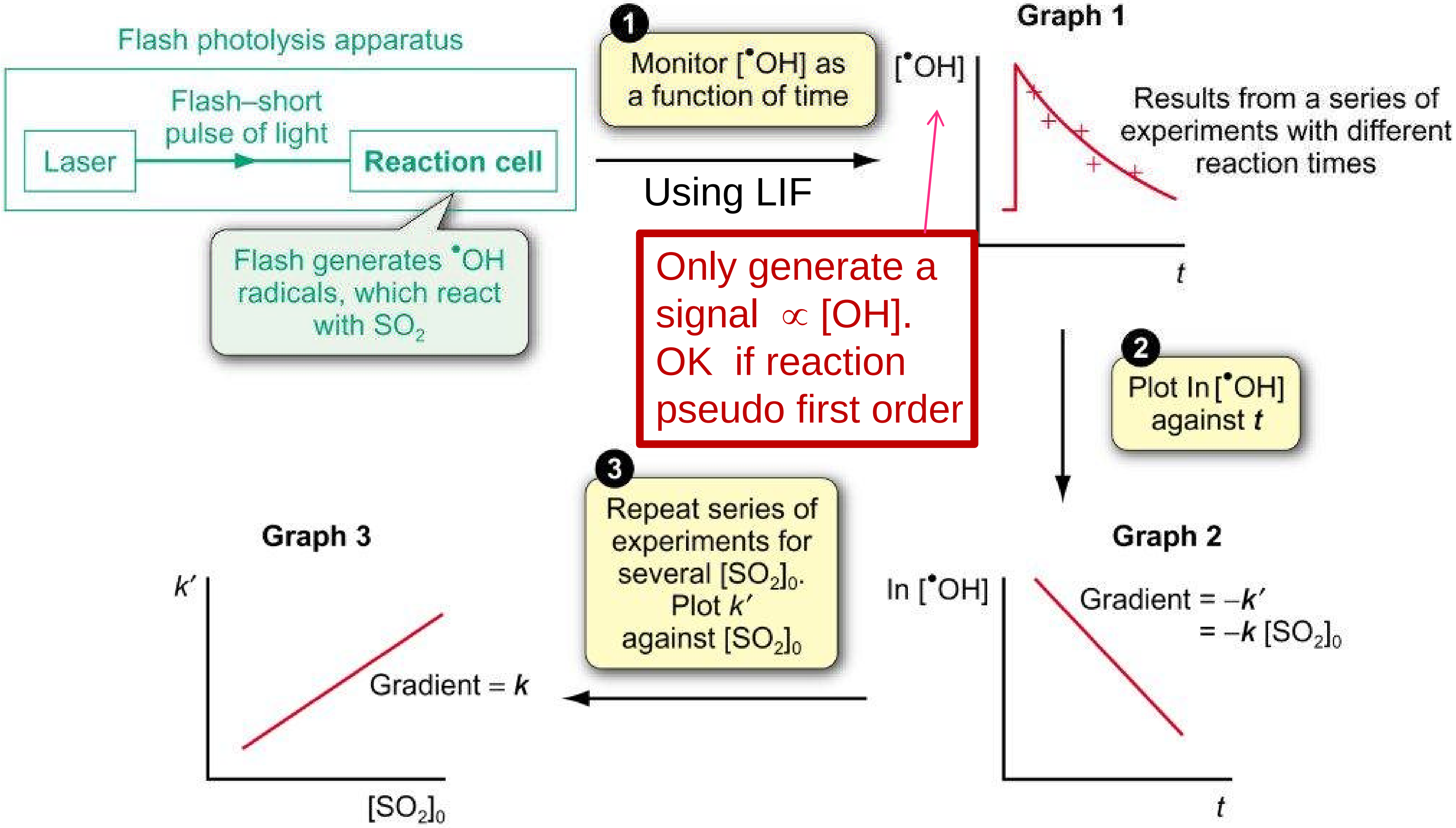
Pulse generator

Boxcar

Signal ∝ exp(-*kt*)

Set delay between Photolysis laser and Probe laser; repeat wit different delay times

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



Flash generates $^{\bullet}OH$ radicals, which react with SO_2

❶ Monitor $[^{\bullet}OH]$ as a function of time

Using LIF

Results from a series of experiments with different reaction times

Only generate a signal $\propto$ [OH]. OK if reaction pseudo first order

❷ Plot $\ln[^{\bullet}OH]$ against t

Gradient $= -k'$
$= -k\,[SO_2]_0$

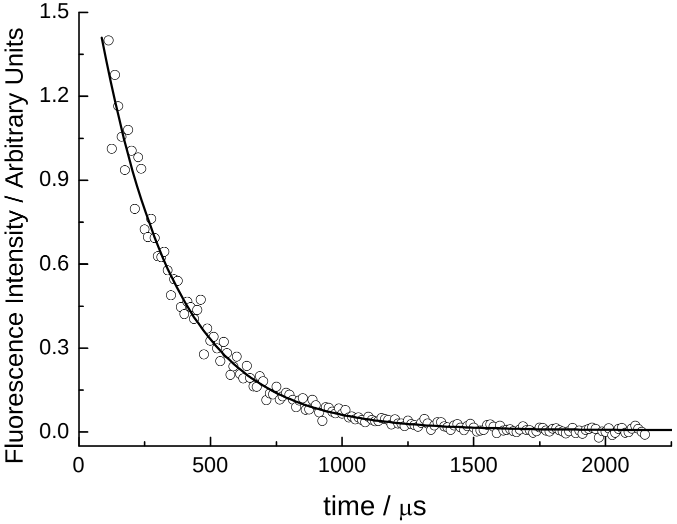
❸ Repeat series of experiments for several $[SO_2]_0$. Plot k' against $[SO_2]_0$

