Hydrogen oxide photochemistry in the northern Canadian spring time boundary layer

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Received 14 June 2011; revised 11 September 2011; accepted 13 September 2011; published 22 November 2011.

[1] Measurements of OH and HO₂ concentrations were made at the surface of the eastern coast of the Hudson Bay during the COBRA campaign from February 18th to March 8th 2008. Diurnally averaged OH and HO₂ concentrations peaked at $1.16 (\pm 1.02) \times 10^6$ molecule cm⁻³ and $1.42 (\pm 0.64) \times 10^8$ molecule cm⁻³ respectively. A box-model, constrained to supporting observations, is used to access the radical budget in this cold, northerly environment. Formaldehyde (HCHO) photolysis is found to be the dominant daytime radical source, providing 74% of the observed HO_x . A considerable (>80% of the total source) surface HCHO source is required to reconcile the model and observed HCHO concentrations. Model simulations also suggest significant roles for the heterogeneous loss of HO_2 and for halogen chemistry in the cycling of HO₂ to OH. The formation of HO₂NO₂ is identified as an important radical reservoir, reducing HO_x concentrations during the day and enhancing them at night. This impacts both local oxidizing capacity and reduces local ozone production by approximately 30%. The sensitivity of the local chemistry to uncertainties in these processes is explored. The majority of these processes are not currently represented in global chemistry models.

Citation: Edwards, P., et al. (2011), Hydrogen oxide photochemistry in the northern Canadian spring time boundary layer, *J. Geophys. Res.*, *116*, D22306, doi:10.1029/2011JD016390.

1. Introduction

[2] The largest recent changes in surface air temperatures have been seen at the poles [Solomon et al., 2007]. Average Arctic temperatures have increased by almost twice the global mean over the last century, with simulations predicting an averaged warming of the Arctic by the year 2100 of 9°C, compared with 3°C for the tropics [Solomon et al.,

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2007]. These changes can be partially attributed to changes in the concentration of tropospheric ozone, which alters local radiation fluxes [*Mickley et al.*, 1999; *Quinn et al.*, 2008]. The concentration of tropospheric ozone in the Arctic is controlled by a balance between transport into and out of the region, and local processes. This local chemistry is generally considered to be controlled by the chemistry of oxides of hydrogen (OH and HO₂ \equiv HO_x) and oxides of nitrogen (NO and NO₂ \equiv NO_x). In this paper we investigate the processes controlling HO_x at the surface using observations of OH and HO₂ during a surface field campaign in the Canadian high latitudes during the spring of 2008.

[3] For much of the troposphere the major source of HO_x is the photolysis of ozone, and subsequent reaction of $O(^1D)$ with water vapor to form the hydroxyl radical [*Levy*, 1972].

(R1)
$$O_3 + hv \rightarrow O(^1D) + O_2$$

R2)
$$O(^{1}D) + H_{2}O \rightarrow 2OH$$

However, in the low temperatures typical of high latitudes the water vapor concentrations are often low. This leads to other sources of HO_x becoming important. These include the photolysis of formaldehyde (HCHO) (R3), nitrous acid (HONO) (R4) and hydrogen peroxide (H₂O₂) (R5), and the

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ozonolysis of alkenes (R6) [*Atkinson and Aschmann*, 1993; *Paulson and Orlando*, 1996; *Ariya et al.*, 2000].

(R3)
$$\operatorname{HCHO} + hv(+2O_2) \rightarrow \operatorname{CO} + 2\operatorname{HO}_2$$

(R4)
$$HONO + hv \rightarrow OH + NO$$

(R5)
$$H_2O_2 + hv \rightarrow 2 OH$$

$$O_3 + R = R \rightarrow Carbonyl + [ROO]^* \rightarrow Products + OH.$$

(R6)

[4] Once HO_x radicals are formed they undergo rapid interconversion through reactions of OH with CO or hydrocarbons, and HO_2 with NO and O_3 . Under 'low NO_x ' conditions radical loss occurs through the self reaction of peroxy radicals (reactions (R7) and (R8)) to form peroxides which due to their solubility generally deposit to the surface. Under high NO_x conditions OH radicals react with NO_2 to form HNO_3 (reaction (R9)) which again can undergo deposition [*Dollard et al.*, 1987].

$$(R7) \qquad \qquad HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

$$(R8) \qquad \qquad RO_2 + HO_2 \rightarrow ROOH + O_2$$

$$(R9) \qquad \qquad OH + NO_2 + M \rightarrow HNO_3 + M$$

The loss of HO₂ to aerosol surfaces can also be an important HO_x sink in some environments [*Cantrell et al.*, 1996; *Martin et al.*, 2003; *Whalley et al.*, 2010; *Mao et al.*, 2010], although the rates and mechanisms of this process are highly uncertain [*Jacob*, 2000]. The recent ARCTAS campaign (the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites), which took place over the Arctic during spring 2008, propose that heterogeneous loss might be the dominant loss process for HO₂ at altitudes above 5 km [*Mao et al.*, 2010].

[5] The first observations of high latitude HO_x occurred in the Antarctic during the Sulfur Chemistry in the Antarctic Troposphere Experiment (SCATE) in the austral summer of 1994. Measurements were made on the rocky coast of Anvers Island, at the U.S. Palmer Research Station. These observations supported the view that polar oxidation chemistry was relatively inactive, with daytime average OH concentrations of 3×10^5 molecule cm⁻³ [Jefferson et al., 1998]. Comparison with model-predicted concentrations of OH gave agreement to within 30%, with OH-production dominated by $O(^{1}D) + H_{2}O$ (reactions (R1) and (R2)) and the major OH sinks being the reactions with CO and CH₄. More recent field studies however, have shown that despite the cold temperatures and high solar zenith angles experienced at high latitude, the photochemistry is often more active than might be expected. This is partly due to complex chemistry within the snowpack which releases photochemically active species (e.g., NO_x , HCHO, H_2O_2 and HONO) into the boundary layer [Sumner and Shepson, 1999; Davis et al., 2001; Zhou et al., 2001; Jacobi et al., 2002; Yang et al., 2002; Grannas et al., 2007]. These compounds can have a large effect on local oxidation [Chen et al., 2004, 2007; Bloss et al., 2007] and the concentrations of trace species in these

snow covered environments. A campaign at the Summit Research Station, located at an altitude of over 3000 m on the Greenland ice cap during the summer of 2003 [Sjostedt et al., 2007], was the first to make OH measurements above the Arctic snowpack, and reported an average concentration at noon of 8.4×10^6 molecule cm⁻³. The observed concentrations were much higher than those during SCATE, and could not be reproduced by the chemical model used, which consistently under-predicted OH levels by, at best, a factor of 2. Sources of OH were found to be from $O(^{1}D) + H_{2}O$ and photolysis of species such as HCHO and H₂O₂, contributing 41% and 40% respectively [Chen et al., 2007]. The high observed concentrations of HO_x precursors, such as H₂O₂, HCHO and HONO (mean noontime values of 1800 pptv, 181 pptv and 13 pptv, respectively) were attributed to emissions of these species from the snowpack. A review of polar chemistry is provided by Grannas et al. [2007].

