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**The chemistry of OH
and HO₂ radicals in
the boundary layer**

L. K. Whalley et al.

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

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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, 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. IO and BrO, although present only at a few pptv, constituted ~23% of the instantaneous sinks for HO₂. Modelled HO₂ was sensitive to both HCHO concentration and the rate of heterogeneous loss to the ocean surface and aerosols. However, a unique combination of these parameters could not be found that gave optimised (to within 15%) agreement during both the day and night. The results imply a missing nighttime source of HO₂. The model underpredicted the daytime (sunrise to sunset) OH concentration by 12%. Photolysis of HOI and HOBr accounted for ~13% of the instantaneous rate of OH formation. Taking into account that halogen oxides increase the oxidation of NO_x (NO → NO₂), and in turn reduce the rate of formation of OH from the reaction of HO₂ with NO, OH concentrations were estimated to be 10% higher overall due to the presence of halogens. The increase in modelled OH from halogen chemistry gives an estimated 10% shorter lifetime for methane in this region, and the inclusion of halogen chemistry is necessary to model the observed daily cycle of ozone destruction that is observed at the surface. Due to surface losses, we hypothesise that HO₂ concentrations increase with height and therefore contribute a larger fraction of the ozone destruction than at the surface.

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The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1 Introduction

The OH radical is the dominant oxidant in the troposphere; its presence being felt most in tropical regions where high levels of humidity and solar irradiance lead to high rates of OH production:



Around 80% of methane, the third most abundant greenhouse gas, is processed within the tropical troposphere by the OH radical with the tropical marine lower troposphere contributing ~25% to the total tropospheric methane removal rate (Bloss et al., 2005a).

10 The loss of methane is disproportionately high in the lower tropical troposphere owing to the large temperature dependence of the reaction between methane and OH; the reaction rate being ~24 times greater at the surface than at the tropopause in the tropics.

15 Despite the importance of the lower marine tropical troposphere, OH measurements in this region, and also those of HO₂, which is closely coupled to OH through the reaction cycles shown in Fig. 1, are sparse. Aircraft measurements of OH and HO₂ were made during the Pacific Exploratory Missions (PEM) (Hoell et al., 1996, 1997, 1999; Raper et al., 2001), with OH midday concentrations between 6–8 × 10⁶ molecule cm⁻³ recorded in the tropical marine boundary layer (MBL) using the Selected Ion Chemical Ionisation Mass Spectrometer (SICIMS) technique (Mauldin III et al., 1999, 2001).
20 Modelling studies (using a photochemical box model and a photostationary state point model) indicated that Reaction (R2) was the major source of HO_x (OH+HO₂) (contributing 81%), while the major sinks involved the formation and subsequent loss of the peroxides of H₂O₂ and CH₃OOH (Chen et al., 2001). The models under-predicted the measured marine boundary layer (MBL) OH by 15–20%; no halogen chemistry
25 was included in these models. The primary focus of many of the PEM campaigns was the free-troposphere, and so measurements in the boundary layer were limited. OH

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

measurements using Differential Optical Absorption Spectroscopy (DOAS) have been made onboard the *R/V Polarstern*, as part of the Air Chemistry and Lidar Studies of Tropospheric and Stratospheric Species on the Atlantic Ocean (ALBATROSS) project held in October/November 1996 (Brauers et al., 2001). OH data were collected over the latitudinal range 5° N to 40° S in the Atlantic. OH displayed a distinct diurnal profile with a maximum around local noon of $\sim 7 \times 10^6$ molecule cm^{-3} . A simple photochemical box model, containing just CO and methane as sinks for OH, on average underpredicted OH by 16%, but was within the combined calibration errors associated with the OH, CO and photolysis frequency measurements.

In background marine airmasses, which are low in volatile organic compounds (VOCs) and NO_x, with HO_x generated mainly by Reactions R1–R2 and removed primarily by the formation and subsequent loss of peroxides, modelled and measured OH concentrations are in reasonable agreement. In contrast to OH, however, models often significantly overpredict HO₂ in such airmasses when only this basic chemistry is considered (Sommariva et al., 2004, 2006; Kanaya et al., 2007).

The Southern Ocean Photochemistry Experiment (SOAPEX-2) was held at Cape Grim, in North Western Tasmania, Australia, in 1999 under extremely clean conditions ([NO] < 3 pptv). Two chemical schemes were constructed to describe the free-radical budget; one containing just the oxidation of CO and methane, the other also describing the oxidation of non-methane hydrocarbons (NMHC) that were also measured (Sommariva et al., 2004). Box model calculations of [OH] using these two mechanisms agreed to within 5–10%, implying a minor role for NMHC as an OH sink, and both over-predicted [OH] by 10–20%. [HO₂], however, was overestimated by up to 40%, but model agreement was improved by assuming an HO₂ uptake coefficient to aerosol of unity (Sommariva et al., 2004). This, however, is probably an unreasonable assumption, as recent experimentally determined uptake coefficients for HO₂ on realistic aerosol surfaces range only from 0.01–0.1 (Thornton et al., 2008; Taketani et al., 2008, 2009). During the summer 2002 NAMBLEX project, which took place at Mace Head on the West coast of Ireland, the role of halogen oxides, specifically IO and BrO, in

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

the chemistry of the MBL was confirmed (Bloss et al., 2005b, 2006; Smith et al., 2006). IO and BrO react quickly with HO₂, with rate coefficients at 25°C of 8.6 and 2.1×10⁻¹¹ molecule⁻¹ cm³ s⁻¹ for IO and BrO, respectively (IUPAC, 2006). The HOI and HOBr formed may then either undergo photolysis to yield OH (and a halogen atom) or be taken up onto an aerosol surface. Reaction of HOI and HOBr with halide ions in acidified aerosol can form volatile inter-halogen species (Vogt et al., 1996; Pechtl et al., 2007) which photolyse in the gas phase allowing gaseous halogen chemistry to continue. The inclusion of a halogen scheme has been shown to improve the HO₂ modelled to measured agreement at a number of marine sites (Bloss et al., 2005b; Smith et al., 2006; Sommariva et al., 2006; Kanaya et al., 2007), and could account for the model discrepancy reported during the SOAPEX-2 experiment if realistic HO₂ uptake coefficients are instead used (Haggerstone et al., 2005).

At coastal locations such as Mace Head, the primary source of IO is the photolysis of molecular iodine (Saiz-Lopez and Plane, 2004) and, to a smaller extent, iodocarbons (Chameides and Davis, 1980; Carpenter et al., 1999), which are released by macro-algae exposed at low tide. The iodine atoms generated react rapidly with O₃ to generate the IO radical. At coastal sites where macro-algae are exposed, IO follows a distinct diurnal profile, with concentrations peaking with low tide during the daytime (Alicke et al., 1999; Whalley et al., 2007). The impact of halogens on tropospheric oxidants in regions without tidally exposed macro-algae, for example the open ocean, which covers ~70% of Earth's surface, was until recently, unconfirmed. A number of theoretical and observational studies had inferred indirectly the possible global impact of halogens (Dickerson et al., 1999; Vogt et al., 1999; Galbally et al., 2000; von Glasow et al., 2002a, 2004), but observations in the remote MBL were limited (Allan et al., 2000; Leser et al., 2003). In 2006/2007 an 8 month measurement series of IO and BrO at the Cape Verde Atmospheric Observatory (CVAO) was reported (Read et al., 2008), exhibiting fairly flat diurnal profiles following light intensity; with typical peak concentrations of ~1.4 and 2.5 pptv, respectively. CVAO is thought to be representative of the open ocean tropical MBL and hence these observations provide evidence

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of a potentially global presence of halogen oxides. Although IO and BrO are present at much lower concentrations than observed at coastal sites, for example Mace Head ($[\text{BrO}]_{\text{max}}=6.5$ pptv (Saiz-Lopez et al., 2004) and $[\text{IO}]_{\text{max}}\sim 30$ pptv – Commane et al., 2008) and Roscoff, France ($[\text{IO}]_{\text{max}}\sim 28$ pptv – Whalley et al., 2007), the inclusion of bromine and iodine chemistry was necessary to model adequately the daily O₃ destruction that is observed at Cape Verde (Read et al., 2008).

For $[\text{NO}]<\sim 20$ pptv, O₃, an important greenhouse gas in the troposphere, is photochemically destroyed (Penkett et al., 1997; Lee et al., 2009b) as shown in Fig. 1. At higher levels of NO the regime switches to a net O₃ production via the following reactions:



Read et al. (2008) reported a consistent daytime O₃ destruction cycle at the CVAO with an annually averaged loss of 3.3 ± 2.6 ppbv d⁻¹. In this paper, we present OH and HO₂ measurements made at the observatory as part of the Reactive Halogen in the Marine Boundary Layer (RHAMBLE) project (Lee et al., 2009a). The contribution towards the overall O₃ destruction from the reactions of OH and HO₂ radicals with O₃ is determined directly. A detailed model is used to investigate the impact of the reactions of HO₂ with BrO and IO, and the subsequent recycling to OH via the photolysis of HOBr and HOI. Of interest is the contribution of halogen chemistry to the rate of photochemical destruction of O₃ and the budgets of OH and HO₂ radicals. The significance of halogen chemistry for the global oxidising capacity and hence the removal rate of methane is also examined.

2 Experimental

2.1 Measurement of OH and HO₂ radicals

Fluorescence Assay by Gas Expansion (FAGE) provides a powerful method for the detection of tropospheric OH and HO₂ radicals (Heard and Pilling, 2003). The technique utilises the strong $A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi_i (v''=0) Q_1(2)$ transition at 308 nm for OH laser excitation. HO₂ can also be detected by this method following initial chemical conversion to OH by adding NO and subsequent detection. Laser-induced fluorescence experiments of this type are conducted at low pressures (~ 1 Torr) to extend the fluorescence lifetime of the OH radical sufficiently to allow the fluorescence to be discriminated from the more intense laser radiation. This is achieved by temporal gating of the detector; a channel photo multiplier (CPM) (Perkin Elmer C943P) is used. Switching the CPM off during the laser pulse also helps to prevent detector saturation (Smith et al., 2006). OH fluorescence and scattered light (laser and solar) are recorded by a gated photon counter (SRS SR400) during a 500 ns integration period (Gate A), commencing approximately 50 ns after the end of the laser pulse (FWHM ~ 35 ns). A small fraction of the total laser scattered light, along with solar scattered light and detector dark counts constitute a background signal to the OH fluorescence in gate A. The contribution of the solar scattered light and dark counts can be determined using a second photon counting gate (Gate B), delayed by 50 μ s from the first, at a time when the fluorescence and laser pulse have subsided. Tuning the laser away from resonance with the OH transition (online), to a wavelength where OH does not absorb (offline), allows the signal contribution of the laser scatter to be determined.

