MCM Box Modelling of the OP3 Aircraft Campaign

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Introduction

Tropical forests emit significant amounts of volatile organic compounds (VOCs), of which isoprene (C_5H_8) is dominant

Isoprene and other VOCs removed from atmosphere by oxidation processes

⇒ Largely controlled by **OH** and **HO_2** - **HO_x**

⇒ Isoprene reacts rapidly with OH

⇒ Isoprene and VOCs have significant impacts on HO_x

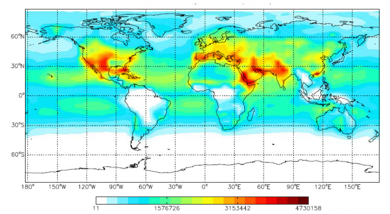
⇒ Changes to HO_x chemistry affect greenhouse gases (e.g. O_3, CH_4)

Models predict low OH concentrations in regions with high isoprene such as Amazonia and Borneo

⇒ GABRIEL project reported unexpectedly high OH over Amazonia

⇒ Models require additional OH sources

⇒ Proposed OH recycling in isoprene oxidation



Lelieveld et al. (2006)

Surface concentrations of OH (molec cm^{-3}) for May 2001 using GEOS-Chem
OH depletion is predicted in regions with high isoprene emissions

Oxidant and Photochemical Processes (OP3) field campaign in Borneo during 2008 aimed to improve understanding of oxidation chemistry in remote tropical regions

Measurements during OP3

Combination of ground, tower and aircraft measurements

Aircraft measurements on NERC FAAM BAe146 aircraft

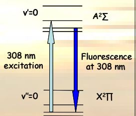
OH and HO_2 measured by low pressure Laser Induced Fluorescence (LIF)

⇒ Fluorescence Assay by Gas Expansion (FAGE)

⇒ On-resonance detection of OH at 308 nm

⇒ HO_2 detection by chemical titration to OH

$HO_2 + NO \rightarrow OH + NO_2$



Measurements include O_3, CO, NO_x, ethane, propane, *i*-butane, ethene, propene, acetylene, methanol, acetone, isoprene, MVK, MACR, RO_2, $J(O^1D)$, $J(NO_2)$)

Aircraft measurements of long-lived species used to constrain box model

Model Approach

Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC) Emmerson & Evans (2009)

⇒ Uses the Kinetic Pre-Processor (KPP) Sandu & Sander (2006)

⇒ Flexible zero dimensional box model constrained to observations

⇒ Photolysis rates calculated from TUV radiation model

⇒ Cloud correction factors using observed $J(O^1D)$ and $J(NO_2)$

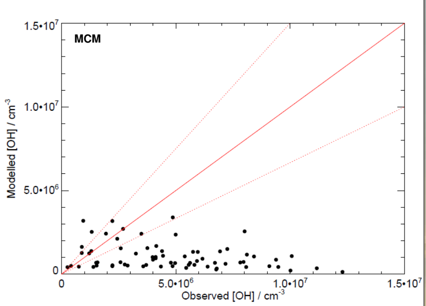
⇒ Model run forwards to diurnal steady state to calculate OH, HO_2

Chemistry described by the Master Chemical Mechanism (MCM) v3.1

⇒ Near explicit degradation schemes

⇒ Approximately 5600 species in over 13,500 reactions

⇒ Represents state of the art in current understanding



Significant underestimate of OH correlated to isoprene

Model Performance

MCM chemistry results in a significant underestimate of OH, with model failure correlated to isoprene

Similar to results obtained for the GABRIEL project in Amazonia Lelieveld et al. (2008)

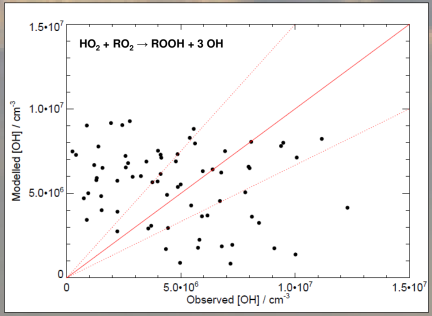
Investigate potential sources of OH for OP3 suggested by recent work
Do these approaches reconcile the model failure for OH during OP3???