[6] Halogens (Cl, Br, I) have been found to significantly impact high latitude boundary layer chemistry, notably during the spring [Barrie et al., 1988; Fried et al., 2004; Bloss et al., 2007, 2010; Saiz-Lopez et al., 2008]. These species (predominantly I and Br) influence HO_x concentrations through the reaction of XO (generic halogen oxide) with HO_2 to form HOX (reaction (10)). HOX can then be photolyzed to produce OH and a halogen atom X (providing a pathway to convert HO₂ into OH (reaction (R11))), or be lost to aerosol thereby acting as a net sink for HO_x (reaction (R12)). The halogen atom formed from reaction (R11) can then react with ozone, via reaction (R13), to re-form the halogen oxide XO and so catalytically destroy ozone. This further impacts HO_x concentrations via a reduction in HO_x production through ozone photolysis (reactions (R1) and (R2)) [von Glasow et al., 2007]. Halogens can also effect the production and partitioning of HO_x by impacting the concentrations of species such as NO_x and HCHO [Grannas et al., 2007; Saiz-Lopez et al., 2008].

(R10)
$$XO + HO_2 \rightarrow HOX + O_2$$

(R11)
$$HOX + hv \rightarrow X + OH$$

(R12)
$$HOX + aerosol \rightarrow loss$$

$$(R13) X + O_3 \to XO + O_2.$$

[7] The CHABLIS (CHemistry of the Antarctic Boundary Layer and the Interface with Snow) project at the Halley research station, Antarctica, took place during the austral summer, January–February 2005, and reported a mean concentration of 3.9×10^5 molecule cm⁻³ for OH, and 1.9×10^7 molecule cm⁻³ for HO₂ [*Bloss et al.*, 2007, 2010]. It was found that the chemistry controlling HO_x in this environment was closely coupled with local halogen chemistry, with RO₂–HO₂–OH interconversions dominated by the action of halogen monoxides.

[8] These previous studies have highlighted some distinct differences in the processes controlling tropospheric photooxidation processes in the high-latitudes compared with the midlatitudes. Understanding these differences is important if we are to understand the processes controlling the local O_3 budget, and hence the radiative impact of O_3 in this region.

Species/Unit	Mean	1 σ Standard Deviation	Instruments Limit of Detection	Observational Time Period
NO ₂ /pptv	39	9	6	10 min
NO/pptv	4	3	4	10 min
O ₃ /ppbv	30	7	0.8	1 min
CO/ppbv	169	37	1	30 s
$C_2H_6/pptv$	3194	217	9	One 5 min sample taken daily
C ₃ H ₈ /pptv	1841	222	3	One 5 min sample taken daily
<i>i</i> -C ₄ H ₁₀ /pptv	288	25	1	One 5 min sample taken daily
$n-C_4H_{10}/pptv$	496	57	1	One 5 min sample taken daily
C ₂ H ₂ /pptv	917	52	3	One 5 min sample taken daily
C ₃ H ₆ /pptv	216	110	3	One 5 min sample taken daily
$C_2H_4/pptv$	245	77	7	One 5 min sample taken daily
HCHO/pptv	363	242	200	10 min
BrO/pptv	<1	-	1	-
IO/pptv	<1	-	1	-
H ₂ O/ppmv	852	462	20	1 min
Aerosol surface area/m ² m ⁻³	8.791×10^{-5}	0.296×10^{-5}	-	10 min
Temperature/°C	-22	6	-	1 min

Table 1. Summary of Supporting Observations^a

^aAll the data have been filtered to remove periods when air coming from the site power generator was being sampled.

The Combined iodine and BRomine release on the Arctic atmosphere (COBRA) project was designed to investigate some of these issues and so measured a wide range of species including OH and HO₂ within the boundary layer. In this paper, the HO_x observations made during COBRA are described. Through the use a box model constrained to supporting measurements, the observations are assessed and the processes important in controlling the HO_x budget in this environment are investigated. We focus on the processes controlling the average diurnal cycle of OH and HO₂ and their representation within a constrained box model.

2. Measurement Site Details

[9] The COBRA field observations were made near the town of Kuujjuarapik, on the eastern coast of Hudson Bay (55.30°N, 77.73°W), between the 18th of February and the 8th of March 2008. The field site is dissimilar to previous cold, remote, high latitude ground based locations where HO_x photochemistry has been studied, notably in Antarctica and at the Summit station in Greenland [Chen et al., 2004; Bloss et al., 2007, 2010; Sjostedt et al., 2007]. This is due to its location on the shore of the ice covered Hudson Bay combined with its proximity to the town of Kuujjuarapik. The sea ice remained intact in the coastal region near the measurement site throughout the observation period, although open leads of water were identified as close as 40 km away for periods during the campaign [Mahajan et al., 2010]. Back trajectories (not shown) for the period showed that the air masses from both land and sea ice origins were sampled throughout the campaign. The combination of air masses that have traveled for several days across the snow and ice covered landscape with local emissions and extremely low temperatures provides a unique data set for the study of radical chemistry in an environment typical of large areas of the Arctic and sub-Arctic.

[10] OH and HO₂ concentrations were measured using the FAGE (Fluorescence Assay by Gas Expansion) technique [*Hard et al.*, 1984], which is discussed in Section 4. Concentrations of NO and NO₂ were measured using a single channel, chemiluminescent analyzer with a photolytic converter [*Moller et al.*, 2010]. O₃ concentrations were mea-

sured using a UV absorption instrument. Concentrations of CO were measured using a VUV fluorescence instrument. A measurement of C₂-C₄ hydrocarbon mixing ratios was made daily by whole air samples, which were later analyzed off site by GC-FID (methodology described by Hopkins et al. [2003]). Photolysis rates were measured using a 2π spectral radiometer. Aerosol surface area was calculated from aerosol size distribution measurements from the University of Manchester's DMPS (Differential Mobility Particle Sizer) and a GRIMM 1.108 dust monitor. All of these observations were made from the roof of the same container laboratory as the FAGE instrument. Measurements of temperature, albedo and water vapor concentration were made from a mast, located approximately 100 m from the container laboratory on the sea ice. Concentrations of HCHO, BrO and IO were measured using the LP-DOAS technique from a second container laboratory, with an optical path of 11 km over the sea ice [Mahajan et al., 2010]. The use of LP-DOAS observations introduce additional uncertainty in the calculations of point HO_x concentrations, due to uncertainties in how representative these numbers are of the point sampled air mass. Table 1 shows the supporting observations used in this study, and the mean values recorded.

3. The Model

[11] In order to investigate the processes controlling HO_x radicals in this environment we use the Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC) box model [*Emmerson and Evans*, 2009] and follow the methodology of *Stone et al.* [2010]. The chemistry scheme used by the model, generated by the Master Chemical Mechanism V3.1 [*Jenkin et al.*, 1997; *Saunders et al.*, 2003], includes detailed inorganic chemistry and a near explicit degradation scheme for the observed hydrocarbons, C₂H₆, C₂H₄, C₃H₈, C₃H₆, *i*-C₄H₁₀, *n*-C₄H₁₀ and C₂H₂ (Figure 1). The halogen scheme used, described in the auxiliary material, has been adapted from that used by *Saiz-Lopez et al.* [2006].¹ Rate coefficients for inorganic reactions

¹Auxiliary materials are available in the HTML. doi:10.1029/2011JD016390.



Figure 1. Observed average diurnals used to constrain the box model, the variability bars indicate ± 1 standard deviation on the observations at each time point.

and three body reactions were updated to recent recommendations [*Atkinson et al.*, 2004; *Sander et al.*, 2006]. For each observed data point the model is integrated forwards using a Livermore solver [*Radhakrishnan and Hindmarsh*, 1993] with a time step of 600 s until a diurnal steady state was reached (the cycles of simulated species exhibit less than 0.01% variation from the previous day).



