# **Direct detection of OH yields from a temperature** dependent study of HOCH, O, + HO, in HIRAC

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### Introduction

- Recent studies have shown the reactions • between organic peroxy radicals (RO<sub>2</sub>) and the hydroperoxyl radical (HO<sub>2</sub>) to be radical propagating [1].
- RO<sub>2</sub> + HO<sub>2</sub> reactions in pristine (low NOx) environments are the major tropospheric sink of RO<sub>2</sub> and key components of the OH-initiated oxidation of isoprene.
- It is thought that they may proceed *via*



#### **Experimental**

- Experiments performed in the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC) (Figure 2).
- Chamber has 8 rows of internal photolysis lamps ( $\lambda \sim 360$  nm) and 4 mixing fans (total mixing time  $\sim$  70 s).
- Experiments conducted at T = 263, 273, 283 and 293 K and p = 1000 mbar and additional experiments to quantify wall loss rates.
- HO<sub>2</sub> and HCHO generated by reacting methanol with chlorine atoms:  $Cl_2 + hv \rightarrow 2Cl$  $CI + CH_3OH \rightarrow CH_2OH + HCI$

OH-recycling mechanisms and hence account for model/measurement discrepancies of  $HO_x$  (OH + HO<sub>2</sub>) [2].

Figure 1: The different product channels of the hydroxymethyl peroxy +  $HO_2$  reaction.

- Reaction with formaldehyde (HCHO) is an important influence on  $HO_2$  in the troposphere, especially at low • temperatures, and is of importance to laboratory experiments where [HCHO] is high. The reaction is a key area of uncertainty in the  $CH_3C(O)O_2 + HO_2$  reaction, which has recently been studied in this laboratory [3].
- The HO<sub>2</sub> + HCHO equilibrium constant (R1) is well established in the literature and the rate constants,  $k_1$  and  $k_{-1}$  have recently been measured directly [4]. However, the fate of HOCH<sub>2</sub>O<sub>2</sub>, which predominantly reacts with HO<sub>2</sub> (R2, Figure 1) is less well characterised.
- OH has been measured indirectly in a chamber study [5], which proposed that the reaction proceeds via • three channels (R2a-c, Figure 1) - the only determination to date of these branching ratios.
- Theoretical calculations have provided further evidence of an OH channel [6]. •
- This work aims to measure the branching ratio of the OH-producing channel of the hydroxymethyl peroxy + HO<sub>2</sub> reaction (channel (2c), Figure 1) and its variation with temperature.

#### $CH_2OH + O_2 \rightarrow HO_2 + HCHO$

<ul> <li>Reactants and products were monitored with a time resolution of ~60 s (Table 1).</li> </ul>	
Instrument	Species measured
FTIR	Methanol, formic acid, formaldehyde
GC-FID	Methanol
Fluorescence Assay by Gas Expansion (FAGE)	OH, HO <sub>2</sub>
Commercial analysers	NO, NO <sub>2</sub> , O <sub>3</sub> (all were below LODs throughout experiments)

Table 1: Instruments used and species measured throughout experiments.



Figure 2: (a) The HIRAC chamber. (b) 8 rows of photolysis lamps inside the chamber.

#### Results

• Direct measurements of OH using FAGE, confirming





**Conclusions and Future Work** 

#### channel (2c).

- Modelling performed in Kintecus using a chemical mechanism based on that described in Jenkin et al. (2007) [5] shows good agreement with measurements at all temperatures (example dataset at T = 273 K shown in Figure 3).
- Branching ratios for R2 included in the model are: Y<sub>2a</sub> = 0.5;  $Y_{2b}$  = 0.3;  $Y_{2c}$  = 0.2, as reported by Jenkin *et al.* (2007) [5].
- No temperature dependence of the OH channel observed,  $Y_{2c} = 0.2$  gave a good model fits to the data at all measured temperatures (Figure 7).
  - Discrepancy between model/measurement of HO<sub>2</sub> at all temperatures (30-50%) over-prediction).
- Measured OH yields at T = 293 K, where [OH] is approaching the limit of detection (LOD) of the FAGE

## **Understanding the mechanism**

- It is important to look at the contribution of individual
  - reactions to overall product formation, to ensure that the
  - overall process is well understood.
- For our system, rate of production (ROP) and rate of



- Successful experiments of the reaction of  $HO_2 + HOCH_2O_2$ at *T* = 263 - 293 K and *p* = 1000 mbar.
- Reactant HO<sub>2</sub> and products OH, HCHO and HCOOH were observed directly.
- Only study to measure both radicals and stable products directly.
- ROP and ROD analyses validate measurements of species; the target reaction is well understood.
- Good agreement between measurements and literature  $(Y_{2a} = 0.5; Y_{2b} = 0.3; Y_{2c} = 0.2 \text{ gave good model fits})$  [5].
- No temperature dependence has been observed between T = 263 - 293 K, good model fits to data where  $Y_{2C} = 0.2$  at all studied temperatures (Figure 7).
- HO<sub>2</sub> measurements need to be scrutinised in more detail.
- Constrain the system to measurements, including OH, and use the model to calculate Y<sub>2C</sub> at all temperatures. Future plans to look at HO<sub>2</sub> + CH<sub>3</sub>CHO equilibrium which is also of importance to the  $CH_3C(O)O_2 + HO_2$  reaction.

# instrument (~ $1.5 \times 10^6$ ), are in good

agreement with the model (Figure 4).



Figure 4: Measured and modelled OH for

experiment at T = 293 K.

destruction (ROD) analyses were carried out for the experimental data for all measurable species.

- Figure 5 shows that the target reaction  $(HO_2 + HOCH_2O_2)$ reaction times.
- dominates OH formation chemistry through to t = 600 s. • Up to t = 600 s, OH loss reactions are well characterised
  - (Figure 6).
  - Because ROP = ROD, which is well characterised, and the
  - target reaction dominates OH production, we understand our target reaction well.
- This is also the case for HO<sub>2</sub>, HCHO and for HCOOH (>99% destruction reactions at different produced from R2b&c, >97% removed by reactor walls). reaction times.

Therefore, experiments are sensitive to  $Y_{2b}$  and  $Y_{2c}$ .







#### References

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