Field measurements and modelling of OH, HO₂ and OH reactivity in low NOₓ environments
Lisa Whalley, 1,2 Trevor Ingham, 1,2 Daniel Stone, 1 Stewart Vaughan, 1 Hannah Bunyan, 1 Ingrid George, 1 Peter Edwards, 1 Mat Evans 3,4 and Dwayne Heard 1,2,
1 School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK
2 National Centre for Atmospheric Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK
3 US Environmental Protection Agency, 109 TW Alexander Drive, Durham, NC 27709, USA
4 ESRL, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, CO 80305-3328, USA
5 Department of Chemistry, University of York, York, YO10 5DD, UK
6 National Centre for Atmospheric Chemistry, University of York, YO10 5DD, UK
*Corresponding author: d.a.heard@leeds.ac.uk

Introduction

The abundance of OH controls the photochemical turnover rate and the lifetimes of trace gases in the atmosphere. Field measured concentrations of OH and HO₂ radicals, and comparison with the results of box model simulations, for example using the detailed Master Chemical Mechanism (MCM), provide a sensitive test of our understanding of the rates of atmospheric processes. Field measurement of OH reactivity enables quantification of sinks for OH which are missing in models. Here we present results and model calculations from recent field experiments in a range of low NOₓ environments.

Technique

Field observations of the radicals were made using Laser Induced Fluorescence (LIF) spectroscopy at low pressures (FAGE technique):
- Ambient air drawn into a low pressure cell (< 4 Torr)
- Laser beam passed perpendicular to air stream
- On resonance 308 nm OH fluorescence detected by PMT
- HO₂ titrated to OH by reaction with NO
- OH reactivity measured in a turbulent flow reactor, with a movable OH injector coupled to a LIF detector

1. Seasonal Oxidants Study

- Tropical regions have high HO₂ production rates due to high solar irradiance, warmth and humidity
- Estimated that ~ 80 % of global CH₄ oxidation occurs in the tropics (Bloss et al. 2005)
- SOS took place at the Cape Verde Atmospheric Observatory in 2009 and provided the first seasonal measurements of both OH and HO₂ in a tropical marine environment (Vaughan et al., 2012)

- The summer months typically exhibited highest concentrations of OH and HO₂
- OH and HO₂ exhibited a strong correlation with the rate of ozone photolysis
- Radical concentrations were sensitive to small concentrations of halogen oxides (|IO| = 1.4 ppt, [BrO] = 2.5 ppt observed at the site using DOAS)

2. Oxidant and Particle Photochemical Processes

- In tropical forested environments where biogenic VOC emissions are high and NOₓ concentrations are low, low OH concentrations and extended CH₄ lifetimes are predicted due to rapid reactions of OH with sink species such as isoprene (Lelieveld et al., 2002)
- To assess the oxidative capacity of tropical forests, observations of OH, HO₂ and OH reactivity in and above the Borneo rainforest were made as part of the OP3 project in 2008 and compared to model predictions:
  - MCM chemistry underpredicts OH for air masses impacted by isoprene (ground level and aircraft) suggesting missing OH sources in the model (Stone et al., 2011, Whalley et al., 2011)
  - HO₂ concentrations are well replicated suggesting that the missing chemistry does not generate HO₂
  - The model underestimates the measured OH reactivity; this discrepancy is reduced if the lifetimes of modelled intermediates are extended demonstrating the importance of the VOC oxidation products

3. Role of Nighttime chemistry in controlling the Oxidising Capacity of the Atmosphere

- Night time chemistry, driven primarily by the nitrate radical NO₃, plays a significant role in governing the composition of the troposphere
- RONO₂ represents the first aircraft-based night-time measurements of OH, HO₂ and NOₓ. Flights were made during summer and winter around the UK and aimed to assess the importance of OH and HO₂ at night and the processes controlling radical concentrations
- [HO₂] was strongly correlated to [NO₃]
- OH was not measured above the limit of detection of the instrument (6.4 - 18 x 10⁶ molecule cm⁻³)
- Tendency for model to under-predict [HO₂]
- NOₓ important for radical initiation and radical propagation
- Models need to include appropriate NOₓ + alkene and NOₓ + RO₂ chemistry to model nighttime oxidation chemistry with success

4. Hill Cap Cloud Thuringer-2010

- Clouds occupy ~15% of the troposphere and can potentially reduce gas-phase oxidation by efficient uptake of radicals into droplets (Lelieveld & Crutzen, 1990, 1991; Tilgner et al., 2005).
- Gas-phase measurements of OH and HO₂ were made at Mt. Schmucke, Thuringer Wald both in-cloud and out of cloud and observations have been compared with simple model predictions:
  - ~ 65% reduction in [OH] on average during cloud events
  - low concentrations of OH were observed out of cloud, but concentrations were below the limit of detection in-cloud
  - ~ 90% reduction in [HO₂] during cloud events observed on average
  - Model is able to replicate [HO₂] out of cloud but over-estimates [HO₂] in-cloud
  - To replicate [HO₂] in-cloud observations, a first order loss rate of HO₂ to clouds = 0.2 s⁻¹ is needed suggesting that heterogeneous processes in clouds do perturb gas-phase radical chemistry

6. References

7. Acknowledgements

The authors would like to thank all fieldwork participants for their help during the projects and the Leibniz-Institut für troposphärenforschung, ITF, for funding HCIT. This work is supported by the National Environmental Research Council and the National Centre for Atmospheric Science.