Figure 2. Concentrations of key bromine and iodine species calculated by the base model. Daytime IO and BrO concentrations are consistent with the LP-DOAS instrument limit of detection.

[12] For each observed data point, concentrations of observed long-lived species are kept constant, except for short-lived nitrogen and halogen oxides. For short-lived reactive nitrogen species, each integration point within an individual day of integration has the concentration of reactive nitrogen (defined as NO + NO₂ + NO₃ + 2 N₂O₅ + $HONO + HO_2NO_2$) kept constant, while the concentration of individual reactive nitrogen species is free to vary according to changes in photolysis rates etc. At the end of each day the calculated concentration of one individual NO_x species (NO₂ used in this study) is compared to the equivalent measured concentration and the concentration of all reactive nitrogen species is fractionally increased or decreased so that the measured and the modeled concentrations of the observed species match. As the model simulation runs forwards and a diurnal steady state is reached the fractional change in reactive nitrogen becomes increasingly smaller.

[13] Recent observations have indicated that halogen chemistry is occurring throughout the Arctic [*Liao et al.*, 2011; *Stutz et al.*, 2011]. Halogen chemistry has therefore been included in the base model simulation at levels equivalent to the lower detection limit of the LP-DOAS instrument to provide an upper limit on the impact of halogens. The sensitivity of the HO_x budget to the presence of elevated bromine and iodine oxide species is investigated in Section 6. As with reactive nitrogen species, halogen oxides also have to be treated differently due to their diurnal variation.

The lack of BrO and IO concentration measurements, due to both species being below the 1 pptv detection limit of the LP-DOAS instrument for the majority of the campaign [*Mahajan et al.*, 2010], also complicates their inclusion. Instead the model was initializing with Br_2 and I_2 mixing ratios of 3 pptv and 1.7 pptv, respectively, to give daily maximum (BrO and IO concentration of approximately 1 pptv). The partitioning of halogen species throughout the day was then determined by the chemistry scheme alone (see auxiliary material), which conserves Br and I (no physical loss processes are considered). Figure 2 shows the model calculated diurnal concentrations of the key halogen species in the base model run.

[14] Calculated photolysis rates (using the mean measured albedo of 0.85, average observed O₃ column density of 448.5 ± 50.0 Dobson unit, and the TUV radiation model [*Madronich*, 1998]) were scaled to the observed $j(NO_2)$ and $j(O^1D)$. The ratio between the measured and modeled $j(NO_2)$ was applied to all photolysis rates other than $j(O^1D)$. During the measurement campaign, complications with the spectral radiometer meant that only one day of $j(O^1D)$ data and ten days of $j(NO_2)$ were collected. Predominantly clear sky conditions throughout the campaign, however, resulted in the observed day-to-day noon time $j(NO_2)$ having a maximum deviation of 28% from the mean. This level of variability was deemed acceptable to be able to use the limited photolysis data available to scale calculated photolysis rates.



Figure 3. Sensitivities of the instrument to OH (black) and HO₂ (red) $(10^{-7} \text{ cts s}^{-1} \text{ mW}^{-1} \text{ molecule}^{-1} \text{ cm}^3)$ against H₂O mixing ratio (ppmv), the blue dashed lines represent the water range experienced during COBRA. The linear fits to the data are used to normalize the change in sensitivity due to water vapor. Error bars indicate the error on the calculated sensitivity and on the measurement of H₂O mixing ratio.

[15] The rate of heterogeneous loss to aerosol surfaces within the model is described as [Sander and Crutzen, 1996]

$$\frac{dX_g}{dt} = -\left(\frac{r}{D_g} + \frac{4}{\gamma\omega}\right)^{-1} AX_g \tag{1}$$

where X_g is the number density of gas phase species X (molecule cm⁻³), r is the particle radius (cm), D_g is the gas phase diffusion coefficient, (cm² s⁻¹), γ is the reaction probability, ω is the mean molecular speed of X (cm s⁻¹) and A is the aerosol surface area density $(cm^2 cm^{-3})$. The observed size distribution is used to calculate the aerosol surface area, and the average diurnal median observed particle radius (shown in Figure 1) is used. Although aerosol composition measurements were not made it is believed that the majority of the observed surface area came from windblown snow or ice. For this reason a reaction probability of $\gamma_{\rm HO_2} = 0.025$ has been chosen for HO₂ uptake [Cooper and Abbatt, 1996]. The heterogeneous uptake of HO_2 is assumed to be a direct loss mechanism for radicals within the model. A series of model runs to assess the sensitivity of the HO_x budget to $\gamma_{\rm HO_2}$ are described in Section 6.

[16] In order to represent the non-chemical loss of species either through deposition or mixing, a lifetime with respect to a physical first order loss of 24 h ($k_{loss} = 1.16 \times 10^{-5} \text{ s}^{-1}$) is applied to all calculated species (apart from halogen species). A series of runs were carried out in order to gauge the models sensitivity to this rate. The rate coefficient was varied between 2.78×10^{-4} and $1.65 \times 10^{-6} \text{ s}^{-1}$, corresponding to atmospheric lifetimes between 1 h and 1 week respectively. A 1 week lifetime caused an increase in total noon time HO_x by ~10%, due to increases in the concentrations of HO₂ precursor species such as H₂O₂, and was found to have a less than 1% effect on nighttime HO_x. A 1 h deposition lifetime reduced both noon and nighttime HO_x by ~13% and ~15% respectively, this is largely through the rapid loss of HO_x radical reservoir species such as HO₂NO₂. and is discussed in Section 6.2. As there are no observations of these species to allow a true deposition rate to be found, a 24 h deposition lifetime was chosen for all base runs presented here. The uncertainty due to the deposition rate used is small when compared to uncertainties such as photolysis rates ($\sim 28\%$), and does not change any of the conclusions of this work.

[17] The focus of this work is on the diurnal variation of OH and HO₂ radicals. Thus simulations were constrained to average diurnal cycles of observed O₃, NO₂, CO, HCHO, H₂O vapor and temperature. All these data were first filtered to remove periods where the sampled air mass was being influenced by the site power generator. This was done using wind-sector analysis to remove all 10 min averaged data points where the wind direction was between $170-240^{\circ}$ (the direction of the generator and the town of Kuujjuarapik). This filtered data were then averaged into 30 min time bins to create the average diurnals for each of the species to be constrained (Figure 1).

[18] The hydrocarbons (C_2H_6 , C_2H_4 , C_3H_8 , C_3H_6 , $i-C_4H_{10}$, $n-C_4H_{10}$ and C_2H_2) were all constrained to the observed campaign mean values (Table 1). The methane concentration was set to 1920 ppb, from NOAA observations at Barrow for February–March 2008 (ftp://ftp.cmdl.noaa.gov/ccg/ch4/in situ/brw/), and hydrogen to 550 ppb [*Novelli et al.*, 1999] for all simulations. Total reactive nitrogen was constrained using the mean NO₂ observations, as described above. All other constrained species were maintained at their mean observed concentrations throughout the average diurnal cycle, as shown in Figure 1.

