

Uncertainties in Atmospheric Chemical Mechanisms

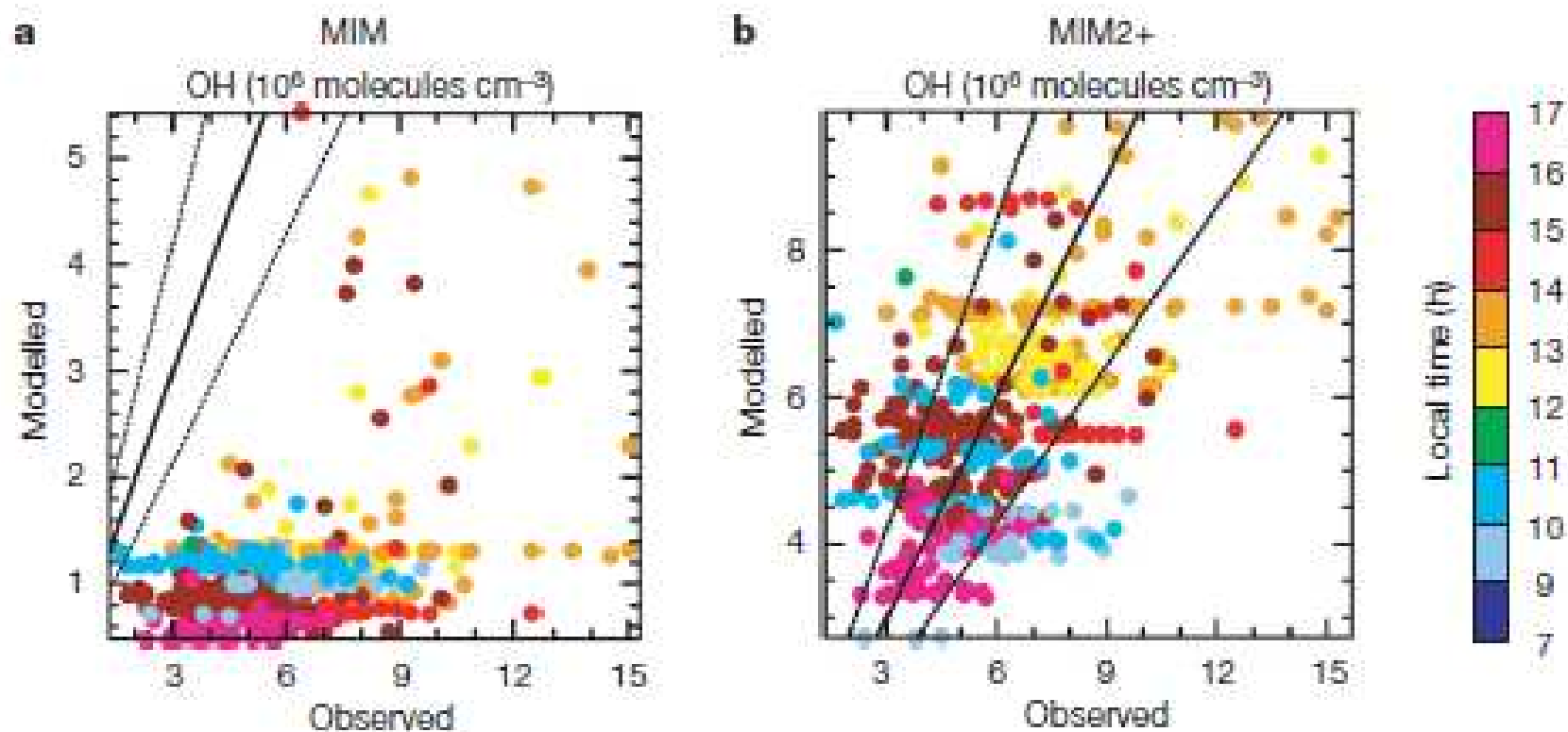
Mike Pilling
University of Leeds

Urban Air Quality and Traffic, Paris, October 6th, 2009

Synopsis

- Outline recent field experiments that indicate routes to OH that are unrecognised in current chemical mechanisms
- Discuss proposed routes to OH via H atom transfer in peroxy radicals.
- What evidence is there for such reactions: pressure and pressure independent chemical activation, thermal isomerization in combustion (autoignition)
- Implications for approaches to mechanism development and deployment. Cautionary tale from aromatic oxidation.

Lieleveld et al., Gabriel campaign Guyanas, 2005.
Nature, April 2008; Atmos. Chem. Phys., 8, 4529-4546,
2008.



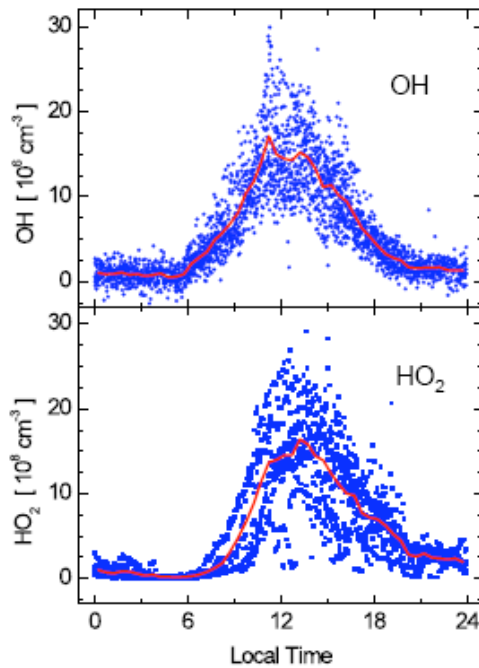
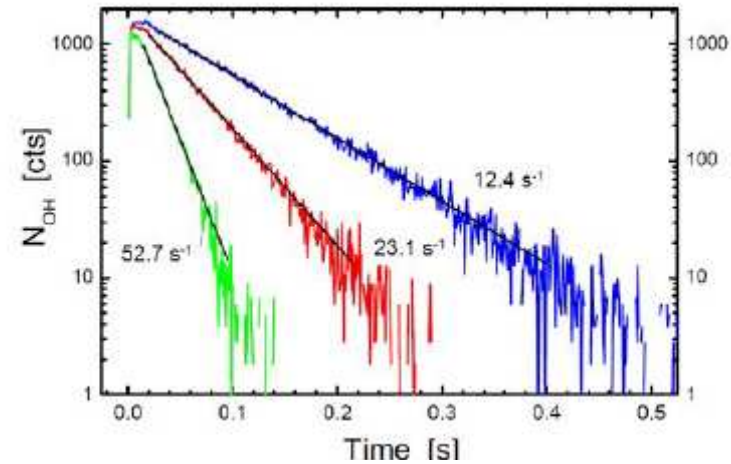
Conclusions from Gabriel analyses

1. OH recycling of about 40-50% (compared with 5-10% in current generation isoprene oxidation mechanisms) is necessary in order for modelled OH to approach the lower error bounds of the OH observed.
2. "To explain the observed isoprene concentrations, the effective rate constant for the reaction of isoprene with OH be reduced by about 50% compared with the lower bound of the range recommended by IUPAC. A reasonable explanation for this lower effective rate constant could be the segregation of isoprene and OH in the mixed layer."

Combine measurement of OH reactivity with measurement of [OH], [HO₂] and concentrations of OH sources (ozone, HONO....). Check budget balance.

- Pearl River Delta, 3 - 30 July 2006
Photochemistry study with measurements of HO_x in China (PRIDE-PRD 2006) ~ 60 km outside of Guangzhou City (23.5°N)
- Forschungszentrum Jülich, Peking University, Beijing, RCEC, Taiwan University of Tokyo
- Science. 2009; 324:1702-1704.

