

# Direct detection of OH yields from a temperature dependent study of HOCH<sub>2</sub>O<sub>2</sub> + HO<sub>2</sub> 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 NO<sub>x</sub>) 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* OH-recycling mechanisms and hence account for model/measurement discrepancies of HO<sub>x</sub> (OH + HO<sub>2</sub>) [2].
- Reaction with formaldehyde (HCHO) is an important influence on HO<sub>2</sub> 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<sub>3</sub>C(O)O<sub>2</sub> + HO<sub>2</sub> 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.

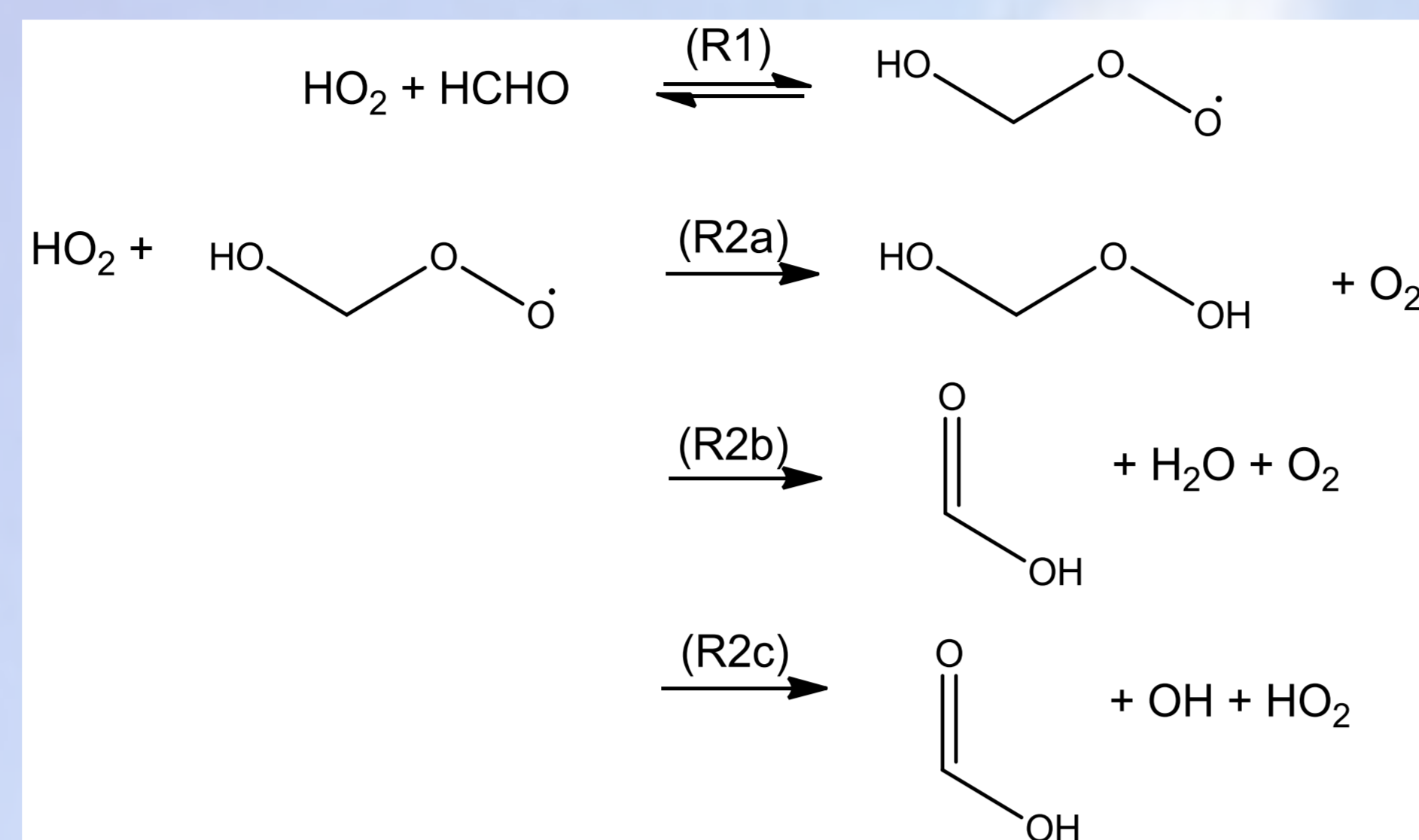


Figure 1: The different product channels of the hydroxymethyl peroxy + HO<sub>2</sub> reaction.