4. Observations of OH and HO₂ Concentration

[19] OH and HO₂ were measured using the Fluorescence Assay by Gas Expansion (FAGE) technique [*Hard et al.*, 1984], which uses on-resonance pulsed laser-induced fluorescence at low pressures to directly measure concentrations



Figure 4. (a) The 10 min averaged campaign time series for HO_2 . (b) The 1 h averaged campaign time series for OH.

of OH. HO_2 concentrations are measured after its conversion to OH via titration with NO. The instrument used during COBRA was the University of Leeds aircraft FAGE system, which is described in detail by *Commane et al.* [2010]. It was located in a sea-container laboratory that had been modified to house the inlet, detection cells and gating boxes in an insulated box on the roof. The laser, pumps and control equipment were located inside the container laboratory, with optical fibers (length 4 m) used for delivery of the laser beam to the detection cells. The pump line was extended, resulting in a cell pressure of *ca.* 533 Pa (4 Torr) with a 1 mm diameter sampling nozzle. The exhaust line from the pumps was first passed through a Sofnofil (Molecular Products Ltd) trap, to remove residual NO, and was then piped away from the measurement site in the direction of the power generator. The instrument performed throughout the majority of the campaign, with measurements being made on 17 of the possible 22 measurement days.

[20] The sensitivity of the FAGE instrument is dependent on water vapor, as water vapor quenches excited state OH radicals ~22 times more efficiently than N₂ [*Hofzumahaus et al.*, 1996; *Creasey et al.*, 1997; *Faloona et al.*, 2004]. Mixing ratios of water vapor experienced during COBRA were much lower than those experienced at lower latitude field sites (<0.1% compared with ~1–2% at lower latitudes). Hence the instrument was calibrated at lower water vapor concentrations than usual. Figure 3 shows that the dependence of the calibration constants $C_{\rm OH}$ and $C_{\rm HO2}$ (see equations (4) and (5) of *Commane et al.* [2010]) on water vapor to be approximately linear over the range observed during COBRA.



Figure 5. Probability distribution of all 5 min averaged nighttime OH observations (black), bin size of 1×10^5 molecule cm⁻³. The red line is a calculated distribution showing the predicted variability on observations with a mean of zero and a standard deviation equal to the calculated precisional error on the observations during COBRA.

[21] Figure 4 shows the time series of 10-min averaged HO₂ and 1 h averaged OH concentrations. Campaign mean noontime (± 0.1 of a day around local solar noon) HO₂ concentrations of $(1.34 \pm 0.62) \times 10^8$ molecule cm⁻³ (at 1 σ) were measured, with an average peak of $(1.42 \pm 0.64) \times$ 10^8 molecule cm⁻³, and nonzero concentrations of (0.14 ± $(0.09) \times 10^8$ molecule cm⁻³ at night (±0.1 of a day on local solar midnight). The campaign mean OH concentration of $(0.26 \pm 0.87) \times 10^6$ molecule cm⁻³ is below the instrument's 1 σ limit of detection ((0.64 ± 0.13) × 10⁶ molecule cm⁻³). Concentrations increased above the limit of detection only around local solar noon. Mean noontime OH concentrations of $(0.77 \pm 1.05) \times 10^6$ molecule cm⁻³ were observed, reaching an average peak of $(1.16 \pm 1.02) \times 10^6$ molecule cm⁻³, and dropping to approximately zero, $(-0.04 \pm 0.76) \times 10^6$ molecule cm⁻³, at night (Figure 5). The mean 5 min limit of detection (as derived in equations (9) and (10) of Commane et al. [2010]) was $(0.09 \pm 0.02) \times 10^8$ molecule cm⁻³ and $(0.64 \pm 0.13) \times 10^6$ molecule cm⁻³ for HO₂ and OH respectively.

[22] If we assume that the nighttime OH concentrations are essentially zero, the standard deviation (assuming Poisson statistics) in observed OH concentrations at night should be explained by the instrumental noise, which can be described by

$$\sigma_b = \sqrt{(S_{lb} + S_{sb} + S_{ds})} \tag{2}$$

where S_{lb} is the laser induced background signal (cts), S_{sb} is the solar stray-light background signal (cts), which should equal zero at night, and S_{ds} is the dark count signal of the photomultiplier (cts) [*Holland et al.*, 1995]. This instrumental noise has been calculated to be $\sigma_b = 0.64 \times 10^6$ molecule cm⁻³.

[23] Figure 5 shows the probability distribution function of the nighttime (3 h either side of local solar midnight) OH observations (black) compared with that predicted from instrument characterization at a concentration of zero $(\sigma_b = 0.64 \times 10^6 \text{ molecule cm}^{-3})$ (red). The agreement between the nighttime OH observations and the calculated variability due to instrument precision gives confidence in the assessment of the instrument characterization and indicates that within the sensitivity of the instrument no OH was seen at night.

5. Analysis of HO_x Observations

[24] Average diurnal HO₂ and OH observations have been compared with concentrations calculated by the model described in Section 3. Figure 6 shows the campaign mean diurnal concentration for observed HO₂ (black) compared with the model calculated HO₂ concentrations (blue). The model reproduces the measurements to within the 1 σ observed variability for all but 3 points, with the model peaking at 1.5×10^8 molecule cm⁻³ compared with the observed (1.34 ± 0.62) $\times 10^8$ molecule cm⁻³, and a mean modeled nighttime HO₂ concentration of 0.1×10^8 molecule cm⁻³ compared with the observed (0.14 ± 0.09) $\times 10^8$ molecule cm⁻³.

[25] Figure 7 shows the mean diurnal model to measurement comparison for OH. The large variability on the observations (as indicated by the ±1 standard deviation variability bars) is due to the instrumental noise being comparable to the observed signal, and makes comparison with the model difficult. However, the average peak OH concentration of $(1.16 \pm 1.02) \times 10^6$ molecule cm⁻³ was reproduced to within the observed uncertainty, with a model peak of 1.4×10^6 molecule cm⁻³. The zero OH concentration observed at night is also reproduced by the model. There appears to be a ~2 h delay in the daily maximum calculated OH compared with the observations. No ready explanation for this exists but it is likely a feature of the highly variable OH data set and the uncertainties associated



Figure 6. Comparison of observed HO₂ concentrations averaged into 30 min time bins to give a mean diurnal (black with variability indicated by ± 1 standard deviation) with base case model calculated HO₂ concentrations (blue).

with the observed photolysis rates (described in Section 3). However, the model is within 1σ of the observations for all bar 1 point.

[26] Overall the model reproduces the measured campaign mean diurnal for OH and HO_2 to within the observed variability. Diagnosis of the model thus provides useful insight into the processes controlling the radical budget. To separate the processes controlling the daytime and nighttime chemistry, we first analyze the processes occurring at local noon and then at local midnight.

6. Processes Controlling the Radical Budget

6.1. Daytime Radical Chemistry

[27] To determine the main processes affecting total radical concentrations in this environment, a wider HO_x radical

family has been defined including all species involved in their cycling so that $RO_x = [OH] + [HO_2] + \Sigma[RO_2] +$ $[HO_2NO_2] + [HOI] + [HOBr] [Evans et al., 2003]$. In this way the primary radical production and loss mechanisms can be identified. Figure 8a is a Rate of Production and loss Analysis (ROPA) for RO_x , showing the magnitude of the ten largest RO_x sources and sinks at local noon within the model. This analysis identifies the production of radicals within the model during the day to be dominated by the photolysis of HCHO, with an average noon time rate of 8.3×10^5 molecule cm⁻³ s⁻¹ accounting for around 74% of the total noon RO_x production. The formation of RO_x via the photolysis of ozone in the presence of water vapor (R1 - R2) accounts for approximately 6% of the total noon time RO_x production rate, with a rate of 0.7×10^5 molecule cm⁻³ s⁻ This is due to the low water vapor and $i(O^{1}D)$ (Figure 1). The



Figure 7. Comparison of observed OH mean diurnal concentrations (black with variability indicated by ± 1 standard deviation) with base case model calculated OH concentrations (blue).



