



Biomass Burning Combustion of N containing Species

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1. Introduction

1. Natural/anthropogenic crop/forest burning
2. Controlled biomass burning for heat and power

2. Pollutant formation – Amines – RNH_2

3. Contrast between carbon only and carbon/nitrogen combustion mechanisms – Amides – $\text{R}-\text{C}(\text{O})\text{NH}_2$

4. Conclusions and Outlook

1. Introduction



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Plant or forest burning



- Natural or manmade
- Flaming or smouldering
- Air Quality Issues
- Climate Change Issues

Biomass Burning for Power



- Good or bad for climate and air quality?

1. Controlled Biomass Burning for Power



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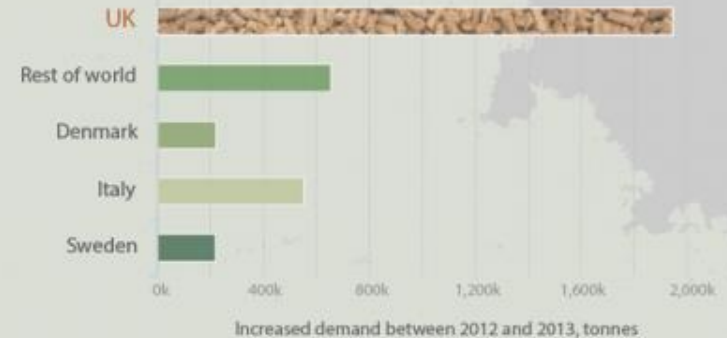
The US is the world's largest exporter of wood pellets



The UK is the largest wood pellet importer



The UK is driving increased demand for pellets



Drax says 80% of its wood pellets come from these sources



Drax is the largest power station user of wood pellets in the UK



BIOMASS IN BRITAIN

Sources: FAOSTAT, Ofgem, Drax bit.ly/biomassinbritain

1. Good or Bad for Climate?



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- Primarily depends on the origin of the wood
- Waste wood and 'forest residue' low emission or even negative (decay in forest environment leads to methane)
- Mature wood is a better sink for carbon
- Land use change can impose a huge carbon debt that can take decades to repay.
- As with biofuels, it may be worth working with lower efficiency to encourage development and infrastructure for the future. CCS?
- Talk from Drax 4 pm 12th June.

1. Wildfires – Flaming vs Smouldering



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Flaming vs Smouldering



Emissions Relative to CO₂

Emission	Flaming	Smouldering
CO ₂	63	37
CO	16	84
CH ₄	27	73
VOCs	33	67

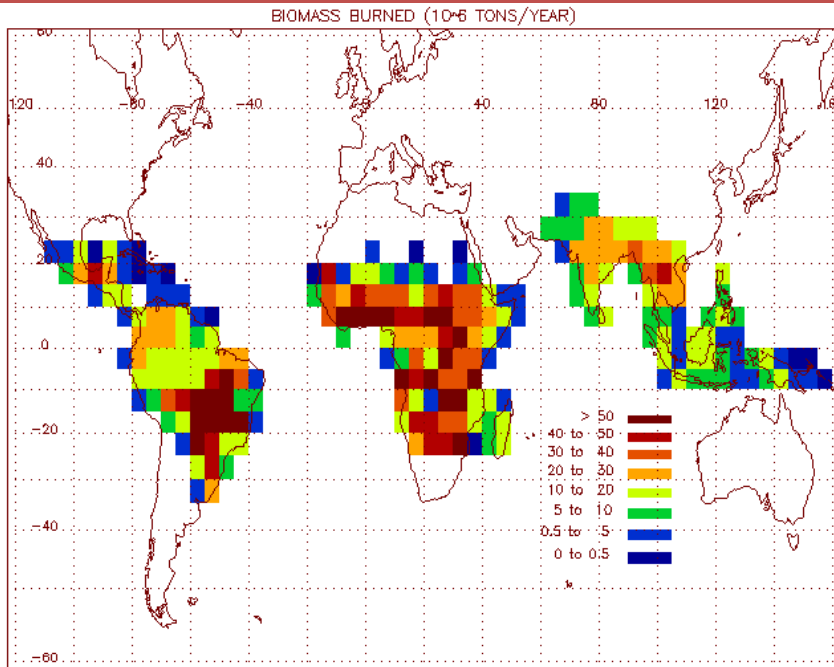
Emission	Flaming	Smouldering
CO ₂	100	100
CO	6.7	12.1
CH ₄	0.64	1.2
VOCs	0.66	1.08

Typically smouldering phase lasts longer

1. Distribution and Role of Biomass Burning



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- 18% of CO₂ Emissions
- 6- 15% of CH₄
- ~30% CO
- ~20% NO_x
- 24% NMHC (ex isoprene)
- 86% elemental carbon
- N₂O
- 5 – 10% of worldwide Air Quality mortalities