Ambient OH and HO₂ measurements have been made using the University of Leeds ground-based FAGE instrument since 1996 (Heard and Pilling, 2003). Details of the instrument have previously been reported (Smith et al., 2006), and are only considered briefly here. The operating conditions encountered at the CVAO were challenging and a modified operating procedure was necessary. The instrument is housed in an instrumented 20 ft sea container (Fig. 2), and comprises a laser system, an OH reference

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



cell for calibration of the laser wavelength, fluorescence cells which are housed on the roof of the sea container at a height of 3.5 m, and data acquisition and calibration systems.

During the RHaMBLe project, the instrument was located at the CVAO (16.85° N, 24.87° W), located at Calhau on a northeast facing rocky foreshore on the island of São Vicente within the Cape Verde archipelago. The island shores shelve steeply and very little tidal variability is apparent near to the site. A detailed map of Cape Verde and the layout of the site can be found in Lee et al. (2009a). The site is adjacent to the ocean, the University of Leeds ground-based FAGE instrument was approximately 50 m from the water's edge and the inlet was positioned approximately 3.5 m above sea level (a.s.l.). A wavelength tuneable Nd:YAG pumped Ti:Sapphire laser (Photonics Industries DS 20-532) was used to generate UV light at 308 nm. The Nd:YAG produces ~9 W of 532 nm radiation at a pulse repetition rate of 5 kHz, and is used to pump a Ti:Sapphire laser which generates up to 1.6 W of broadband near-IR radiation. Selecting a wavelength close to 924 nm, by changing the incident angle of an intra-cavity diffraction grating, and frequency tripling, by passing the light through two non-linear harmonic generation stages, generates the required radiation close to 308 nm for OH excitation. The time taken for the Ti:Sapphire laser to build up sufficient gain for laser output was found to change significantly in this campaign. When optimally aligned, the delay between the 532 nm pump pulse and the Ti:Sapphire laser output can be as short as 200 ns, but as laser optics become damaged or alignment shifts (possibly due to temperature changes) this delay can increase. The time between the Ti:Sapphire laser pulse, t_{308} , and the time when the fluorescence photons are counted (beginning of gate A) is critical, and must be maintained constant to ensure that the instrument sensitivity and background laser scatter does not change. A counter timer (Agilent Technologies, 225 MHz universal counter) triggered at the same time (t_0), as the laser, and coupled to a photodiode (Hamamatsu, S6468 series), which monitors the onset of the pulse of frequency tripled 308 nm light (t_{308}), was implemented during this project to measure the delay $t_{308} - t_0$. This system allowed any drift in $t_{308} - t_0$ to be directly

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



monitored in real time and a correction added to or subtracted from the time of the trigger controlling the start of the fluorescence photon counting gate A. The correction was applied prior to the beginning of each data acquisition cycle, which lasted ~ 450 s.

During this campaign a number of the optical coatings within the laser became damaged as a result of the high intensity laser beam hitting dust or sea-salt particles that had deposited on the optics. Although this problem occurs, to a certain extent, in all environments, the effect was particularly exacerbated at the CVAO, which is exposed to the elements being close to the water's edge and subject to wind-speeds regularly in excess of 10 ms^{-1} . The resultant optical damage led to a reduction in laser power at 308 nm from ~ 40 mW to < 20 mW as the project progressed. The stability of the delay time $t_{308} - t_0$ was significantly worse than had been observed previously (or since). In addition, tuning the laser wavelength by 0.006 nm (the interval between the online and offline positions) significantly changed $t_{308} - t_0$ and hence the position of gate A relative to the laser. As a result, the laser power and hence the laser scattered light changed significantly between the online and offline positions. The timing drift precluded OH measurements during the first half of the project, and the HO_2 measurements were subject to a larger uncertainty during this period. The timing problem was eventually ameliorated by reducing the interval between the online and offline wavelengths to 0.004 nm, for which the change in $t_{308} - t_0$ was much reduced.

Upon exiting the laser, the light was split by a dielectrically coated beam-splitter (CVI Optics Ltd). 80% was directed to a fluorescence cell via a fibre launcher (Elliot GoldTM series), fibre optic (Elliot Scientific) and collimation assembly (Oz Optics), and 19% to an OH reference cell, designed to aid the precise tuning of the laser wavelength to the peak of the $Q_1(2)$ OH transition. A large concentration of OH is generated by the pyrolysis of H_2O vapour, using a flow of humidified air over a heated filament. Light exiting the reference cell was directed on a UV sensitive photodiode (New Focus 2032) to determine the laser power for subsequent normalisation of the ambient LIF signal; a cut-off filter was placed in front of the photodiode to prevent visible light reaching it. The remaining UV light (1%) was directed onto a fast photodiode (Hamamatsu, S6468

The chemistry of OH and HO_2 radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



series), which was used as input to the counter-timer to correct for any drift in the laser timing.

The laser light entered the detection cell on the roof of the container via a baffled side arm and intersected the ambient air stream, drawn through a 0.8 mm diameter nozzle sat on a 25 mm turret, on an axis perpendicular to the fluorescence detection axis containing the CPM. The laser light then exited the cell via a second baffled sidearm and was reflected onto a second UV sensitive filtered photodiode (New Focus 2032), the output of which was monitored to check good laser alignment was being maintained through the cell. Ambient temperature fluctuations can cause the voltage output from photodiodes to drift, this precluded the use of the detection cell photodiode (located on the roof) to normalise the LIF signal to laser power. High solar intensities were experienced at the Cape Verde site (the solar zenith angle at solar noon in June at the site was $\sim 5^\circ$) leading to a large amount of solar scattered light detected within the cell by the CPM. A solar shade, consisting of a sheet of black aluminium (10 cm \times 10 cm) was placed 15 cm above the nozzle, which reduced the solar counts that reached the detector by an order of magnitude. Without the shade, solar counts at solar noon could reach >200 counts s^{-1} , the random fluctuations of which are larger than the typical signal from OH, making measurements extremely difficult. The windspeed at the site was ~ 10 ms $^{-1}$ (and rarely dropped below 5 ms $^{-1}$), thus the average time an air parcel spent under the shade was ~ 0.01 s, much shorter than the lifetime of either OH or HO₂ radicals, and should not perturb their concentrations.

Normally, the University of Leeds ground-based FAGE instrument utilises two fluorescence cells for simultaneous OH and HO₂ measurements (Smith et al., 2006). Due to low laser power, coupled with a CPM failure in the OH cell, only one cell was operable during the project and was used instead to make alternating sequential measurements of the two radicals. This set-up has been successfully utilised on a number of previous field projects, for example during the recent CHABLIS project (Bloss et al., 2007). Signals from the photon counter were integrated for 1 s periods. Online data were acquired for 200 s and consisted of 100 s of fluorescence from OH, followed by

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



100 s of fluorescence from both OH and converted HO₂ (NO added to the cell). The offline signal was then collected for a further period of 100 s, with NO added after 50 s to measure any additional signal caused by the addition of NO, for example from enhanced scattering (there was no extra signal). The [OH] did not vary significantly during a single data acquisition period, and, therefore, the signal due to HO₂ could be determined by subtracting the OH online signal from the HO_x online signal. In total, one data acquisition cycle (including the time taken to find the peak of the OH transition) took ~450 s.

Calibrations were performed every two to three days throughout the campaign. A zero air generator (EcoPhysics PAG 003) was coupled to a zero air trap (Megatech CE-500KF-O-4R Gas Purifier) which reduced the levels of NO_x, VOCs and CO to <1 pptv and following humidification in a liquid water bubbler, this flow was directed down a 60 cm long quartz glass tube (internal diameter 22 cm) past a Hg pen-ray lamp (LOT Oriel model 6035), under roughly laminar flow conditions (Reynolds Number=646). The 184.9 nm radiation emitted by the pen-ray lamp photolysed H₂O vapour, generating OH and HO₂ (in the presence of O₂) in equal quantities. A few ppbv of O₃ was generated from O₂ photolysis and the subsequent O+O₂ recombination reaction, and this was used as a chemical actinometer for the 184.9 nm flux. When calibrating for HO₂ a 100 sccm flow of CO (BOC, 1% CO in N₂) was added to the humidified air flow to rapidly convert all OH radicals to HO₂ (~2.5×10⁻³ s OH lifetime). Approximately 5 slm of the central portion of the flow within the tube was drawn into the detection cell, via the 0.8 mm sampling nozzle, the excess flow (~7 slm) was directed towards an O₃ analyser (Thermo Environmental Instruments (TEI) 42C) and Dewpoint Hygrometer (General Eastern 1311DR sensor). Determining [H₂O] and [O₃] enabled the radical concentration to be calculated using:

$$[\text{OH}] = [\text{HO}_2] = \frac{[\text{O}_3][\text{H}_2\text{O}]\sigma_{\text{H}_2\text{O}}\phi_{\text{HO}_x}}{[\text{O}_2]\sigma_{\text{O}_2}\phi_{\text{O}_3}P} \quad (1)$$

where $\sigma_{\text{H}_2\text{O}}$ and σ_{O_2} are the 184.9 nm absorption cross sections of H₂O vapour

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



and O₂, determined experimentally to be $(7.1 \pm 0.2) \times 10^{-20}$ molecule⁻¹ cm² and $(1.37 \pm 0.14) \times 10^{-20}$ molecule⁻¹ cm², respectively, for the same pen-ray lamp used during the field measurements. $\phi_{\text{HO}_x} = 1$ is the quantum yield for production of OH or HO₂ in the absence of added CO, and $\phi_{\text{HO}_x} = 2$ for HO₂ in the presence of added CO. P is the profile factor, which is discussed further below. With the pen-ray lamp switched off ($[\text{HO}_x] = 0$) it was found that there was no additional signal above the background when NO was added to the FAGE cell, ruling out the presence of any significant artefact due to HO_x production either directly from photolysis of impurities (e.g. HNO₃) in the NO, or from the photolysis of species desorbed from the walls after exposure to NO.