Figure 8. Rate of production and loss analysis (ROPA) at local noon in the average diurnal base model simulation for (a) total RO_x ([OH] + [HO₂] + [RO₂] + [HOI] + [HOBr] + [HO₂NO₂]), showing the dominant reactions controlling the overall radical budget, and (b) HO_x ([OH] + [HO₂]) highlighting processes important in the cycling of OH and HO₂ via inorganic reservoirs, the shading indicates magnitude of HO_x cycling and HO_x sink via these reactions. (c) OH and (d) HO₂ showing the most important production and loss reactions for these individual species. The dominant source reactions of MCM species shown in ROPAs are indicated if >90% of the species production is from one source.

importance of HCHO as a source of HO_x is further discussed in Section 6.4. The fraction of the RO_x source ROPA labeled "other" consists predominantly of ozone + alkene reactions and steps in the OH initiated oxidation of the constraining VOCs that regenerate more than one RO_x radical species. The major day time loss of RO_x is the HO₂ self reaction, with a rate of 2.8×10^5 molecule cm⁻³ s⁻¹, accounting for approximately 26% of the total radical losses. The second largest sink for daytime radicals is the reaction of HO_2NO_2 with OH, accounting for approximately 12% of the total calculated noon RO_x loss. The reaction with OH accounts for 28% of the total noontime losses of HO2NO2, with 66% undergoing thermal decomposition to $HO_2 + NO_2$ and the remaining 6% being lost to physical deposition. The role of HO₂NO₂ is discussed in Section 6.3. The heterogeneous loss of HO₂ also accounts for approximately 12% of the total calculated noontime RO_x radical sink, with a rate of 1.4×10^{5} molecule $cm^{-3} s^{-1}$. The sink fraction labeled "other" on the RO_x ROPA consists predominantly of a multitude of peroxy + peroxy radical self reactions.

[28] Figure 8b is a ROPA for noon time HO_x (= [OH] + [HO₂]) radicals. It identifies processes controlling the cycling between short-lived HO_x reservoirs and OH and HO_2 . The dominant cycling mechanism is through the production and photolysis of HOI, accounting for 21% and 19% of the HO_x losses and sources respectively. The imbalance in this cycling is due to the 8% of the HOI formed which undergoes heterogeneous uptake to aerosol. This heterogeneous process recycles a reactive halogen atom but is a net sink for HO_x . HO_x is interconverted more efficiently by IO than by BrO, due to the lower mean molecular speed of IO resulting in a reduced rate of uptake compared with BrO. The cycling through BrO accounts for 5% and 4% of the HO_x losses and sources respectively. The importance of these halogen reactions in background conditions is highly uncertain given the observations, and is discussed further in Section 6.6. Figure 8b also identifies the loss and re-release of HO₂ through HO₂NO₂ as a factor controlling the concentration of HO₂, with 10% of HO_x reacting with NO₂ to form HO₂NO₂.

[29] Figures 8c and 8d are the individual ROPAs for noontime OH and HO₂ respectively. The Figures show that the direct cycling of HO2 to OH via reaction with NO is still the dominant reaction controlling the OH to HO₂ ratio, accounting for 63% of the noontime OH source compared to 15% and 2% from HOI and HOBr photolysis respectively and 6% from the reaction of O_3 with HO₂. The reaction of O(¹D) with water vapor accounts for only 2% of the OH sources. The dominant reaction in cycling OH through to HO_2 is the reaction of OH with CO (56% of the OH reactions). Propene is identified as the major VOC reaction for OH, representing 11% of the OH sink. This is partly due to the negative temperature dependence of the OH + propene reaction compared with the positive temperature dependence of the OH + methane reaction. This temperature dependence results in the OH + propene reaction rate constant being 17.7×10^3 times higher than that for OH + methane at 250 K, compared with a difference of a factor of 4.7×10^3 at 298 K.

[30] During the daytime HCHO photolysis acts as the dominant radical source, with small contributions from

ozone and H_2O_2 photolysis and the ozonolysis of alkenes. HO₂ self reaction, the reaction of HO₂NO₂ with OH and the heterogeneous loss of HO₂ to aerosol are the dominant HO_x radical sinks. The remaining radical losses are largely through HO₂ + peroxy radical reactions and the loss of HOBr and HOI to aerosol. Even at the low concentrations used here halogens play an important role in the cycling of OH and HO₂. We now turn our attention to the chemistry occurring during the night.

6.2. Nighttime HO_x and the Role of HO_2NO_2

[31] The chemistry controlling HO_x within the model changes at night. The observed nonzero nighttime HO₂ concentrations were reproduced to within 1σ . The model also simulates approximately zero OH, consistent with the available observations (Section 5). Following the same analysis procedure used for the daytime chemistry, Figure 9a is a ROPA for total nighttime RO_x radicals. This shows the ozonolysis of propene to account for approximately 92% of the total RO_x radical source during the night (the bi-radicals formed in the two possible channels for O_3 addition to the propene carbon double bond are represented by "CH₂OOB" and "CH₃CHOOA"). The remaining sources are predominantly the ozonolysis of other alkenes or nitrate radical oxidation of VOCs. Due to the reduction in total radical concentration at night, the second order peroxy radical self reaction that dominates the ROx radical sink during the day becomes less important, with the first order heterogeneous loss of HO₂ now found to account for 31% of the total RO_x sink during the night. The physical deposition of HO_2NO_2 is identified as the second largest RO_x sink at 16%, this being sensitive to the physical deposition rate used in the model (Section 3). The remaining sinks are made up largely of peroxy radical self reactions.

[32] The halogen-catalyzed HO_x cycling present during the day no longer exists in the nighttime HO_x ROPA (Figure 9b) as XO concentrations are essentially zero. The dominant reservoir for radicals at night is HO_2NO_2 , the cycling between HO₂ and HO₂NO₂ accounts for 50% of the HO_x radical losses and 74% of the HO_x radical sources. The net imbalance of these two terms identifies the thermal decomposition of HO₂NO₂ to account for 24% of the total nighttime HO_x radical source. The remaining HO_x radical source consists predominantly of the decomposition of propene derived bi-radicals. Figures 9c and 9d are the ROPAs for OH and HO₂ respectively, showing the only direct cycling of HO₂ to OH to be the reaction of O₃ with HO₂ due to the lack of any NO or XO in the model during the night. Of the small amount of OH produced during the night, its main sink remains CO followed by propene.