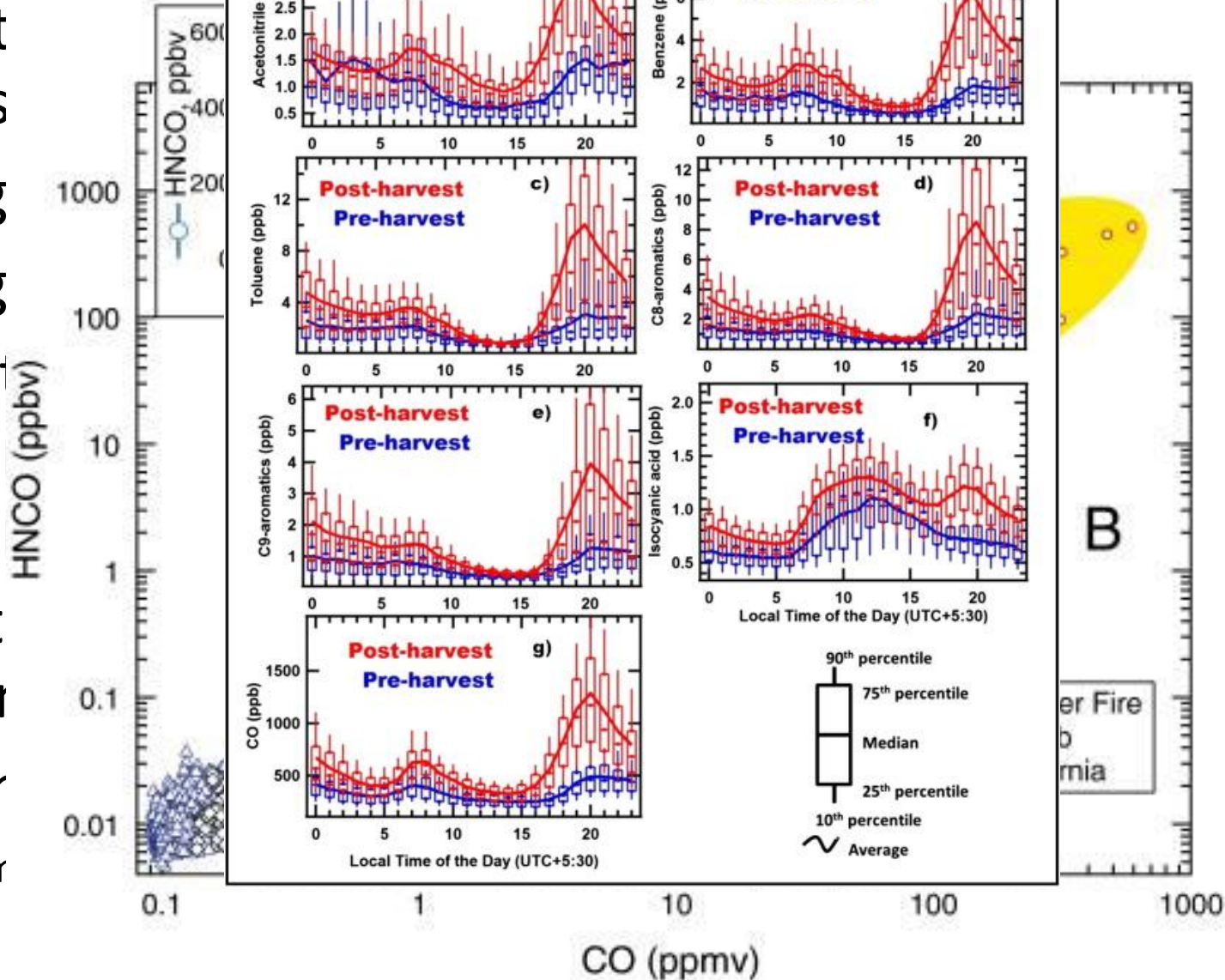


1. Nitrogen and Biomass Burning



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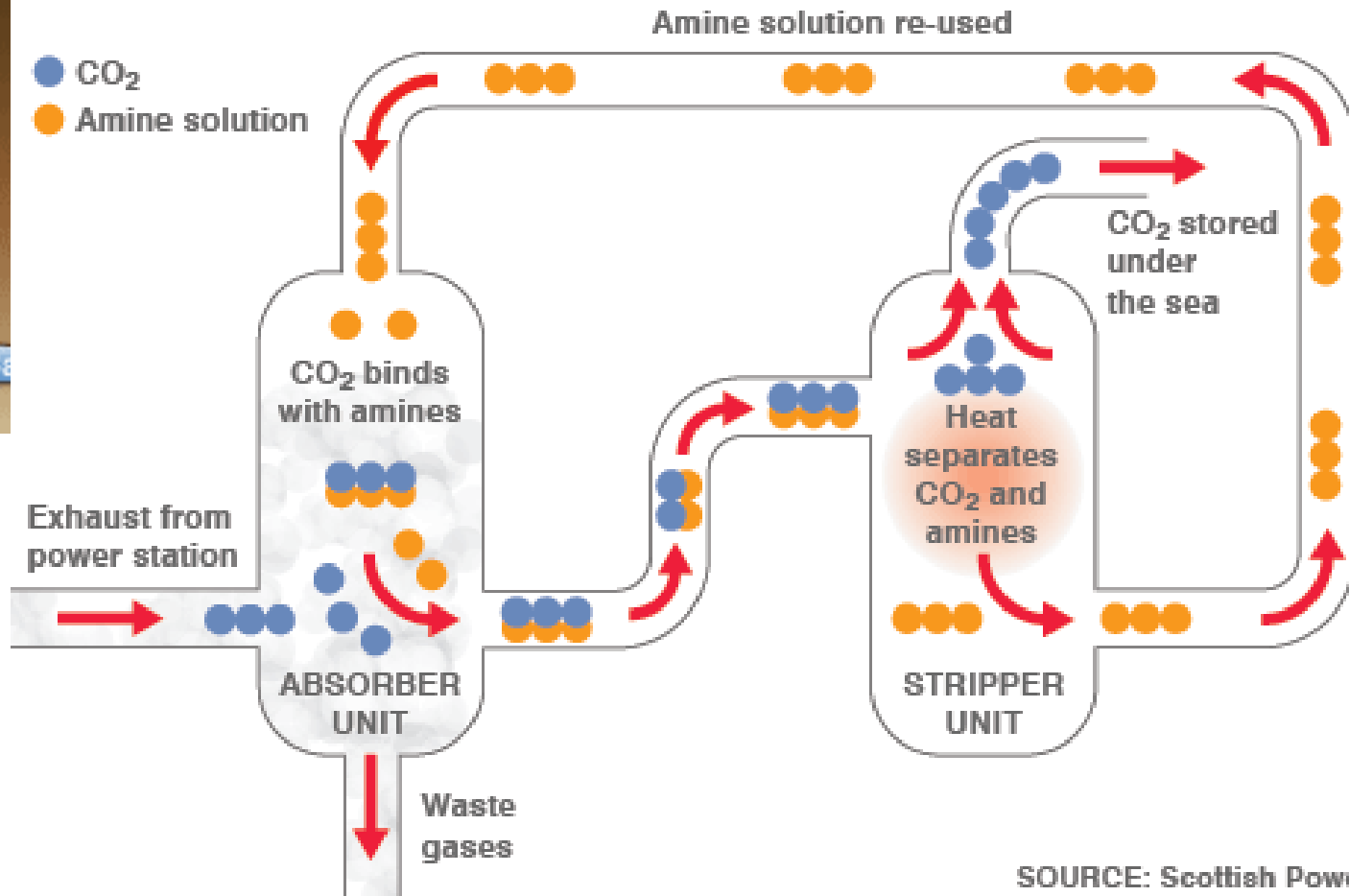
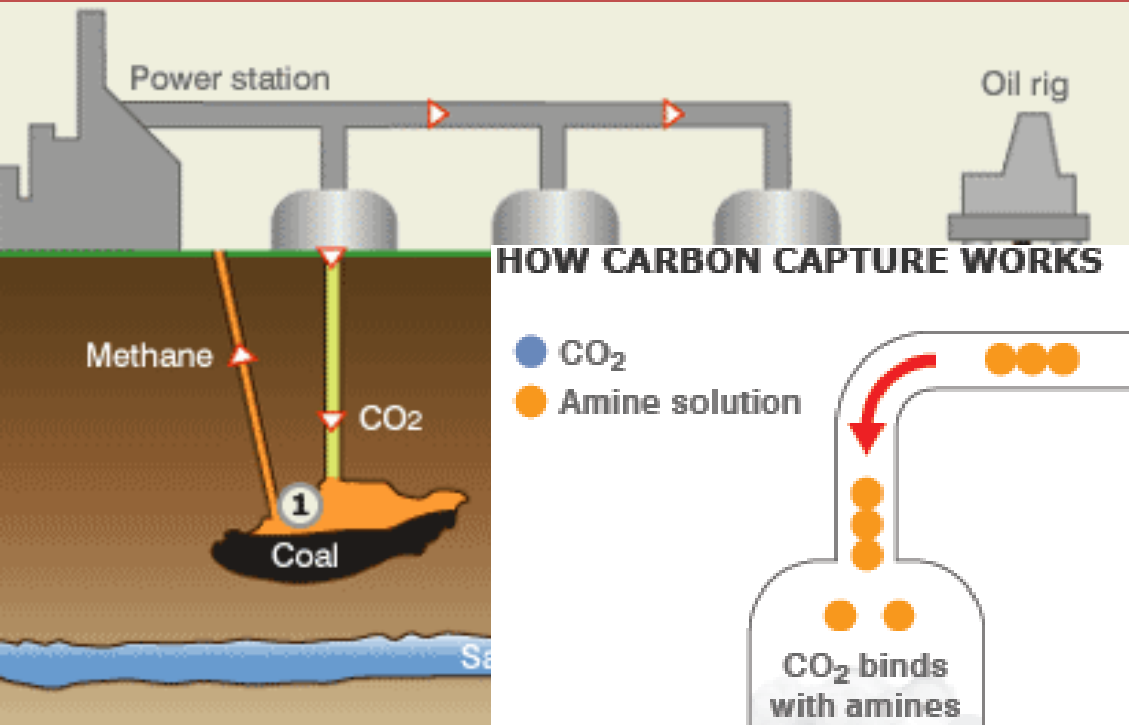
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2. AMINE CHEMISTRY AND POLLUTANT FORMATION

Methylamine – CH_3NH_2

2. Principles of CCS



2. Questions to address



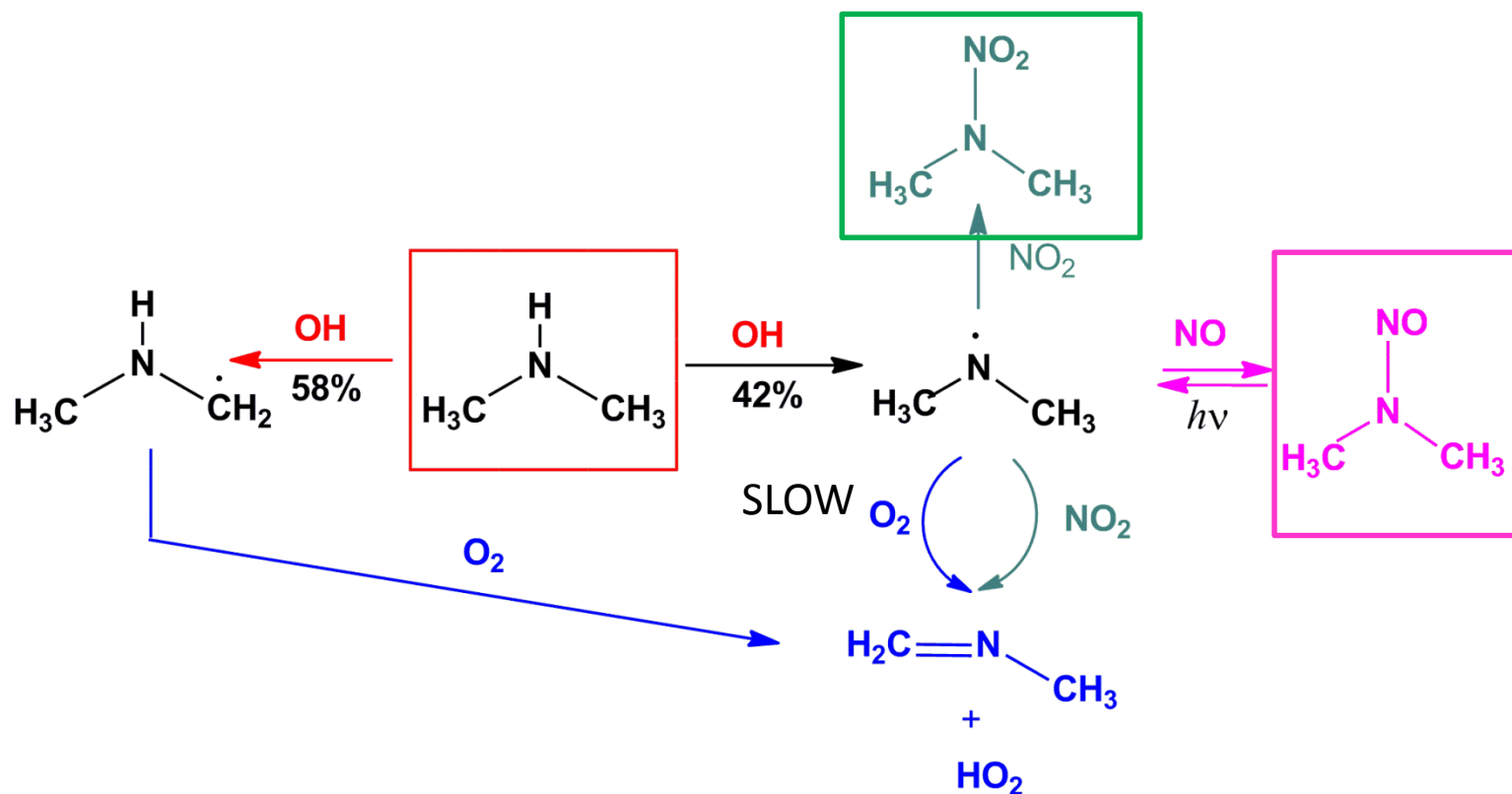
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- In the atmosphere amines will be removed by reaction with the OH radical
 - $\text{OH} + \text{HOCH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{H}_2\text{O} + \text{product}$
- Do amines react preferentially in the gas phase with OH or via uptake into water?
- What is the mechanism of amine oxidation?
- What is the potential for formation of toxic products? Requires knowledge of initial OH abstraction site.