OH lifetime measurements:
 Measure $\tau = 1/k_{OH}$
 Where k_{OH} is the pseudo 1st order k for loss of OH
 Rate of loss of OH = $k_{OH}[OH]$

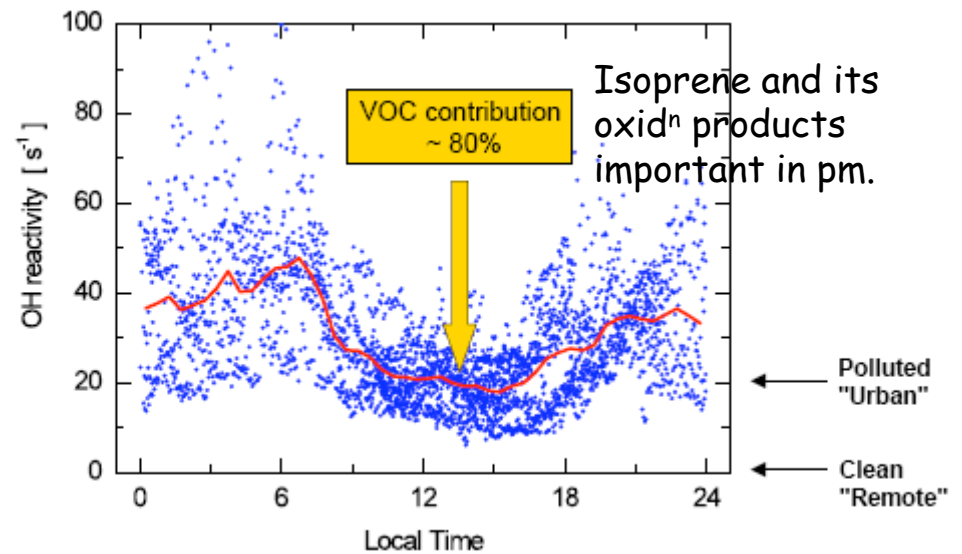
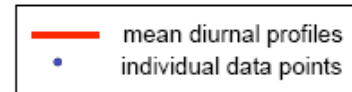


Mean Diurnal Profiles

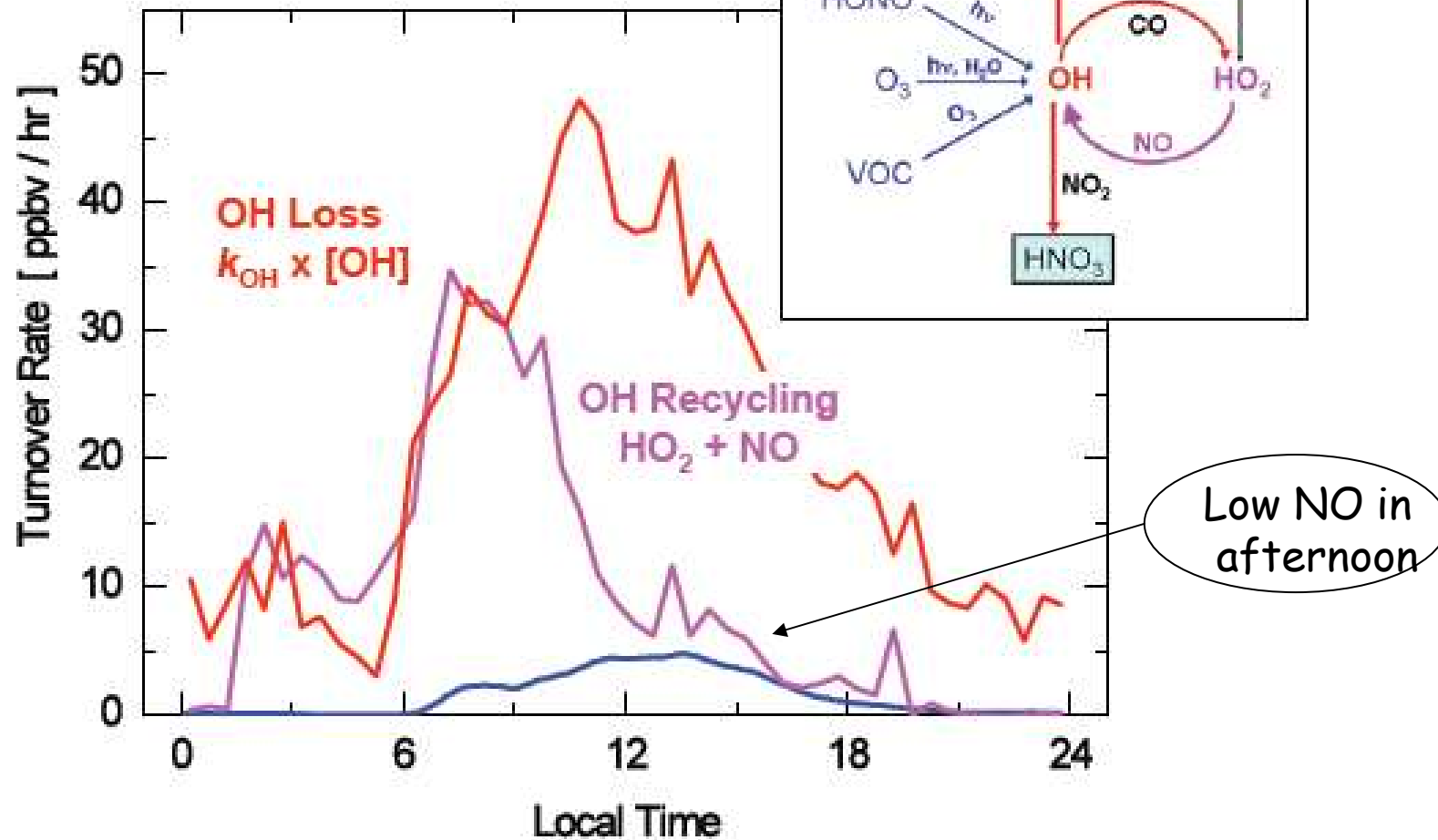
OH peak values
 2×10^7 molecules / cm³
 ~ 0.8 pptv

High photochemical activity !

HO₂ peak values
 ~ 80 pptv



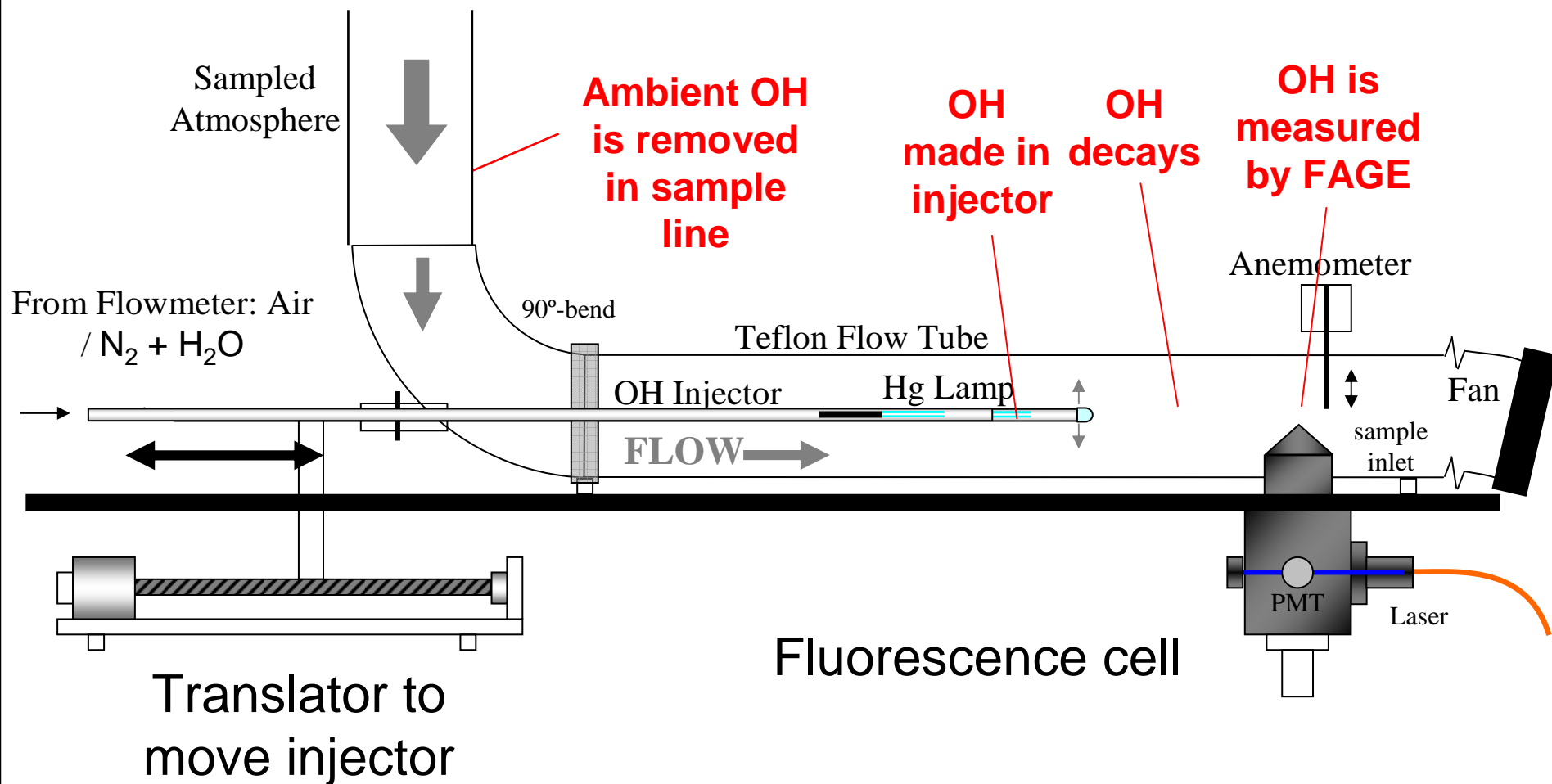
Chemical Turnover



- Radical budget closed in morning - OH recycling is very efficient.
- No closure in afternoon. Since HO_2 , NO and OH loss are directly measured, observation indicates additional source of OH

Measurement of OH reactivity: Leeds OH reactivity (lifetime) instrument (Dwayne Heard et al.)