[33] Within the model HO_2NO_2 plays a significant role in the nighttime chemistry. It is formed in the atmosphere through the association of NO_2 and HO_2 [*Niki et al.*, 1977]

$$(R14) \qquad HO_2 + NO_2 + M \rightarrow HO_2NO_2 + M$$

It is removed via thermal decomposition, photolysis in the UV [Knight et al., 2002] and near IR [Roehl et al., 2002],



Figure 9. Rate of production and loss analysis (ROPA) at local midnight in the average diurnal base model simulation for (a) total RO_x ([OH] + [HO₂] + [RO₂] + [HOI] + [HOBr] + [HO₂NO₂]), showing the dominant reactions controlling the overall radical budget, and (b) HO_x ([OH] + [HO₂]) highlighting processes important in the cycling of OH and HO₂ via inorganic reservoirs, the shading indicates magnitude of HO_x cycling and HO_x sink via these reactions. (c) OH and (d) HO₂ showing the most important production and loss reactions for these individual species. The dominant source reactions of MCM species shown in ROPAs are indicated if >90% of the species production is from one source.

reaction with OH, and dry deposition (reactions (R16)-(R18))

$$(R15) \qquad \qquad HO_2NO_2 + M \rightarrow HO_2 + NO_2 + M$$

(R16a)
$$HO_2NO_2 + hv \rightarrow HO_2 + NO_2$$

 $(R16b) \longrightarrow OH + NO_3$

$$(R17) \qquad OH + HO_2NO_2 \rightarrow H_2O + O_2 + NO_2$$

$$(R18) \qquad \qquad HO_2NO_2 \rightarrow Deposition$$

HO₂NO₂ has previously been identified as an important short-term reservoir of HO_x and NO_x radicals in the stratosphere and upper troposphere [Wennberg et al., 1999; Faloona et al., 2000; Murphy et al., 2004]. However, due to its short lifetime with respect to thermal decomposition, approximately 20 s at 1 atm and 20°C [DeMore et al., 1997], it is considered to be insignificant at lower altitudes, except under very high NO_x conditions [Spencer et al., 2009]. Boundary layer observations of HO₂NO₂ at the South Pole during the Investigation of Sulfur Chemistry in the Antarctic Troposphere (ISCAT) 2000 experiment however measured peak concentrations of 54 pptv with an observed mean of 25 pptv [Slusher et al., 2001, 2002]. This indicated a potentially significant role for HO₂NO₂ in photochemistry at low altitudes in cold, polar regions. Assessments of the HO_x budget during ISCAT 1998 and 2000 [Chen et al., 2001, 2004] found the physical deposition of HO₂NO₂ combined with its reaction with OH accounted for ~45% and 28% of the total HO_x sinks for the two studies respectively. The magnitude of this HO_x sink is dependent on both the rate of production of HO₂NO₂ and the relative rates of HO₂NO₂ loss through thermal decomposition, photolysis, deposition and reaction with OH. The conditions during COBRA were significantly different to those during ISCAT. Lower NOx concentrations compared with the ISCAT campaigns results in both lower rates of HO₂NO₂ production and lower concentrations of OH to react with HO₂NO₂. Thus HO₂NO₂'s importance for HO_x loss is reduced in these conditions. Also, warmer temperatures during COBRA (average temperature of -21.8°C compared with -27.7°C during ISCAT 2000 [Slusher et al., 2002]) result in a faster rate of thermal decomposition of HO₂NO₂ during COBRA, thereby reducing the fraction of HO₂NO₂ to be lost though the channels which result in HO_x loss. The lifetime with respect to physical deposition for HO₂NO₂ for all three studies has been assumed to be equivalent to that of HNO₃. The work described here uses a physical loss lifetime of 24 h (described in Section 3), which, given the observed 400 m boundary layer height [Moller et al., 2010], gives a deposition velocity of approximately 0.5 cm s^{-1} . This is consistent with the values used in previous studies [Hauglustaine et al., 1994; Chen et al., 2001; Slusher et al., 2002], however using a different physical deposition rate for HO₂NO₂ would impact calculated nighttime HOx concentrations. These different conditions during COBRA result in the combination of physical deposition of HO₂NO₂ and its reaction with OH accounting for only 7% of the total HO_x radical sink.

[34] Although HO_2NO_2 does not provide the dominant HO_x sink, the temperatures during COBRA were sufficiently cold for HO₂NO₂ to have a calculated lifetime with respect to thermal decomposition of approximately 3.6 h. This is enables concentrations to build up to a peak \sim 56 pptv during the day and remain above 10 pptv during the night. Thus HO₂NO₂ acts as a reservoir for HO₂, providing a mechanism to transfer HO_x from the daytime to the night. Figure 10 shows the effect of turning off HO₂NO₂ production within the model on HO₂ concentrations. This results in an increase in noon HO₂ concentrations from 1.5×10^8 to 1.6×10^8 molecule cm⁻³, due to a reduction in the amount of HO₂ present in reservoir species. Noon time calculated OH is also increased from 1.0×10^6 to 1.2×10^6 molecule cm^{-3} , through increased HO₂ and NO_x concentrations, resulting in greater conversion to OH, as well as the removal of the $OH + HO_2NO_2$ sink reaction. Nighttime HO_2 concentrations are reduced by approximately 50% through the removal of the nighttime source from HO_2NO_2 decomposition, consistent with the net HO₂NO₂ term in Figure 9b.

[35] The effect of HO₂NO₂ production on local ozone production has also been suggested to have a significant impact in cold environments, through reductions in daytime HO_x and NO_x concentrations. This was reported during the Free Tropospheric Experiment (Freetex'98) study, where it was estimated that ozone production was reduced by ~20% through the loss of NO₂ to HO₂NO₂, favored by the cold temperatures (c.a. -10° C) experienced high in the Swiss Alps [*Carpenter et al.*, 2000]. To assess the impact of HO₂NO₂ on the local ozone production efficiency a free running model, unconstrained to both NO_x and O₃, has been run for 2 days with and without HO₂NO₂ production. This found that HO₂NO₂ production resulted in a 30% reduction in the in situ O₃ production rate from approximately 0.2 ppbv day⁻¹ in the base model run.

[36] During the night therefore the dominant source of nighttime radicals is the ozonolysis of propene, with the main RO_x radical losses being the heterogeneous loss of HO_2 to aerosol and the physical deposition of HO_2NO_2 . HO_2NO_2 has also been found to play an important role in transferring HO_x radicals made during the day into the night, with implications for both local ozone production and oxidizing capacity. The following sections further investigate some of the processes found to be important for HO_x radical chemistry in this environment.

6.3. Impact of HCHO Concentrations

[37] The RO_x ROPA in Figure 8a showed that the photolysis of HCHO is the dominant source of radicals in this environment. The average HCHO concentration of 386 pptv measured during COBRA is high when compared with limited previous observations in high latitude environments, although still within the range reported in the literature *[Hutterli et al.*, 1999; *Sumner and Shepson*, 1999; *Riedel et al.*, 1999, 2005; *Jacobi et al.*, 2002; *Frey et al.*, 2005]. In general the major source of HCHO in the troposphere is the oxidation of hydrocarbons [*Lowe and Schmidt*, 1983; *Fried et al.*, 2003]. However, the sources of HCHO in the Arctic boundary layer have been shown to be dominated by emissions from snow surface [*Sumner and Shepson*, 1999]. The results of running the model with HCHO production



Figure 10. Comparison of observed 30 min averaged HO₂ mean diurnal concentrations (black with variability indicated by ± 1 standard deviation) with model calculated HO₂ concentrations. The blue trace is the base model run where HO₂NO₂ production is included in the chemistry scheme. The green trace is the model run with no HO₂NO₂ production.

only via the oxidation of the constraining hydrocarbon species and no surface HCHO source (i.e., not constraining model HCHO to observations) on the HCHO and HO₂ concentrations are shown in Figures 11 and 12 respectively. This simulation gave a mean noon steady state HCHO concentration of 61 pptv compared with the mean observed used in the base model of 386 pptv. This results in a reduction in peak modeled HO₂ of 60% and OH of 48%. This inability to reproduce the observed HCHO, and thus HO_x , concentrations with hydrocarbon oxidation alone indicates the importance of a surface source of HCHO [*Sumner and Shepson*, 1999; *Hutterli et al.*, 1999]. A HCHO source scaled to *j*NO₂, with an approximate daily averaged rate equivalent to the flux calculated by *Sumner and Shepson* [1999] (4.9 × 10⁹ molecule cm⁻² s⁻¹) and a boundary layer height of 400 m [*Moller et al.*, 2010] leads to



Figure 11. Observed HCHO mean diurnal concentrations (blue with observation variability indicated by ± 1 standard deviation) compared with, model calculated HCHO concentrations (light blue) from the oxidation of hydrocarbons within the model; model calculated HCHO with an added emission source of HCHO of the approximate strength of that reported by *Sumner and Shepson* [1999] (green); model calculated HCHO with an added emission source of HCHO of approximately twice the strength of that reported by *Sumner and Shepson* [1999] (red).