2. Oxidation of dimethylamine (DMA)



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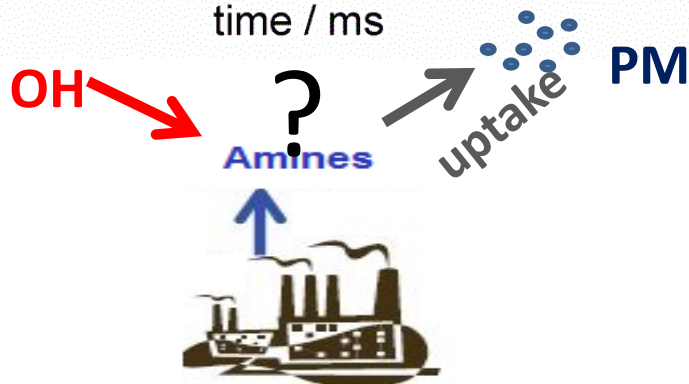
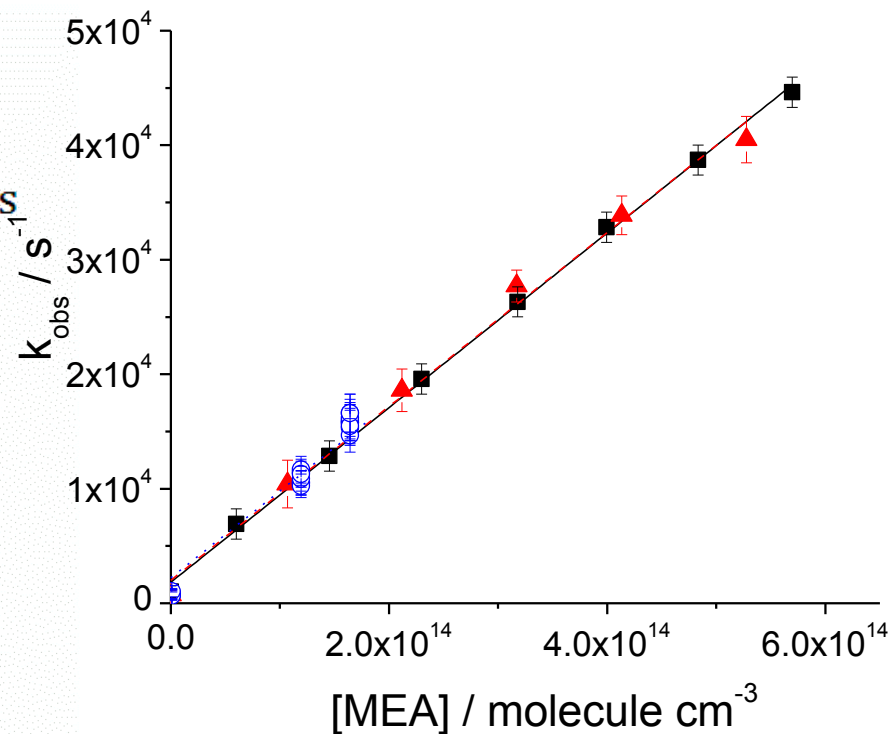
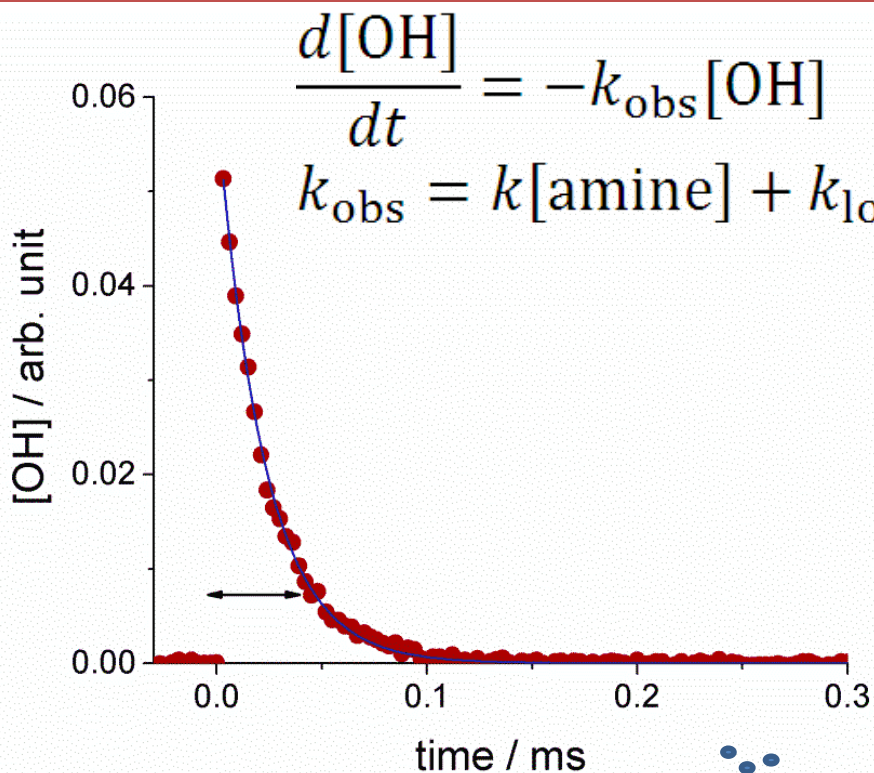


adapted from
Nielsen, Herrmann and Weller
Chem. Soc. Rev **2012**

2. OH + MEA (monoethanolamine)



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$$k = (7.59 \pm 0.31) 10^{-11} \text{ s}^{-1} \text{ cm}^{-3}$$

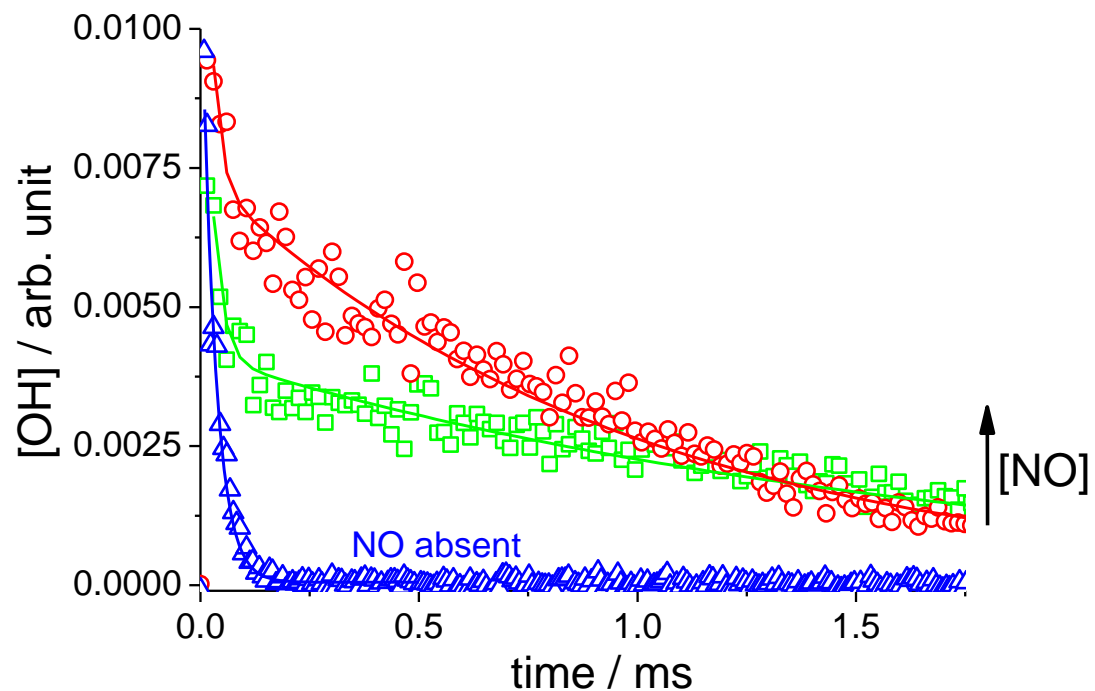
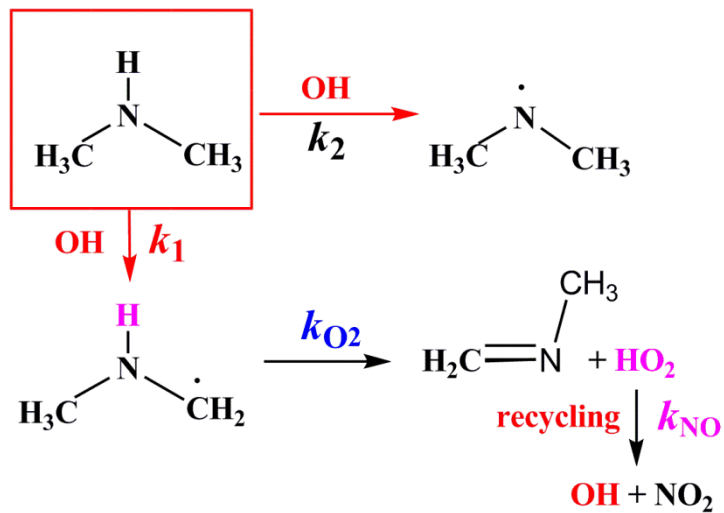
Fast!