A correction needs to be applied to account for the parabolic distribution of radial flow velocities across the calibration tube under laminar flow conditions. The central portion of the flow sampled by the detection cell has a higher velocity and hence spends less time in the photolysis region compared with the remainder of the flow (excess) that is sampled by the O₃ analyser from regions of the tube with a lower velocity. This radial flow distribution leads to more O₃ in the excess air relative to that in the FAGE sampled air at the centre. Any variability in the flux of the 184.9 nm light across the tube can also perturb the O₃ and radical profile in the tube. The profile factor, defined as $P = [\text{O}_3]_{\text{excess}} / [\text{O}_3]_{\text{central}}$, has been experimentally measured as 1.57 ± 0.09 (Smith, 2007), and is used in Eq. (1) to calculate [OH] and [HO₂].

The sensitivity of the cell towards OH and HO₂, in units of cts s⁻¹ mW⁻¹ molecule⁻¹ cm³, is given by:

$$C_{\text{OH}} = \frac{S_{\text{OH}}}{[\text{OH}] \times P_{\text{wr}}} \text{ and } C_{\text{HO}_2} = \frac{S_{\text{HO}_2}}{[\text{HO}_2] \times P_{\text{wr}}} \quad (2)$$

S_{OH} and S_{HO_2} are the measured fluorescence signals (cts s⁻¹) due to OH (in the absence of added CO and NO) and HO₂ (in the presence of added CO and NO), respectively. P_{wr} is the laser power entering the cell in mW, which decreased from ~19 to ~7 mW during the RHaMBLe campaign. The average instrument sensitivity was 1.1×10^{-7} cts s⁻¹ mW⁻¹ [OH]⁻¹ for OH and 4.4×10^{-8} cts s⁻¹ mW⁻¹ [HO₂]⁻¹ for

HO₂, with the 2σ uncertainty estimated as ~40% for OH and HO₂ (Smith, 2007). The cell pressure was optimised for OH detection rather than for conversion of HO₂. The detection limit (LOD) is given by:

$$\text{LOD} = \frac{\text{SNR}}{\text{Pwr} \times C} \sqrt{\left(\frac{1}{m} + \frac{1}{n}\right) \frac{S_{\text{back}}}{t}} \quad (3)$$

5 where SNR is the signal-to-noise ratio (1), *m* is the number of online data points (100), *n* is the number of offline points (50), *S*_{back} is the background signal comprising laser scattered light (~20 cts s⁻¹), solar scattered light (max. ~20 cts s⁻¹ at noon) and CPM dark counts (0 cts s⁻¹) and *t* is the integration of each data point (1 s). Using the above values and Pwr=9 mW, LOD of 1.1×10⁶ molecule cm⁻³ and 2.8×10⁶ molecule cm⁻³
10 were calculated for OH and HO₂, respectively.

2.2 Ancillary measurements

A number of ancillary measurements were made to permit a detailed characterisation of the atmospheric composition at the site and to constrain the box model. Details of these measurements are listed in Table 1 and are discussed further in Lee et al. (2009a). The majority of these measurements are part of a long term dataset made continuously at the Cape Verde Observatory since October 2006. The halogen oxide measurements made using Long Path-Differential Optical Absorption Spectroscopy (LP-DOAS) were part of an 8 month dataset, covering the period November 2006 to June 2007 (Read et al., 2008).
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2.3 Box model using the Master Chemical Mechanism

A box model was used to calculate OH and HO₂ concentrations, and contained a near explicit chemical scheme for the oxidative degradation of C1–C5 hydrocarbons, extracted from the Master Chemical Mechanism (MCM) version 3.1 (Saunders et al., 2003). The entire MCM treats the degradation of 125 VOCs and considers oxidation by
20

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



OH, O₃ and NO₃. The degradation continues until CO₂ and H₂O vapour form as the final oxidation products. The mechanism uses the latest kinetic and photochemical data and complete details are available at the MCM website (MCM, <http://mcm.leeds.ac.uk/MCM/home>). A halogen chemical scheme as indicated in Fig. 1 (and listed explicitly in supplementary information <http://www.atmos-chem-phys-discuss.net/9/15959/2009/acpd-9-15959-2009-supplement.pdf>) was added to the MCM to assess the effect of IO, BrO and related species on the budgets of OH, HO₂ and O₃ concentrations. The mechanism contains photolysis of O₃, NO₂, HOI, HOBr, IO, aldehydes, ketones, H₂O₂ and organic hydroperoxides (RO₂H), but only measurements of $j(\text{O}^1\text{D})$ were used to constrain the model. The other photolysis rates were calculated based on a two-stream scattering model (Hough, 1988) and assuming clear-sky conditions. Under cloudy conditions calculated J values were scaled to the ratio of observed $j(\text{O}^1\text{D})$ to clear sky $j(\text{O}^1\text{D})$. Dry deposition terms for H₂O₂ (1 cm s⁻¹) (Junkermann and Stockwell, 1999), RO₂H (0.9 cm s⁻¹) (Junkermann and Stockwell, 1999), HNO₃ (0.8 cm s⁻¹) (Ganzeveld and Lelieveld, 1995), CH₃OH (0.09 cm s⁻¹) (Carpenter et al., 2004) and HCHO and aldehydes (0.33 cm s⁻¹) (Brasseur et al., 1998) were included in the model. The model was constrained with measured VOCs, NO_x, O₃, CO, CH₄, HCHO, $j(\text{O}^1\text{D})$ and meteorological parameters (Table 1). The halogen scheme was constrained using measurements of the diurnal cycle of [IO] and [BrO] averaged for May 2007. It was necessary to use an average because of incomplete data coverage primarily arising from IO and BrO being detected by DOAS in different wavelength regions and, therefore, not being measured simultaneously. A H₂ concentration of 500 ppbv was used, similar to that measured in the remote marine boundary layer at other locations, for example during SOAPEX-2 at Cape Grim (Sommariva et al., 2004), and used in OH model calculations during the ALBATROSS campaign (Brauers et al., 2001). The unmeasured intermediate species, generated from the oxidation of VOCs and other species used to constrain the model, were initialised at zero. The model was constrained to hourly averages of the basic chemical parameters described above and the simultaneous rate equations were solved using the FACSIMILE integrator (Curtis and Sweetenham,

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



1987). The model was allowed to run to steady state (~4 days) to stabilise the concentrations of any unmeasured intermediate species, e.g. alkyl nitrates, unmeasured carbonyls and peroxides, before the OH and HO₂ modelled data were compared to the measurements.

5 The rate of heterogeneous loss of HO₂ and a number of halogenated species (supplementary information <http://www.atmos-chem-phys-discuss.net/9/15959/2009/acpd-9-15959-2009-supplement.pdf>) to aerosol surfaces has been evaluated using this model (see Sect. 3.4 for further details). A simple scheme was used, based on a first-order loss to aerosol surfaces (Ravishankara, 1997):

$$10 \quad k'_{\text{loss}} = \frac{c_g A \gamma}{4} \quad (4)$$

where k'_{loss} is the heterogeneous loss rate, A is the aerosol surface area per unit volume, and γ is the uptake coefficient. In this model the uptake coefficients are assumed independent of aerosol diameter and a constant aerosol surface area of $1 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$ was used, based on average aerosol surface area observed at the
15 CVAO at a height of 30 m during the project (Allan et al., 2009). c_g is the mean molecular speed of the gas molecules (cm s^{-1}), given by:

$$c_g = \sqrt{\frac{8RT}{\pi M_w}} \quad (5)$$

where R is the universal gas constant, T is temperature and M_w is the molecular weight of the gas.

20 More recently, this scheme was extended by Sommariva et al. (2006) and Haggerstone et al. (2005) to incorporate loss rates that were dependent upon the measured aerosol size-distribution, using an expression which incorporated the transition between control by gas-phase diffusion and molecular uptake (Sander, 1999). In the background marine environment, the particle diameters are small. Under such conditions, mass transfer is limited by interfacial mass transport and Eq. (4) provides a
25

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

reasonable estimation of the aerosol uptake coefficient (Haggerstone et al., 2005). The impact of heterogeneous loss of HO₂ is discussed in Sect. 3.4.

A surface deposition term for HO₂ was also considered in a number of model scenerios (Sect. 3.4). The deposition velocity (V_D) of HO₂ was estimated using the NOAA/COARE air/sea gas exchange parameterization (Fairall et al., 2007). The deposition velocity of HO₂ is related to the flux (F) of HO₂ at a given height above the surface (z) by:

$$F = -V_D \times [\text{HO}_2]_{(z)} \quad (6)$$

V_D can be determined given knowledge of the sum of air-side (R_a) and water-side (R_w) resistances (Fairall et al., 2000):

$$V_D = \left(\frac{1}{R_a + (R_w/\alpha)} \right) \quad (7)$$

where α is the dimensionless solubility (a function of species, temperature and salinity). The air-side resistance, R_a , represents the sum of the aerodynamic resistance (R_1) and gas-phase film resistance (R_2). Assuming that the atmospheric surface layer is neutrally stable then R_1 can be determined using Eq. (8):

$$R_1 = \frac{U_{(z)}}{u_*^2} = \frac{1}{\kappa u_*} \ln \left(\frac{z}{z_0} \right) \quad (8)$$

where $U_{(z)}$ is the mean wind-speed at height (z), κ is the von Karman constant (0.4), u_* , is the friction velocity, and z_0 , is the aerodynamic roughness length (Stull, 1988). The gas-phase film resistance (R_2) is determined by Eq. (9):

$$R_2 = \frac{5}{u_*} S_C^{2/3} \quad (9)$$

where S_C is the Schmidt number.

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The water-side resistance (R_w) can be determined by Eq. (10) (assuming the influence of turbulence is negligible relative to chemical reaction time-scale of HO_2 in water):

$$R_w = \frac{1}{\sqrt{aD_w}} \quad (10)$$

5 where a is the reaction time-scale for HO_2 in water (assumed to be sufficiently fast that turbulence is neglected) and D_w is the diffusion coefficient of HO_2 in water.

Many of the variables in Eqs. (7)–(10) can be estimated by the NOAA/COARE algorithm given an input of boundary layer depth (~ 1000 m) (Read et al., 2008), atmospheric pressure (~ 1010 mbar), wind-speed (0 – 20 m s^{-1}), height of wind-speed data
10 (10 m), Henry's law coefficient (1.2×10^3 M atm^{-1} – Schwartz, 1984) and rate coefficients for reactions of HO_2 in water (ionisation of HO_2 forming O_2^- and H^+ (Bielski, 1978) and chemical reaction of HO_2 with O_2^- forming HO_2^- (Bielski, 1978) were considered). The water-side Schmidt number and diffusion coefficient were assumed to be similar to those of O_3 (500 and 1.2×10^{-9} $\text{m}^2 \text{s}^{-1}$ – Chang et al., 2004). The HO_2
15 water-side reaction rate was varied from 10^3 – 10^5 s^{-1} to determine the sensitivity of V_D to it. For HO_2 , the solubility is sufficiently large that the deposition velocity is essentially air-side controlled and the flux is insensitive to the water side turbulence and reaction rate.

