

MEASUREMENTS OF OH AND HO₂ RADICALS AT A TROPICAL MARINE LOCATION AS PART OF THE

SOLAS SEASONAL OXIDANT STUDY

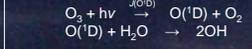
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1. Introduction

Reliable measurements of OH and HO₂ (collectively known as HO_x) in tropical regions, where the warm, humid conditions lend themselves favourably to the generation of OH radicals through the reaction of O(¹D) with water vapour



are important for accurate predictions of future climate change. For radiatively-important species such as methane, CH₄, the primary oxidation pathway is via reaction with OH. In fact, it has been estimated from field measurements of [OH] that the majority of the total occurring in the marine lower troposphere.^{1,2} A seasonal study of the variation of HO_x in the tropics would allow a better understanding of the oxidising capacity in that region, leading to the more accurate prediction of seasonal CH₄-lifetimes in the troposphere and, in turn, the long-term climate trends on a global scale.

This poster presents the first long-term, seasonal measurements of HO_x made at the Cape Verde Atmospheric Observatory (CVAO) using sensitive laser-induced fluorescence (LIF) spectroscopy taken as part of the Seasonal Oxidant Study (SOS), compared with LIF measurements made during a similar period in 2007 (see section 3), and comparisons are made with the model predictions of [HO_x] for the SOS1 and 2 (section 4).

3. Seasonal observations of OH and HO₂

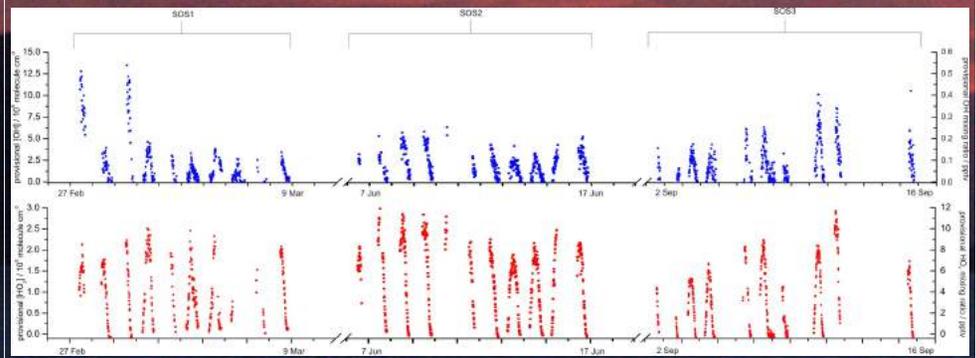


Figure 1. Plots showing the diurnal variation in the levels of OH (blue) and HO₂ (red) for each of the three measurement periods.

Figure 1 shows that a total of 31 days of HO_x measurements were made during 2009, excluding periods when the instrument was not performing within acceptable tolerances and when measurements were influenced by bad weather or local conditions.

OH showed the greatest day-to-day variation, with concentrations over 10⁷ molecule cm⁻³ observed on two days in SOS1. SOS3 was characterised by very unstable weather, which may explain why the levels of both OH and HO₂ were so variable. The mean levels of [HO_x] were relatively consistent over the three mini-campaigns (see Figure 2). The peaks are provisionally lower than those observed in the summer of 2007,⁴ although they do agree within the 2σ confidence bands dictated by the errors in the respective calibrations and are not statistically different. Both OH and HO₂ tend towards zero concentration at night, although the number of night-time measurements during SOS was restricted.

In the only previous long-term study of OH behaviour, Rohrer and Berresheim were able to show that a 5-year dataset of [OH] in Germany could be simply described the equation³

$$[\text{OH}] = (a \times J(\text{O}^1\text{D})^b) + c$$

Our values of [OH] shows a reasonable correlation with J(O¹D) with a value of *b* close to 1 (see Figure 3), suggesting that the levels of OH are heavily influenced by the reaction of O¹D with water vapour. HO₂ shows a very good correlation with J(O¹D), with *b* close to 0.5, suggesting that its concentration is controlled by its self-reaction.

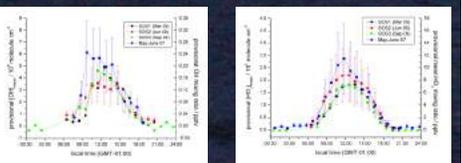


Figure 2. Average diurnals from 2007 and 2009 (hourly-averaged data). The error bars symbolise the 2σ confidence limits of the calibrations.

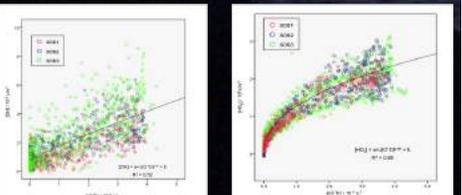


Figure 3. Plots of concentration against J(O¹D) for each HO_x species. The lines represent the non-linear fit to the data described by the equations.

2. LIF Detection of OH and HO₂

The OH radical was detected by on-resonance (at λ ~ 308 nm) LIF carried out at low pressures (*P* < 4 Torr). The low pressure extended the fluorescence lifetime of OH sufficiently to allow discrimination (in time) between the fluorescence and laser pulse. The HO₂ radical was 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 was drawn into the low pressure cells via pinhole nozzles, the laser beam passed perpendicular to the air stream and the fluorescence was imaged, along a 3rd axis, onto the photocathode of a gated channel photomultiplier.