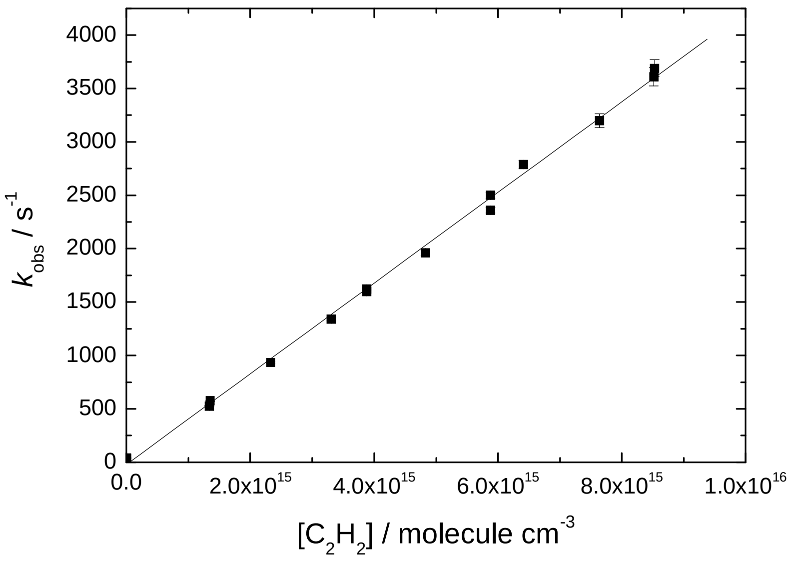
Gradient $= k$

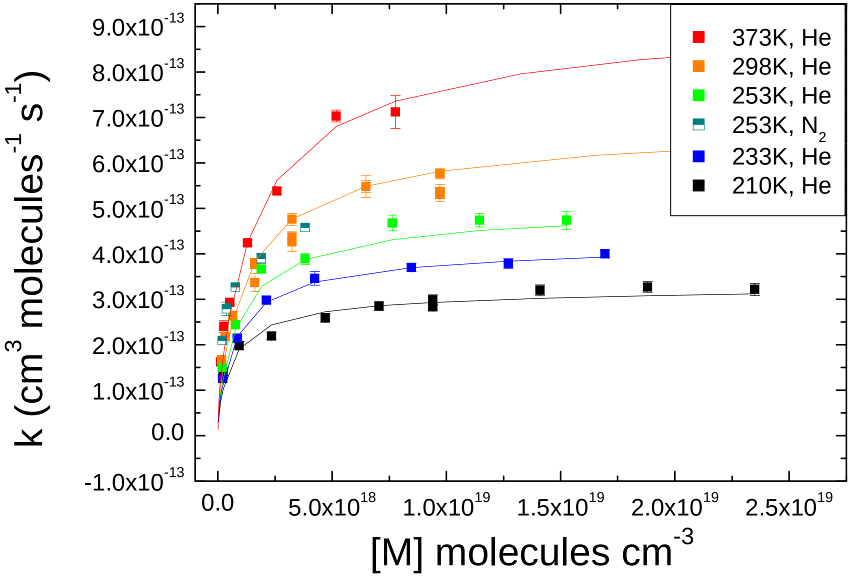
$OH + C_2H_2 + M \rightarrow C_2H_4OH$

Cleary et al. Phys. Chem. Chem. Phys., 2006, 8, 5633-5642

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

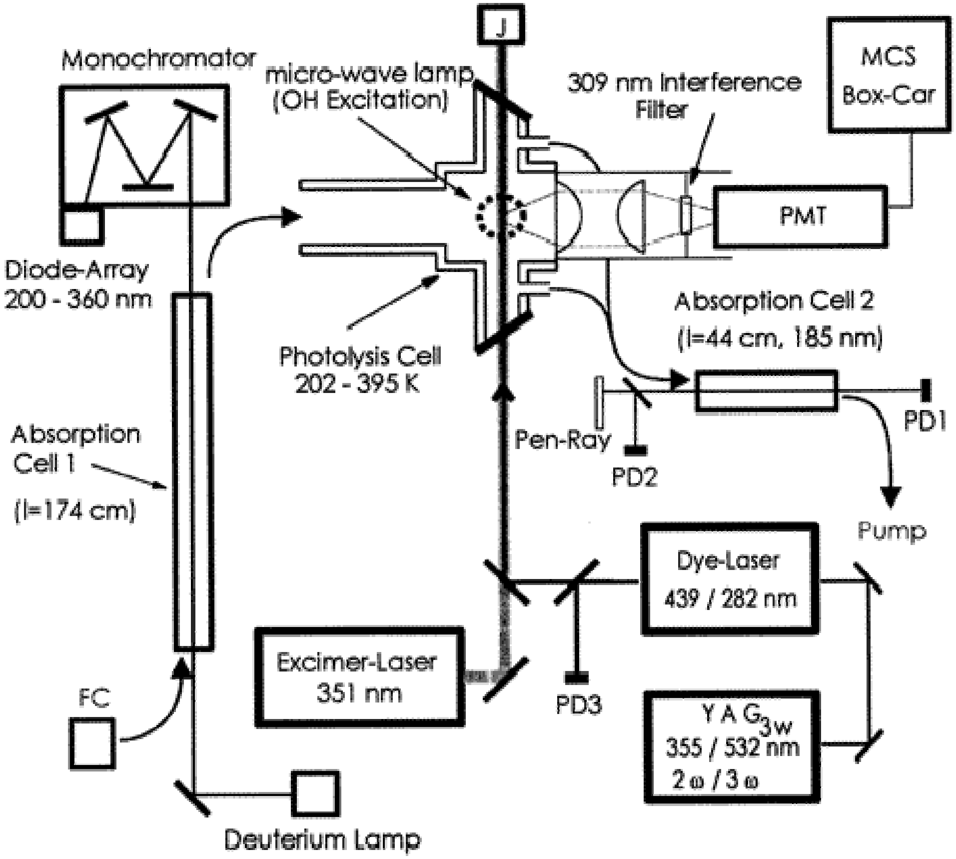


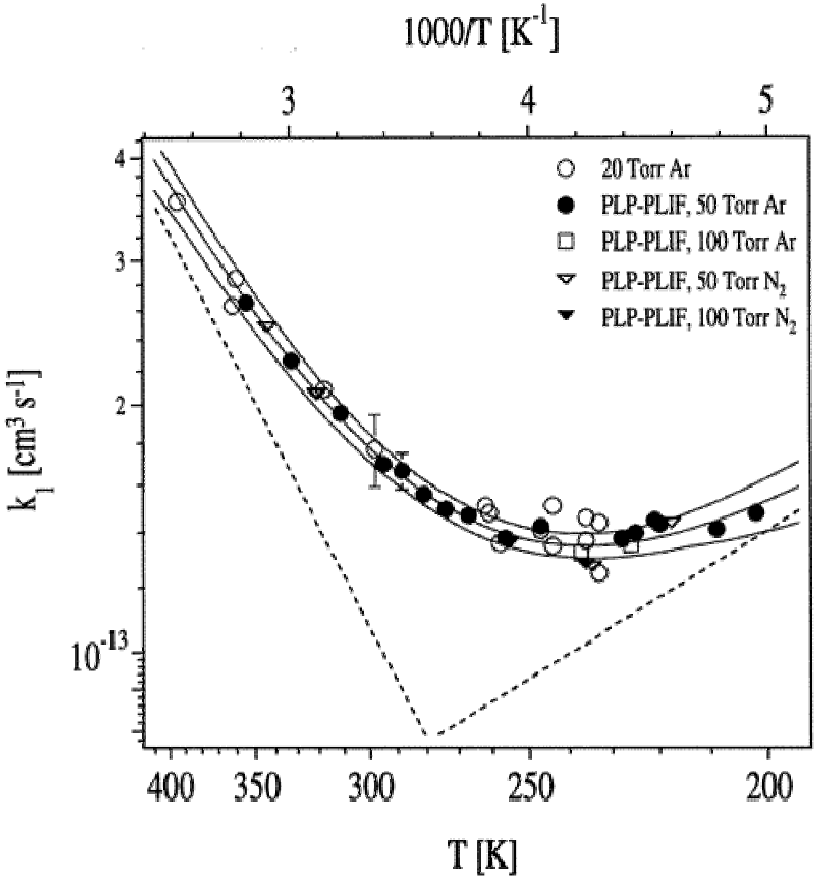




OH + acetone, J N Crowley, JPCA, 2000, **104**,2695

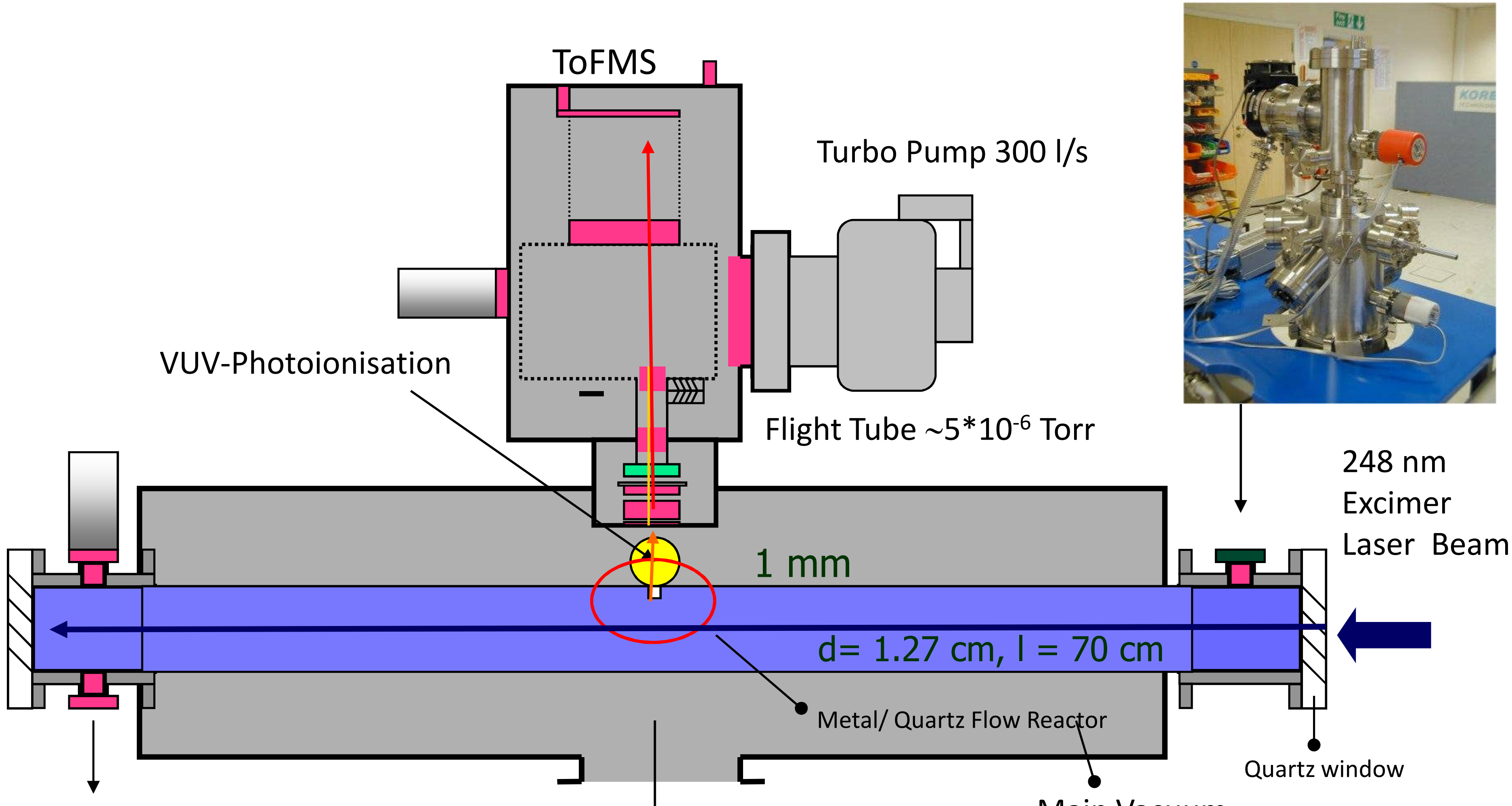
laser flash photolysis, resonance fluorescence/laser induced fluorescence. Optical measurement of [OH] before and after reactor.





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

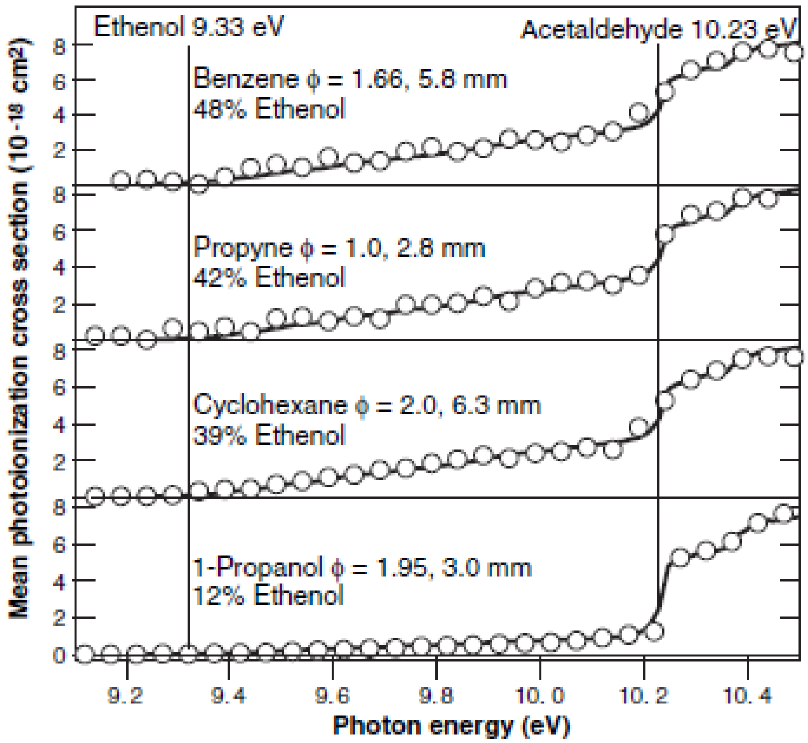
Main Vacuum
Chamber 10^{-3}-10^{-4}
Torr

Application of advanced light source (ALS) to distinguish isomers in flames.

- 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

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

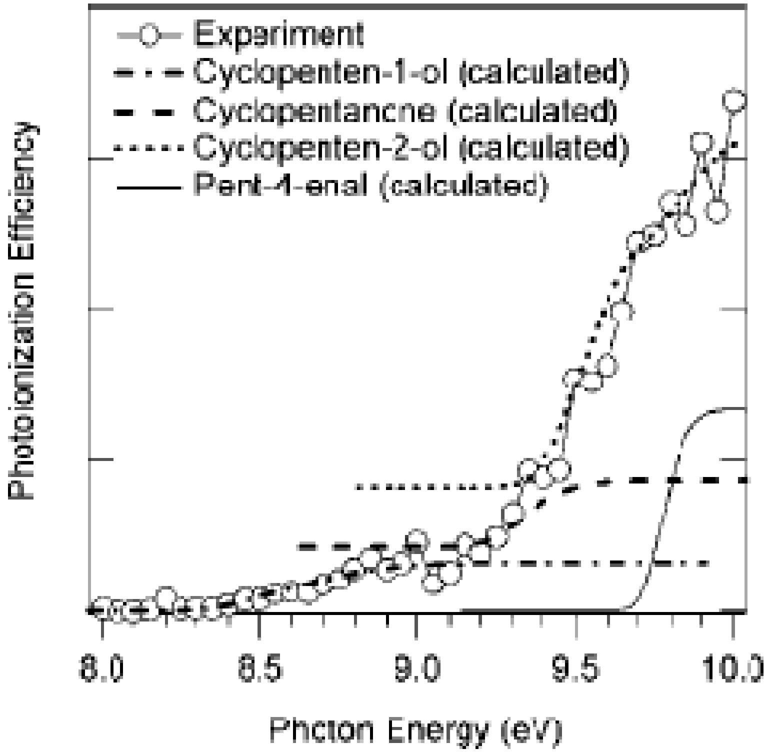
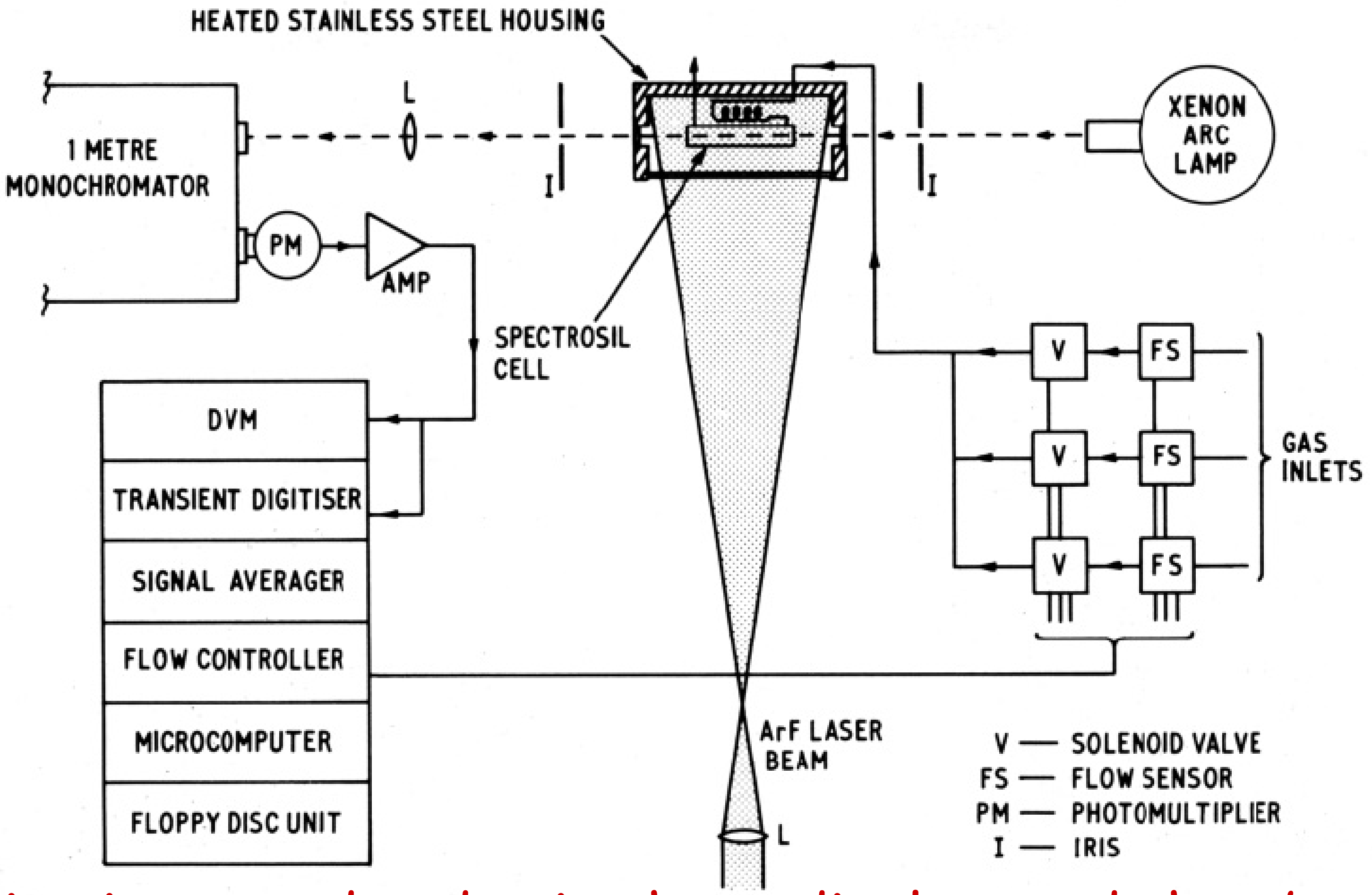


Figure 2. Schematic decomposition of the best fit to the experimental photoionization efficiency spectrum into the substituent calculated photoionization efficiency curves of the three isomers: 1-*c*-C_5H_7OH, *c*-C_5H_8=O, and 2-*c*-C_5H_7OH. The isomeric photoionization efficiency curves are scaled by their weighting in the fit to the overall spectrum (see Figure 1) and vertically displaced for clarity. The photoionization efficiency spectrum of pent-4-enal is shown for reference; no evidence of its formation is seen and it is not included in the fit.