## 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:
 
$$\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$$

$$\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{OH} + \text{HCl}$$

$$\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{HCHO}$$
- Reactants and products were monitored with a time resolution of  $\sim 60$  s (Table 1).

| 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.

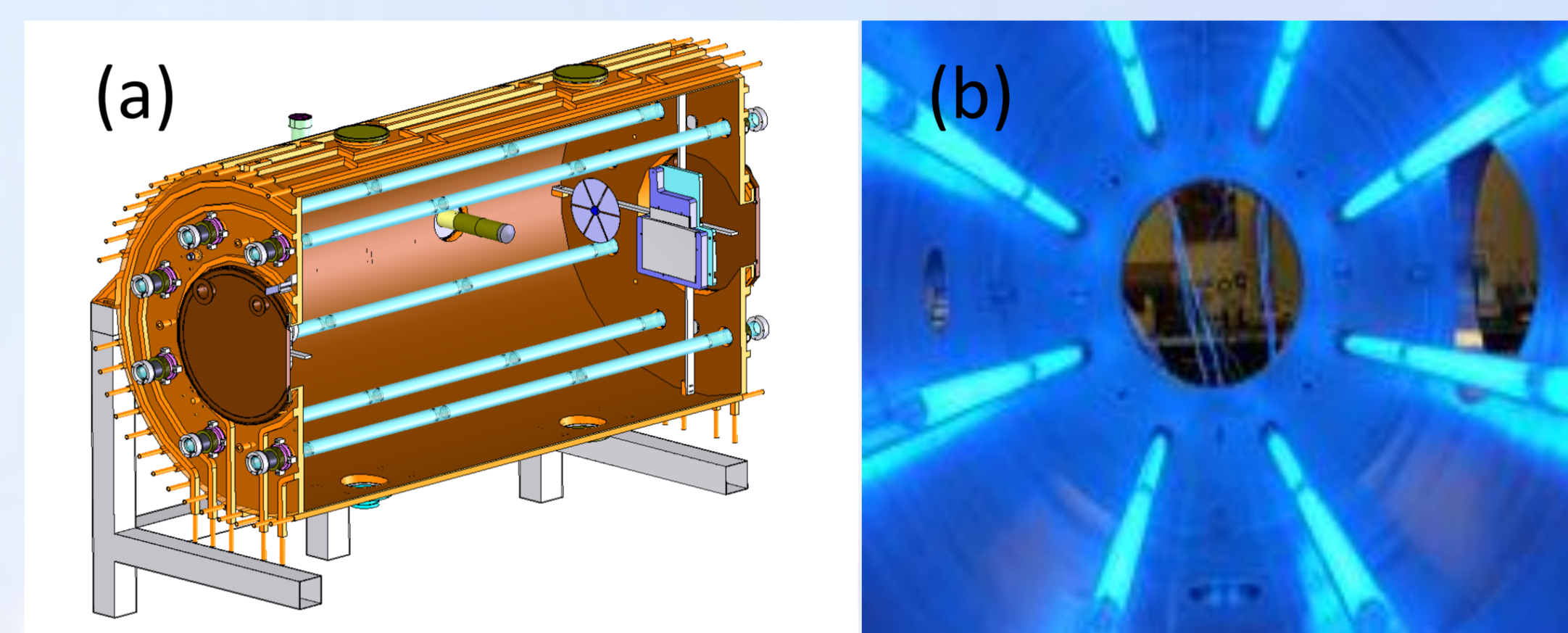


Figure 2: (a) The HIRAC chamber. (b) 8 rows of photolysis lamps inside the chamber.

## Results

- Direct measurements of OH using FAGE, confirming 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:  $Y_{2a} = 0.5$ ;  $Y_{2b} = 0.3$ ;  $Y_{2c} = 0.2$ , 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 instrument ( $\sim 1.5 \times 10^6$ ), are in good agreement with the model (Figure 4).