Gas phase oxidation **will** compete with aerosol uptake

2. Dimethylamine (DMA) + OH + O₂ + NO



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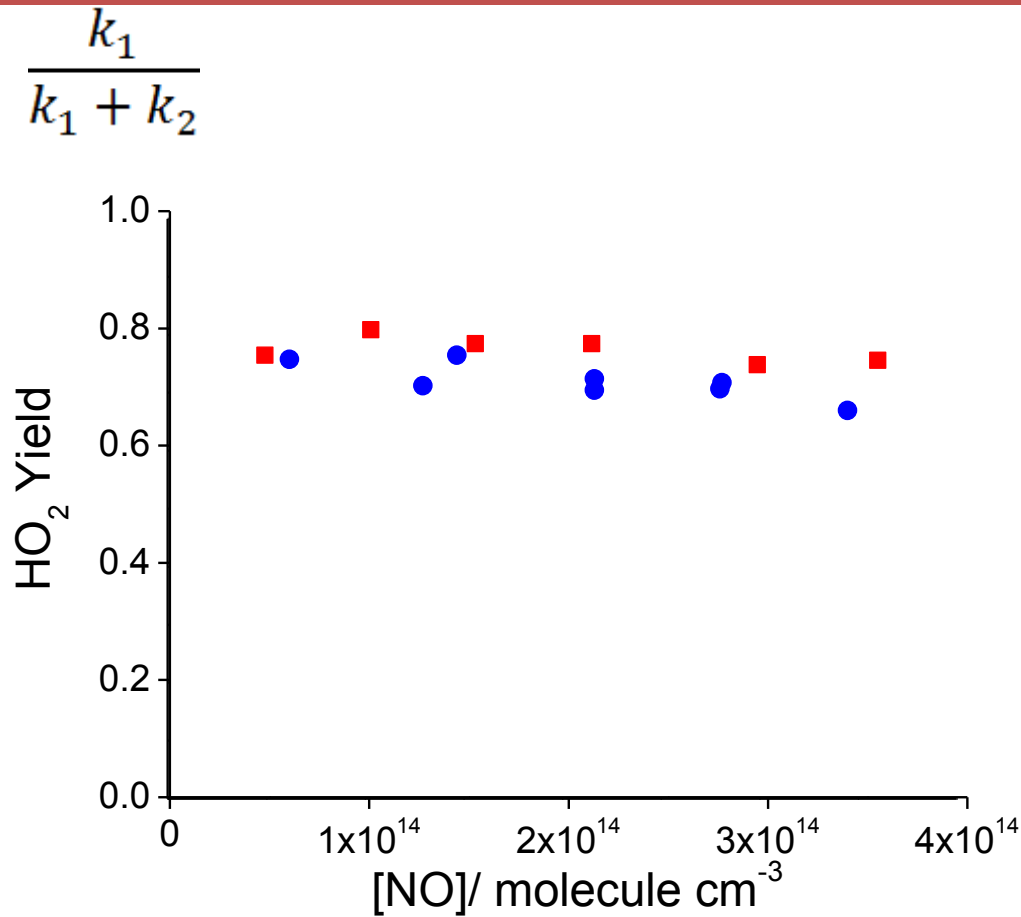


$$\text{HO}_2 \text{ Yield} = \frac{k_1}{k_1 + k_2} = (73 \pm 5)\%$$

2. DMA/MA + OH + O₂ + NO

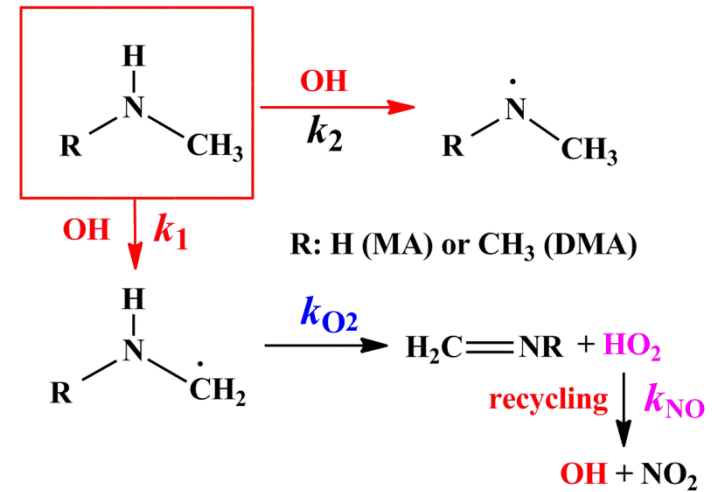


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(80 ± 5) % MA

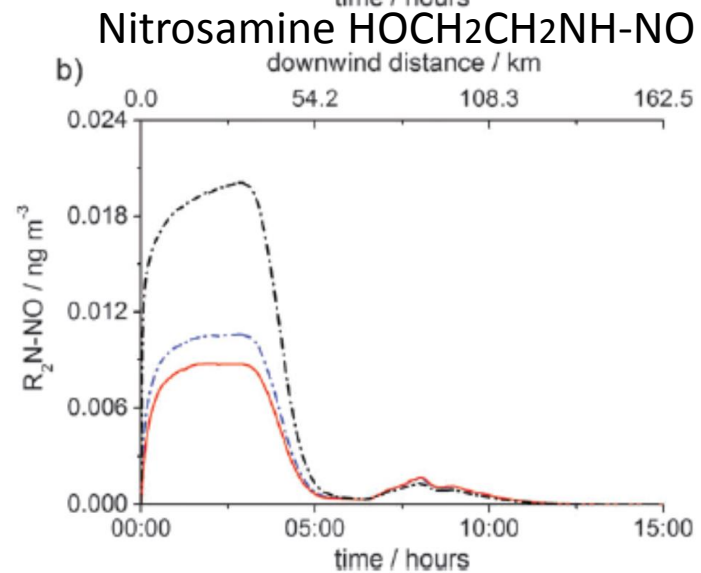
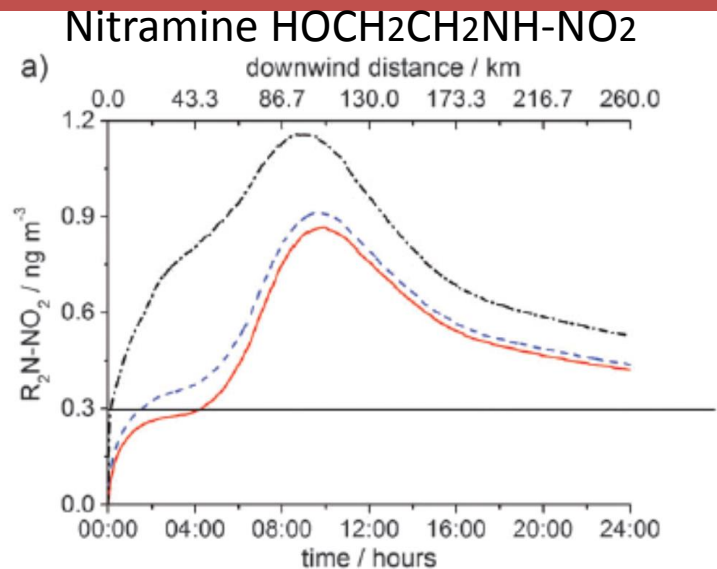
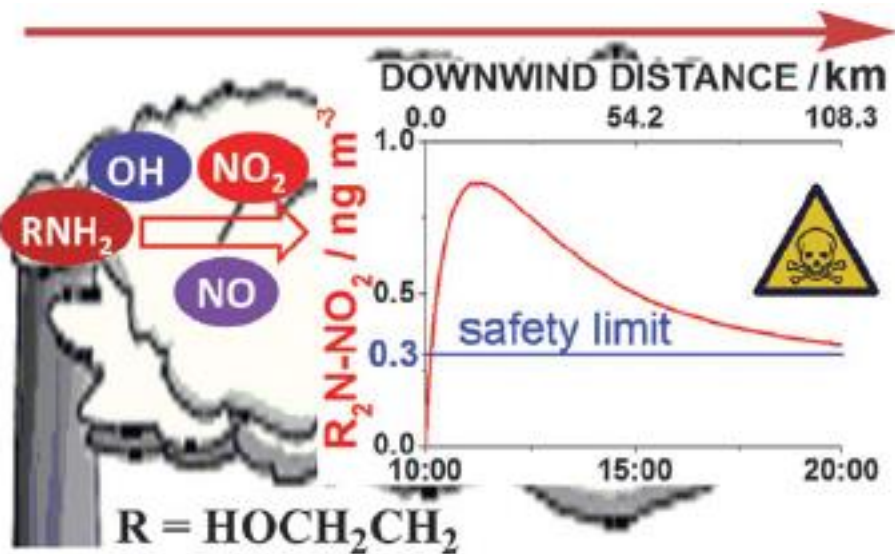
(73 ± 5) % DMA



2. Pollutants downwind from a power plant



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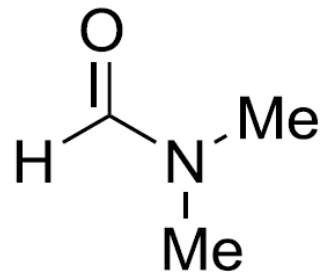