The sensitivity of the instrument was determined in the field at Cape Verde as regularly as possible by a calibration method that allowed the generation of known concentrations of HO_x. Typical instrumental conditions for the three campaigns (SOS1–3) are shown in the right-hand table, as well as the average peak values of J(O¹D), measured using a radiometer.

	SOS1	SOS2	SOS3
Dates	27 th Feb – 8 th Mar	6 th – 16 th June	1 st – 15 th Sep
Days of OH/HO ₂	10	11	10
5-minute LOD OH (SN=1) [†]	3 × 10 ⁵ cm ⁻³	3 × 10 ⁵ cm ⁻³	7 × 10 ⁵ cm ⁻³
4-minute LOD HO ₂ (SN=2) [†]	6 × 10 ⁵ cm ⁻³	5 × 10 ⁵ cm ⁻³	7 × 10 ⁵ cm ⁻³
Average peak J(O ¹ D) / s ⁻¹	2.6 × 10 ⁵	3.5 × 10 ⁵	3.2 × 10 ⁵

[†] Provisional values based on calibrations performed in the field but subject to further laboratory checks

* Campaign-averaged calibration factors were used

4. Modelling analysis

A zero-dimensional box model based on the Master Chemical Mechanism (MCM) has been used to interpret the observations of OH and HO₂ during SOS1 and 2. The model was constrained to the supporting measurements of NO_x, CO, O₃, H₂O, J(O¹D) and some hydrocarbons, including acetaldehyde.

The base model run had the following parameters:

- (i) no halogen oxide chemistry
- (ii) no aerosol uptake
- (iii) 24 hr deposition of all species, but observed values always used

This model was then altered to ascertain the effects of a constant heterogeneous loss of HO₂. Both IO (~1.5 ppt) and BrO (~2.4 ppt) were observed at the site in 2007⁴ and different diurnal schemes of halogen oxides were included in the model based on those measurements:

- (a) Square top-hat 1.5 ppt IO, 2.4 ppt BrO (i.e. halogen oxides 'switch on' at -09:00 GMT and 'switch off' at -18:00 GMT)
- (b) Smoothed top-hat 1.5 ppt IO, 2.4 ppt BrO
- (c) Square top-hat 5 ppt each IO and BrO
- (d) Constant 5 ppt each IO and BrO

Presently, the model follows the diurnal trends in OH and HO₂ quite well (e.g. R² = 0.70 – 0.96). The model over-estimates daytime (i.e. 10:00 to 18:00, GMT) [OH] and [HO₂] for SOS1 and 2, but inclusion of aerosol losses and halogen oxide chemistry does reduce the modelled-to-observed ratios for both species. It must be noted that it is difficult to draw strong conclusions until laboratory verification of the field calibrations of the instrument have been performed. However, these preliminary modelling studies do suggest that aerosol and halogen oxide chemistry are important for the control of HO₂ and, to a lesser extent, OH.

Work is currently on-going to model the HO₂-observations from SOS3. Also, once the laboratory checks have taken place, the model's agreement with the observations can be fully assessed. A long-term variance analysis will then be applied to the full dataset to show the impact of seasonal changes on the variability of HO_x.

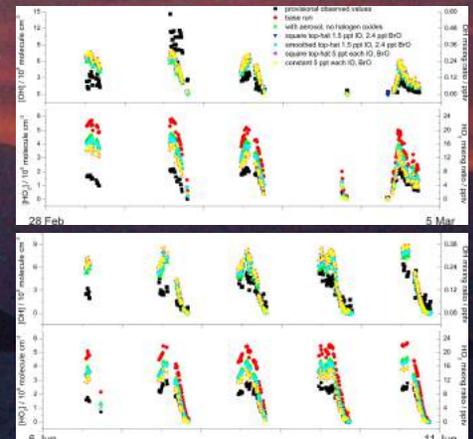


Figure 4. Comparison of observed [HO₂] with model predictions

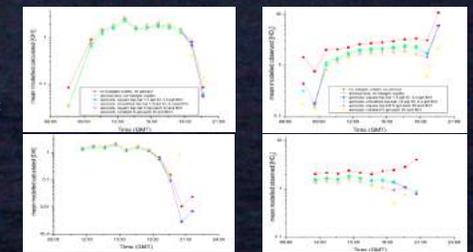


Figure 5. Averaged diurnal modelled-to-calculated [HO₂]

5. References and Acknowledgements

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The authors would like to acknowledge Dr James Lee and Dr Katie Read (Univ. York) for the core data used in the models, Prof. Lucy Carpenter (York) for co-ordinating the Seasonal Oxidant Study, and Bruno Faria, Luis Mendes and Gisela Duarte for their logistical assistance in Cape Verde. We would also like to thank Dr Andrew Goddard and the staff of the technical workshops at the School of Chemistry, Leeds, for their continued support. The Cape Verde Atmospheric Observatory is part of a bilateral German-UK initiative to undertake long-term ground- and ocean-based observations in the tropical Eastern North Atlantic Ocean region. It links with the international programme SOLAS, the EU-funded TENATSO (Tropical Eastern North Atlantic Time-Series Observatory) project, and with the German SOPRAN (Surface Ocean Processes in the Anthropocene) project.