Flow-tube reactor with the atmosphere as the reagent

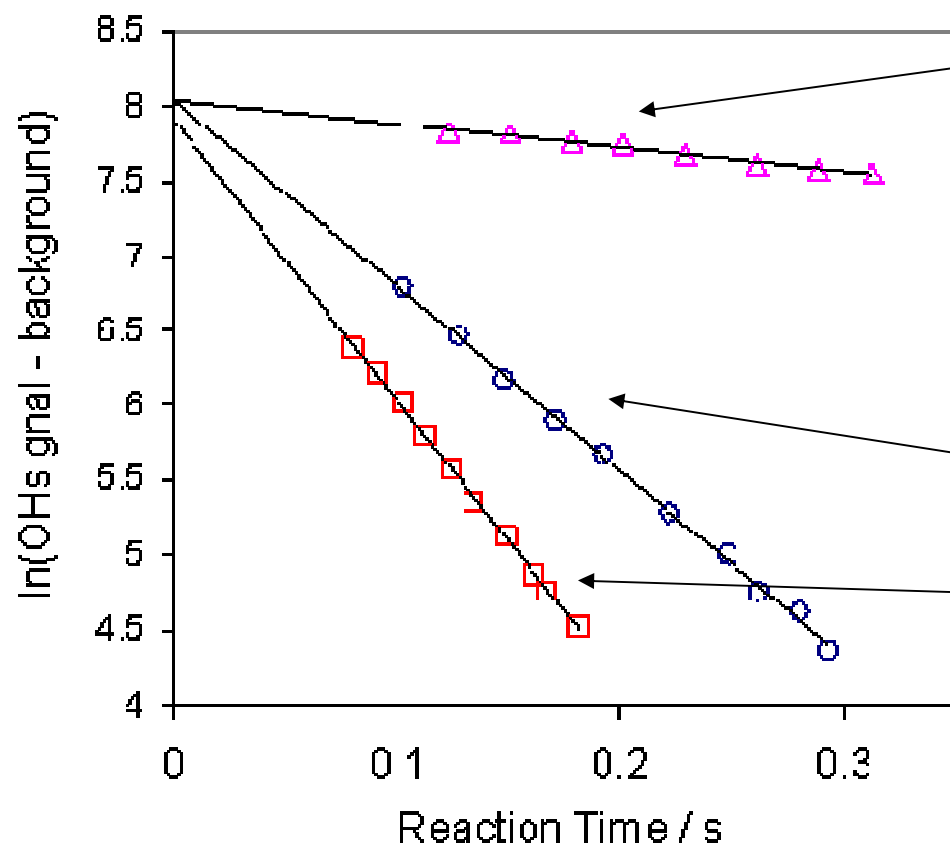


Semi-log decay of OH

$$k'_{\text{OH}} = \sum_i k_i [\text{VOC}]_i$$
$$= 1/\tau_{\text{OH}}$$

$[\text{OH}] = [\text{OH}]_0 \exp(-k'_{\text{OH}} t)$. Obtain k'_{OH} from semi-log plot

Change t by moving injector position



Physical loss (zero air)
 $k' = 1.88 \pm 0.09 \text{ s}^{-1}$

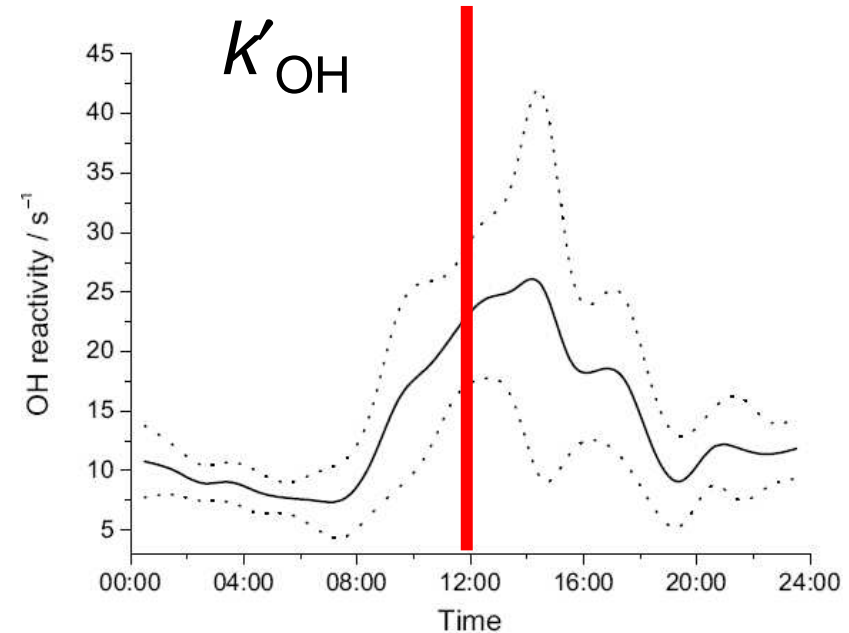
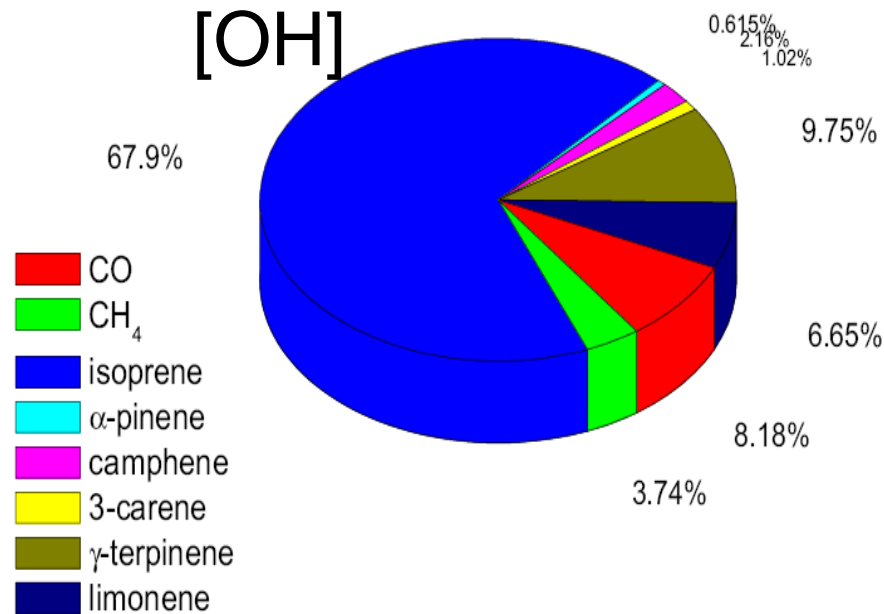
Field measurements

$12.46 \pm 0.15 \text{ s}^{-1}$

$18.59 \pm 0.21 \text{ s}^{-1}$

UK OP3 campaign, Borneo, 2008

Average diurnal for [OH] and OH reactivity (Dwayne Heard)



[OH] peaks before noon, K'_{OH} after noon (isoprene dominates)