2. Summary

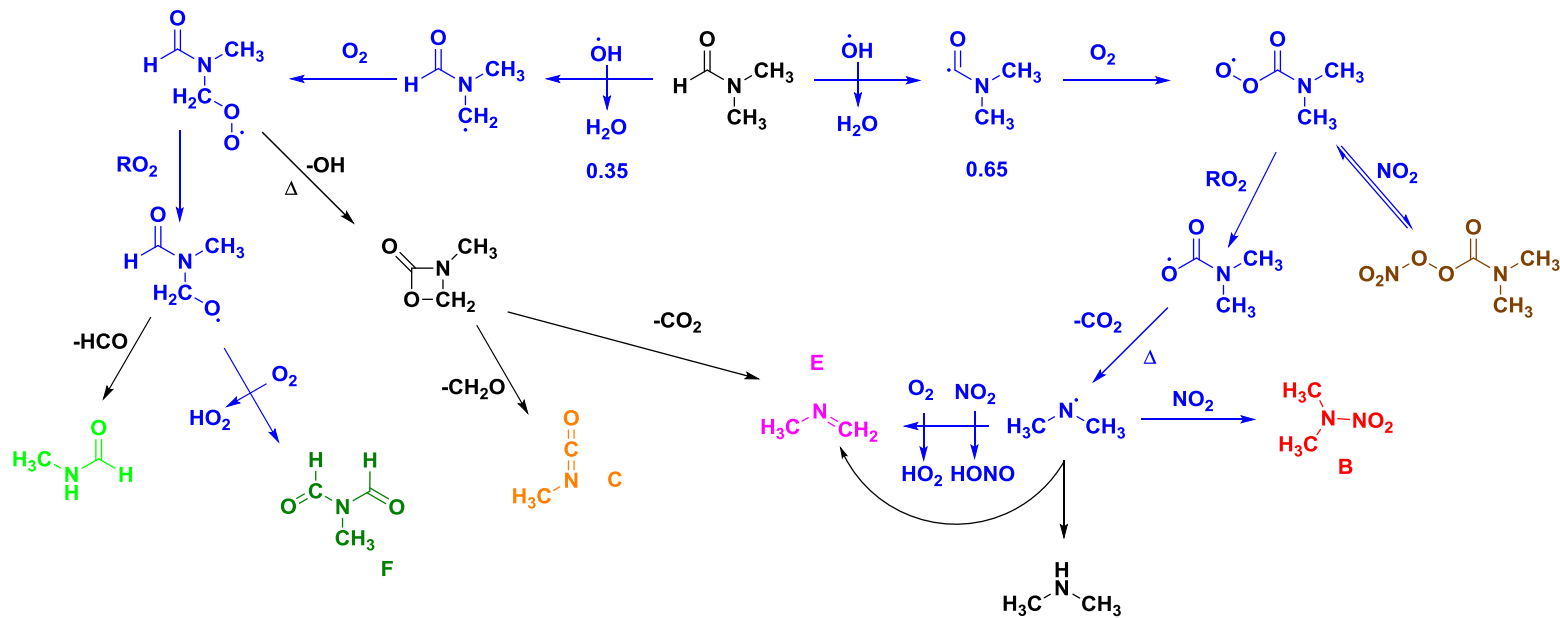


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- Amines react rapidly in the gas phase. Gas phase processing will compete with heterogeneous uptake.
- For simple amines, abstraction at the C-H grouping dominates. Needs to be studied as a function of temperature.
- Despite not being the dominant route, sufficient N-H abstraction occurs for nitramine levels to be significant.



3. COMBUSTION CHEMISTRY OF AMIDES

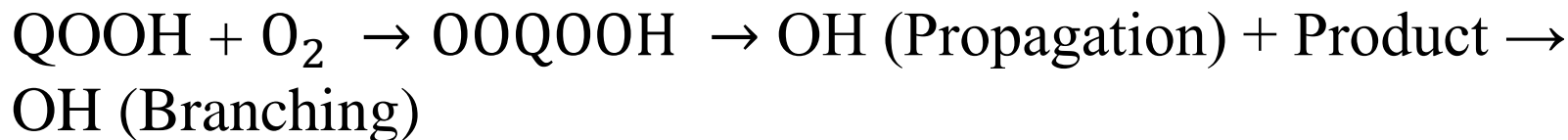
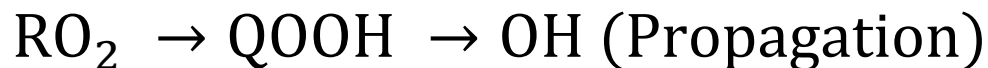
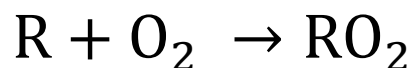
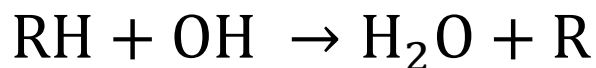


3. Introduction – Chain Branching mechanism



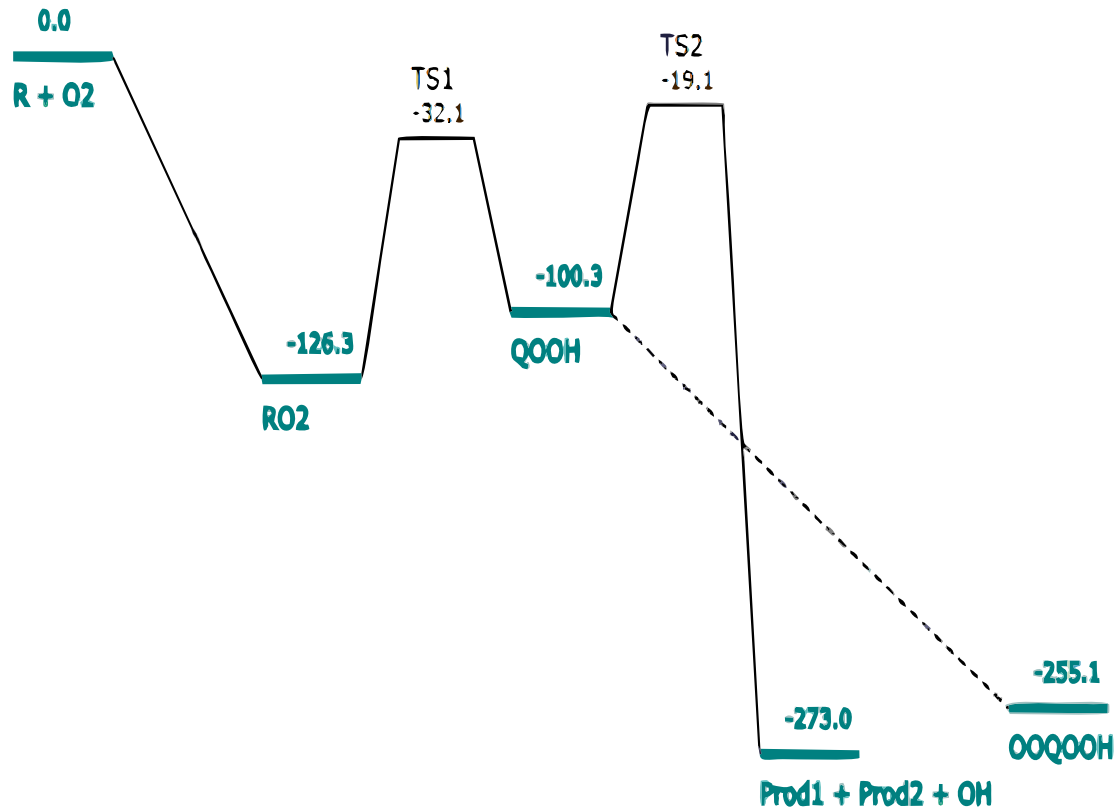
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- Some stabilised QOOH species have been observed.
- Stable QOOH tend to be less reactive towards O_2 addition.





3. Standard PES

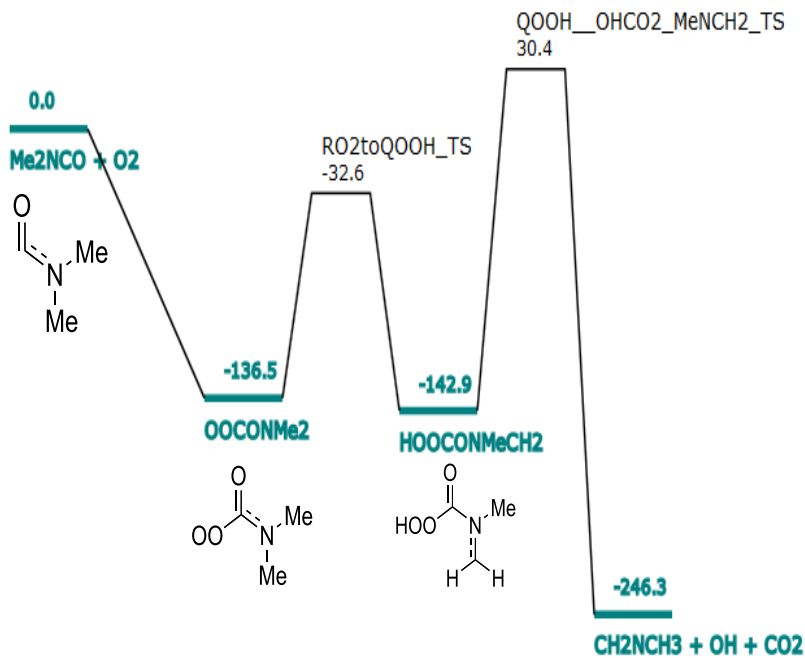


Energies in kJ/mol

- QOOH higher in energy than RO₂
- Barrier to Isomerisation and barrier to OH below entrance energy.
- Low population of QOOH well.
- Competition between QOOH fragmenting to give OH and being intercepted by O₂ to form OOQOOH.