3 Results

20 3.1 Time series of measured and modelled OH and HO_2

Figure 3 shows the values of $j(\text{O}^1\text{D})$, CO, NO, NO_2 , O_3 , HO_2 and OH measured at the CVAO during the summer 2007 campaign. Box model calculations using the MCM for OH and HO_2 are compared with measured values in Fig. 4. OH measurements were made on 5 days (28th May to 2nd June) and HO_2 on 11 days (21st May to 2nd

The chemistry of OH and HO_2 radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

June). The first 4 days of HO₂ measurements were characterised by elevated levels of CO (~130 ppbv); for the remainder of the measurement period the concentration of CO dropped and remained at ~100 ppbv (Panel a, Fig. 3). A 5-day back trajectory analysis for this period indicates a switch in air-mass origin (Lee et al., 2009a). During the first 4 days of HO₂ measurements, air was influenced by long-range transport from America, this then changed to a more typical air-mass (influenced by the marine background) that tends to dominate at the site for the majority of the year (Lee et al., 2009a). Throughout the measurement period maximum $j(\text{O}^1\text{D})$ levels were relatively constant, at $3.5 \times 10^{-5} \text{ s}^{-1}$ (Panel a, Fig. 3) with very little cloud cover observed throughout the campaign. O₃ concentrations between 35–40 ppbv were recorded (Panel b, Fig. 3) (Lee et al., 2009a).

During 3 out of the first 4 days of measurements [HO₂] was elevated relative to data taken later in the campaign, due to the elevated CO during this time, with a maximum of $\sim 6 \times 10^8 \text{ molecule cm}^{-3}$ (~24.5 pptv) recorded on 24th May (Panel c, Fig. 3). MCM model estimates of [HO₂] over this period are also elevated relative to model estimates for later in the campaign (Panel a, Fig. 4), although peak MCM modelled [HO₂] from this period is only $\sim 4 \times 10^8 \text{ molecule cm}^{-3}$ suggesting either a missing source of HO₂, or an over-estimation of the HO₂ sinks in the model. On the 22nd May, measured [HO₂] was significantly lower at $\sim 3 \times 10^8 \text{ molecule cm}^{-3}$, but this was not reflected in the model. The lack of variability in the modelled HO₂ over this 4 day period compared to measurement may be due, in part, to the use of a constant average diurnal cycle for IO and BrO. As discussed below, reaction of HO₂ with these species represents a significant sink, and any daily variability in their concentrations will not be captured in modelled HO₂. During the 8 months of IO and BrO measurements, the mean day-time maxima were 1.4 pptv and 2.5 pptv respectively although there was considerable variability displayed, ± 0.8 (1 σ) pptv for IO and ± 1.1 (1 σ) pptv for BrO (Read et al., 2008). In addition, the model was constrained using a constant HCHO concentration of 500 pptv, this is the typical HCHO concentration observed, as measured using the LP-DOAS during its 8 month deployment at the observatory. It should be noted, how-

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

ever, that throughout the 8 months [HCHO] were variable, dropping below the LOD of the LP-DOAS (~200 pptv) at times and elevated in polluted air-masses. Reaction of OH with HCHO, and also HCHO photolysis are sources of HO₂, HCHO concentrations may have been higher than 500 pptv, particularly in the long-range transport of American air-masses from 21–24 May, yet this will not be reflected in modelled HO₂. After 26th May, peak measured [HO₂] ~2–4 × 10⁸ molecule cm⁻³ were lower, and mirrored by the model, although there is now a model over-prediction.

OH measurements were also made during the second measurement period (Panel c, Fig. 3). Peak concentrations of 6–9 × 10⁶ molecule cm⁻³ were recorded; the midday [OH] gradually decreasing over the 5 days. The modelled [OH] was in good agreement with the measurements, with the peak agreeing to within 15% (Fig. 4, Panel b) and also decreasing over the 5 days.

3.2 Rate of production and destruction analysis

Figure 5 shows the instantaneous rates of production (ROPA) and rates of destruction analyses (RODA) for OH and HO₂ at solar noon (averaged for the period 12:00–13:00 local time) as determined by the MCM. The ROPA and RODA are averaged over all days for which there are respective measurements of OH and HO₂. Figure 6 shows the diurnal variation of the MCM calculated rates of production and destruction of OH and HO₂ for different chemical processes, again averaged over the days when there are radical measurements. It should be noted that several of the pathways serve to inter-convert OH to HO₂, or visa versa, and so, overall, do not lead to an increase or decrease in the total HO_x.

The photolysis of O₃ and subsequent reaction with H₂O vapour represents the dominant OH source, accounting for ~76% of its production at solar noon. The photolysis of H₂O₂ and CH₃OOH, which, when allowed to run to steady state, in the MCM reach levels of ~500 pptv and ~1 ppbv respectively, similar in magnitude to observations of peroxides at Cape Grim (Ayers et al., 1996; Monks et al., 1998) and also in the Cape Verde region during the ALBATROSS cruise (Weller et al., 2000). The recycling of

HO₂ to OH, via reaction with NO and O₃, also act as small additional OH sources. The hypohalous acids, HOI and HOBr, which are generated by the reaction of HO₂ with IO and BrO respectively (Fig. 1), may be photolysed to OH or taken up on aerosol surfaces. An uptake coefficient for HOI and HOBr loss onto aerosols of $\gamma_{\text{HO}_x} = 0.061$ was assumed, consistent with experimental data (Mossinger and Cox, 2001). Under this scenario, the photolysis of HOI and HOBr contributes ~13% to the instantaneous OH formation. There is some uncertainty in the γ_{HO_x} assumed, with some studies speculating that it may be an order of magnitude higher in the MBL (Abbatt and Waschewsky, 1998; Wachsmuth et al., 2002). Under such a scenario ($\gamma_{\text{HO}_x} = 0.61$), the photolysis of HOI and HOBr contributes ~9% to the instantaneous OH formation.

The reactions of OH with CO and acetaldehyde are the major OH losses (~28% and ~25% respectively), with other oxygenated VOCs that were measured (acetone and methanol) playing only a minor role (contained within “other” in Fig. 5). Other sinks include reaction with methane, H₂, O₃, HO₂, HCHO and peroxides. Reaction of OH with NO₂, C₂–C₅ hydrocarbons (NMHC) and MCM calculated chemical intermediates from OH oxidation of NMHC (oxygenated VOCs and organo-nitrates) all account for a small fraction of the OH loss, and are contained within the “other” segment.

HO₂ sources are dominated by the reaction of OH with CO (~41%) and, to a smaller extent, CH₃O with O₂ (~16%); the source of CH₃O is from the reaction of CH₃O₂ with NO. The reaction of HCHO with OH, combined with the photolysis of HCHO, can contribute up to 20% of the HO₂ at solar noon. Other smaller HO₂ sources include OH+H₂, OH+O₃, CH₃OH+OH, $j(\text{CH}_3\text{CHO})$, OH+H₂O₂ and HO₂NO₂ thermolysis.

The reaction of HO₂ with IO and BrO accounts for a combined, instantaneous, HO₂ loss of ~23%, despite these species only being present at ~1.4 pptv and ~2.5 pptv (peak daytime levels) respectively. The major HO₂ sink is the reaction with RO₂ (R=CH₃–C₅H₁₁) (Reaction R10), typical of low NO_x environments (Carpenter et al., 1997; Penkett et al., 1997), which together with the self reaction (R11) accounts for over 50% of the total HO₂ loss. The presence of a small quantity of NO (~1.5 pptv) at the site serves to slightly enhance HO₂ levels, because although HO₂+NO removes HO₂,

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



this is offset at these low levels of [NO] by a larger overall rate of $\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2$ (followed by rapid HO_2 production from $\text{RO} + \text{O}_2$) leading to a net production of HO_2 (Reactions R7–R8) (Poppe, 1999). If NO concentrations were to increase further, $[\text{RO}_2]$ would decrease (Fleming et al., 2006) and $\text{HO}_2 + \text{NO}$ (Reaction R4) would begin to dominate over $\text{RO}_2 + \text{NO}$ (Reaction R8) (as $k_4 = 8.9 \times 10^{-12} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ is $> k_7 = 7.7 \times 10^{-12} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ – IUPAC, 2006). Under this regime, reactions involving NO would act as an HO_2 sink rather than a source.



The presence of halogen oxides can perturb this HO_x/NO_x chemistry. IO and BrO serve to reduce the NO:NO₂ ratio through Reactions (R11) and (R12), this in turn reduces the rate of Reactions (R4) and (R7) and decreases the rate of formation of OH via Reaction (R4). Although the photolysis of HOI and HOBr acts as a significant OH source (Fig. 5), it has recently been suggested that the presence of halogen oxides can actually lead to a reduction in [OH] (Keene et al., 2009) by the reduction in the secondary formation of OH via Reaction (R4). Modelling studies indicate that NO_x levels could approximately double in the absence of halogen oxides in environments similar to Cape Verde (Keene et al., 2009). To simulate the overall impact of halogen oxides, taking into account that NO_x levels may be significantly perturbed due to the presence

of halogens, a model run, initialised with no halogens and a factor of two increase in the NO_x concentration, has been performed. In contrast to Keene et al. (2009), OH concentrations were found to be 10% larger in the presence of halogen oxides compared to in the absence of halogen oxides (but with double $[\text{NO}_x]$); the perturbation of the NO_x chemistry by halogen oxides offsets the instantaneous OH formation via HOI and HOBr photolysis by $\sim 3\%$. Keene et al. (2009) consider the impact of BrO and ClO only; no IO measurements were made. The rate coefficient for reaction of ClO with HO_2 ($5 \times 10^{-12} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ – IUPAC, 2006) is a factor of two times smaller than the rate coefficient for reaction of ClO with NO ($1.7 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ – IUPAC, 2006). Depending on $[\text{HO}_2]$ and $[\text{NO}]$, the presence of ClO can effectively lead to a reduction in $[\text{OH}]$, as presented by Keene et al. (2009). Conversely, the rate coefficient for reaction of IO with HO_2 ($8.4 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ – IUPAC, 2006) is larger than the rate coefficient for reaction of IO with NO ($1.96 \times 10^{-11} \text{ molecule}^{-1} \text{ cm}^3 \text{ s}^{-1}$ – IUPAC, 2006) and so the presence of IO, in low NO_x environments, serves to increase $[\text{OH}]$. The absence of IO chemistry in the model used by Keene et al. (2009) could account for the differences in the modelled impacts of halogens on $[\text{OH}]$.