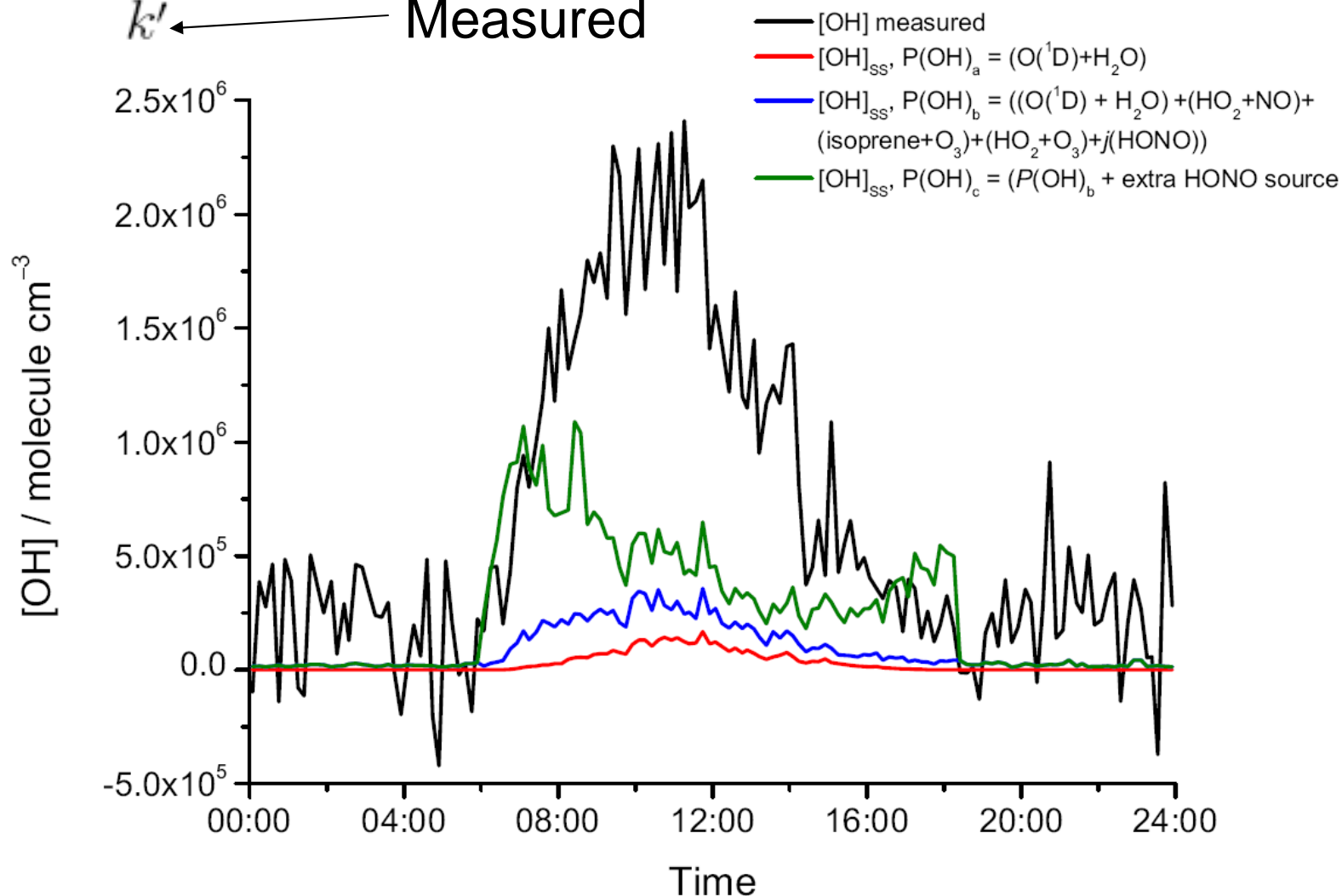
But - calculated reactivity gives a maximum only of $K' = 8.0 \text{ s}^{-1}$

Some OH sinks remain unmeasured – as seen in other forests

Using measured k'_{OH} to calculate [OH]

$$[\text{OH}]_{\text{ss}} = \frac{P(\text{OH})}{k'}$$

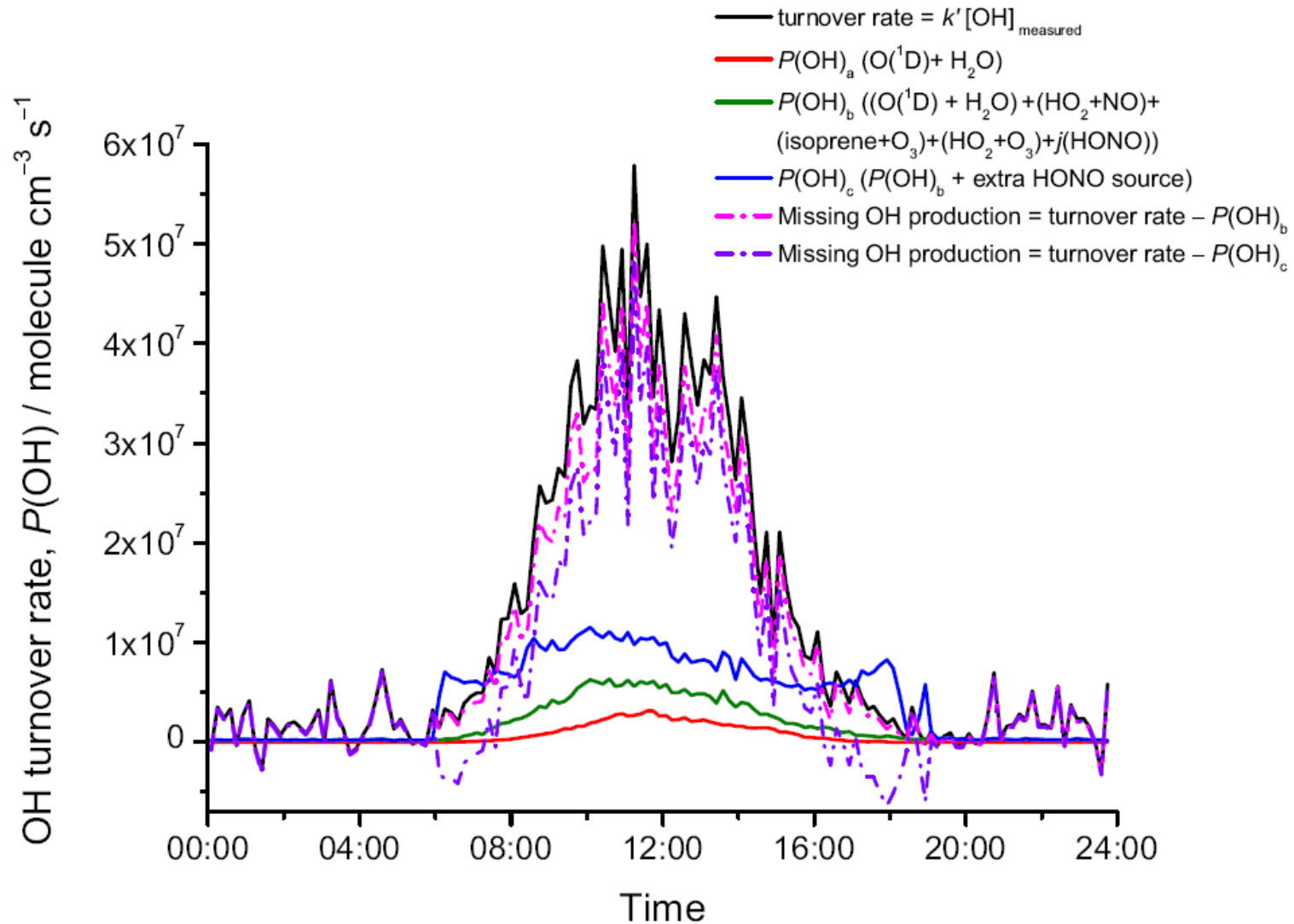
← Measured



Implies significant OH sources are missing

Using measured $[OH]$ and k'_{OH} to calculate a "measured" OH turnover rate

$$K_{OH} [OH] = L(OH) = P(OH) = \text{OH turnover rate}$$

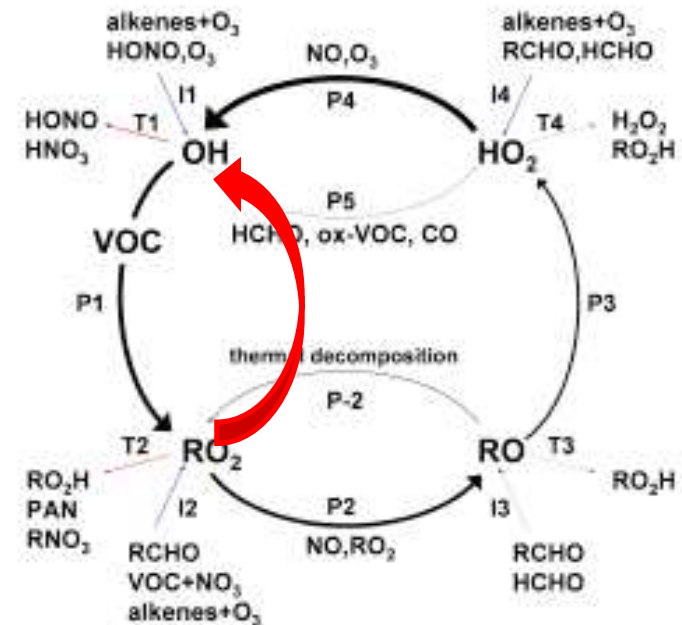


Aircraft measurements in Borneo

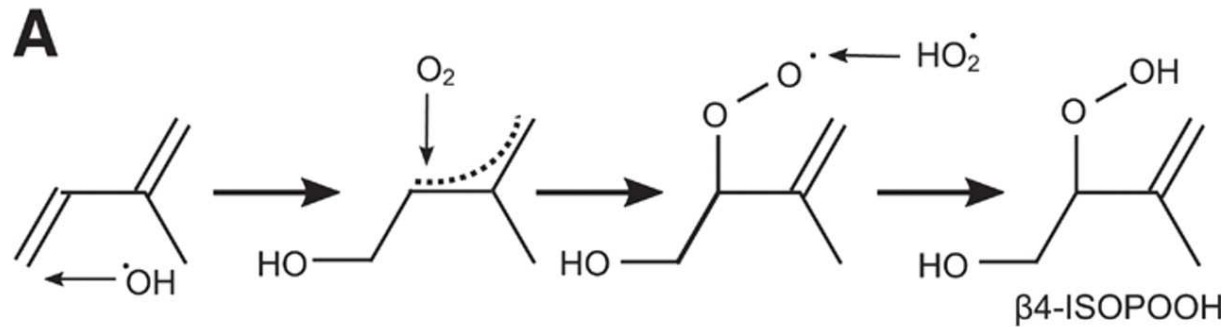
- No reactivity measurements. Detailed modelling of [OH] and [HO₂] using MCM by Mat Evans.
- Model constrained to measured concentrations of trace gases including VOCs
- Good agreement between measurements and model for [HO₂].
- Model considerably and consistently underestimates [OH].