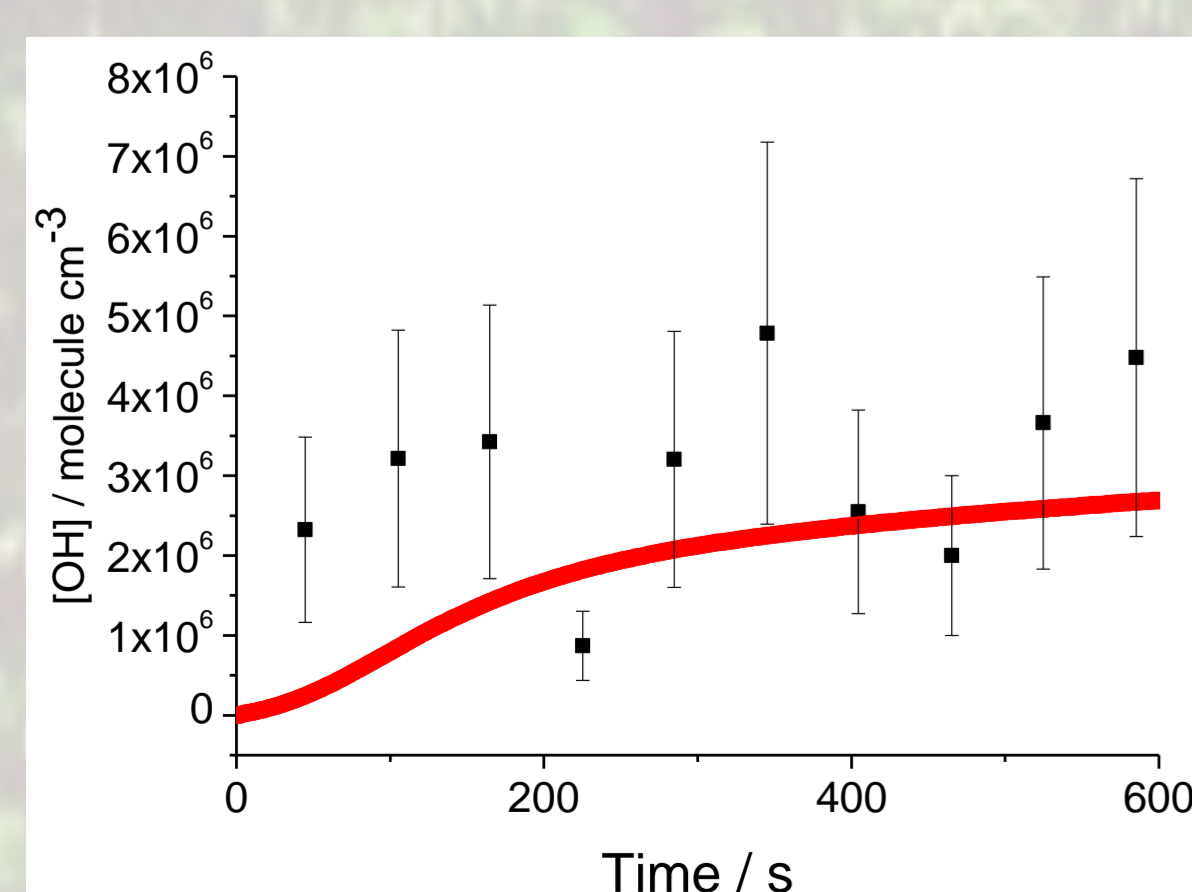


Figure 4: Measured and modelled OH for experiment at  $T = 293$  K.