Over a 24 h period, the relative contribution of the HO_x sources and sinks remains fairly consistent, as shown in Fig. 6. There is some deviation from the trend discussed above, and displayed in Fig. 5, for example the reaction of OH with CH_3CHO and reactions involving HO_2NO_2 peak in the afternoon, reflecting the afternoon peak in the concentrations of CH_3CHO and NO_2 as measured at the site. In the morning and evening (when the concentration of HO_2 is low) the reaction of HO_2 with O_3 dominates over the HO_2 self reaction promoting radical recycling rather than radical termination. The reaction of HO_2 with IO and BrO exhibits a broad diurnal cycle that reflects light intensity.

The chemistry of OH and HO_2 radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.3 Diurnally averaged measured and modelled profiles

Figure 7 shows the average diurnal profile for both measured and modelled [OH] and [HO₂], together with the modelled-to-measured ratios. The model is averaged only for times when radical measurements exist. Only daytime OH data are available on 5 days due to the instrumental difficulties outlined in Sect. 2, which limits the scope of the discussion of the model performance. Although the absolute noon [OH] and afternoon decrease is captured well, the model under-predicts [OH] in the mid-morning, and during the very late afternoon and evening, although for the latter OH levels are close to the LOD of the instrument. HO₂ was measured on 11 days and 2 nights, enabling a complete 24 h average diurnal profile to be built up. The model contains the halogen scheme and is constrained to 500 pptv HCHO, but does not include heterogeneous loss for HO₂ by surface deposition or uptake to aerosol, which are discussed below. HO₂ was measured (~0.6 pptv), above the detection limit throughout the night, consistent with previous measurements in other remote locations in the marine boundary layer (Salisbury et al., 2001), and in reasonable agreement with the model. On average HO₂ is under-predicted by 20% at night, although there are significant excursions in the modelled-to-measured ratio. During the daytime the model-to-measured HO₂ is fairly constant, with the model over-predicting [HO₂] by an average of 35%. We discuss this systematic overprediction below.

3.4 Sensitivity analysis of modelled HO₂ concentrations

A number of key parameters that control the production and loss of HO₂ have been varied to determine the impact on modelled [HO₂]. Table 2 lists the changes made and their impact on modelled [HO₂], and Fig. 8 shows the impact on the diurnal variation of the modelled-to-measured ratio of [HO₂].

As seen in Figs. 5 and 6, the photolysis of HCHO and reaction of HCHO with OH accounts for up to 20% of the HO₂ source in the daytime. Reducing the HCHO concentration from 500 pptv (value used to constrain the model) to 100 pptv decreases

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

[HO₂] by ~14% during the daytime, reducing the model-measurement discrepancy, but has relatively little effect at night (~2% decrease). HCHO was detected using LP-DOAS, and typically ~500 pptv was observed (J. M. C. Plane, personal communication, 2009.). Consistent with this, when HCHO is left unconstrained in the model it builds up to a steady state concentration of ~530 pptv. During the ALBATROSS cruise, up to 1 ppbv of HCHO was observed in the tropical mid-Atlantic (Brauers et al., 2001), whereas ~750 pptv was recorded in the Cape Verde region (Weller et al., 2000). At Cape Grim, Tasmania during the SOAPEX-2 campaign, and during clean conditions, [HCHO] was measured around noon from 217–352 pptv (with 50% error) (Sommariva et al., 2004). Given these measurements, it seems unlikely that [HCHO] can be as low as 100 pptv during the measurement period, although any variability in [HCHO] during the course of the campaign could account for the variability observed in the measured [HO₂], which will not be captured by the model. Specifically, [HCHO] may have been elevated in the air-masses originating over North America encountered at the start of the HO₂ measurement period. More frequent measurements of HCHO at the site in the future would be beneficial to better constrain the box model.

Heterogeneous loss of HO₂ represents another significant uncertainty in the model. In the model comparison thus far, no uptake onto aerosols has been considered. A $k'_{\text{loss}} = 4.37 \times 10^{-3} \text{ s}^{-1}$ from aerosol loss was found to optimise the daytime HO₂ modelled to measured ratio if surface deposition of HO₂ (see below) was included also. Using this value, the [HO₂] is reduced on average in the daytime by ~26%. Using Eq. (4), an uptake coefficient of $\gamma_{\text{HO}_2} = 0.4$, combined with the typical measured aerosol surface area, $A = 1 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$, is required to realise this. Literature values for the HO₂ uptake coefficient suggest that a value of γ of ~0.1 is more appropriate (Thornton et al., 2008; Taketani et al., 2008). If $\gamma = 0.1$ is used in the model then, from Eq. (4), a correspondingly increased aerosol surface area (from $1 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$ to $4 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$) is required to maintain the optimised agreement of the daytime modelled to measured ratio of HO₂. The particle radius and number population, used to determine the aerosol surface area, were measured with a Scanning Mobility Parti-



cle Sizer (SMPS) (0–1 μm) and a Aerosol Particle Sizer (APS) (1–10 μm) (Allan et al., 2009). For particles of 0–1 μm diameter (which encompasses the bulk of the aerosols at the site) a dry aerosol distribution was determined. At an average ambient humidity of $\sim 80\%$ the radius of sea-salt aerosols are expected to grow by a factor of ~ 1.4 (Allan et al., 2009), leading to the aerosol surface area increasing roughly by a factor of 2 (radius²) for this size range.

A strong gradient in the aerosol surface area at the ground (where the HO_x measurements were made) to a height of ~ 12 m has recently been recorded at the site (R. von Glasow, personal communication, 2009). The aerosol measurements used here were made above this high aerosol region at a height of 30 m. The aerosol sampling position could account for the remaining discrepancy between the measured aerosol surface area and the optimal modelled aerosol surface area of $4 \times 10^{-6} \text{ cm}^2 \text{ cm}^{-3}$. Using a k'_{loss} of $4.37 \times 10^{-3} \text{ s}^{-1}$ leads to a large under-prediction of nighttime HO₂ levels, although it must be stressed that both the modelled and measured values are already very low. To calculate the heterogeneous loss of HO₂ to aerosol satisfactorily, measurements of the aerosol size distribution at the radical measurement height are required.

In addition to heterogeneous loss to aerosols, surface deposition of HO₂ to the surrounding ocean has also been considered by the method described in Sect. 2.3. Using the RODA presented above, the chemical lifetime of HO₂ is calculated to be 51 s, and so surface deposition can compete with chemical loss. With HO₂ measured at a height of 3.5 m from the ground, and for a windspeed of 7 ms^{-1} , the HO₂ concentration is reduced by $\sim 12\%$ in the daytime due to deposition. Prior to reaching the FAGE cell, the sampled air also passed over ~ 50 m of surf zone and rocks, in addition to the open ocean, and as this area is likely to have an increased surface roughness, leading to higher turbulence and hence contact with the ground, the surface deposition assuming loss to the ocean only is likely a lower limit for this region. Inclusion of surface deposition of HO₂ improves the daytime model agreement with measured HO₂, but worsens the nighttime agreement.

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



3.5 Nighttime source of HO₂

The inclusion of heterogeneous loss of HO₂ via surface loss to aerosol or deposition improves the daytime model-to-measured agreement, but causes the model to under-predict HO₂ at night. As reported by Read et al. (2008) a daily O₃ destruction cycle is observable at the CVAO, with the majority of this loss due to photolysis of O₃ and subsequent reaction of O(¹D) with H₂O and via catalytic cycles involving IO and BrO. The O₃ concentration is replenished during the night by entrainment of air from the free troposphere that is richer in O₃, followed by advection to the site (Read, et al., 2008). The HO₂ concentration was observed to decrease to a minimum at ~21:30 and then slowly increase throughout the remainder of the night, analogous to the observed nighttime O₃ profile, suggesting that the entrained air during the night is providing a source of radicals.

The nighttime generation of OH and HO₂ in the MCM box model is from reactions of O₃ with alkenes, specifically propene (~72%) and isoprene and its oxidation products (~25%). The reaction of NO₃ with alkenes is not a significant source of HO₂, unlike Mace Head (Salisbury et al., 2001). The OH generated from O₃+alkene reactions reacts with acetaldehyde and methane, leading to the formation of peroxy radicals, which in turn, through self reaction or reaction with NO generate HO₂. Alternatively, OH reacts with CO, generating HO₂ directly. The OH and HO₂ radicals are strongly coupled at night with ~37% of OH formed from the O₃+HO₂ reaction. The model underestimation of HO₂ at night may derive from an unmeasured alkene, possibly one that is biogenic in origin. Phytoplankton in oceans are known to produce a large suite of VOCs (Moore et al., 1994; Shaw et al., 2003). It is likely, however, that this source would also be present in the daytime, and so would have to be included as an OH sink.

The entrainment of peroxyacetyl nitrate (PAN) may also act as a nighttime (as well as daytime) source of radicals. In the modelling presented thus far, PAN is unconstrained in the model, and the modelled concentration peaks at ~100 pptv at ~15:00, corresponding to the peak in NO₂ and then decreases to ~10 pptv during the night.

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The thermal decomposition lifetime of PAN is just 20 min at 300 K (Bridier et al., 1991), and entrainment of air from the cooler free troposphere (where the PAN lifetime will be much longer) could lead to the rapid decomposition of the molecule, leading to an additional source of radicals. To test this hypothesis, the PAN concentration was constrained in the model to a constant 100 pptv (during both the day and night). Running the model with constrained PAN and heterogeneous loss improves the modelled to measured HO₂ throughout the day and night (Fig. 8) Jacobi et al. (1999) have reported PAN concentrations measured during a cruise of the *R/V* Polarstern from Cape Town (South Africa) to Bremerhaven (Germany) in May/June 1998. Whilst cruising a maximum of 500 km west of the African coast, corresponding to 20° W–15° E, (CVAO is ~500 km west of the coast) PAN concentrations north of 10° N (CVAO is at 16°51'49) only dropped below 100 pptv on two days. In contrast to these findings, Gallagher et al. (1990) found that between 7° N–64° N and 20° W–50° W in late summer that PAN concentrations in the north Atlantic ranged from <1 pptv–40 pptv. The proximity of the measurement sites to the African coast seems to strongly influence the PAN content of the sampled air-masses (Jacobi et al., 1999). Trajectory analysis from the RHAMBLE campaign indicated that for 21st–25th May (during which time the nighttime measurements of HO₂ were made) the air-masses intercepted at the CVAO were influenced by the US continent. In such air-masses the PAN content may have been enhanced, and, therefore, could act as an important radical source. Measurements of PAN at the site are necessary to confirm this hypothesis.