Other possible sources of OH

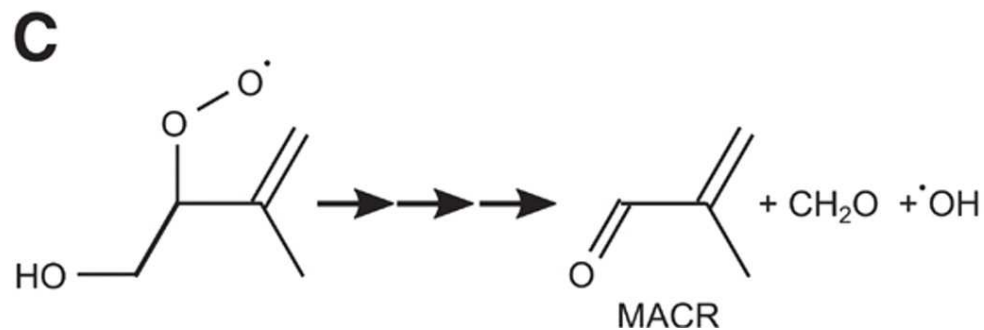
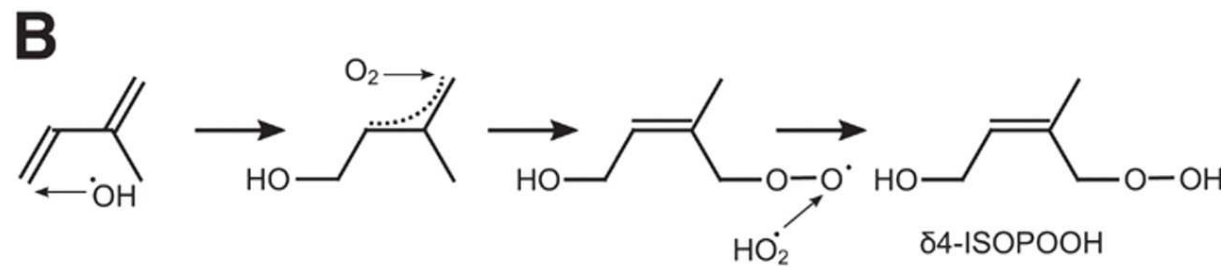
- The main requirement is to form OH without going through HO_2 , since that route is quantified through the measurement of $[\text{HO}_2]$ and NO.
- ? Unrecognised photolysis routes to OH
- $\text{RO}_2 \rightarrow \text{QOOH} \rightarrow \text{OH} + \text{product}$: the 'combustion route', via weak C-H and O-H bonds, c.f. reactions in ethers and acetylene.
- $\text{RC(O)O}_2 + \text{HO}_2 \rightarrow \text{OH}$. Recent experiments by Tyndall and Orlando show 100% OH yield from methacryloylperoxy + HO_2
- Both mechanisms less efficient at high NO_x



Examples of main reactions of peroxy radicals in early stages of isoprene oxidation in MCM



Low NO_x



High NO_x

HO_x radical regeneration in the oxidation of isoprene

Peeters et al., PCCP 2009

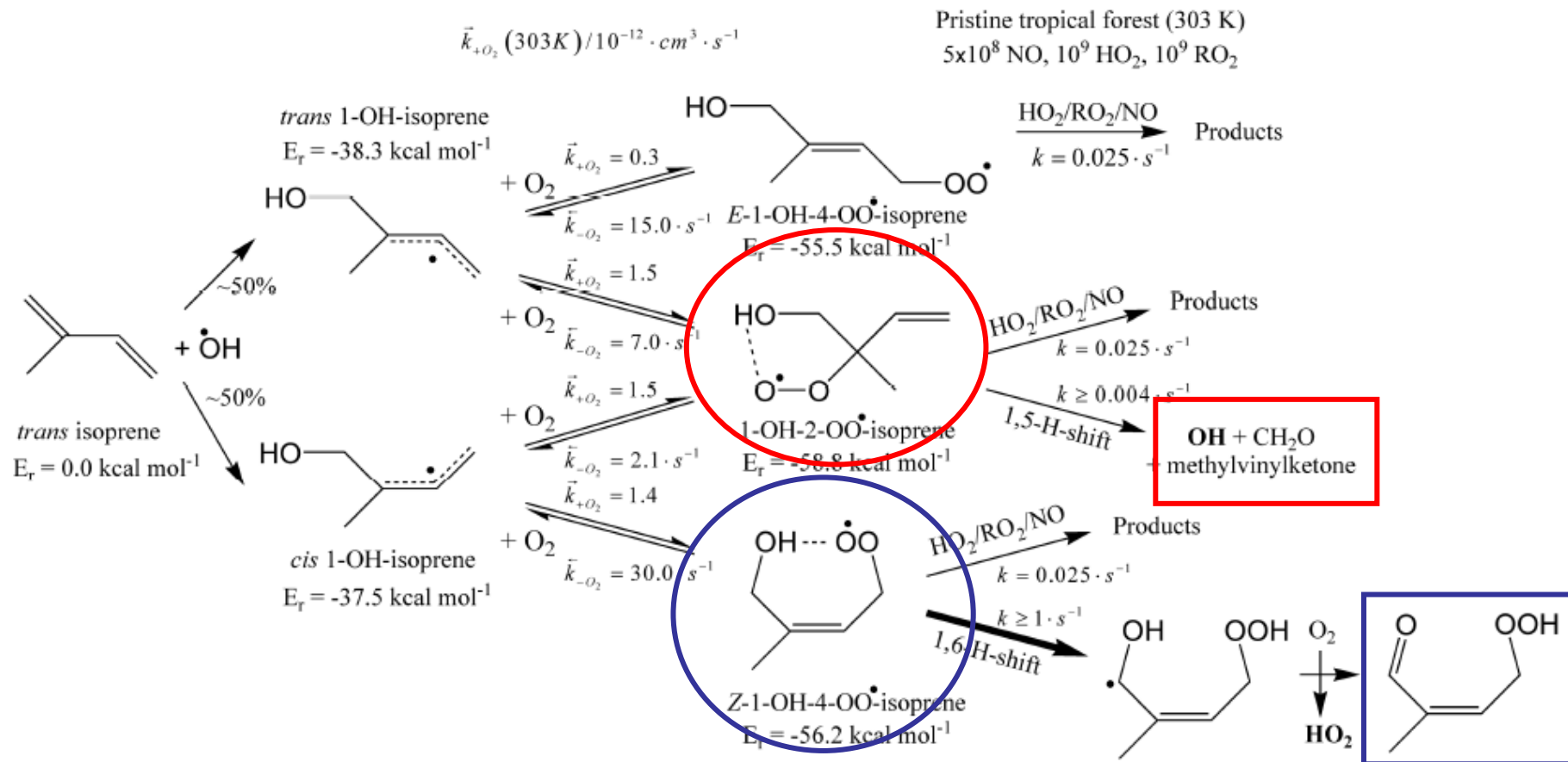
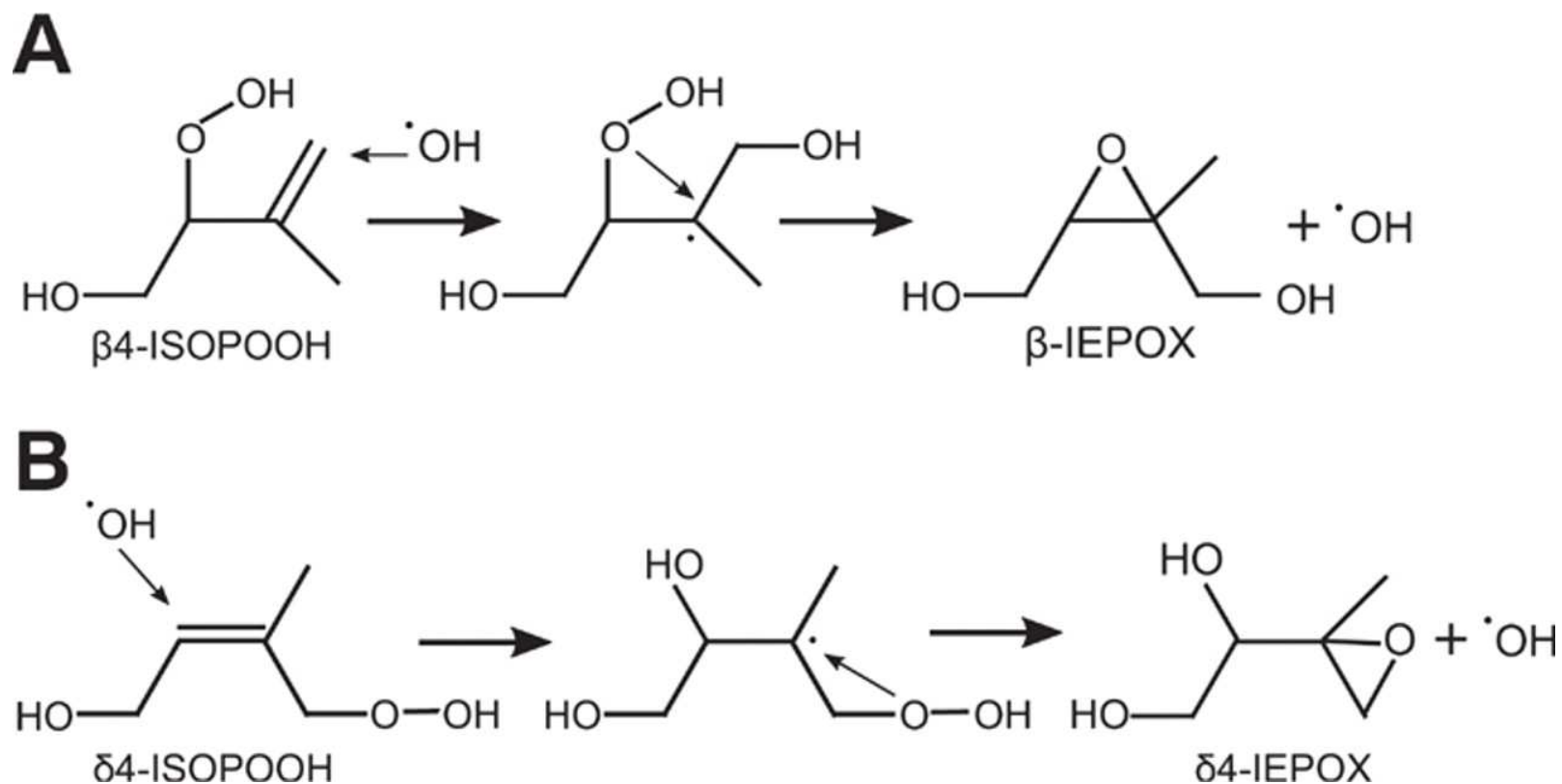