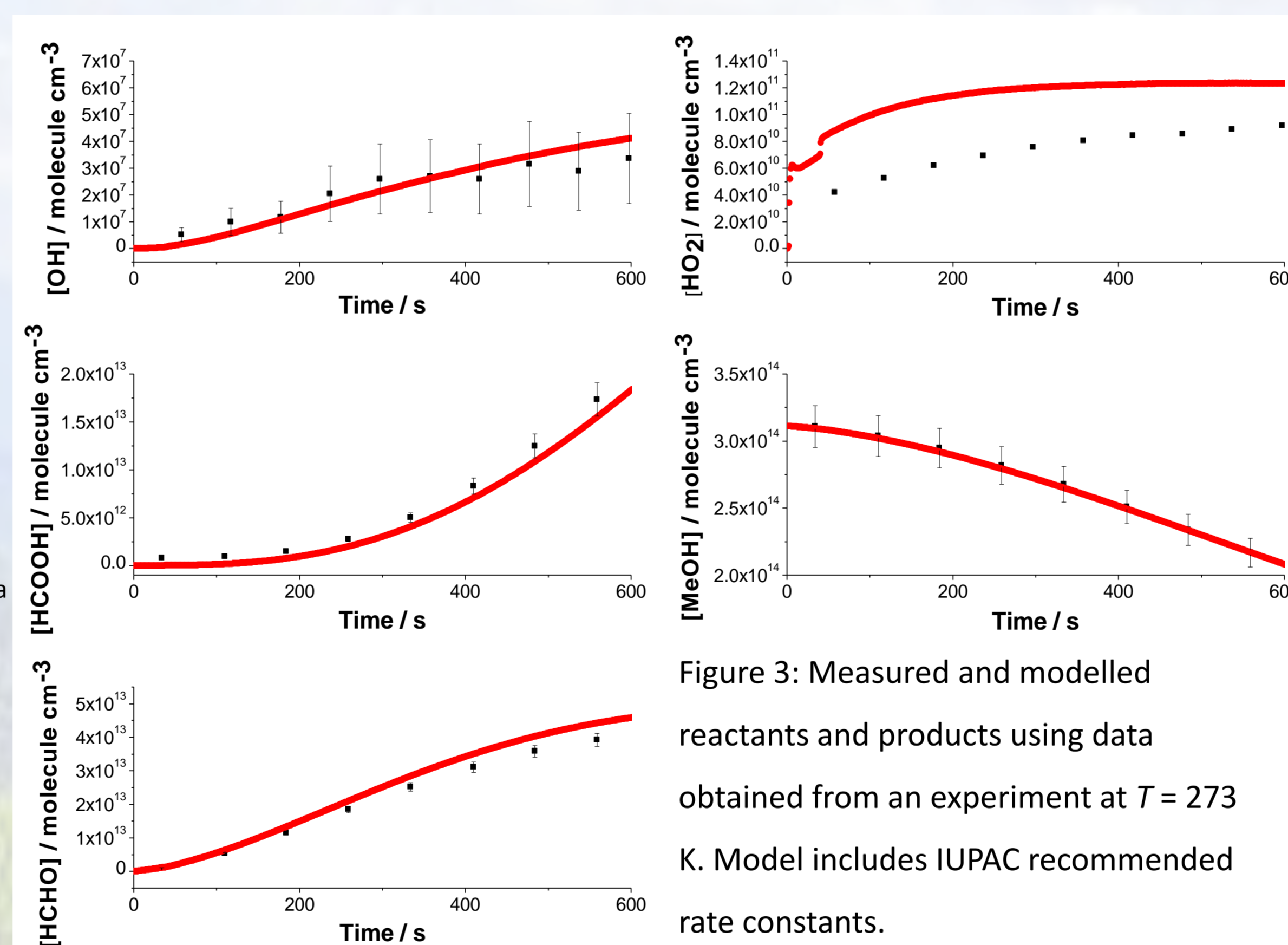


Figure 3: Measured and modelled reactants and products using data obtained from an experiment at  $T = 273$  K. Model includes IUPAC recommended rate constants.

## 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 destruction (ROD) analyses were carried out for the experimental data for all measurable species.
  - Figure 5 shows that the target reaction (HO<sub>2</sub> + HOCH<sub>2</sub>O<sub>2</sub>) 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% produced from R2b&c, >97% removed by reactor walls).
- Therefore, experiments are sensitive to  $Y_{2b}$  and  $Y_{2c}$ .