Radical detection using absorption spectroscopy: $C_3H_5 + C_3H_5$

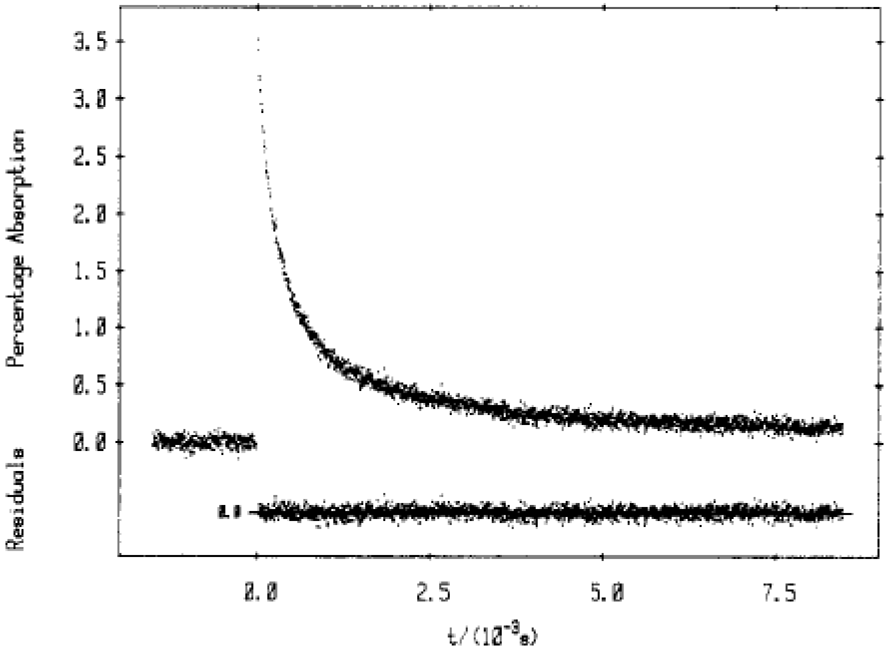


Reaction is <u>second order</u> in the radical – need the <u>absolute concentration</u> To determine *k*.

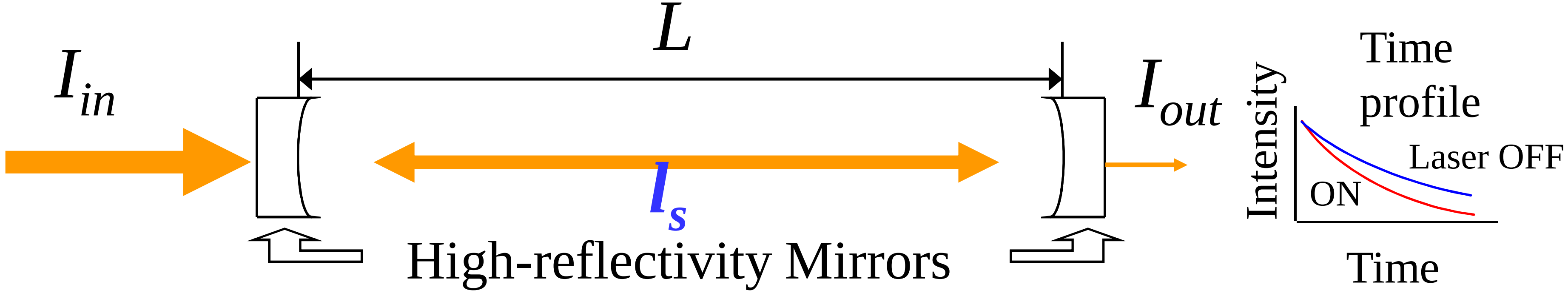
Tulloch et al. *J.* ***Phys. Chem. l982, 86, 3812-3819***

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)
- $I/I_0 = \exp(-\sigma[C_3H_5]l)$



Detection of HCO using cavity ring down spectroscopy (CRDS)