4 Discussion and implications for MBL photochemistry

Tropospheric ozone is an important greenhouse gas, providing a similar radiative forcing to methane, and ~25% of that due to CO₂ (Forster et al., 2007), and in the troposphere forms via the catalytic oxidation of CO, methane and other VOCs in the presence of NO_x. O₃ production predominantly occurs in continental regions where NO_x is elevated, whereas in the remote tropical marine boundary layer O₃ is destroyed

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

primarily through photolysis and subsequent reaction of the excited state oxygen atom with H₂O vapour (Read et al., 2008). During the RHaMBLe project at the CVAO, a daily O₃ loss was observed of the order of ~3.5 ppbv d⁻¹. Taking the daytime average for the relevant measured species from the period 21st May–2nd June 2007, the relative contributions to the observed chemical loss were calculated, as shown in Fig. 9. The photolysis of O₃ and subsequent reaction with H₂O accounts for ~40% of the daily O₃ destruction. The reaction of O₃ with OH (9%) and HO₂ (12%) also contributes to its loss, owing to the relatively high concentrations of the radicals at the site, and reaction with IO (22.5%) and BrO (16.5%) also destroy ozone via the cycles shown in Fig. 1. Table 3 highlights the relative importance of the reactions which contribute to the chemical destruction of O₃. When combined, BrO and IO together destroy ~1.5 ppbv d⁻¹, whilst the loss due to the combined reaction with OH and HO₂ is just under 1 ppbv d⁻¹, in good agreement with estimates reported by Read et al. (2008) for the month of May. Read et al. (2008), however, used a box model to calculate OH and HO₂ for the purposes of calculating the rate of O₃ destruction, rather than using the in-field measurements, as presented here.

Aircraft measurements of O₃ made above the CVAO during the RHaMBLe project (Read et al., 2008) demonstrated that the O₃ destruction observed at ground level occurs throughout the entire MBL, which typically extends to ~1 km altitude. The IO and BrO, observed by the LP-DOAS at the site, originate from the photolysis of organo-iodine compounds volatilised from the ocean and the acid-catalysed activation of bromine from sea-salt aerosols, respectively (Read et al., 2008). There is some evidence to suggest that [BrO] may increase with altitude in the MBL (von Glasow et al., 2002b) owing to an increase in the acidity of sea salt aerosols with altitude which enables acid catalysed bromine activation to occur more efficiently (von Glasow and Sander, 2001). It is uncertain, given the surface source of organo-iodine compounds and the short atmospheric lifetime of IO (~50 s), whether this molecule also prevails throughout the MBL. The rate of heterogeneous loss of HO₂ by uptake to aerosol surfaces and by surface deposition to the ocean (and/or rocky foreshore) will be at a max-

imum at ground level. The HO₂ measurements were made just 3.5 m above sea level and, as discussed above, heterogeneous losses could reduce [HO₂] at the ground by ~30%. As a consequence of this, the HO₂ concentration could increase with altitude in the boundary layer, and hence the rate of destruction of ozone by the HO₂+O₃ reaction will also increase with altitude. Further increases in [HO₂] with height may be expected as a consequence of a reduction in the [IO] with height.

A model scenario in which [IO], and heterogenous losses are set to zero and [BrO] is increased by a factor of 1.4 to simulate chemistry at the top of the MBL predicts that [HO₂] could be 45% higher than at the surface. Table 3 and Fig. 9, right panel highlight the impact these changing parameters may have upon O₃ destruction. A reduction in temperature (~5°C) is also considered as this has a small effect on the rate coefficients used. An O₃ loss rate of ~3.95 ppbv d⁻¹ is predicted at the surface and an O₃ loss rate of ~3.53 ppbv d⁻¹ at the top of the MBL (~1 km); this is consistent with the observed O₃ loss during the campaign. The increase in HO₂ and BrO concentrations is sufficient to compensate for the loss of IO at higher altitudes. Aircraft measurements of HO₂ made over the Pacific during the Transport and Chemical Evolution over the Pacific (TRACE-P) campaign (Cantrell et al., 2003) provides some evidence that HO₂ concentrations increase over the first couple of kilometres. However, it is difficult to draw strong conclusions from the dataset due to the limited number of boundary layer observations that were made. Leser et al. (2003) have reported MAX-DOAS measurements of BrO taken onboard the *R/V Polarstern* north of the Canary Islands. Significant boundary layer BrO was observed, of the order of 1 pptv, although the vertical distribution within the boundary layer cannot be determined. Future, simultaneous observations of O₃, HO₂ and halogen oxides from 0–1 km from an aircraft platform, therefore, would be extremely beneficial.

Methane is removed from the atmosphere through oxidation by OH (Levy, 1971) with ~25% of this removal occurring in the tropical MBL (Bloss et al., 2005a). In this work the important parameters which control the OH concentration in this region have been quantified, a number of which, until recently, have been overlooked, for example chem-

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ical processes involving halogen species. Although the vertical extent in the MBL of the impact of halogen oxides on the HO_x and O₃ budgets, particularly for IO, remains uncertain, these species constitute a significant source of OH. Photolysis of HOBr and HOI lead to an increase in the OH concentration of ~13%, although this increase is offset slightly (~3%) by the perturbation of the NO_x chemistry (lowering [NO]) by halogen oxides as discussed in Sect. 3.2. Overall, this work suggests that the methane lifetime is reduced by ~10% due to the presence of halogen oxides leading to an increase in [OH]. In the current atmosphere, one added methane molecule absorbs infra-red radiation ~25 times more efficiently than one added CO₂ molecule (Lelieveld et al., 1993) as CO₂ is approximately 200 times more abundant in the atmosphere and, as a consequence, many of its absorption bands are saturated. Current estimates suggest that methane contributes a radiative forcing of +0.48 (±0.05) Wm⁻² (Forster et al., 2007), which is ~33% of that due to CO₂. Radiative forcing from methane increases approximately as the square root of its concentration (Forster et al., 2007), and it is estimated that without halogen oxides, the lower [OH] would lead to an increase in the radiative forcing by methane by ~3.5×10⁻³ Wm⁻². A key remaining question is the range of altitudes over which halogen oxides, particularly IO, extend. To fully determine the global impact of the halogen oxides on the oxidising capacity of the tropical MBL, manifested through their effect on [OH], the vertical profile of these species in this region is required.

5 Summary

Measurements of OH and HO₂ radicals, together with a suite of supporting measurements, were made at the Cape Verde Atmospheric Observatory on the island of Sao Vicente during May and June 2007.

A model using the Master Chemical Mechanism, and constrained to the supporting measurements, was used to predict OH and HO₂ concentrations and to probe the chemistry controlling the radicals at the observatory. The halogen oxides, despite their

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



low concentrations, were found to act as a significant HO₂ sink (23%), with the subsequent photolysis of the hypohalous acids increasing the modelled [OH]. The model was able to capture daytime [OH] reasonably well (12% underprediction) but overestimated the daytime [HO₂] by 35% despite inclusion of the detailed halogen scheme.

The addition of heterogeneous loss in the model improved the daytime modelled to measured HO₂ agreement, but reduced the nighttime agreement. The entrainment of PAN from the cooler free troposphere may act as a source of radicals and inclusion of 100 pptv of PAN improves the nighttime HO₂ agreement considerably.

Active halogen chemistry over the tropical oceans, where photochemical oxidation is most prevalent, can significantly impact the global oxidising capacity via its effect on [OH]. From this work, the calculated methane lifetime could be as much as 10% shorter in this region if halogen chemistry is included in the calculation of [OH]. Currently, halogen chemistry is not routinely included in chemistry-transport models used to predict, for example, global distributions of tropospheric methane and ozone.

Further measurements of OH and HO₂ coupled with concurrent measurements of halogen oxides, VOCs, HCHO, HONO, NO_x, NO_y and aerosol number and size distributions are needed to describe the chemistry of this region more fully and further test the hypotheses raised here. Vertical profiles of the concentrations of IO, BrO, OH, HO₂ and O₃ are needed to discover if halogen chemistry has an impact on the budgets of OH, HO₂ and O₃ throughout the MBL.

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The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



References

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The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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The chemistry of OH and HO₂ radicals in the boundary layerL. K. Whalley et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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The chemistry of OH and HO₂ radicals in the boundary layerL. K. Whalley et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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The chemistry of OH and HO₂ radicals in the boundary layerL. K. Whalley et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Table 1. Listing of the concurrent measurements made during the RHaMBLe project and used to constrain the box model.

Measurements	Instrument	Typical Concentration ^a	Averaging Time	LOD (2 σ)	Reference
O ₃	TEI 42c, UV absorption	33 ppbv	1 min	1 ppbv	(Lee et al., 2009a)
CO	Aerolaser, VUV resonance fluorescence	110 ppbv	1 min	–	(Lee et al., 2009a)
CH ₄	Flask Samples, Gas Chromatography analysis	1821 ppbv	–	–	(Lee et al., 2009a)
NO	Chemiluminescence detector	1.5 pptv	1 h	1.5 pptv	(Lee et al., 2009b)
NO ₂	Chemiluminescence detector	15 pptv	1 h	4.1 pptv	(Lee et al., 2009b)
Ethane	Gas Chromatography – Flame Ionisation Detection (GC-FID)	925±29 pptv	1 h	2.5 pptv	(Read et al., 2009)
Propane	GC-FID	60±2.0 pptv	1 h	2.5 pptv	(Read et al., 2009)
Iso-butane	GC-FID	3.0±0.3 pptv	1 h	2.5 pptv	(Read et al., 2009)
n-butane	GC-FID	4.0±0.3 pptv	1 h	2.5 pptv	(Read et al., 2009)
Acetylene	GC-FID	125±3.5 pptv	1 h	2.5 pptv	(Read et al., 2009)
Ethene	GC-FID	27±1.8 pptv	1 h	2.5 pptv	(Read et al., 2009)
Propene	GC-FID	20±0.8 pptv	1 h	2.5 pptv	(Read et al., 2009)
Isoprene	GC-FID	7.0±0.7 pptv	1 h	1.0 pptv	(Read et al., 2009)
Acetaldehyde	GC-FID	970±161 pptv	1 h	18 pptv	(Read et al., 2009)
Methanol	GC-FID	950±146 pptv	1 h	7 pptv	(Read et al., 2009)
Acetone	GC-FID	840±77 pptv	1 h	3 pptv	(Read et al., 2009)
IO	LP-DOAS	0.6 pptv	20–30 min	0.3–0.5 pptv	(Read et al., 2008)
BrO	LP-DOAS	1.4 pptv	20–30 minutes	0.5–1 pptv	(Read et al., 2008)
HCHO	LP-DOAS	500 pptv	20–30 min	200 pptv	(Plane and Saiz-Lopez, 2006)
J(O ¹ D)	Filter Radiometer	3.5×10 ⁻⁵ s ⁻¹	1 min	–	(Lee et al., 2009a)
Aerosol	Scanning Mobility Particle Sizer (SMPS) & Aerosol Particle Sizer (APS)	1×10 ⁻⁶ cm ² cm ⁻³	30 min	–	(Allan et al., 2009)
Relative Humidity	Campbell Met Station	76%	1 min	–	(Lee et al., 2009a)
Temperature	Campbell Met Station	296 K	1 min	–	(Lee et al., 2009a)
Pressure	Campbell Met Station	1016 hPa	1 min	–	(Lee et al., 2009a)

^a Typical 24 h average concentration.

