1. Introduction

Field measurements of the short-lived radical species OH and HO₂ (referred to collectively as HO₂) are vital for our understanding of the oxidative capacity of the Earth’s atmosphere. Such observations are used to validate atmospheric chemical models. In particular, as a means of testing our current understanding of the complex chemical processes that occur in the troposphere. Reliable measurements of HO₂ in tropical regions, where the warm, humid conditions lend themselves favourably to the generation of OH radicals through:

$$\text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2 \text{OH}$$

are important as it has been estimated that the majority of tropospheric methane is oxidized in this region. However, there have been no long-term study of the seasonal variation of HO₂ in the tropics.

Laser-induced fluorescence (LIF) (section 2) has been used to sensitively detect HO₂ radicals in the field by several groups worldwide and at a variety of locations. This poster presents field measurements of HO₂ at the Cape Verde Atmospheric Observatory (CVAO, ~17° N, 24° W) using LIF taken over the course of this year as part of the Seasonal Oxidant Study (SOS). The observations made during the summer study (SOS2) are compared with LIF measurements taken during a similar period in 2007 (see section 4), and comparisons are made with the model predictions of [HO₂] for the first two campaigns (section 5).

2. LIF Detection of OH and HO₂

The OH radical is detected by on-resonance (at 308 nm) LIF carried out at low pressures (<4 Torr). The low pressure extends the fluorescence lifetime of OH sufficiently to allow discrimination (in time) between the fluorescence and laser pulse. The HO₂ radical is converted to OH by titration with NO and detected by the same method.

The radicals were detected in situ from the roof of a standard shipping container converted into a temporary mobile laboratory. Air is drawn into the low pressure cells via pin-hole nozzles, the laser beam passes perpendicular to the air stream and the fluorescence is imaged, along a 3rd axis, onto the photocathode of a channel photomultiplier.

The sensitivity of the instrument is determined as regularly as possible by a calibration method that allows the channel photomultiplier.

The authors would like to acknowledge J. Lee and K. Read (Univ. York) for the core data used in the models.

3. Seasonal observations of OH and HO₂

Plots showing the hourly averages of OH and HO₂ for each of the three campaigns; the error bars are the 1σ of the hourly-averaged data and represent the day-to-day variance in the concentrations. Local time = GMT -1.0h.

Interestingly, the seasonal trend in OH is similar to that observed in [HO₂]/[HO₂] by the Leicester PERCA instrument (www.leicester-perca.co.uk) measuring the peroxy radical in the eastern tropical Atlantic boundary layer. (Kaimsalatsa, Paris, the Wednesday session).

The figures below show how the concentrations of OH and HO₂ behave as a function of J(O1D). The error bars are close to 1 for OH suggesting the reaction J(O1D) + HO₂ is controlling [OH] and 0.5 for HO₂ (i.e. [HO₂] is being constrained by its self-reaction).

4. Comparison with RHaMBLe 2007

There appears to be excellent agreement between the observed concentrations of HO₂, but the noontime average [OH] was lower in SOS2 compared to 2007.

5. Modelling studies of SOS1/2

•BrO and IO levels set constant to 5ppt, when included
•Aerosol losses of other halogen species and HO₂ included

Plots of the mean diurnal observed and model-predicted HO₂ for SOS1/2 are shown on the left-hand side; the error bars represent the 2σ errors on the calibrations. Plots of the mean diurnal modelled observed HO₂ are shown on the right-hand side; the median and RF values are over all points for each campaign, not the hourly averages.

6. References and Acknowledgements

1. Lawrence et al., Atmos. Chem. Phys., 2001
2. Blos et al., Faraday Discussions, 2005
4. Whalley et al., Atmos. Chem. Phys. Discuss., 2009

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