L

I_{in}

I_s

I_{out}

High-reflectivity Mirrors

Time profile

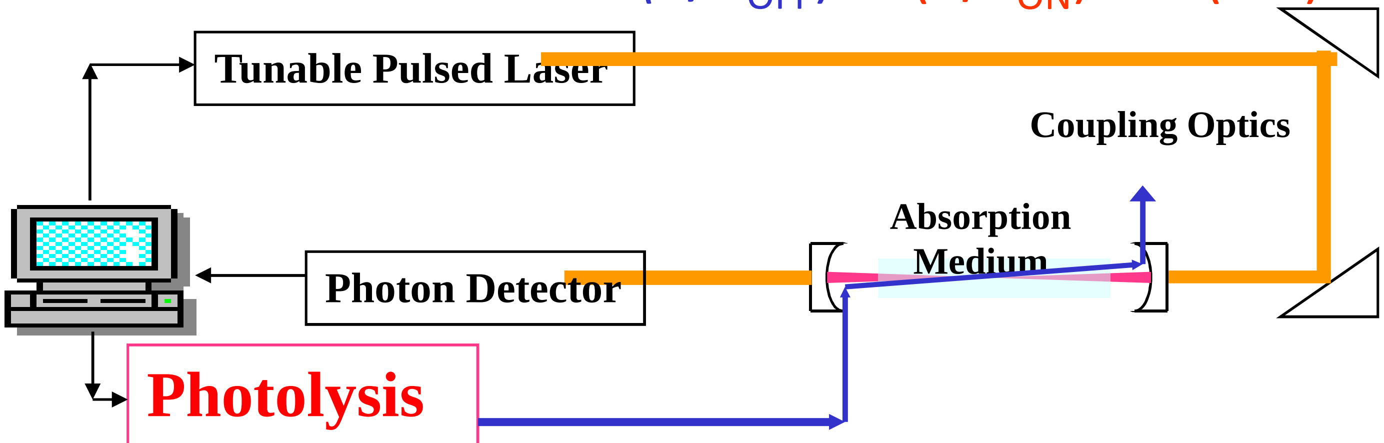
Intensity

Laser OFF

ON

Time

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



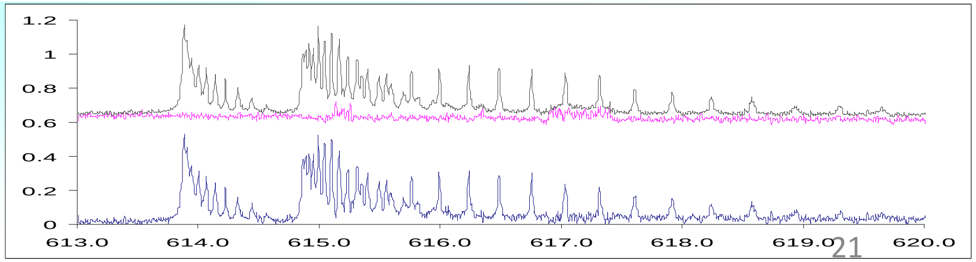
Tunable Pulsed Laser

Coupling Optics

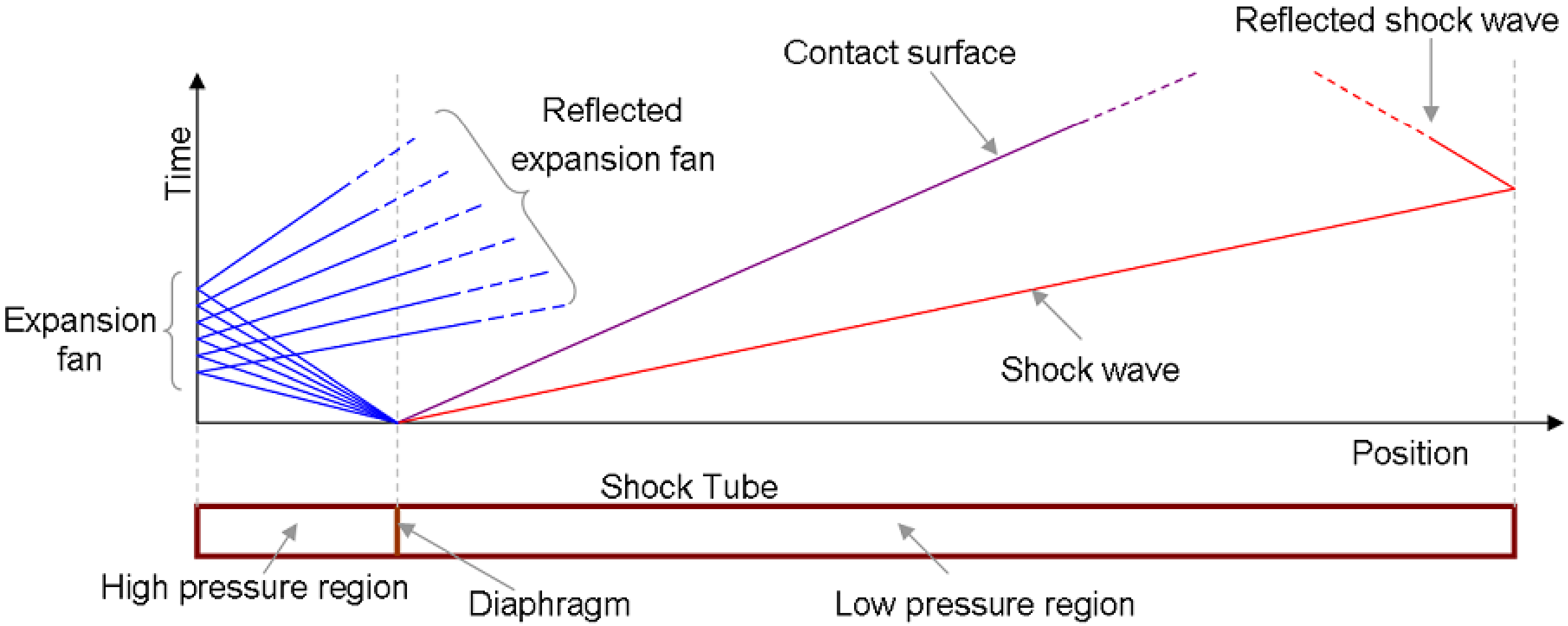
Absorption Medium

Photon Detector

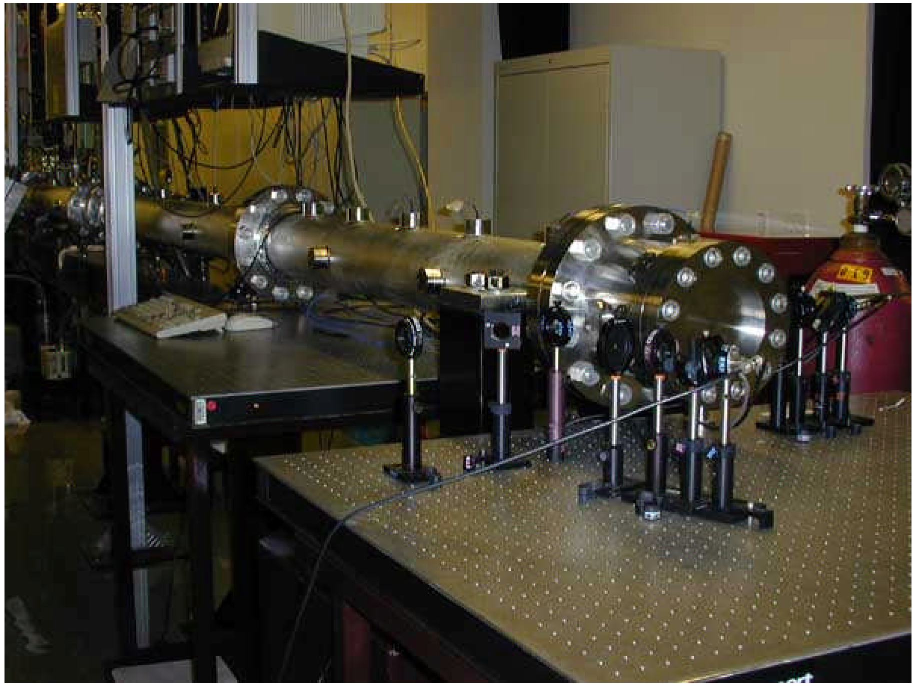
Photolysis (Dye) Laser

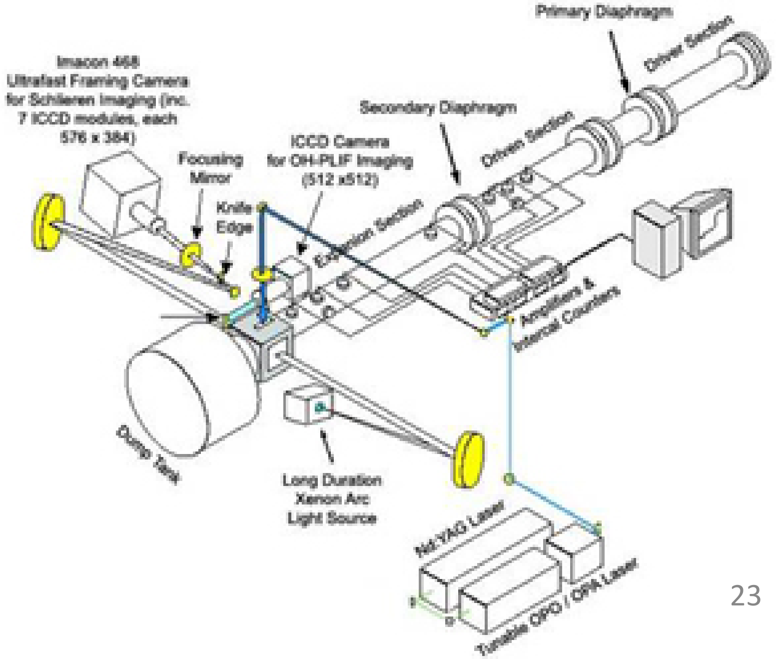


Shock tube - basics



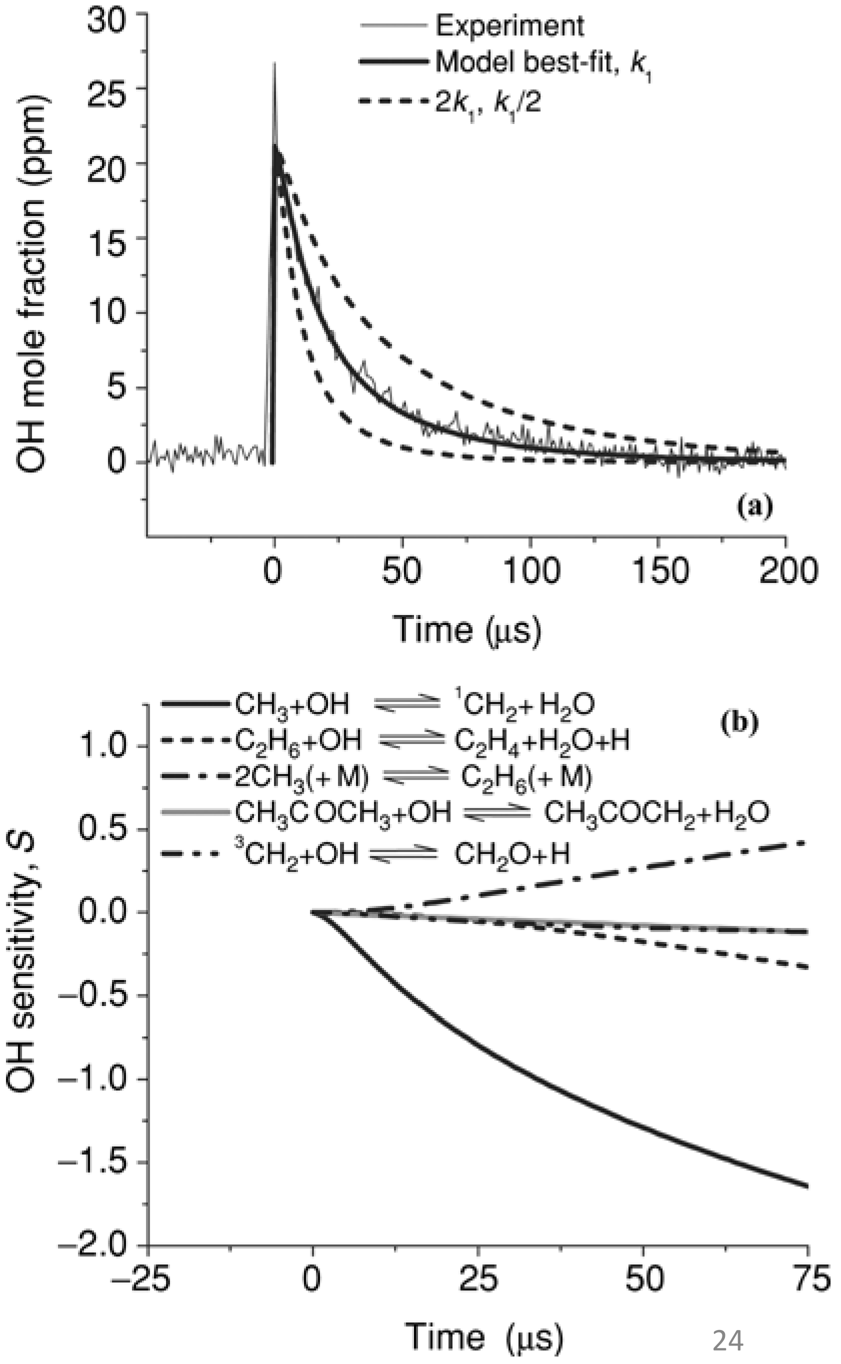
Shock tube:
Hanson lab at Stanford





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

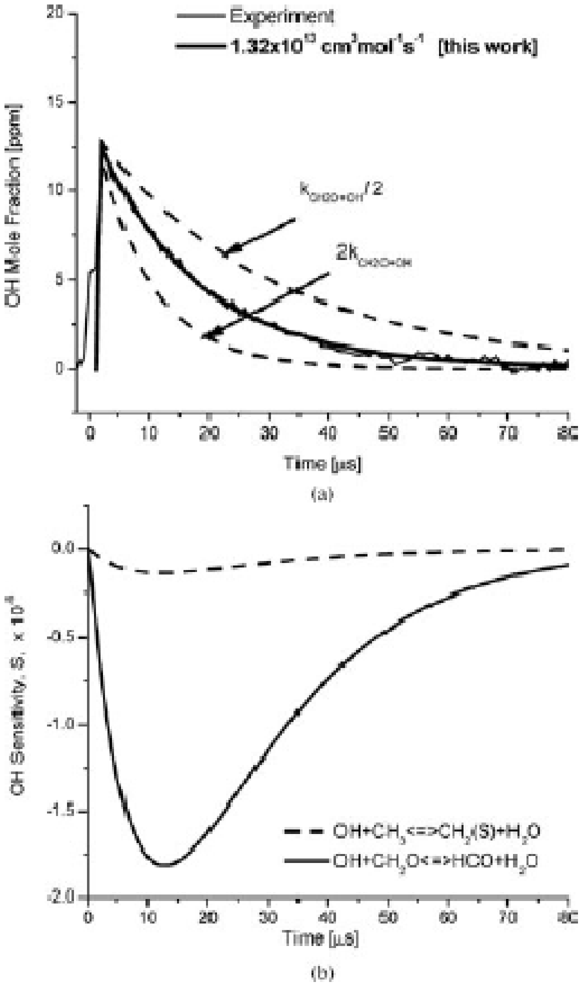


Figure 2 (a) OH concentration time history. 13.25 ppm TBHP, 80 ppm $(CH_2O)_3$, Ar; initial reflected shock conditions: 1229 K, 1.64 atm. (b) Sensitivity analysis. 13.25 ppm TBHP, 80 ppm $(CH_2O)_3$, Ar; initial reflected shock conditions: 1229 K, 1.64 atm. $S = (dX_{OH}/dk_i)(k_i)$, where k_i is the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

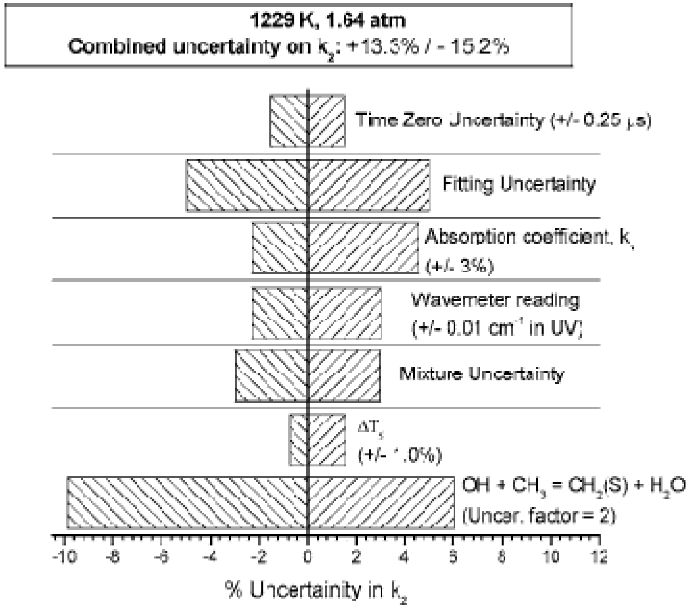
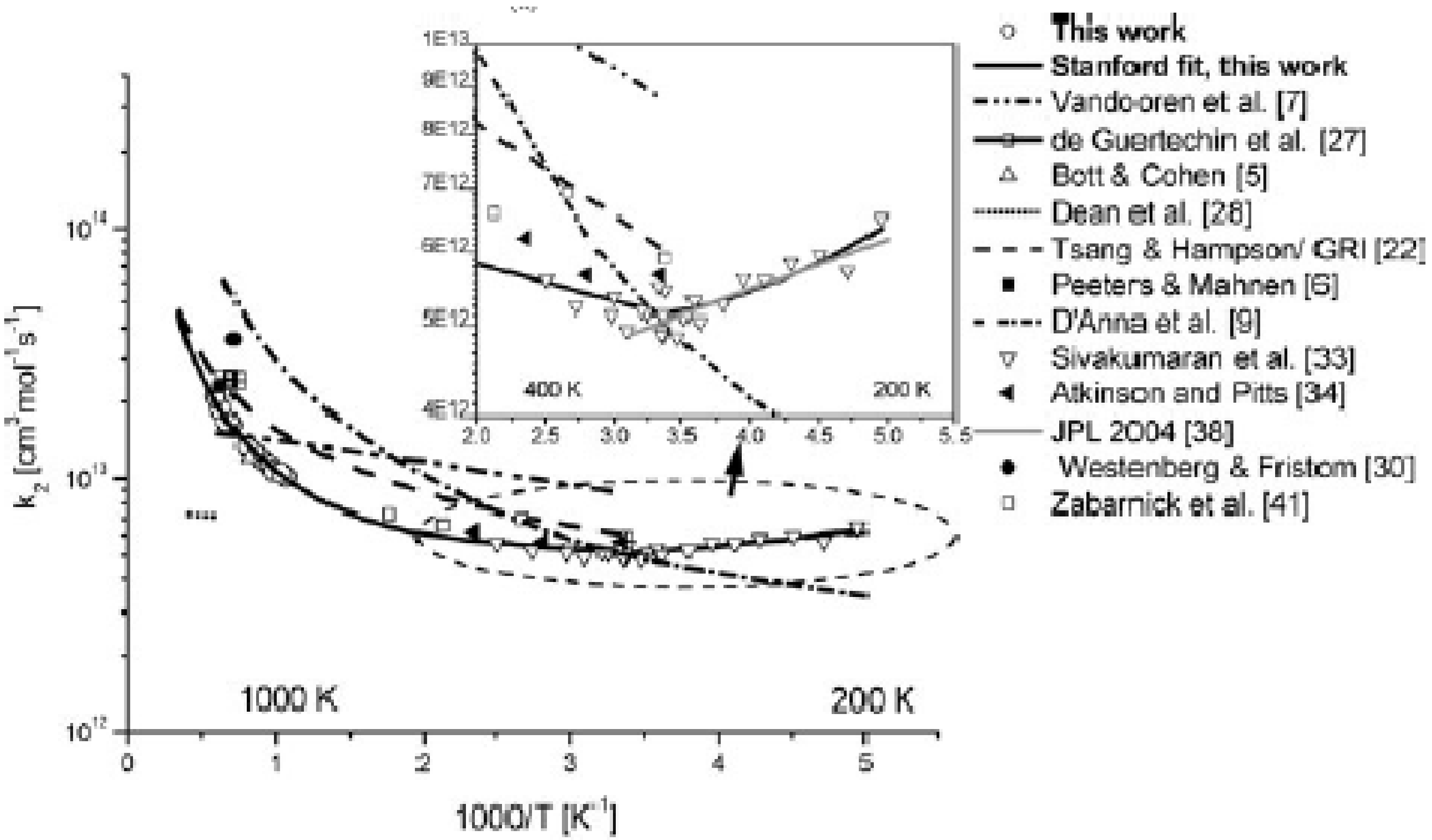