Figure 12. Comparison of observed HO₂ mean diurnal concentrations (black with variability indicated by ± 1 standard deviation) with model calculated HO₂ concentrations. The blue trace is the base model run where HCHO is constrained to observations; the light blue trace is the model calculated HO₂ where HCHO is left unconstrained with the only source being the oxidation of hydrocarbons within the model; the green trace is the model calculated HO₂ with HCHO left unconstrained + an added emission source of HCHO of the approximate strength of that reported by *Sumner and Shepson* [1999]; the red trace is the model calculated HO₂ with HCHO left unconstrained + an added emission source of HCHO approximately twice the strength of that reported by *Sumner and Shepson* [1999].

a mean modeled HCHO concentration of 194 pptv, approximately half that observed during COBRA (see Figure 11). This increases the calculated average noon HO₂ concentration to within 30% of the observations. In order to get the calculated average daily HCHO concentration to agree to within < 20% of the observations and calculated noon HO₂ concentration to be within 10% of the observations, an emission flux of approximately 1×10^{10} molecule cm⁻² s⁻¹ is required (see Figure 11). Although a factor of 2 higher than the HCHO flux reported by Sumner and Shepson [1999], this required emission flux of HCHO from the snowpack is thought to be highly dependent on the local levels of organic precursors within the snow [Grannas et al., 2007], and thus a degree of variability is to be expected. Although largely within the 1σ variability on the observed HCHO concentrations, it is visible from Figure 11 that the model-calculated HCHO concentrations do not follow the same diurnal trend as the observations. This is most likely due to a misrepresentation of the processes controlling the snowpack emissions of HCHO and variations in the boundary layer height, and without direct flux observations it is difficult to investigate this further. However, the available evidence points to the snow source of HCHO being the dominant source of radicals in the polar spring boundary layer. This is a process currently missing from global models of atmospheric chemistry.

6.4. Impact of the Heterogeneous Uptake of HO₂

[38] Figure 8 highlights the importance of the heterogeneous loss of HO₂ on the HO_x budget. This is consistent with the study by *Mao et al.* [2010] which found HO₂ uptake by aerosol to be the dominant HO_x sink at altitudes above 5 km, during the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) campaign in 2008, and the third most important HO_x sink below 5 km after HO₂ + HO₂ and HO₂ + CH₃O₂ peroxy radical self reaction. The value of γ_{HO_2} for different aerosol types is highly uncertain, being dependant on factors such as aerosol composition, physical state of the aerosol and temperature [*Jacob*, 2000]. *Mao et al.* [2010] calculated values of γ_{HO_2} ranging from less than 0.05 near the surface to 0.4 in the upper troposphere using a scheme by *Thornton et al.* [2008].

[39] Due the lack of observations of aerosol composition and state during COBRA, there is considerable uncertainty in the value chosen for $\gamma_{\rm HO_2}$ in the model simulation. Observations of $\gamma_{\rm HO_2}$ on various aerosols have yielded values between 0.025–1 [*Cooper and Abbatt*, 1996; *Jacob*, 2000] depending on the state and composition of the aerosol. Figure 13 shows the model sensitivity to possible values of $\gamma_{\rm HO_2}$. The model best fits the observations with a $\gamma_{\rm HO_2}$ of between 0.025 and 0.05. Reaction probabilities of 0.1 and above resulting in a failure of the model to reproduce the observed nighttime HO₂ concentrations to within the observed variability.

[40] Thus we conclude that within the reasonable range of $\gamma_{\rm HO_2} 0.025 \rightarrow 0.1$ there is a 50% uncertainty in our simulation of HO₂, and 65% in OH, with the model fitting the observations best on the range $\gamma_{\rm HO_2} 0.025 \rightarrow 0.05$.

6.5. Effect of Halogens

[41] In the base model simulations 1 pptv noon time IO and BrO mixing ratios were used to represent an upper limit on background halogen concentrations. These result in the formation and photolysis of HOI being an important cycling



Figure 13. Comparison of observed HO₂ mean diurnal concentrations (black with variability indicated by ±1 standard deviation) with model calculated HO₂ concentrations using different values of γ_{HO_2} . Red trace $\gamma_{HO_2} = 0$; blue trace $\gamma_{HO_2} = 0.025$ [*Cooper and Abbatt*, 1996] for HO₂ on ice surfaces; purple trace $\gamma_{HO_2} = 0.05$; green trace $\gamma_{HO_2} = 0.1$; light blue trace $\gamma_{HO_2} = 1$.

process for HO_x radicals. For the majority of the campaign concentrations of IO and BrO remained below the LP-DOAS 1 pptv limit of detection. However, elevated concentrations up to a maximum of 28 pptv BrO and 3.4 pptv of IO [*Mahajan et al.*, 2010] were observed on a few occasions which correlated with depletion of ozone down to approxi-

mately 5 ppbv. Unfortunately the infrequency of these 'halogen events' combined with incomplete data coverage from the FAGE instrument during these time periods meant that insufficient data were collected to allow a detailed assessment of the effects of elevated BrO and IO levels on the HO_x budget.



Figure 14. Sensitivity of modeled HO₂ concentrations to reactive iodine and bromine concentrations within the model. Plot shows observed HO₂ mean diurnal concentrations (black with variability indicated by ± 1 standard deviation); base model calculated HO₂ concentrations includes reactive halogens equivalent to daily peaks of IO and BrO of 1 pptv (blue); model calculated HO₂ concentrations with no halogen species in the model (red); model calculated HO₂ concentrations from simulation with reactive halogens equivalent to daily peaks of 3.4 pptv and 28 pptv for IO and BrO respectively (green).



Figure 15. Sensitivity of modeled OH concentrations to reactive iodine and bromine concentrations within the model. Plot shows observed OH mean diurnal concentrations (black with variability indicated by ± 1 standard deviation); base model calculated OH concentrations includes reactive halogens equivalent to daily peaks of IO and BrO of 1 pptv (blue); model calculated OH concentrations with no halogen species in the model (red); model calculated OH concentrations from simulation with reactive halogens equivalent to daily peaks of 3.4 pptv and 28 pptv for IO and BrO respectively (green).