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Table 2. List of parameters that have been varied to optimise the HO₂ modelled to measured agreement. The daytime % change was averaged from 08:44–19:44; the nighttime % change was averaged from 19:44–08:44.

Model Parameter	Parameter Change	Av.% Change in HO ₂ (day)	Av.% Change in HO ₂ (night)
HCHO	500 pptv→100 pptv	–14	–2
Aerosol Uptake	$\gamma=0\rightarrow\gamma=0.4^*$	–26	–67
Surface Deposition	Not included→Included*	–12	–42
PAN Entrainment	~10 pptv at night→~100 pptv*	0	+124
Heterogeneous loss+PAN Entrainment	See above*	–30	–10

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

Table 3. The rates of the rate-limiting O₃ destruction steps and their percentage contribution towards O₃ destruction both in the surface layer and at the top of the MBL (1 km), see text for details.

O ₃ destruction rate determining step	Contribution to O ₃ destruction at the surface (molecule cm ⁻³ s ⁻¹)	Contribution to O ₃ destruction at the top of the BL (molecule cm ⁻³ s ⁻¹)
O ¹ D+H ₂ O	9×10 ⁵ (40%)	9×10 ⁵ (45%)
OH+O ₃	2.1×10 ⁵ (9%)	1.8×10 ⁵ (9%)
HO ₂ +O ₃	2.7×10 ⁵ (12%)	3.7×10 ⁵ (18%)
IO+IO	7.2×10 ⁴ (3%)	0%
IO+HO ₂	3.7×10 ⁵ (16%)	0%
IO+NO	2.7×10 ⁴ (1%)	0%
IO+BrO	1.1×10 ⁵ (5%)	0%
BrO+BrO	1.4×10 ⁴ (1%)	2.7×10 ⁴ (1%)
BrO+HO ₂	2.2×10 ⁵ (10%)	4.4×10 ⁵ (22%)
BrO + NO	6.7×10 ⁴ (3%)	9.4×10 ⁴ (5%)
Total	2.3×10 ⁶ (3.95 ppbv d ⁻¹)	2.0×10 ⁶ (3.53 ppbv d ⁻¹)

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

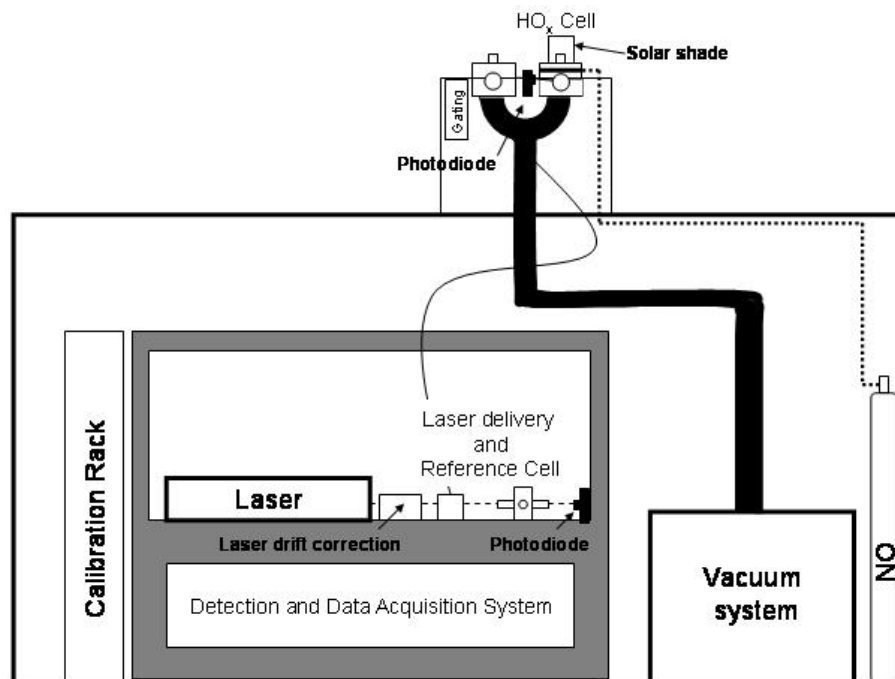


Fig. 2. Schematic of the FAGE laboratory set-up during RHaMBLe (see text for details).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

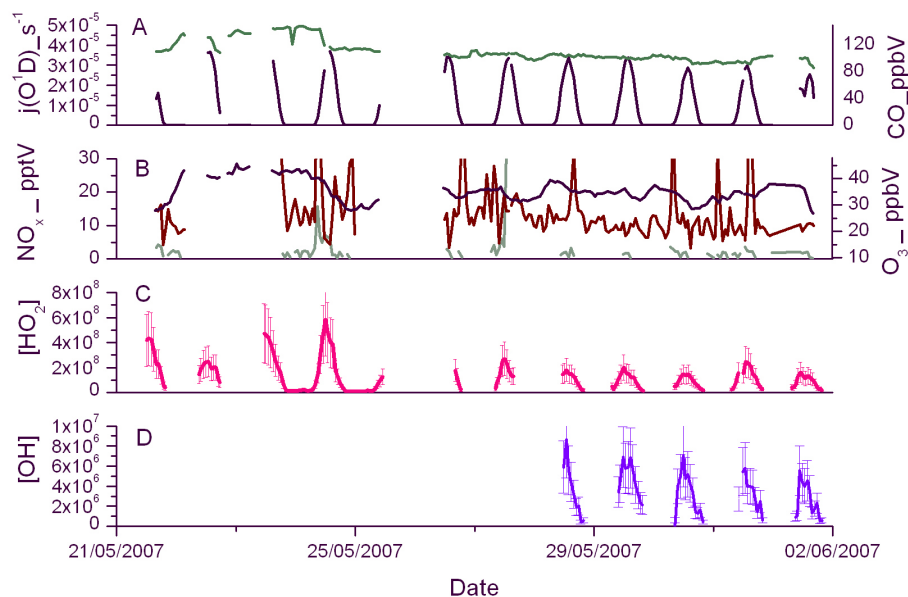


Fig. 3. (A) Time-series of $j(\text{O}^1\text{D})$ (black line) and CO (blue line) from the HO_x measurement period (gaps in data are due to power failures). (B) Time-series of NO (green line), NO₂ (brown line) and O₃ (black line) from the HO_x measurement period (gaps in data are due to power failures or instrument down-time). (C) Time-series of measured HO₂ in molecule cm⁻³ (pink line) with the 2 σ standard deviation shown. (D) Time-series of measured OH in molecule cm⁻³ (purple line) with the 2 σ standard deviation shown. All data are hourly averaged.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

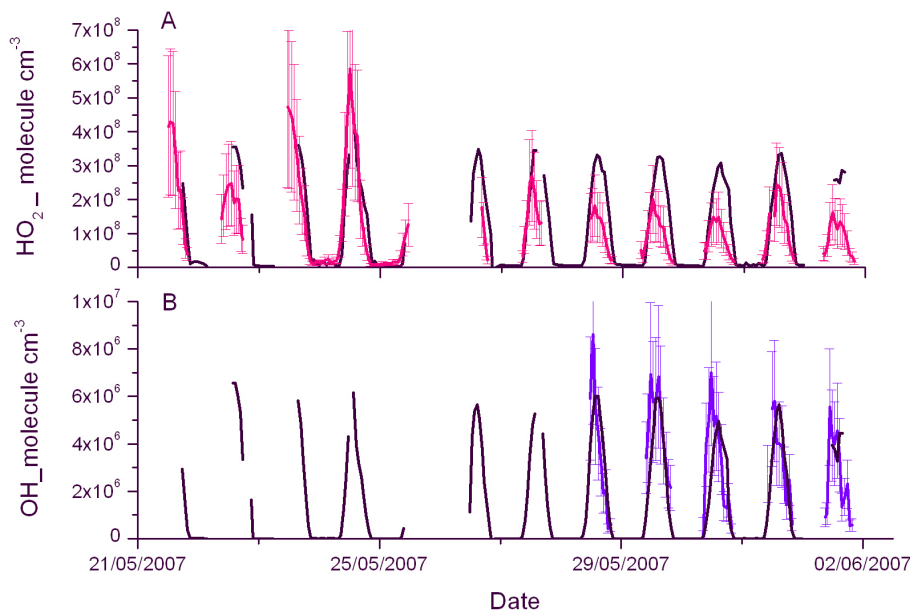


Fig. 4. (A) Time-series of measured HO₂ in molecule cm⁻³ (pink line) with the 2- σ standard deviation shown and MCM calculated [HO₂] (base-case scenario, see text for details) (black line). (B) Time-series of measured OH in molecule cm⁻³ (purple line) with the 2- σ standard deviation shown, and MCM [OH] estimate (base-case scenario, see text for details) (black line). All data represent a 1 h average.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