Figure 3 Uncertainty analysis for rate coefficient of $CH_2O + OH - HCO + H_2O$. Initial reflected shock conditions: 1229 K, 1.64 atm; individual error sources were applied separately and their effect on the rate of reaction (2) was determined. Uncertainties were combined to yield an overall uncertainty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

Arrhenius plot for OH + HCHO



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

Determination of product yields by Laser Flash Photolysis 1

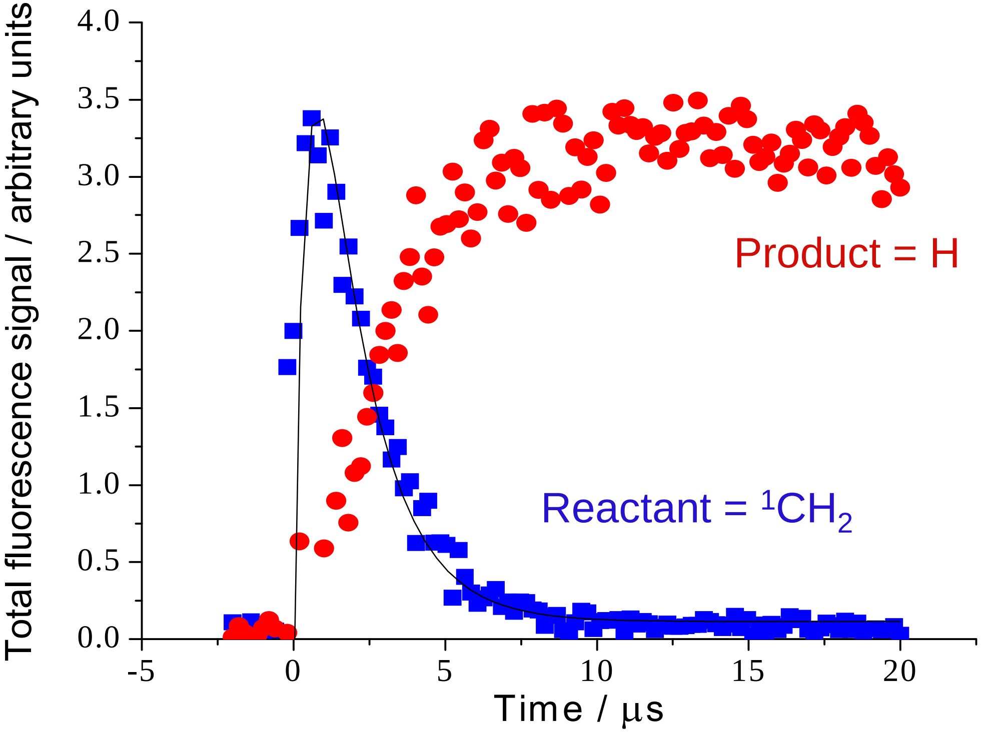
- Use laser pulse to generate radical on short timescale (~10 ns)
- Observe radical concentration vs time. Obtain kinetics from decay time constant
- Also observe product – calibration gives channel yield for a multi channel reaction:

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

Detection technique : laser induced fluorescence for CH_2 and H

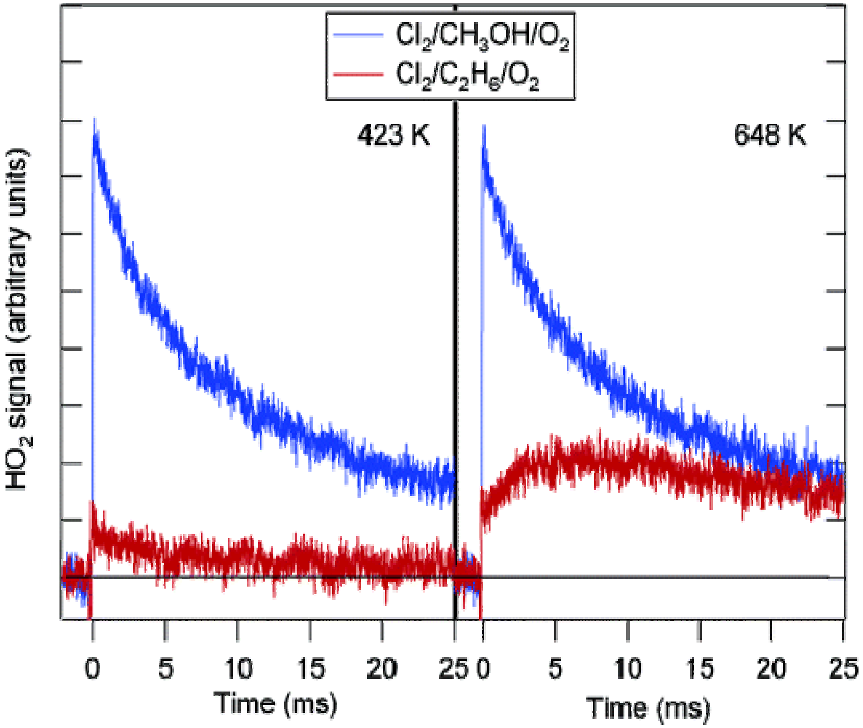
H atom signal calibrated against H formation $^3CH_2 + NO$

$^1CH_2 + H_2 \rightarrow CH_3 + H$



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



$$C_2H_5 + O_2 \rightarrow C_2H_5O_2^*$$
$$C_2H_5O_2^* + M \rightarrow C2H_5O_2 + M$$
$$C_2H_5O_2^* \rightarrow C_2H_4 + HO_2$$
$$C_2H_5O_2 + M \rightarrow C_2H_4 + HO_2$$

Westbrook p67:

We focus on three distinct chain branching pathways

1) $H + O_2 \rightarrow O + OH$ High T

2) $H + O_2 + M \rightarrow HO_2 + M$ Medium T

$RH + HO_2 \rightarrow R + H_2O_2$

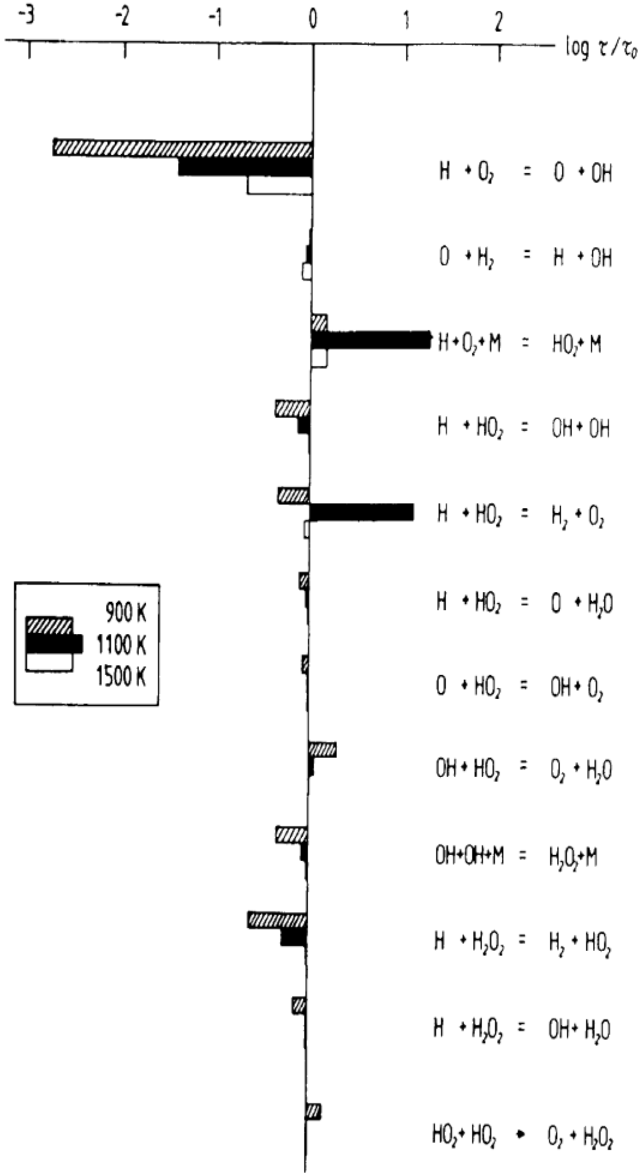
$H_2O_2 + M \rightarrow OH + OH + M$

3) $R + O_2 \rightarrow RO_2$ Low T

$RO_2 \rightarrow QOOH \rightarrow O_2QOOH \rightarrow$ 3+ radicals

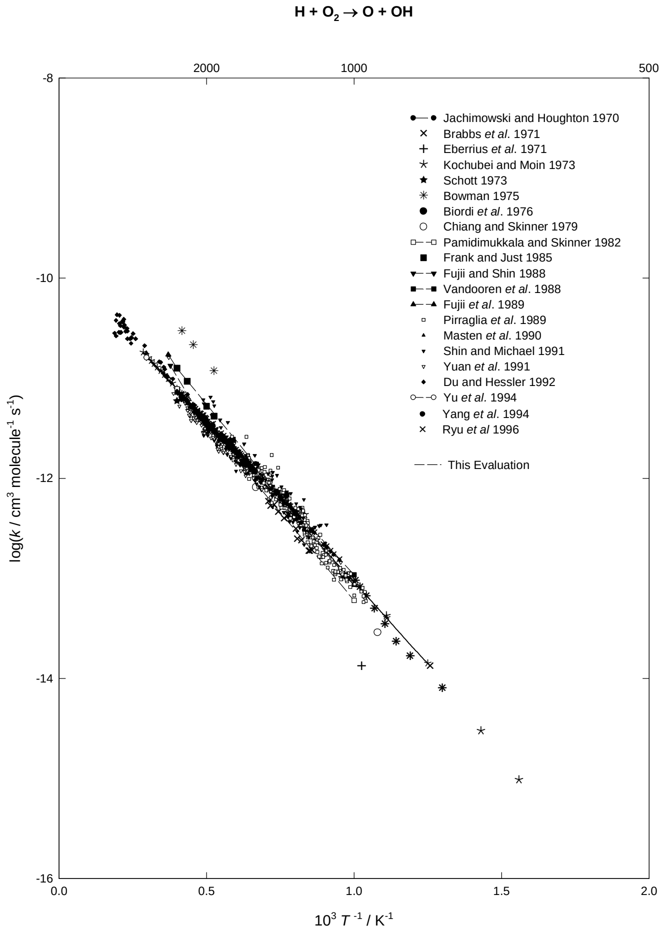
Hydrogen oxygen system

- 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



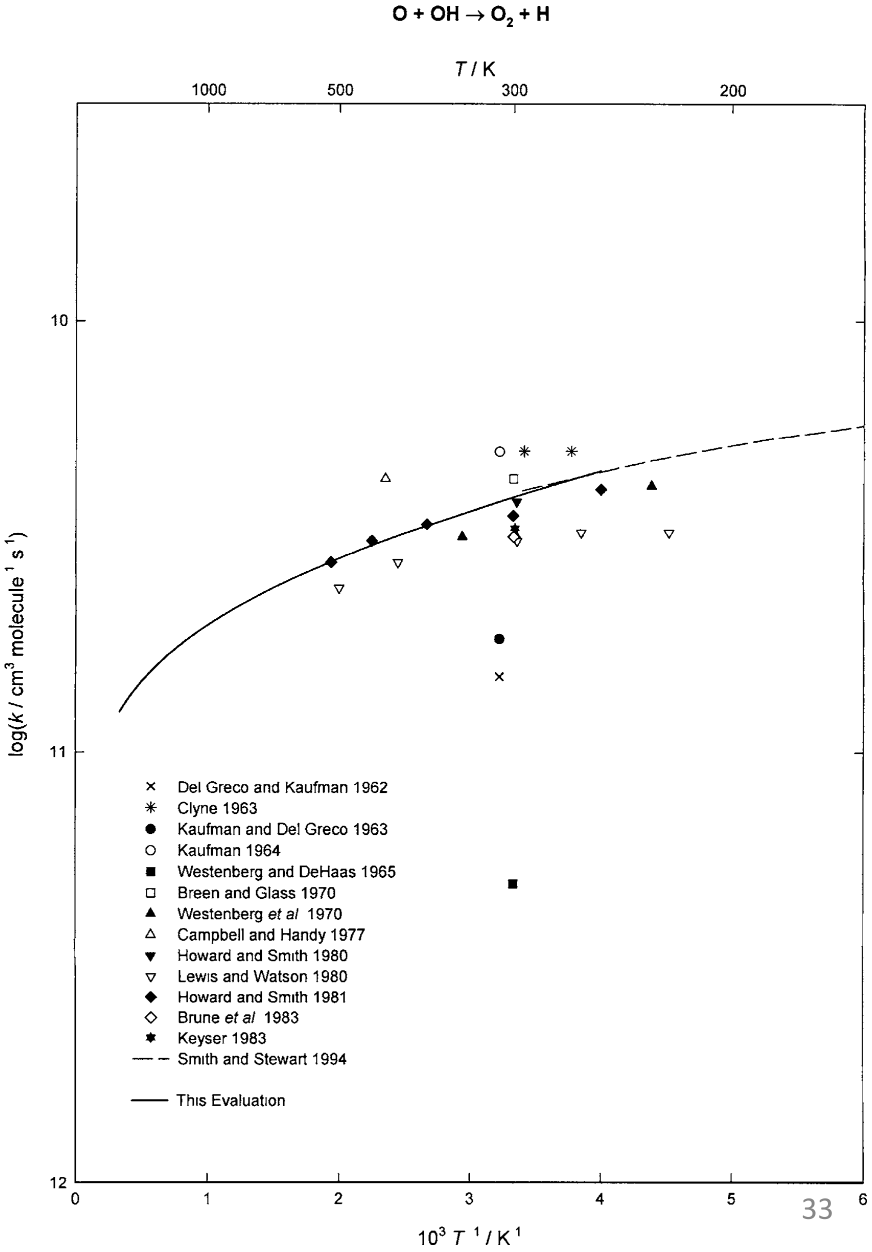
Evaluation of experimental data for $H + O_2 \rightarrow OH + O$

- Evaluation discussed on Wednesday.
- Large number of separate experimental investigations for this reaction, mainly shock tube
- Evaluation provides recommended rate coefficient: $k = 3.43 \cdot 10^{-10}\ T^{-0.097} \exp(-7560/T)$ cm^3 molecule^{-1} s^{-1} over the range 800-3500 K.
- Uncertainty estimate also given: $\Delta \log k = \pm 0.1$ at 800 K, rising to ± 0.2 at 3500 K.



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

- Studied 150 - 500 K, mainly by dischaarge flow / laser flash photolysis.
- Not of great importance in combustion, but provides additional information on reverse reaction through thermodynamics
- $k = 2.00\times10^{-10}\ T^{-0.352} \exp(113/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$ 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

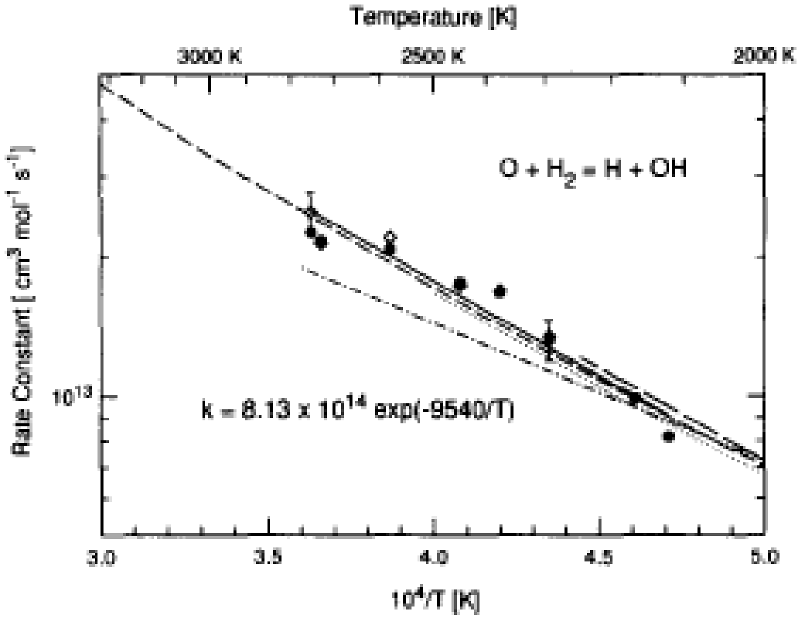
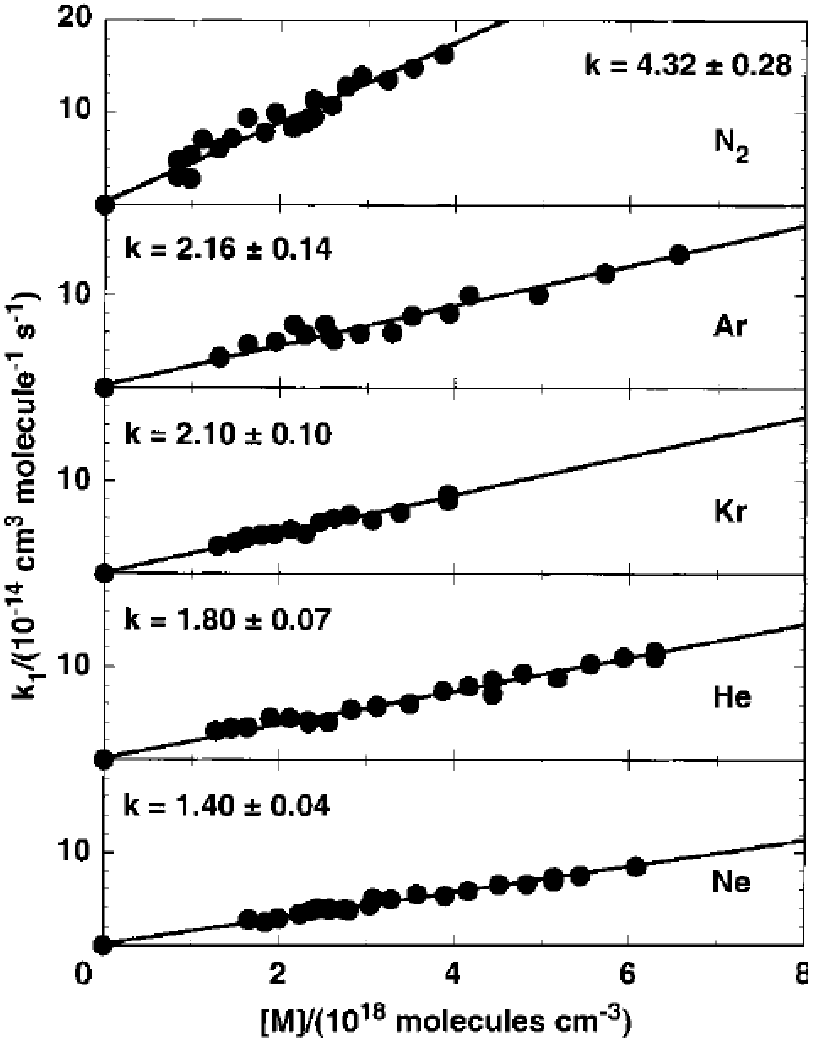


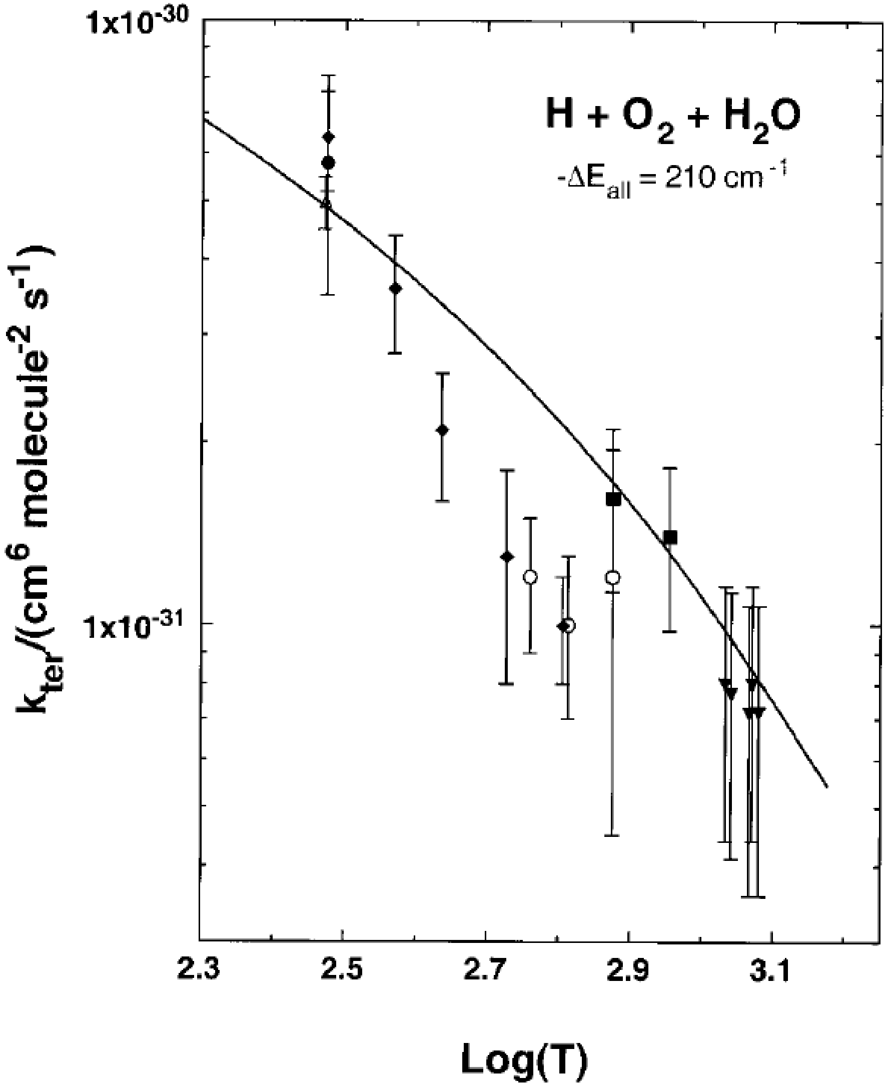
Fig. 2. Arrhenius diagram: $O + H_2 \rightarrow OH + H$. Filled circles—data derived from photolysis method. Open diamonds—data derived from pyrolysis method. Error bars represent ±10%. Solid line—best fit to present data. Dotted line—Sutherland et al. [8]. Dashed line—Nataranjan and Roth [9]. Dot-dashed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