Fig. 1 Reaction scheme for OH and HO₂ radical formation following 1-OH addition to isoprene (60%), in pristine forest BL conditions, at 303 K. Note: to obtain the pseudo-first-order k'_{+O_2} , in these conditions, multiply the k_{+O_2} values listed by $5 \times 10^{18} \text{ cm}^{-3}$.

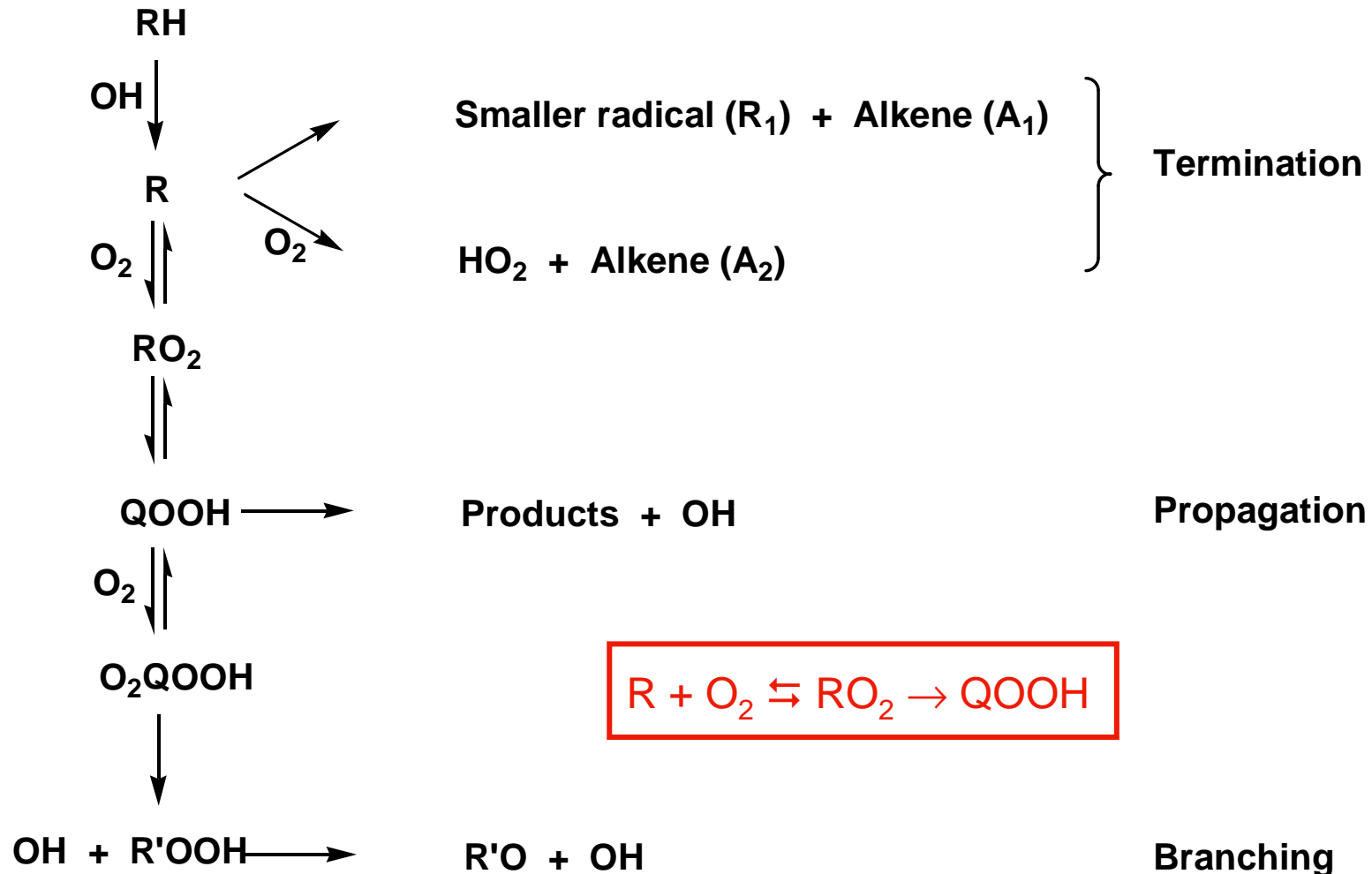
$k(\text{RO}_2 + \text{NO}) \sim k(\text{RO}_2 + \text{HO}_2) \sim 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. For $[\text{NO}] = 400 \text{ ppt}$, $k' \sim 0.1 \text{ s}^{-1}$
For $[\text{HO}_2] = 4 \text{ ppt}$, $k' \sim 10^{-3} \text{ s}^{-1}$.

Unexpected epoxide formation in the gas phase photooxidation of isoprene (Paulot et al. *Science*, 2009, 325, 730)