3. DMF PES



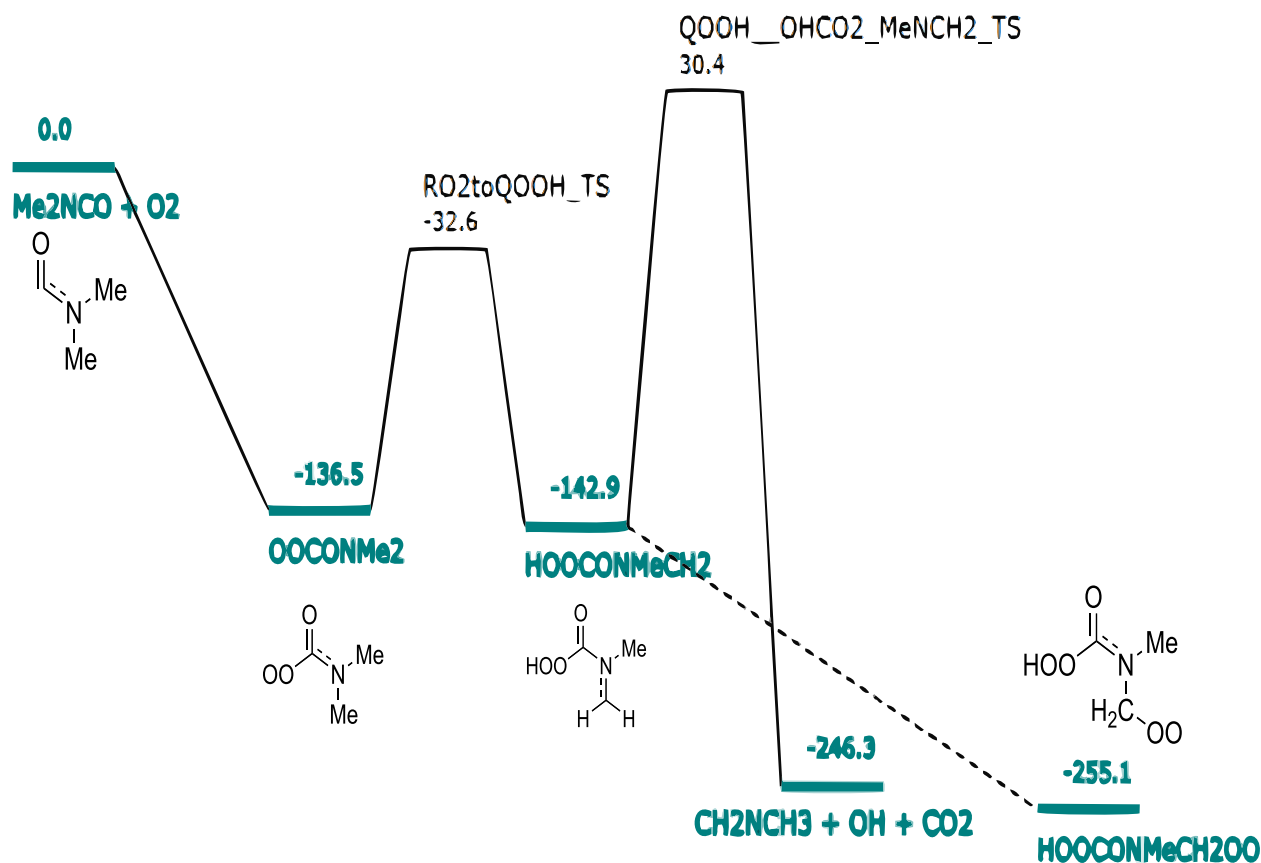
Energies in kJ/mol

- QOOH lower in energy than RO₂
- Barrier to isomerisation below entrance energy.
- Allows for QOOH well to be readily populated at elevated temperatures.
- Barrier to OH well above entrance energy - not a route out to OH.
- Competition between R fragmentation and oxygen interception.

3. DMF PES



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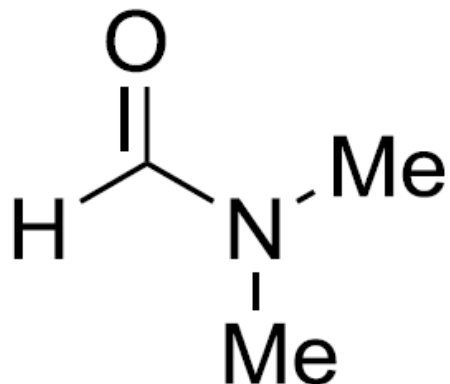


Energies in kJ/mol

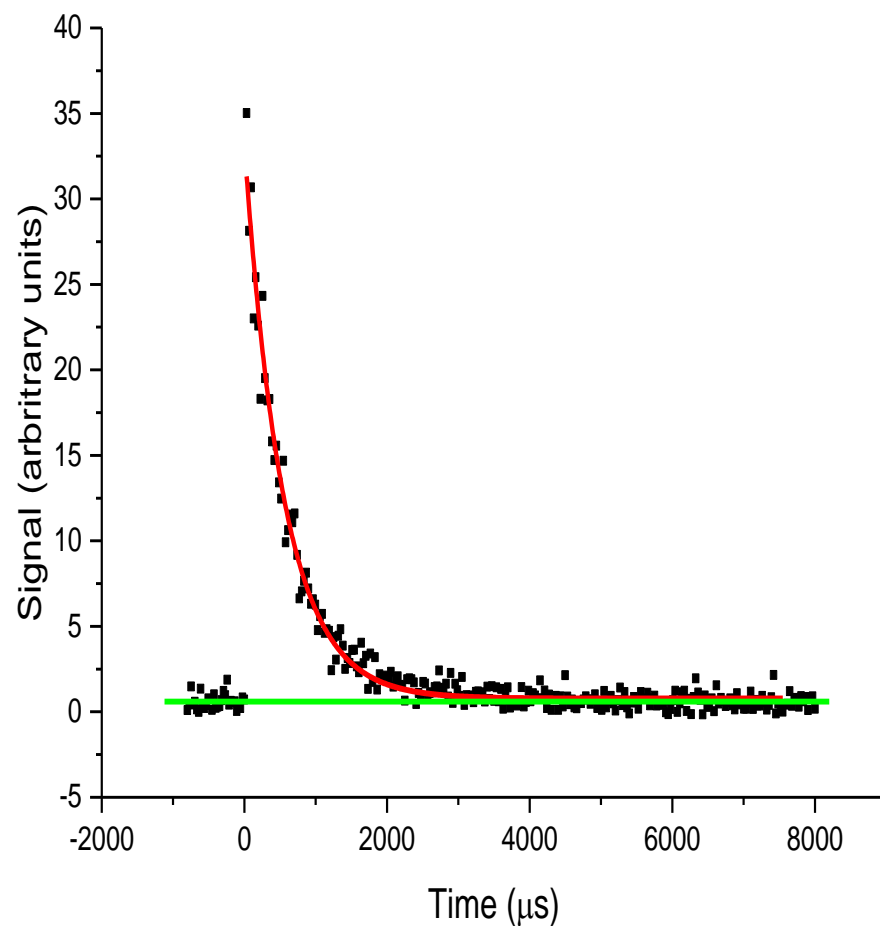
Implications for DMF OH oxidation are:

- At low temperatures RO_2 chemistry will dominate.
- At low temperatures we will generate single exponential traces for the loss of OH.
- At elevated temperatures OH regeneration is not the product of QOOH fragmentation.
- Another route is required to OH.