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

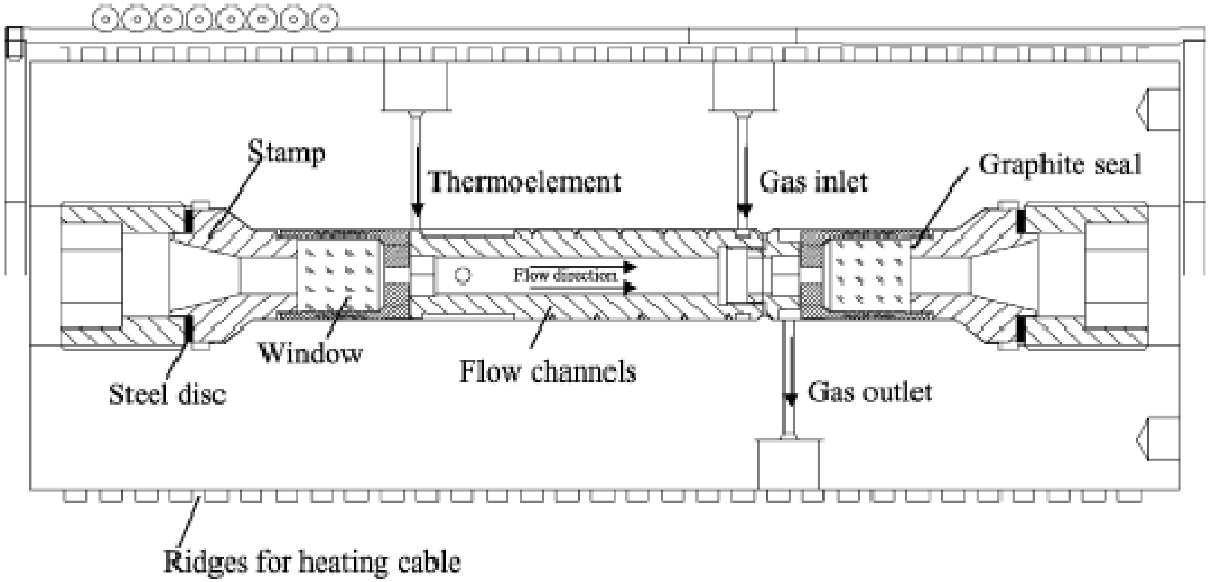




Units of k: 10^{-32} cm^6 molecule^{-2} s^{-1}

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*

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

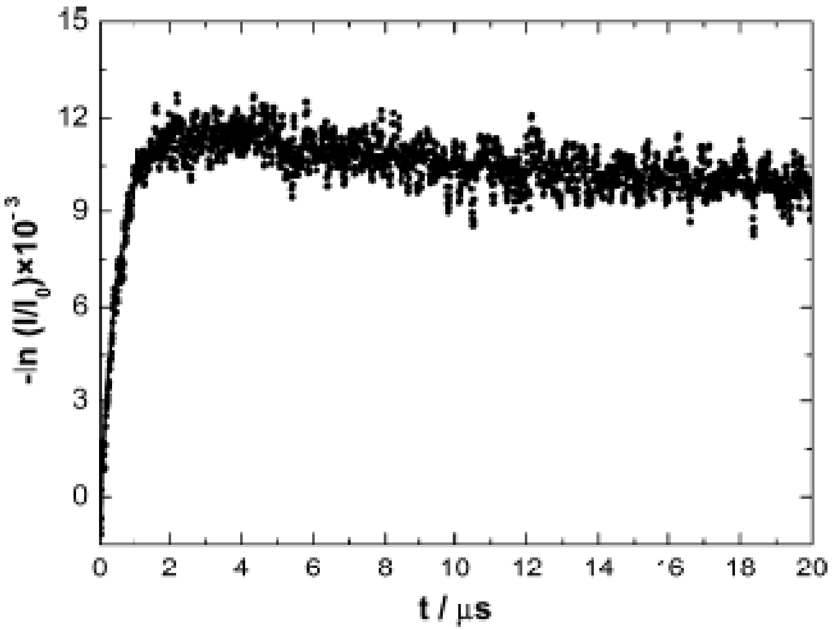


Fig. 2 Absorption–time profile of HO_2 (λ = 230 nm, T = 600 K, p = 300 bar, M = N_2).

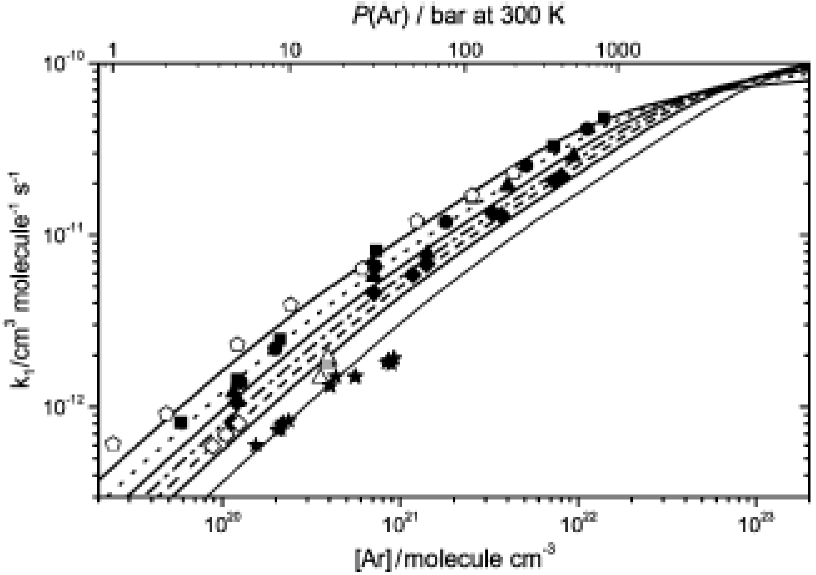


Fig. 5 Falloff curves for the recombination $H + O_2$ (+Ar) → HO_2 (+Ar) (representative upper pressure scale for 300 K; T/K = 300 (■), 400 (●), 500 (▲), and 600 (♦) from this work; 300 (⬠, ref. 19), 820 (◇, ref. 20), 1200 (★, ref. 22), and 1325 (△, ref. 21); the fitted curves at left from top to bottom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

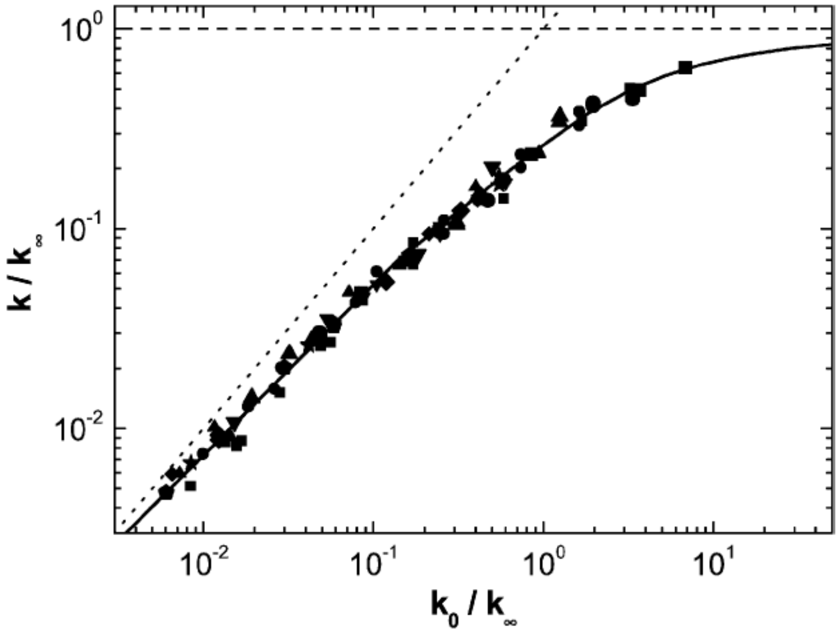


Fig. 7 Doubly reduced falloff curves for the recombination $H + O_2$ $(+M) \rightarrow HO_2$ $(+M)$ in the bath gases M = He, Ar, and N_2 (experimental points from this work from Tables 1–3; T/K = 300 (■), 400 (●), 500 (▲), 600 (▼), 700 (♦), 800 (★), and 900 (⬟), see text).

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
- Significant disagreement > 1000 K

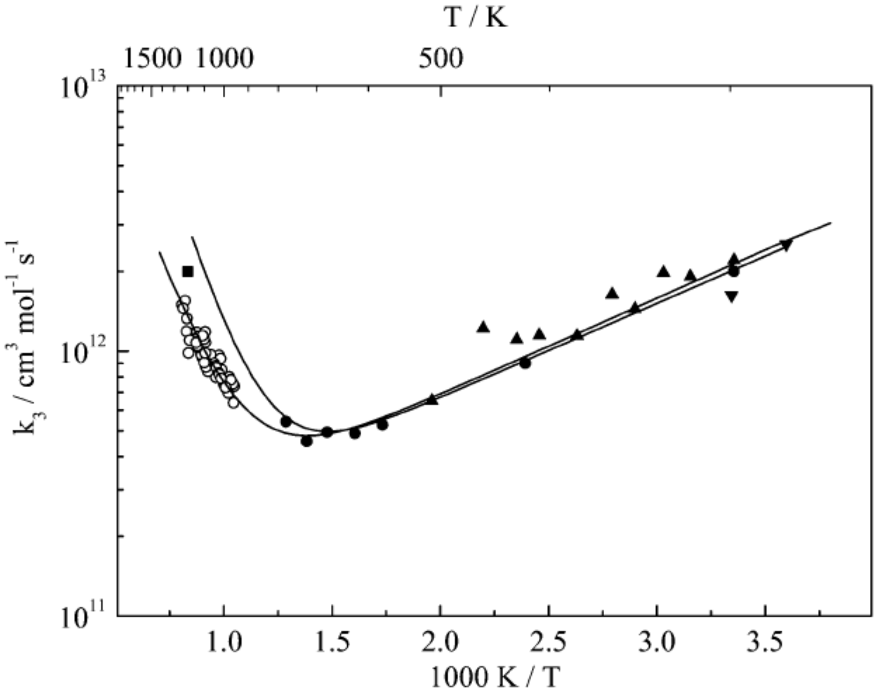


Fig. 10 Rate constants k_3 (■: ref. 2, ▲: ref. 35, ▼: ref. 36, ●: ref. 37, ○ and lower line: this work, upper line: ref. 5).

$H_2O_2 + M \rightarrow 2OH + M$

- 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)

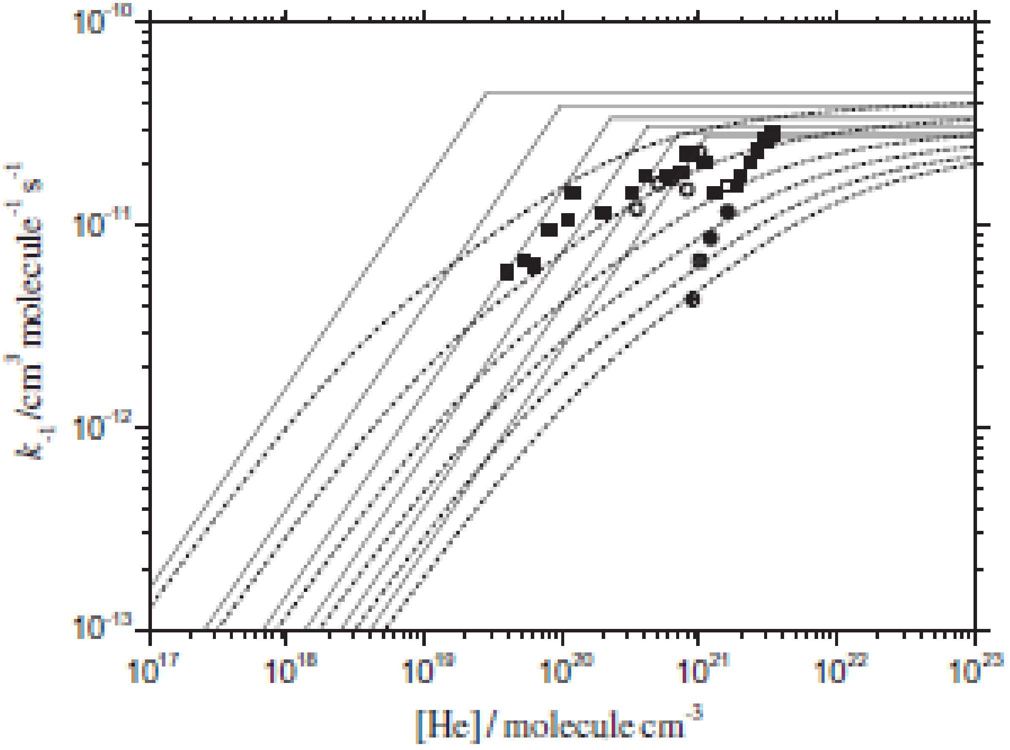
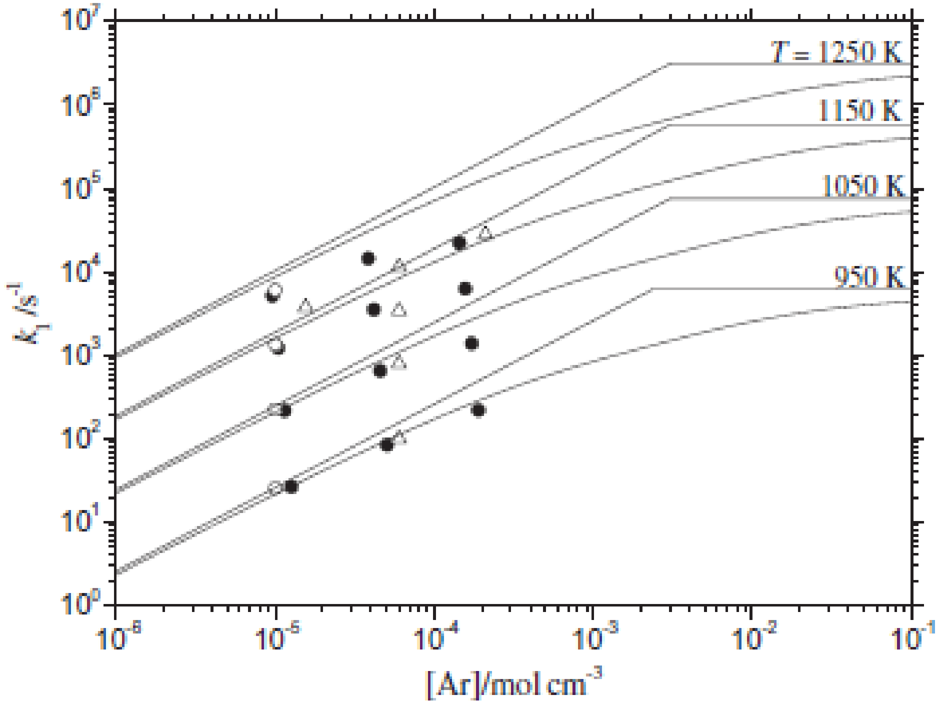


