

Introduction

- The hydroxy radical, OH, is the principal oxidising diurnal radical in the troposphere. OH reacts with Volatile Organic Compounds (VOC) to produce HO_2 and RO_2 .
- In high NO_x (NO + NO₂) conditions, HO₂ and RO₂ rapidly react with NO, recycling OH and generating O_3 .
- In low NO_x conditions OH levels are predicted to be low due to a lack of verified recycling mechanisms.
- However, measurements over rainforests {1-3} have found unexplainable high [OH], correlating with concentrations of biogenic VOC, particularly isoprene, C_5H_8 (see right).
- Isoprene oxidation proceeds via many RO₂ intermediates.
- Previous results {4} indicate that those with C=O substituents (eg. targets B, C & D) react with HO_2 to produce OH.
- Isoprene models require accurate rate coefficients & products yields for key OH recycling routes.

2. RO₂ + HO₂ reactions

• Reactions known to proceed via 3 pathways:

 $RO_2 + H$

• For alkyl peroxy radicals, termination pathway (a) dominates. For several carbonyl substituted RO₂, previous studies show production of $O_3(b) \& OH(c)$ is also efficient {5}.

• Of particular interest are HO₂ reactions with RO₂ produced from isoprene (targets A-D, above):

Target "A" (6 isomeric HO-substituted C5 peroxys) do not produce OH {6}. Targets "B" & "C" are subject of ongoing work at MPIC {7} – indications are they do recycle OH.

Target "D" is acetyl peroxy ($CH_3C(O)O_2$). Produced in the atmosphere from acetaldehyde, acetone & isoprene, its reaction with HO₂ has been studied the most: indirect chamber studies from Hasson et al. {8, FTIR end product analysis} and Jenkin et al. {9, OH scavenging} show good agreement with direct OH detection {4, LIF} from Dillon et al.; OH yield = 0.4 {5}.

• This work: first T & P dependent experiments on HO₂ + RO₂, with direct detection of HO_x, O₃ & VOC precursors / products. The aim is to obtain product yields f(P,T) & a detailed understanding of RO₂ reactions (energetics, P-effects etc.)

3. Experimental – the HIRAC chamber

• Experiments using HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry), a 2.25 m³ stainless steel chamber: - 8 rows of internal photolysis lamps ($\lambda \sim 305$ nm); 4 mixing fans (total mixing time ~ 70 s) — Instruments include FAGE, GC-FID, FTIR, CRDS, commercial O₃, NO_y, CO & H₂O analysers. -P(50 - 760 Torr) & T(225 - 325 K) control.• In this work Fluorescence Assay by Gas Expansion (FAGE) was used to

measure HO_x , whilst VOC (HCOOH, CH_3CHO , $CH_3C(O)OH$, $CH_3C(O)OOH$, HCHO) were detected by FTIR. $O_3 \& NO$ also monitored.

- Experiments conducted at *P* = 200 & 760 Torr (air), *T* = 290 & 325 K.
- HO₂ & RO₂ generation:
- $Cl_2 + hv \rightarrow 2Cl$ $CI + CH_3OH \rightarrow CH_2OH + HCI$ $CH_2OH + O_2 \rightarrow HO_2 + HCHO$ $CI + RH \rightarrow R + HCI$ $R + O_2 + M \rightarrow RO_2 + M$ n.b. $R = CH_3CO$ for most reactions

Pressure and Temperature Dependent Product Study of the $CH_3C(O)O_2 + HO_2$, Reaction Using HIRAC Frank A. F. Winiberg⁽¹⁾, S. Orr⁽¹⁾, S. C. Smith⁽²⁾, T.J. Dillon⁽³⁾, C.B.M. Groß⁽³⁾, T. Ingham⁽¹⁾, D. E. Heard⁽¹⁾ and P. W. Seakins⁽¹⁾

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10 ₂	\rightarrow KOOH + O ₂	
	\rightarrow ROH + O ₃	
	\rightarrow RO + OH + O ₂	



The HIRAC chamber with HIRAC FAGE instrument





{1} J. Lelieveld et al.: Atmospheric oxidation capacity sustained by a tropical forest. Nature, 452, 737–740, 2008. {2} http://www.atmos-chem-phys.net/special_issue88.html. {3} http://www.atmos-chem-phys.net/special_issue163.html ; {4} Terry J. Dillon and John N. Crowley. Atmos. Chem. Phys., 2008, (8), 4877-4889. {5} IUPAC subcommittee for gas kinetic data evaluation: http://www.iupac-kinetic.ch.cam.ac.uk/index.html ; {6} Dillon, Groß and Crowley, manuscript in preparation. {7} Christoph B. Gross, Terry J. Dillon and John N. Crowley.: Kinetic studies of peroxy radical reactions, 21st International Symposium on Gas Kinetics, Leuven, 2010 (Poster) {8} Hasson, A.S., Tyndall, G.S., Orlando, J.J., J. Phys. Chem. A, 108, 5979-5989, 2004. ; {9} Jenkin, M.E., Hurley, M.D., and Wallington, T.J.: Phys. Chem. Chem. Phys., 9, 3149-3162, 2007. {10} <u>http://mcm.leeds.ac.uk/MCM/</u>; {11} D. Taraborrelli, et al. Nature Geoscience 5, 2012, www.nature.com/naturegeoscience



5. Conclusions and Further Work

- Successful experiments into the reaction of HO₂ + CH₃C(O)O₂ at two different pressures and temperatures.
- Reactant HO₂ and products OH, O₃, CH₃C(O)OH & CH₃C(O)OOH were observed directly.
- Further numerical simulations (ATCHEM) required to determine *P* & *T* dependent product branching ratios for $HO_2 + CH_3C(O)O_2$.
- New experiments needed on other "target" RO₂.
- Project development to include theoreticians and modellers update MCM {10} & MIM {11}, assess atmospheric impact.



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Comparison of OH measured using FAGE (points) and modelled OH (line) for $CH_3CO_3 + HO_2$ @ 291 K and 760 Torr



Peak [OH] vs reactant ratios at two temperatures and pressures