3. Room Temperature decay



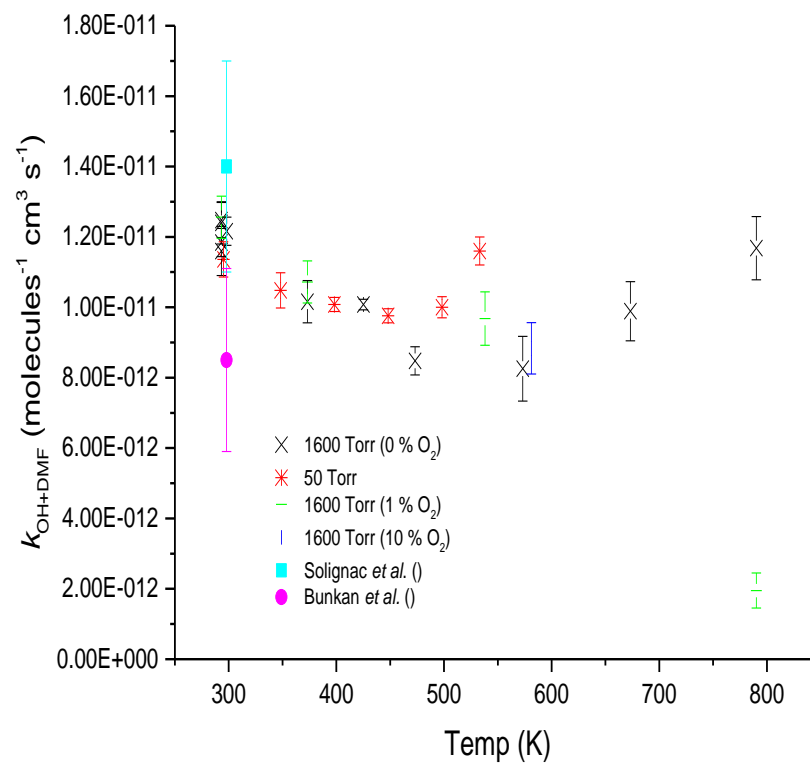
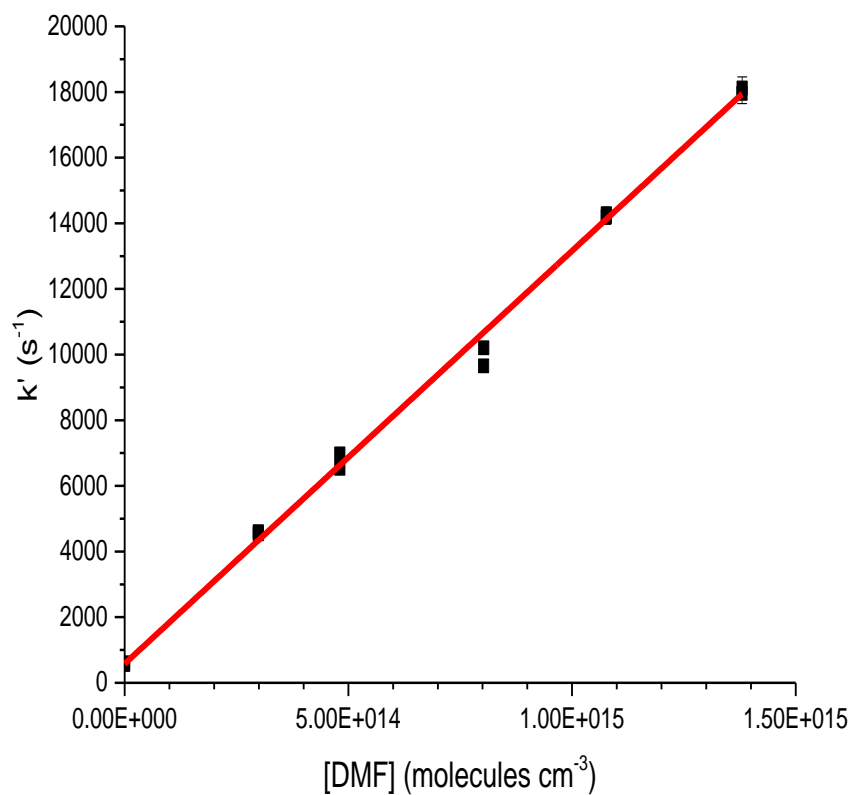
- Good fits for single exponential loss with traces returning to the pre-trigger baseline.
- Photolysis of the RO₂ is not responsible for OH regeneration seen later.



3. Room temperature Oxidation



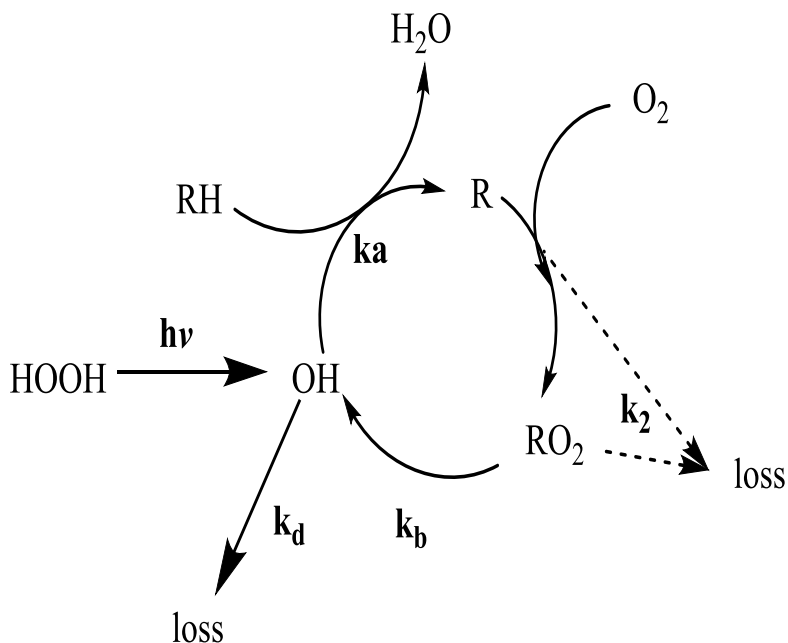
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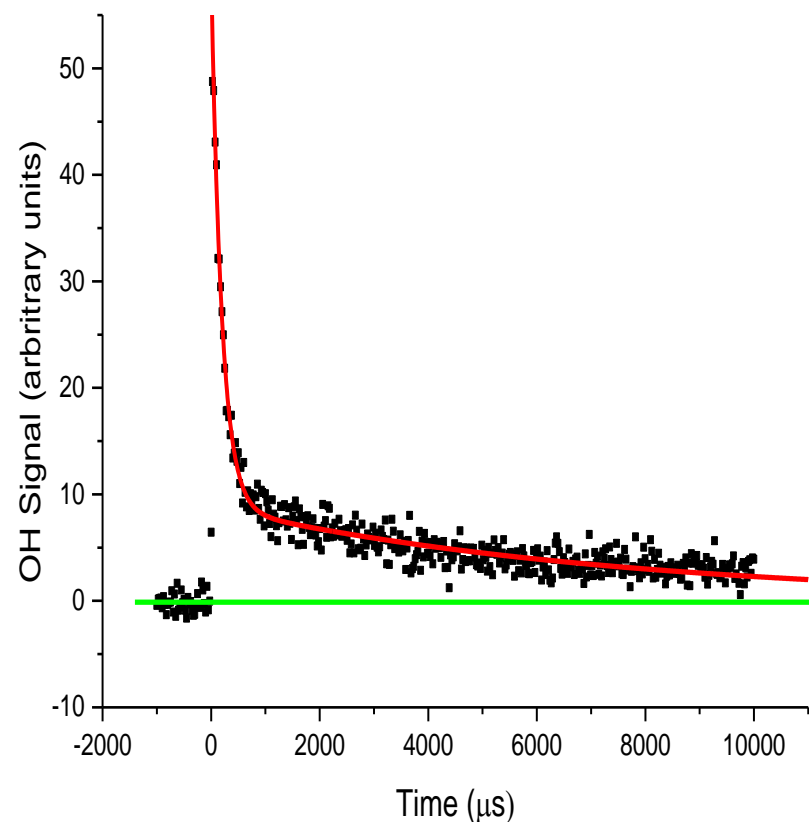
3. OH recycling kinetics



- We recover biexponential decays at temperatures > 500 K
- We fit these using a simplified model.