Fig. 3. Experimental recombination rate coefficients k_{-1} and their modelled falloff representation (M = He, experimental points from Refs. [30,31] at T/K = 210 (○), 298 (■), 406 (□), 510 (●), 614 (⊚), and 694 (⊕); full lines = modelled limiting low and high pressure rate coefficients from Section 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)



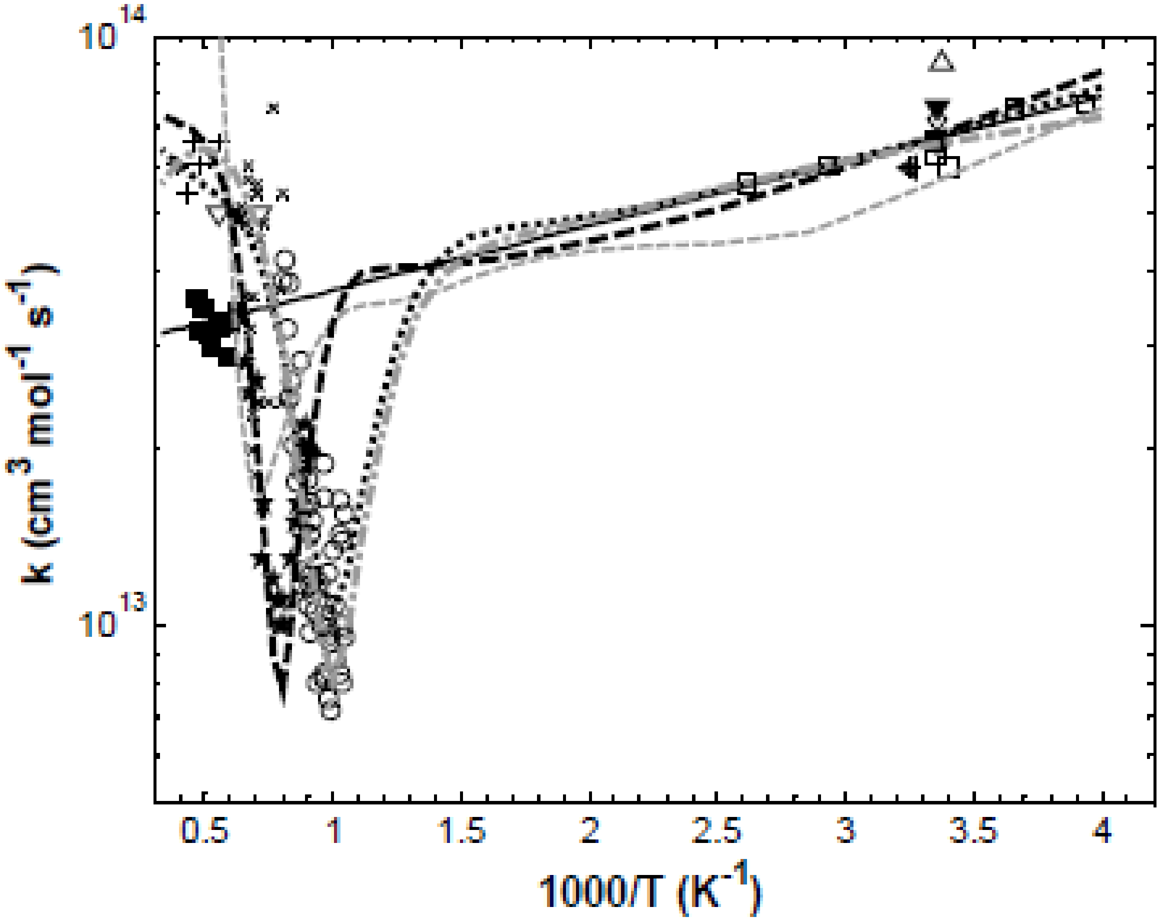
Overall reaction

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

$OH + HO_2 = O_2 + H_2O$. Important chain terminator

- Methods:
  - Discharge flow study. [OH] monitored by LIF and [HO_2] by reaction with NO and LIF detection of the OH produced. $k = 4.8 \cdot 10^{-11} \exp(250/T)$ cm^3 $molecule^{-1}$ s^{-1} 254-382 K
  - Shock tube study using incident and reflected shocks in H_2O_2/Ar mixtures. [HO] monitored by cw laser absorption. Fitting of the [OH] profile by computer simulation used to obtain *k*. 1118-1566 K. Strong positive T dependence

Arrhenius plot



High T behaviour not supported by theory

$$\begin{aligned} H + HO_2 &\rightarrow H_2 + O_2 && (1)\\ &\rightarrow OH + OH && (2)\\ &\rightarrow H_2O + O && (3) \end{aligned}$$

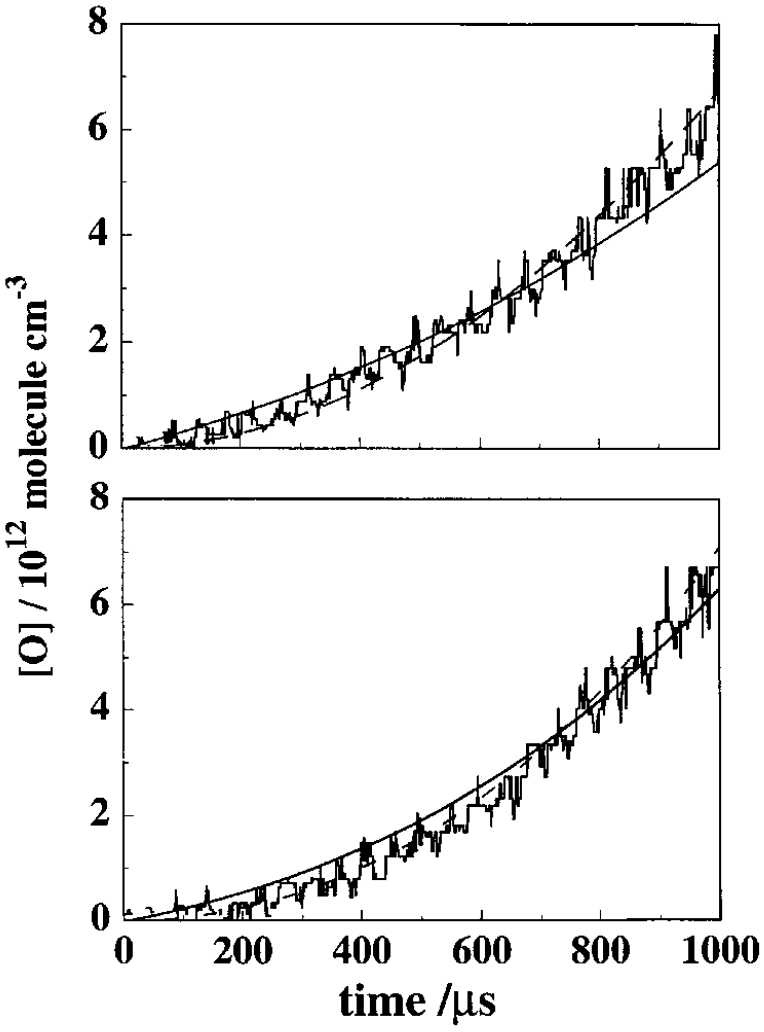
- Methods:
  - Discharge flow study in which HO_2 was generated by the F + H_2O_2 reaction. [H], [O], and [OH] monitored by resonance fluorescence, and [HO_2] by quantitative conversion to OH with an excess of NO.
  - Analysis of $H_2 + O_2$: induction period and maximum rate of the slow reaction, and the second explosion limit.

Recent recommendations (A, n, E):

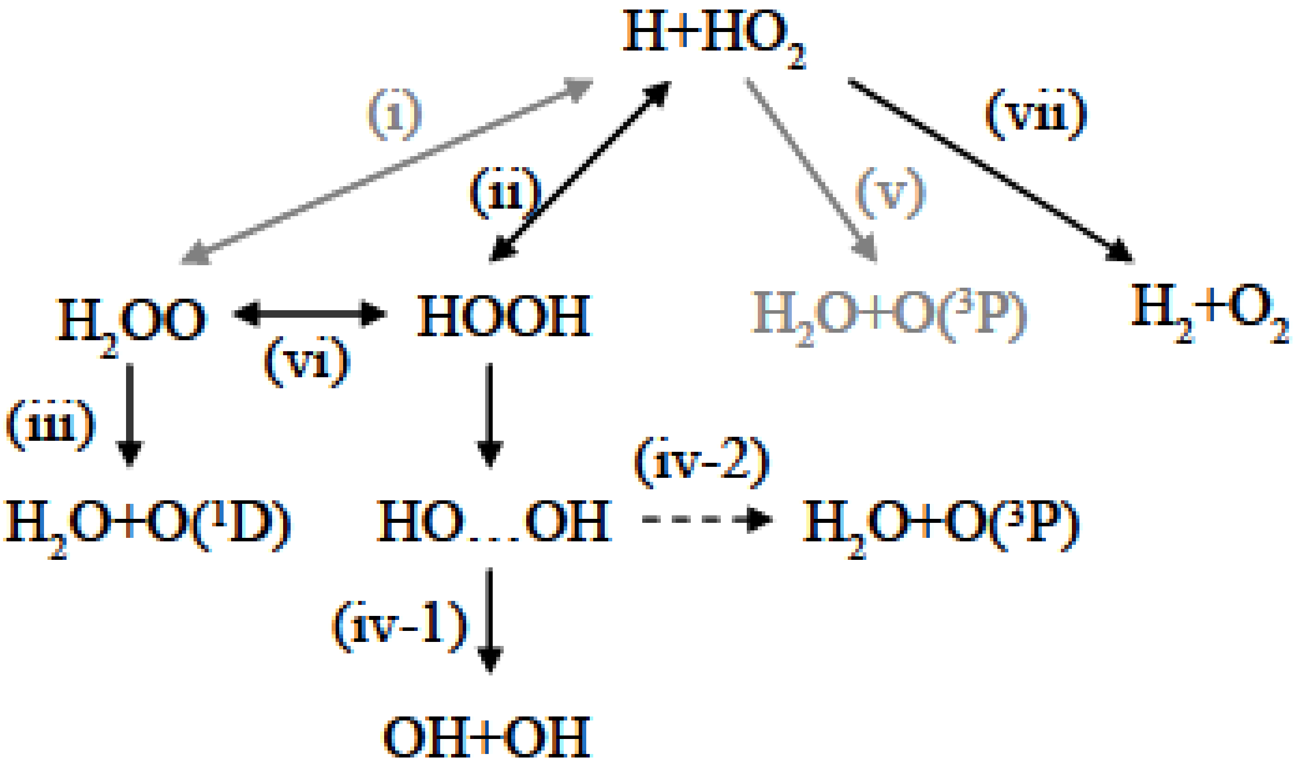
HO_2+H = H_2+O_2	2.75E+06	2.09	-1.45E+03
HO_2+H = OH+OH	7.08E+13	0.00	2.95E+02

Reverse reaction: $H_2 + O_2 \rightarrow H + HO_2$
Michael et al. Proc Comb Inst, 28, 2000, 1471–1478

- reflected shock tube, 1662–2097 K , 400–570 torr Kr
- O ARAS gave absolute [O] ,most secondary reactions negligible. [O] direct result of the rate controlling $H_2 + O_2$ followed by $H + O_2 \rightarrow O + OH$.
- Combined with theory (ab intio + TST) gave $k = 1.228 \times 10^{18}\ T^{2.4328} \exp(-26{,}926\ K/T)\ cm^3\ molecule^{-1}\ s^{-1}$,



Mechanism



Burke et al., Int J Chem Kinet (in press)