Several recent experimental and theoretical studies identify potential sources of OH

$HO_2 + RO_2 \rightarrow OH$ Dillon & Crowley (2008); Lelieveld et al. (2008)

Production of OH has been observed by LIF in certain $HO_2 + RO_2$ reactions

Model discrepancy for GABRIEL reconciled with $HO_2 + ISOPO_2 \rightarrow ISOPOOH + 2\text{-}4\ OH$



Production of OH in $HO_2 + RO_2$ reactions can improve model success for OP3

Significant improvements using $HO_2 + ISOPO_2 \rightarrow ISOPOOH + 3\ OH$

BUT requires branching ratio far greater than observed $\beta = 0.5 \pm 0.2$

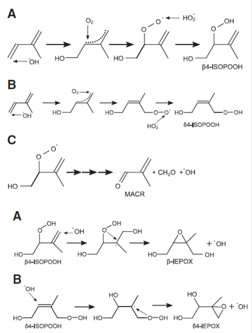
AND only observed with $RC(O)O_2$ radicals, not $ISOPO_2$

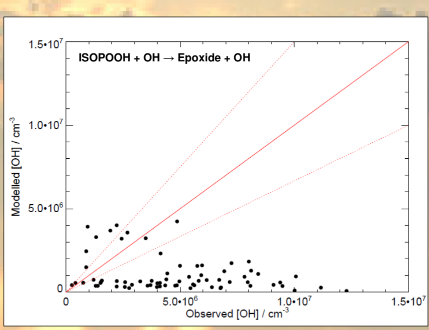
Although model success is improved, production of large amounts of OH from $HO_2 + RO_2$ not substantiated by experimental evidence

Epoxide formation Paulot et al. (2009)

Chamber studies indicate formation of OH + epoxides from OH + C_5H_8

Can lead to aerosol formation



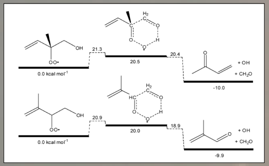


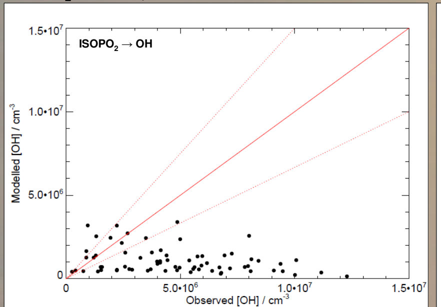
Epoxide formation cannot explain model failure

H-shift in $ISOPO_2 \rightarrow OH$ Da Silva et al. (2010)

Theoretical work suggests H-shifts in $ISOPO_2$ radicals produces OH

Only expected to be important in regions with low HO_2 and low NO_x

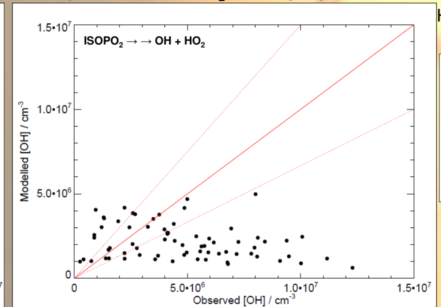




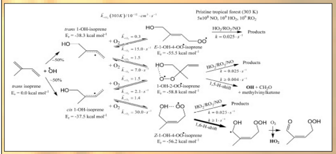
Cannot explain OP3 observations
Requires experimental validation

H-shift in $ISOPO_2 \rightarrow\rightarrow OH + HO_2$ Peeters et al. (2009)

H-shift predicted in $ISOPO_2$ resulting in production of OH and HO_2



H-shifts also expected for MVK and MACR



Greatest increase in modelled OH BUT requires experimental validation

Conclusions

Understanding of OH-initiated oxidation of isoprene is poor

Isoprene chemistry is misrepresented in models

Leads to poor replication of OH observations in high isoprene low NO_x regions

Could have important consequences for global modelling of greenhouse gases

Experimental and theoretical studies indicate several areas for improvement in chemical schemes used in models

H-shift in $ISOPO_2$ radicals producing OH and HO_2 has greatest impact on modelled OH

Experimental validation of theoretical studies required

Further laboratory investigations of isoprene oxidation chemistry required!

Acknowledgements

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References

Lelieveld et al., Nature, 452, 737-740, 2008
Dillon & Crowley, Atmos. Chem. Phys., 8, 4877-4889, 2008
Da Silva et al., Environ. Sci. Technol., 44, 250-256, 2010
Emmerson & Evans, Atmos. Chem. Phys., 9, 1831-1845, 2009
Hewitt et al., Atmos. Chem. Phys., 10, 169-199, 2010
Paulot et al., Science, 325, 730-733, 2009
Peeters et al., Phys. Chem. Chem. Phys., 11, 28, 5935-5939, 2009
Sandu & Sander, Atmos. Chem. Phys., 6, 187-195, 2006