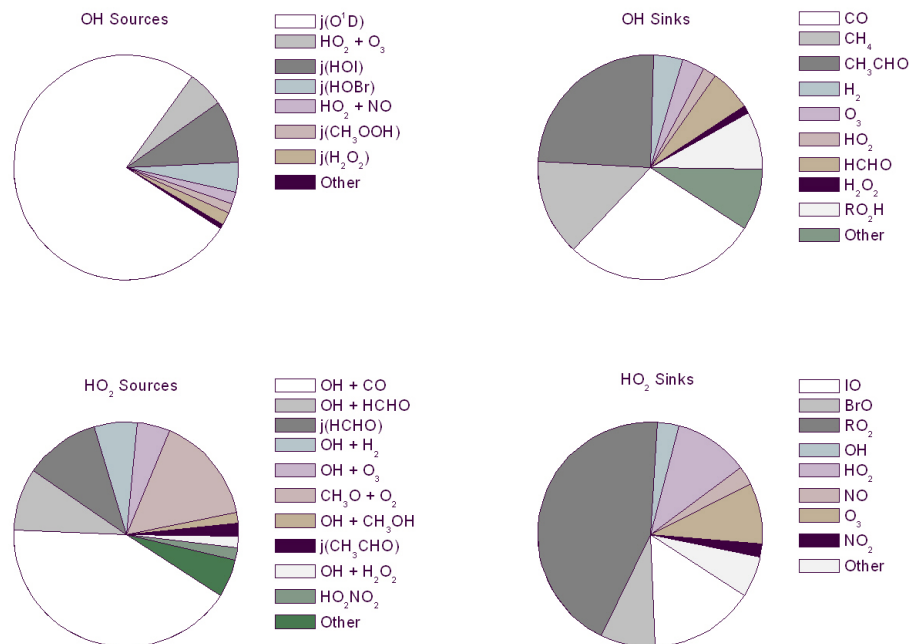


Fig. 5. Pie-charts showing the MCM (base-case scenario, see text for details) average diurnal modelled OH and HO₂ sources and sinks between 12:00–13:00.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

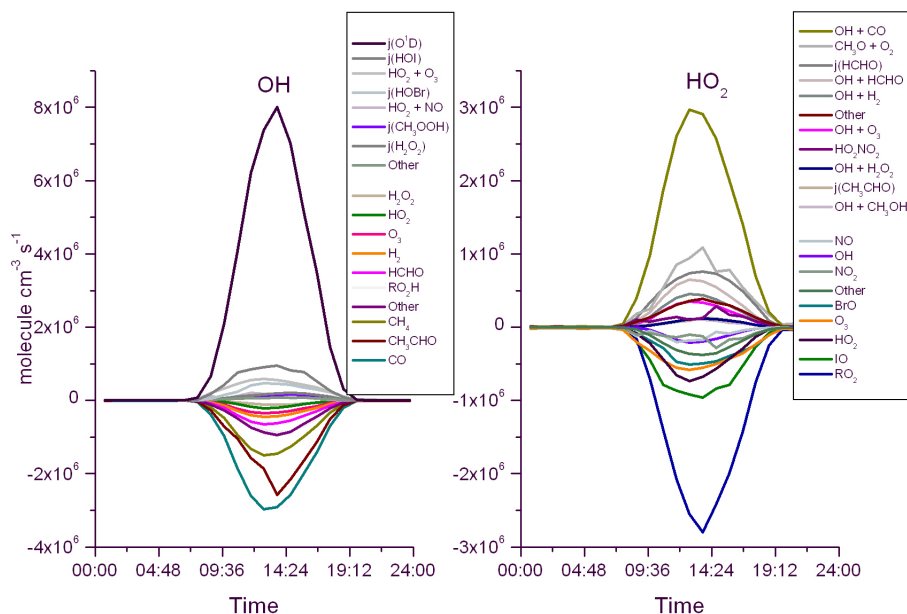


Fig. 6. Left: Diurnal variation of the rate of OH production and loss calculated using the MCM. Right: Diurnal variation of the rate of HO₂ production and loss taken from the MCM (base case, see text for details).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

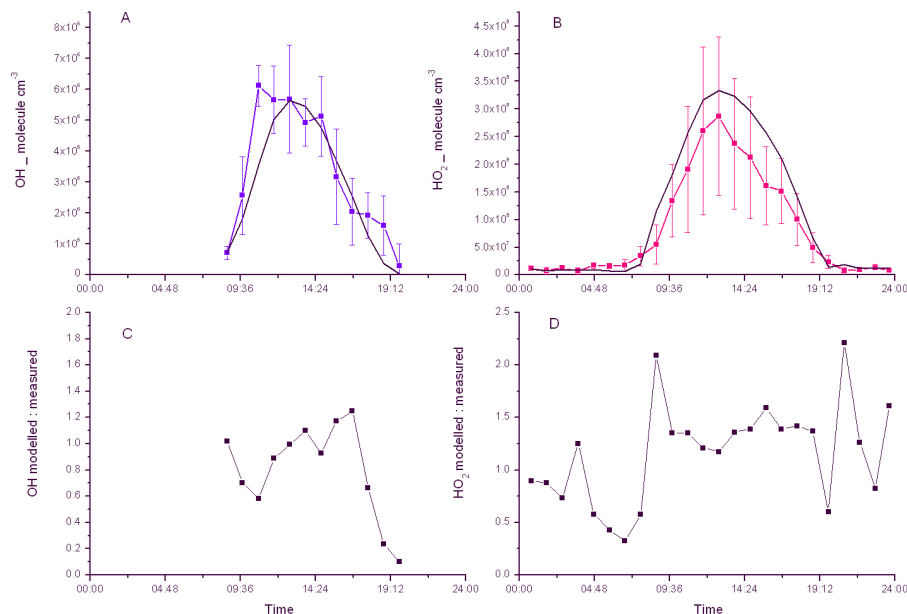


Fig. 7. (A) Average diurnal [OH] calculated for the 5 days of measurements (data on an hourly time-scale); the error bars represent the standard deviation of the data that were averaged (purple points and line). The modelled average diurnal (averaged over the 5 days of OH measurements) is also shown (MCM=grey line). (B) Average diurnal [HO₂] calculated for the 11 days of measurements (data on an hourly time-scale); the error bars represent the standard deviation of the data that was averaged (pink points and line). The modelled average diurnal (averaged over the 11 days of HO₂ measurements) is also shown (MCM=black line). (C) Solid line, with black squares represents the (OH MCM modelled)/(OH measured) ratio averaged for 1 hour over 24 h. (D) Solid line represents the (HO₂ MCM modelled)/(HO₂ measured) ratio averaged for 1 h, for a 24 h period.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

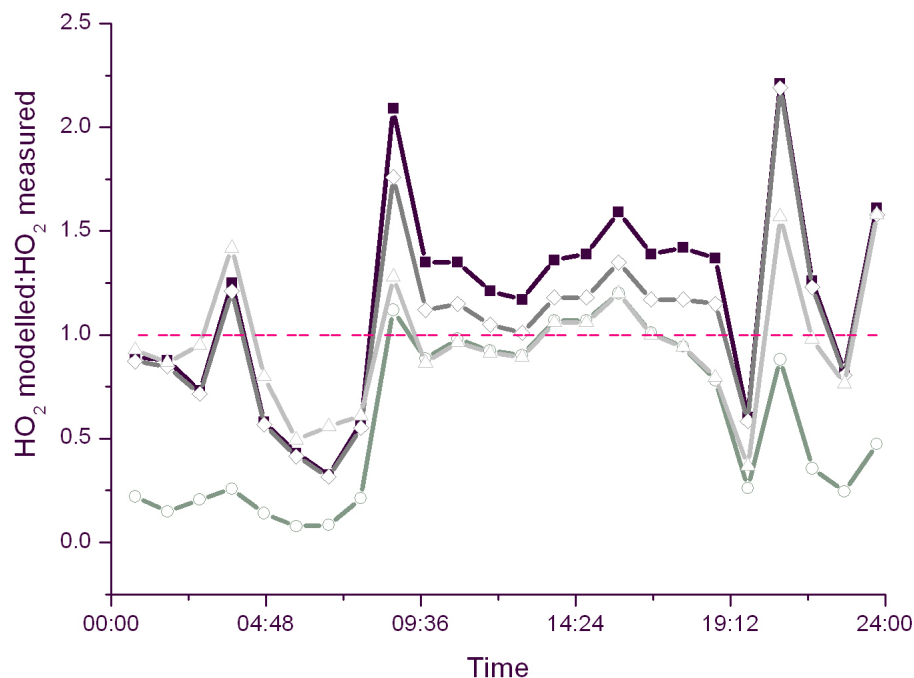


Fig. 8. (HO₂ MCM modelled)/(HO₂ measured) ratio for a number of different model scenarios. Filled squares=base case scenario, open diamonds=HCHO set to 100 pptv, open circles=heterogeneous loss of HO₂ to aerosols ($\gamma=0.4$) and surface deposition, open triangles=heterogeneous loss (loss to aerosol surface+surface deposition) and PAN entrainment. Red dashed line represents an (HO₂ MCM modelled)/(HO₂ measured) of 1. See text and Table 2 for further details.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

The chemistry of OH and HO₂ radicals in the boundary layer

L. K. Whalley et al.

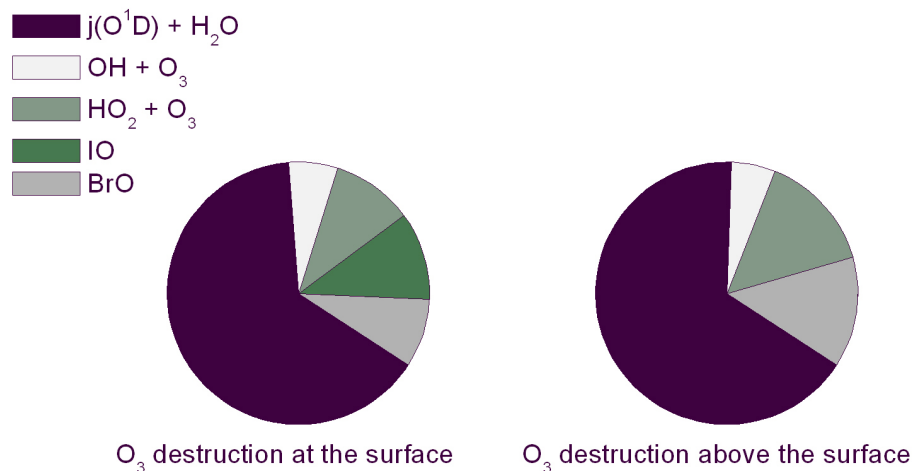


Fig. 9. Pie-charts highlighting the key parameters that cause the daily O₃ destruction that is observed at the CVAO both at the surface (left panel) and at the top of the MBL (right panel). Total O₃ destruction calculated using 12 h averaged, daytime, data was ~4 ppbv at the surface and ~3.5 ppbv at the top of the MBL.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)