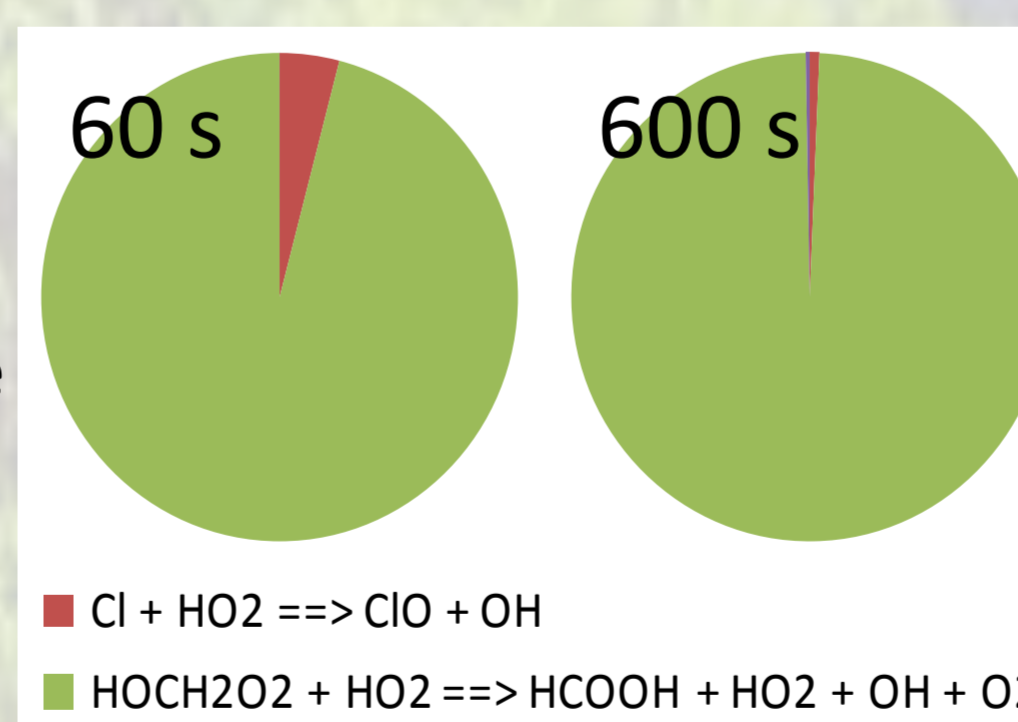


Figure 5: Relative contribution of OH production reactions at different reaction times.

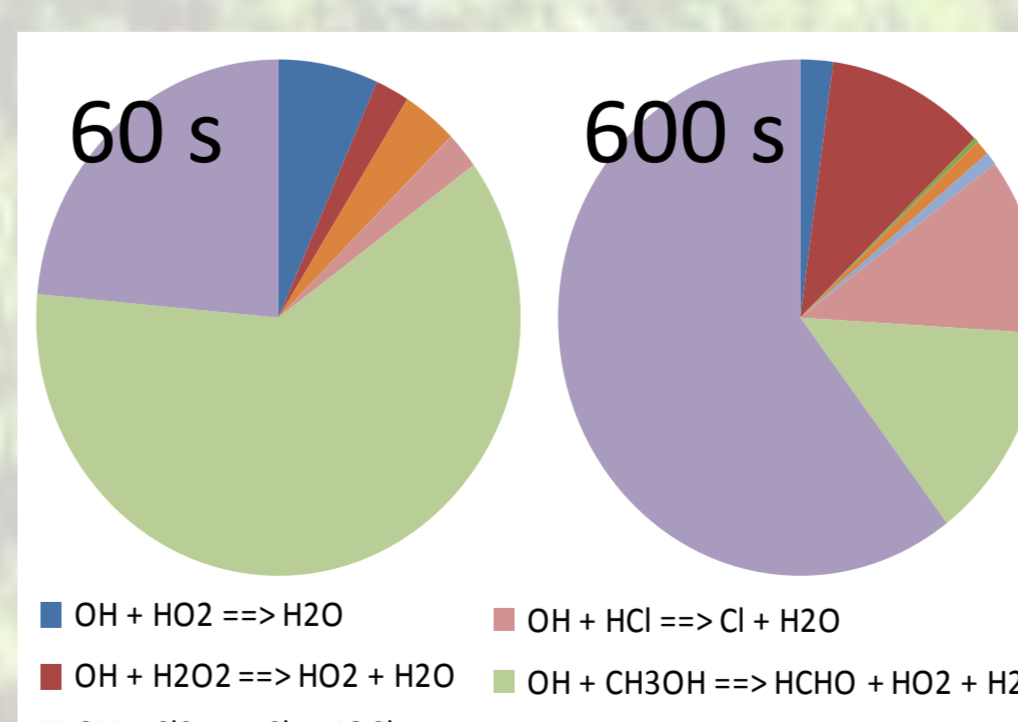


Figure 6: Relative contribution of OH destruction reactions at different reaction times.

## Conclusions and Future Work

- Successful experiments of the reaction of HO<sub>2</sub> + HOCH<sub>2</sub>O<sub>2</sub> 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 ( $Y_{2a} = 0.5$ ;  $Y_{2b} = 0.3$ ;  $Y_{2c} = 0.2$  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  $Y_{2c}$  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<sub>3</sub>C(O)O<sub>2</sub> + HO<sub>2</sub> reaction.