Evidence for peroxy radical isomerisation

Autoignition chemistry



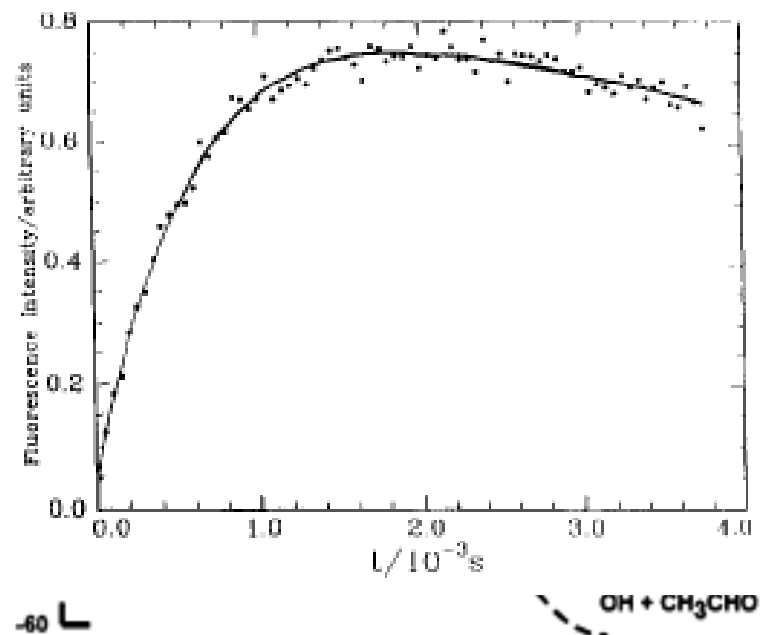
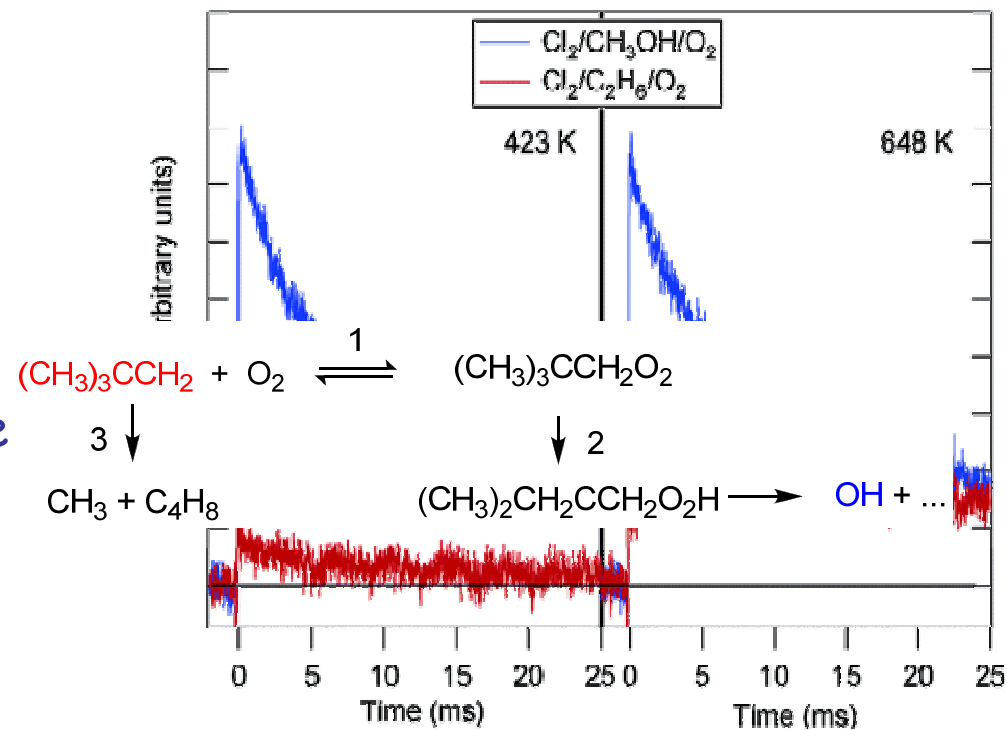
- R.W.Walker and C. Morley, in *Low-Temperature Combustion and Autoignition*; M.J. Pilling, Ed.; 1997; p 1



- Taatjes and coworkers:¹ Observed the formation of OH and HO₂, determining the fractional yields.
- HO₂ yield ↑ as T ↑ and p ↓
- Two timescales at higher T
- OH yield is small.
- Miller and Klippenstein² (ME calcs): 'formally direct' route to HO₂
- $\text{C}_2\text{H}_5 + \text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{O}_2^* \rightarrow \text{C}_2\text{H}_4 + \text{HO}_2$
- For higher alkanes, e.g. neopentane, OH formation is important

¹ J. Phys. Chem. A 104 (2000) 11549 - 11560

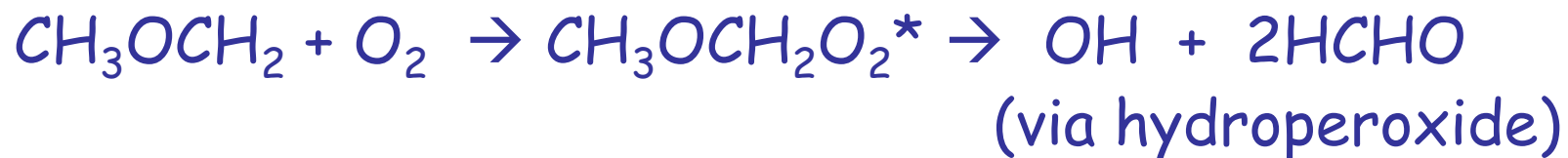
² Int. J. Chem. Kinet. 33 (2001) 654 - 668.



Can such reactions occur at room temperature?

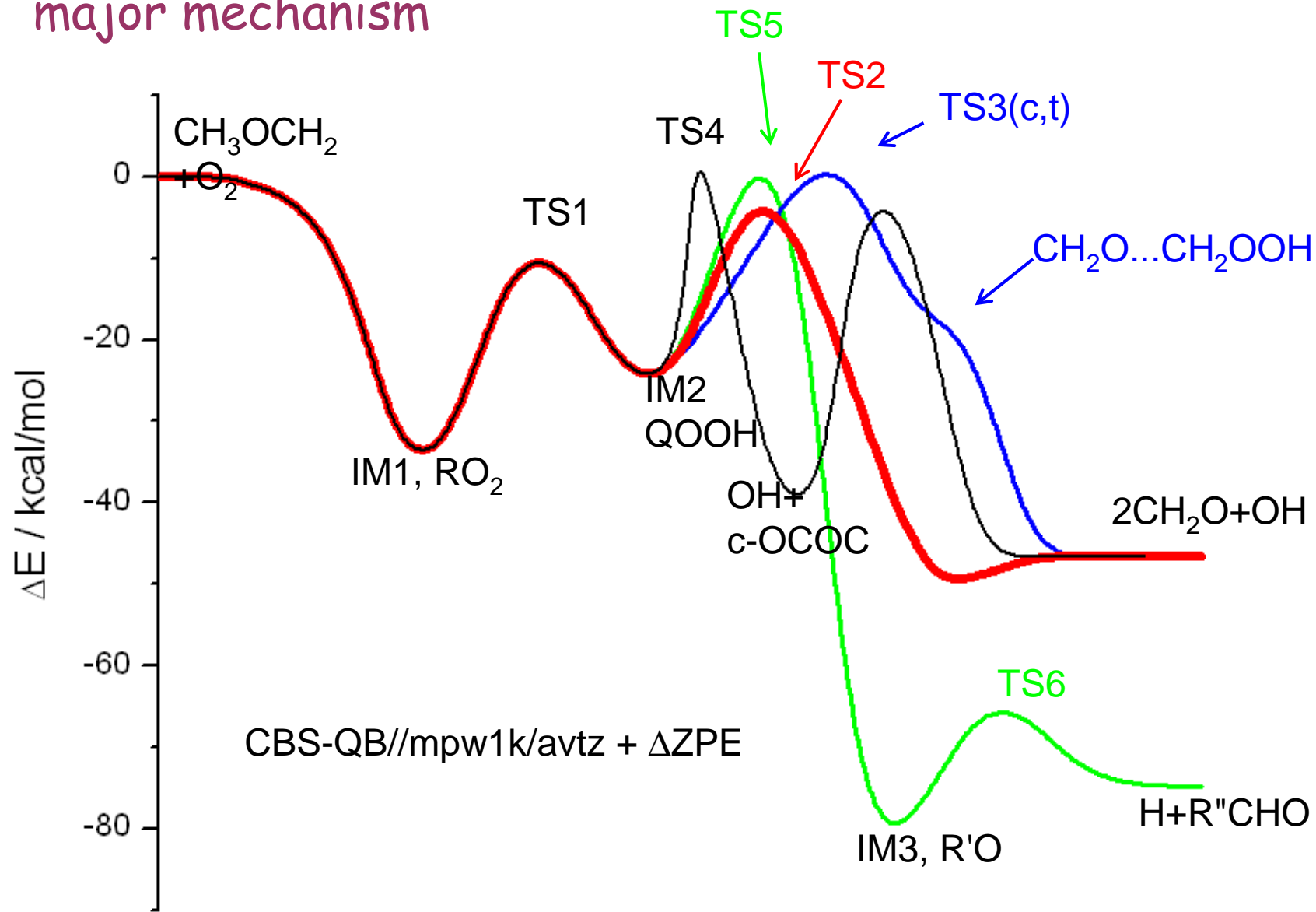
Mechanism of OH formation from $\text{CH}_3\text{OCH}_2 + \text{O}_2$

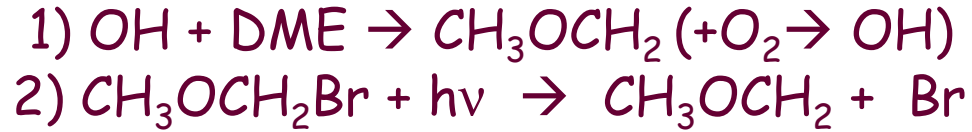
- Chemically activated route ('formally direct'):



- Occurs at room temperature
- OH formation is suppressed as the pressure increases and so this route to OH is not atmospherically significant.
- Example of chemically activated peroxy OH formation that is suppressed in favour of stabilised RO_2 formation as the pressure increases