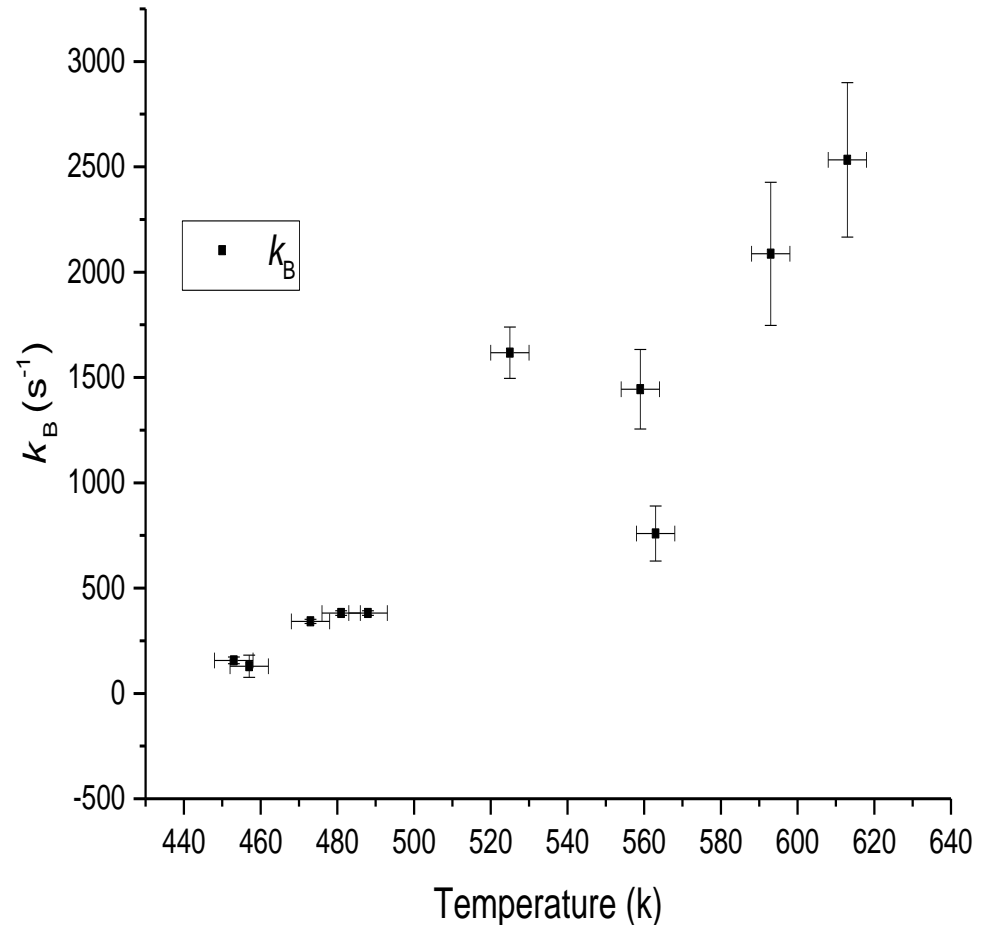
Trace taken at 550 K



3. Temperature dependence of k_B



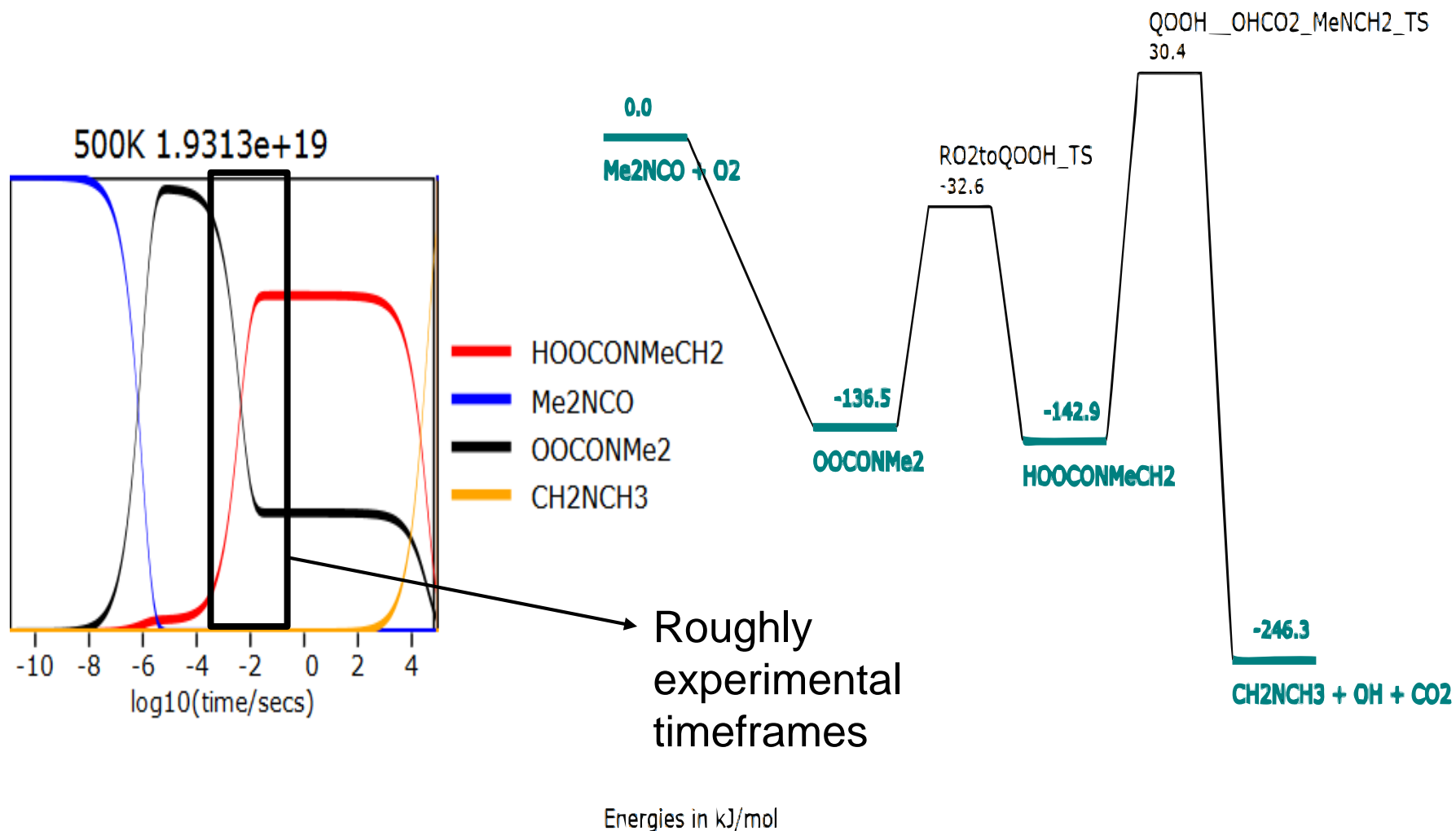
- Initially k_B is a small value and it increases with temperature.
- The temperature dependence of this can be compared with the output of our models.
- At the highest temperatures have over 90 % OH coming back.



3. Modelled output for DMF PES



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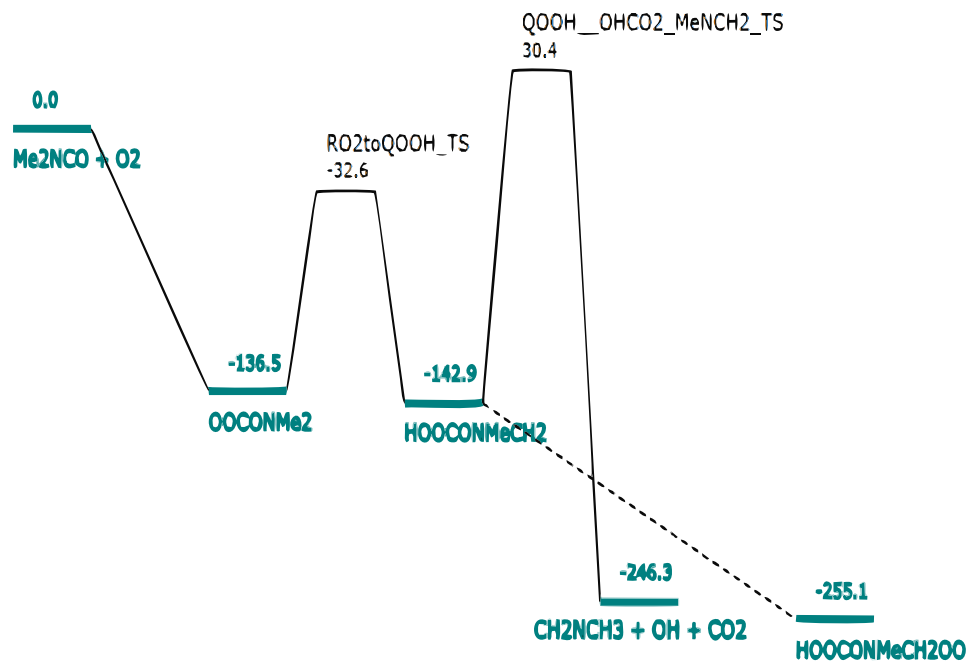


2nd Oxygen addition PES



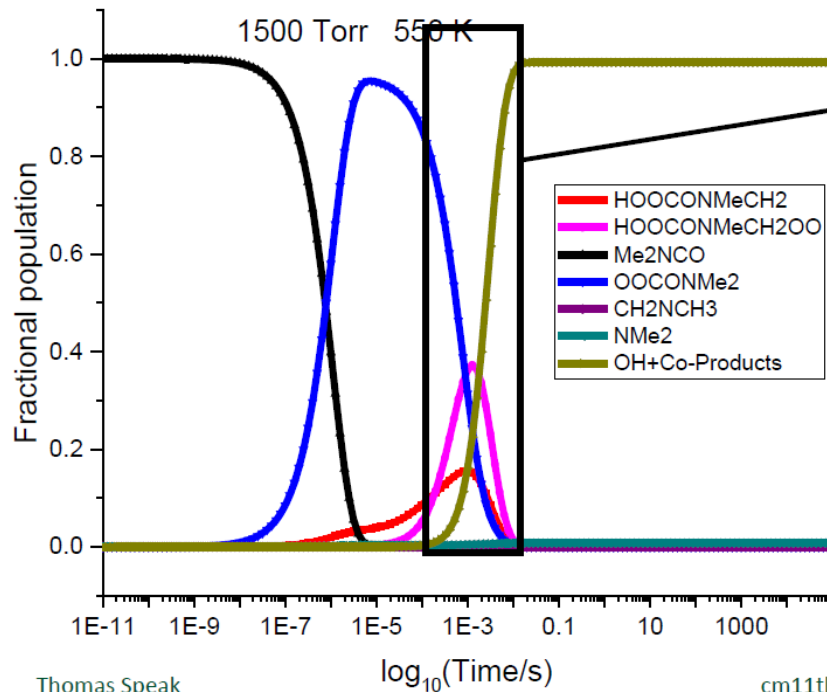
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- $\text{QOOH} + \text{O}_2 \rightarrow \text{OH} ?$
- Rate coefficients for the individual reactions on this PES were used in combination with Kintecus to simulate OH decay curves.



Energies in kJ/mol

Mesmer output for OOQOOH decomposition PES



- Get OH yield on experimental timeframe.

Potential to observe QOOH

3. Amide Chemistry Summary



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- Potential to study/observe critical intermediates lying at the heart of combustion chemistry.



4. SUMMARY AND FUTURE DIRECTIONS

4. Summary



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- Biomass burning contributes strongly to air quality (HCN, HNCO, VOC, O₃, particulates) and Climate Change (CO₂, N₂O, CH₄, particulates)
- Need to understand the details of the chemistry to predict yields.
- Nitrogen chemistry particularly important AND interesting.
- Examples of studies to characterise:
 - branching ratios – OH + amines
 - reaction intermediates – Amide chemistry

4. Future Directions



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- Studies in HIRAC and other environmental chambers. Greater detail on product yields.
- Expand amide studies. Consider potential for direct observation of intermediates.
- Examine chemical mechanisms for biomass burning.

4. Biomass Burning @ Leeds?



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- Leeds is well-placed to expand activity in plant biomass burning
 - CDT looking at controlled biomass burning (input from Engineering, MAPS, E&E)
 - Detailed Chemistry (laboratory and MCM)
 - Field studies capability (COBRA, Dwayne et al.)
 - Modelling