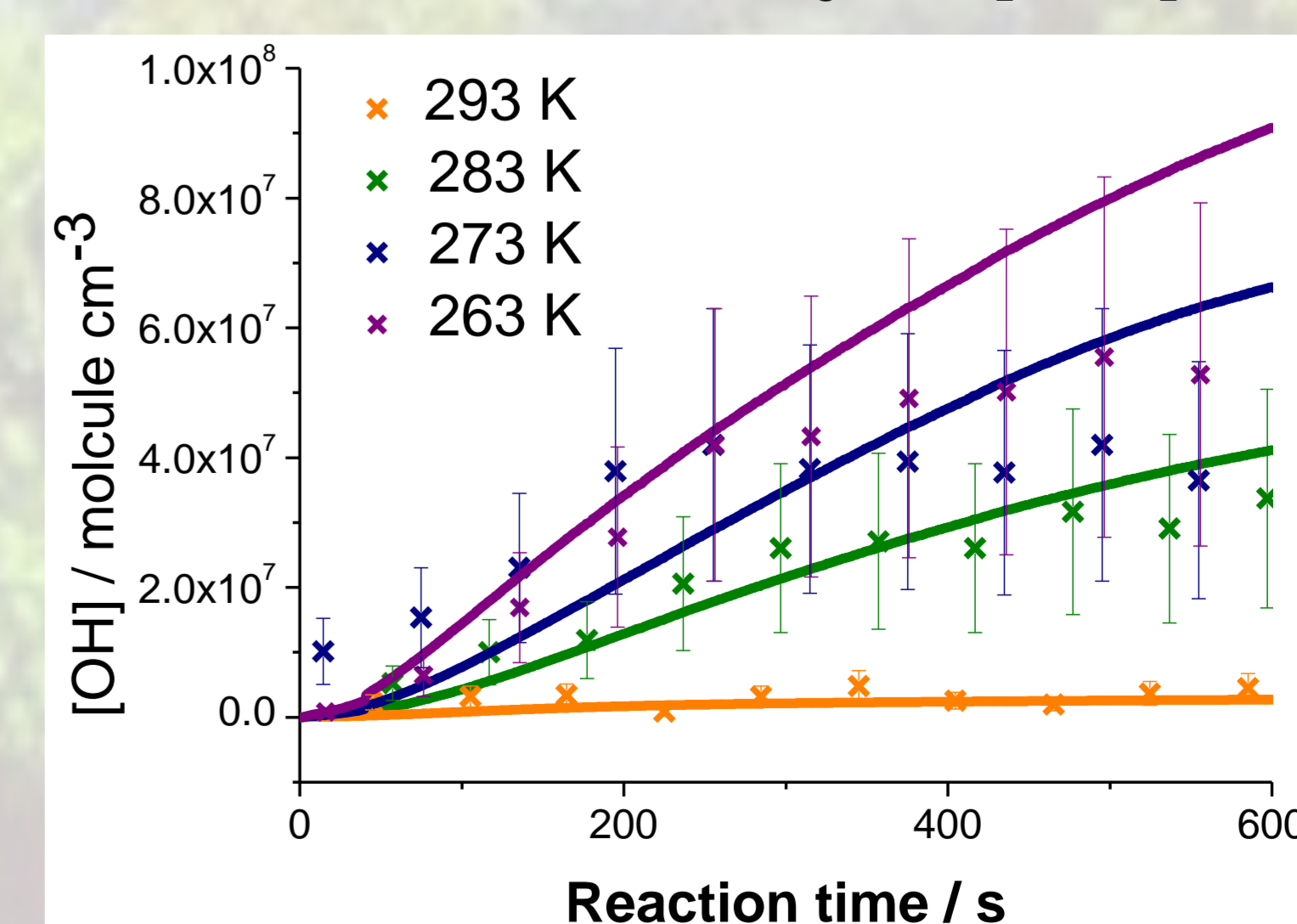


Figure 7: Model/measurement comparisons of [OH] for  $T = 263, 273, 283$  &  $293$  K.

## References

- [1] J. Orlando and G. Tyndall, *Chem. Soc. Rev.* **41**, 6294-6317 (2012); [2] J. Lelieveld *et al.*, *Nature*, **452**, 737-740 (2008); [3] F. A. F. Winiberg, Ph.D Thesis, University of Leeds (2014); [4] P. Morajkar, C. Schoemaeker, M. Okumura and C. Fittschen, *Int. J. Chem. Kinet.* **46**, 245-259 (2014); [5] M. E. Jenkin, M. D. Hurley and T. J. Wallington, *PCCP* **9**, 3149-3162 (2007); [6] T. L. Nguyen, L. Vereecken and J. Peeters, *Z. Phys. Chem.* **224**, 1081-1093 (2010).