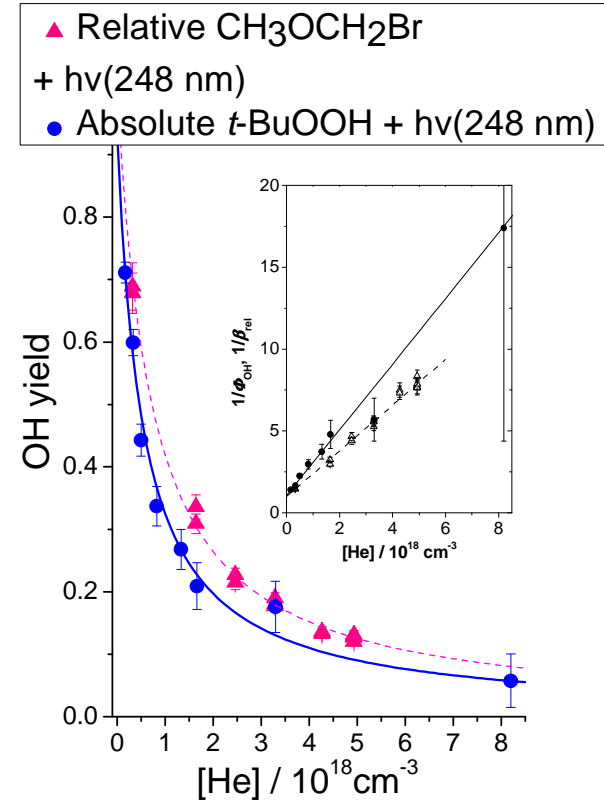
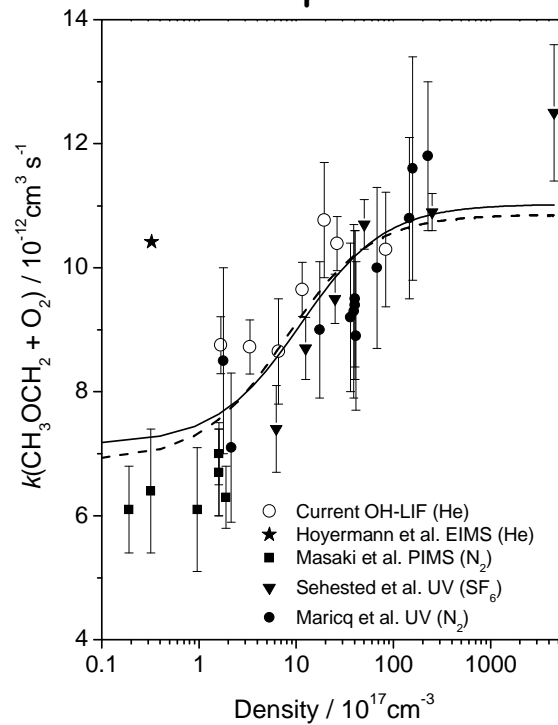
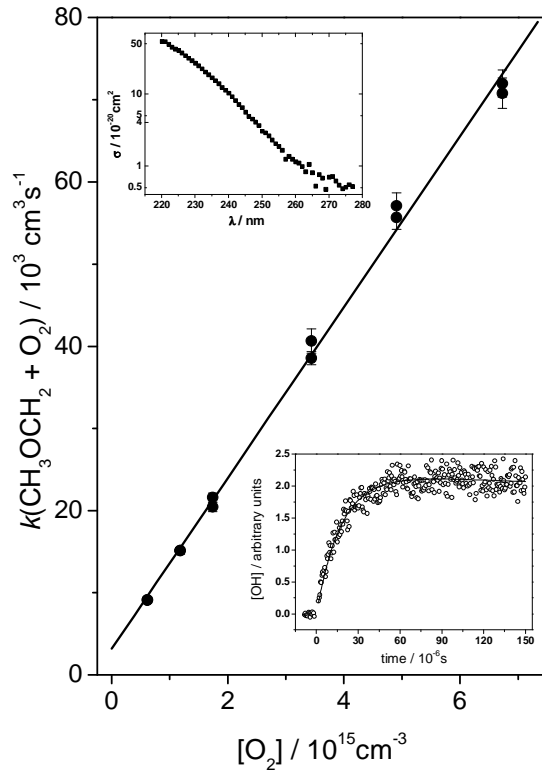
$\text{CH}_3\text{OCH}_2 + \text{O}_2$
major mechanism





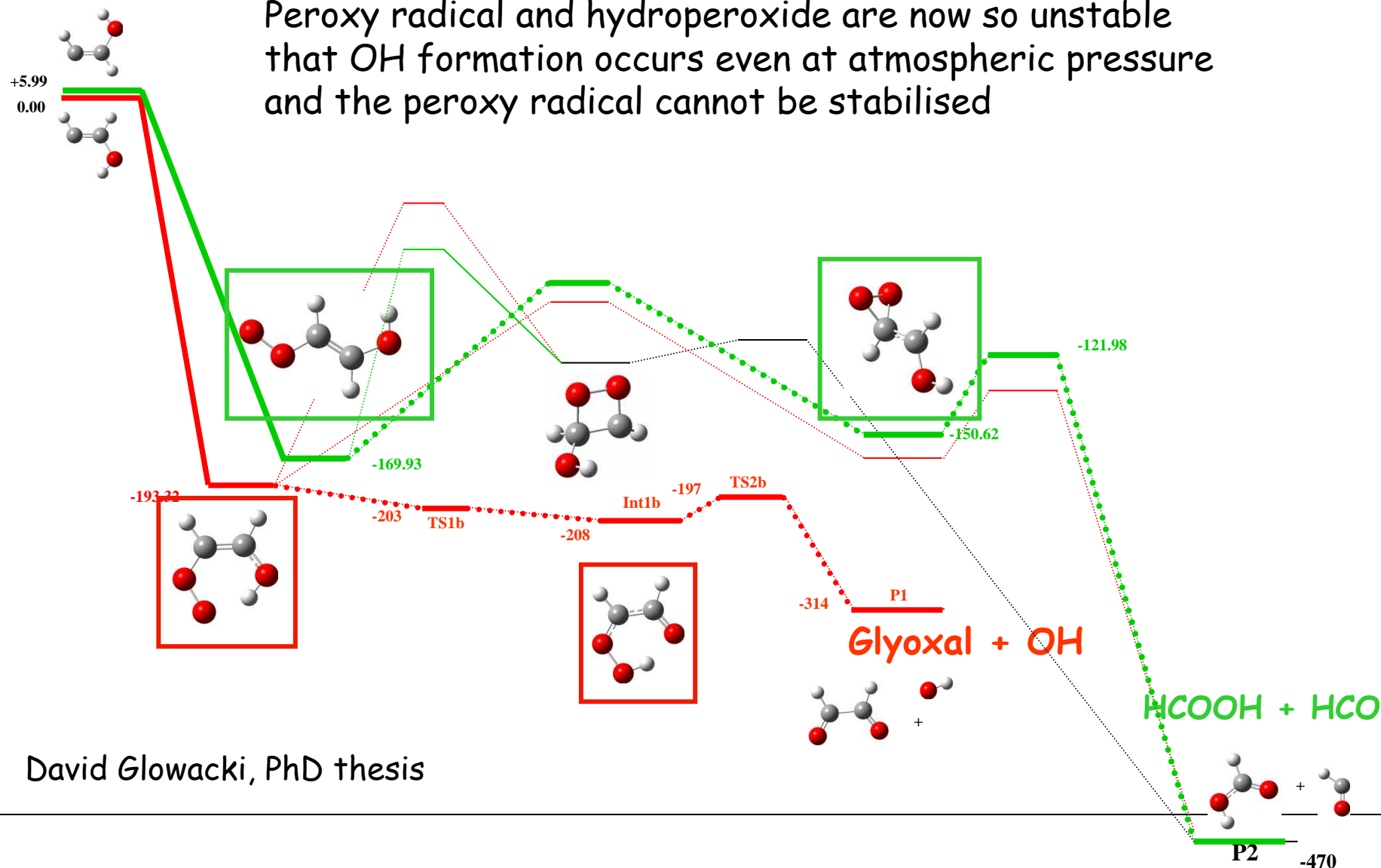
Observe kinetics and Mechanism using OH LIF:

- 1) Apparent rate coefficient decreases on O_2 addition
- 2) Observe OH on addition of O_2 Yield decreases as p increases





Peroxy radical and hydroperoxide are now so unstable that OH formation occurs even at atmospheric pressure and the peroxy radical cannot be stabilised



David Glowacki, PhD thesis

Conclusions

- Chemically activated ('formally direct') isomerization and dissociation in $R + O_2$ reactions known for several systems. Some are atmospherically significant - how widespread are such reactions?
- Thermally activated $RO_2 \rightarrow QOOH \rightarrow OH +$ co-product may be significant in unsaturated systems, with low C-H and O-H bond energies. Such reactions may occur at low NO_x in preference to $RO_2 + H/RO_2$ reactions and provide a route to OH from RO_2 . Evidence derives indirectly from field measurements and from electronic structure calculations.
- Need experimental verification via lab / chamber experiments on a range of timescales (ms - s - h): pulsed photolysis; slow flow / stirred reactor; chamber
- Care needed in design and interpretation.

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