

[Home](#)[Online Library ACP](#)[Recent Final Revised Papers](#)[Volumes and Issues](#)[Special Issues](#)[Library Search](#)[Title and Author Search](#)[Online Library ACPD](#)[Alerts & RSS Feeds](#)[General Information](#)[Submission](#)[Review](#)[Production](#)[Subscription](#)[Comment on a Paper](#)Impact
Factor
4.927ISI
indexed[Volumes and Issues](#) [Contents of Issue 4](#) [Special Issue](#)

Atmos. Chem. Phys., 10, 1555-1576, 2010

www.atmos-chem-phys.net/10/1555/2010/

© Author(s) 2010. This work is distributed under the Creative Commons Attribution 3.0 License.

The chemistry of OH and HO₂ radicals in the boundary layer over the tropical Atlantic Ocean

L. K. Whalley^{1,5}, K. L. Furneaux^{1,†}, A. Goddard¹, J. D. Lee^{2,6}, A. Mahajan¹, H. Oetjen¹, K. A. Read^{2,6}, N. Kaaden³, L. J. Carpenter², A. C. Lewis^{2,6}, J. M. C. Plane¹, E. S. Saltzman⁴, A. Wiedensohler³, and D. E. Heard^{1,5}¹School of Chemistry, University of Leeds, Woodhouse Lane, Leeds, LS2 9JT, UK²Chemistry Department, University of York, Heslington, YO10 5DD, UK³Physics Department, Leibniz Institute for Tropospheric Research, Leipzig, Germany⁴Department of Earth System Science, University of California, Irvine, CA, USA⁵National Centre for Atmospheric Sciences, University of Leeds, Leeds, LS2 9JT, UK⁶National Centre for Atmospheric Sciences, University of York, Heslington, YO10 5DD, UK[†]Sadly passed away 28 July 2009

Abstract. Fluorescence Assay by Gas Expansion (FAGE) has been used to detect ambient levels of OH and HO₂ radicals at the Cape Verde

Atmospheric Observatory, located in the tropical Atlantic marine boundary layer, during May and June 2007. Midday radical concentrations were high, with maximum concentrations of 9×10^6 molecule cm^{-3} and 6×10^8 molecule cm^{-3} observed for OH and HO₂, respectively. A box model incorporating the detailed Master Chemical Mechanism, extended to include halogen chemistry, heterogeneous loss processes and constrained by all available measurements including halogen and nitrogen oxides, has been used to assess the chemical and physical parameters controlling the radical chemistry. The model was able to reproduce the daytime radical concentrations to within the 1σ measurement uncertainty of 20% during the latter half of the measurement period but significantly under-predicted [HO₂] by 39% during the first half of the project. Sensitivity analyses demonstrate that elevated [HCHO] (~ 2 ppbv) on specific days during the early part of the project, which were much greater than the mean [HCHO] (328 pptv) used to constrain the model, could account for a large portion of the discrepancy between modelled and measured [HO₂] at this time. IO and BrO, although present only at a few pptv, constituted $\sim 19\%$ of the instantaneous sinks for HO₂, whilst aerosol uptake and surface deposition to the ocean accounted for a further 23% of the HO₂ loss at noon.

Photolysis of HOI and HOBr accounted for $\sim 13\%$ of the instantaneous OH formation. Taking into account that halogen oxides increase the oxidation of NO_x (NO \rightarrow NO₂), and in turn reduce the rate of formation of OH from the reaction of HO₂ with NO, OH concentrations were estimated to be 9% higher overall due to the presence of halogens. The increase in modelled OH from halogen chemistry gives an estimated 9% shorter lifetime for methane in this region, and the inclusion of halogen chemistry is necessary to model the observed daily cycle of O₃ destruction that is observed at the

[Search ACP](#)

Library Search

Author Search

[News](#)

- [Bringing Down Geoscientific Barriers](#)
- [New Tax Regulation for Service Charges](#)
- [Sister Journals AMT & GMD](#)
- [Public Relations & Background Information](#)

[Recent Papers](#)

01 | ACP, 19 Feb 2010:
Tropospheric photooxidation of CF₃CH₂CHO and CF₃(CH₂)₂CHO initiated by Cl atoms and OH radicals

02 | ACP, 19 Feb 2010:
Estimations of climate sensitivity based on top-of-atmosphere radiation imbalance

03 | ACP, 19 Feb 2010:
Numerical simulations of contrail-to-cirrus transition – Part 2: Impact of initial ice crystal number, radiation, stratification, secondary nucleation and layer depth

surface. Due to surface losses, we hypothesise that HO₂ concentrations increase with height and therefore contribute a larger fraction of the O₃ destruction than at the surface.

■ [Final Revised Paper](#) (PDF, 2496 KB) ■ [Supplement](#) (57 KB) ■ [Discussion Paper](#) (ACPD)

Citation: Whalley, L. K., Furneaux, K. L., Goddard, A., Lee, J. D., Mahajan, A., Oetjen, H., Read, K. A., Kaaden, N., Carpenter, L. J., Lewis, A. C., Plane, J. M. C., Saltzman, E. S., Wiedensohler, A., and Heard, D. E.: The chemistry of OH and HO₂ radicals in the boundary layer over the tropical Atlantic Ocean, *Atmos. Chem. Phys.*, 10, 1555-1576, 2010. ■ [Bibtex](#) ■ [EndNote](#) ■ [Reference Manager](#)