[42] The model sensitivity to halogens is investigated by simulations at the maximum observed BrO and IO concentrations, 28 pptv and 3.4 pptv respectively, and with no halogens. These simulations are a first order approximation of the impact of halogens on local HO_x concentrations, as the concentrations of all other constraining species, including O_3 and HCHO, have been kept the same as in the base model simulation. Elevated halogen concentrations would be expected to impact the concentrations of these other species, which would in turn have consequences for HO_x concentrations [Evans et al., 2003; Liao et al., 2011]. The limited data coverage during these 'halogen events' however makes a detailed study of this full impact of halogens difficult, and therefore only the direct effect on HO_x chemistry is investigated. Figures 14 and 15 show the sensitivity of the modeled HO₂ and OH to the assumed range of halogen loadings.

[43] The removal of halogens from the model leads to a 10% increase in noon-time HO₂ concentrations and a 7%decrease in noon-time OH concentrations. The ROPA for total RO_x radicals at noon in the zero halogens model run is shown in Figure 16. Comparison of the dominant reactions in this zero halogens simulation (Figure 16) with those in the base model run (Figure 8) show that the increase in HO_2 , and hence total HO_x , is due to the removal of reactions of HO₂ with halogen monoxides to form HOBr and HOI. Although these species undergo photolysis to yield OH, therefore recycling HO_x, approximately 8% of HOI and 30% of HOBr undergo heterogeneous reactions on aerosol surfaces, therefore acting as a loss for HO_x. The difference between the fractions of HOI and HOBr lost to aerosol is due to the larger photolysis rate of HOI compared with HOBr [Atkinson et al., 2007]. The decrease in OH concentration when halogen chemistry is not included is due to the removal of this mechanism of cycling HO_2 to OH via HOBr and HOI.

[44] The high halogen concentration simulation was initialized with sufficient I_2 and Br_2 (7.4 pptv and 52 pptv, respectively) to achieve the observed maximum levels of 3.4 pptv of IO and 28 pptv of BrO during the day. The diurnal profiles of these species were controlled by the same chemistry scheme as that used in the base model run, and so show similar diurnal trends to those in Figure 2 but with higher values. The effect of elevated halogen concentrations was to decrease noon-time HO₂ concentrations by 31%, and increase OH concentrations by 27%, thus reducing noontime HO_x by approximately 30%. The noontime HO_x ROPA in Figure 17b shows that BrO becomes the dominant species affecting the cycling of OH and HO₂, due to the \sim 28 fold increase in BrO concentration in this simulation compared with the \sim fourfold increase in IO concentration. Approximately 40% of the total reactivity of HO₂ proceeds through reaction with BrO. Of the HOBr formed in this reaction, 70% is recycled back to OH through photolysis, with the remaining 30% undergoing heterogeneous uptake resulting in the loss of HO_x . The cycling of HO_x through reaction of HO₂ with IO is also increased in this elevated halogen simulation, with 28% of HO₂ reacting with IO to give HOI, of which 92% is recycled to OH. These two processes convert HO₂ to OH while acting as an overall sink for HO_x. The increase in the OH: HO₂ ratio generates more organic peroxy radicals. This increases the rate of RO_x loss through hydro-peroxy – peroxy radical reactions, and hence reduces total HO_x concentrations. It is this increase in peroxy radical self reaction that gives rise to the significant increase in the "other" fraction of RO_x losses in Figure 17a compared with



Figure 16. Rate of production and loss analysis (ROPA) for modeled total RO_x ([OH] + [HO₂] + [RO₂] + [HO₂NO₂]) radicals at noon in the zero halogens average diurnal model run, showing the most important production and loss reactions and associated rates. The dominant source reactions of MCM species shown in ROPAs are indicated if >90% of the species production is from one source.

the base model simulation (Figure 8a). These increased HO_x sinks are slightly offset in the elevated halogens simulation by the increased source from the reaction of HCHO with bromine atoms (reaction (R19)), which accounts for 16% of the total noon RO_x radical source. The importance of the HCHO + Br reaction as a HO_x source, however, is likely a feature of maintaining its constrained concentration. In reality, this enhanced sink for HCHO would instead act to reduce the magnitude of the primary HO_x sink from HCHO

photolysis. For an emitted HCHO molecule photolysis can release 2 HO_x radicals, while reaction with Br releases 1.

$$(R19) \qquad \qquad HCHO + Br \rightarrow HBr + CO + HO$$

The effect of increased halogens on nighttime HO_x chemistry was to reduce HO_2 concentrations by approximately 20%. This was primarily through a reduction in the rate of HO_2NO_2 production during the day, due to lower HO_2



Figure 17. (a) Rate of production and loss analysis (ROPA) at local noon in the maximum halogens model simulation for (a) total RO_x ([OH] + [HO₂] + [RO₂] + [HOI] + [HOBr] + [HO₂NO₂]), showing the dominant reactions controlling the overall radical budget, and (b) HO_x ([OH] + [HO₂]) highlighting processes important in the cycling of OH and HO₂ via inorganic reservoirs, the shading indicates magnitude of HO_x cycling and HO_x sink via these reactions. The dominant source reactions of MCM species shown in ROPAs are indicated if >90% of the species production is from one source.

concentrations, which in turn results in less HO_2 being liberated from this reservoir during the night.

[45] Halogens reducing total HO_x while increasing OH concentrations has been observed previously at coastal locations where halogen chemistry is believed to play an important role in HO_x chemistry [*Bloss et al.*, 2007, 2010; *Whalley et al.*, 2010]. As observations of BrO and IO only increased above the LP-DOAS limit of detection for brief periods during this campaign, we are unable to comment on the overall effect of halogens in this region. However, the modeling carried out has indicated that even at low concentrations halogens play a significant role, and at the maximum levels observed during halogen events can play a dominant role in the cycling of HO_x.

7. Conclusions

[46] OH and HO₂ concentrations were measured by FAGE during February-March 2008 on the coast of the Hudson Bay, as part of the COBRA campaign, with mean noontime concentrations of $(0.765 \pm 1.05) \times 10^6$ molecule cm⁻³ and $(1.34 \pm 0.62) \times 10^8$ molecule cm⁻³ respectively. We are able to reconcile the observed HO_x concentrations with the available observed sources, 74% of the HOx source being from HCHO photolysis, with ~80% of this HCHO coming from a surface source. As discussed earlier the COBRA HCHO observations are higher than the extremely small data set of similar observations. In similar environments other emitted HO_x precursor species (specifically HONO and H_2O_2) have been found to be important radical sources, with H2O2 photolysis found to contribute as much as 37% to the calculated HO_x source during the 2003 Summit campaign (e.g., Yang et al., 2002; Chen et al., 2004, 2007). We have no observational constraints for these alternative radical sources. However, should they be significant in this would suggest either a reduced HO_x source or an enhanced HO_x sink. Given that we have an observational constraint (HCHO concentrations) on the HO_x source this would suggest an enhancement of the HO_x sink. The heterogeneous uptake of HO_x onto aerosol is highly uncertain and should these extra HO_x sources exist this would suggest a higher value for the gamma HO₂ than used here. The ozonolysis of propene is the dominant nighttime radical source. HO₂NO₂ plays an important role as a reservoir for HO_2 , reducing HO_x concentrations during the day and increasing them during the night. Thus HO₂NO₂ impacts both local oxidizing capacity and ozone production.

[47] Overall, model simulations suggest significant roles for halogen chemistry, HO_2NO_2 processes, surface sources of HO_x precursors, and the heterogeneous loss of HO_2 . These processes are very simply or not at all parameterized in the current generation of chemistry or climate models (e.g., GEOS-Chem [*Bey et al.*, 2001]). This leads to significant uncertainties in the chemistry calculated in polar and sub-arctic regions. Thus the usefulness of model derived climate assessments of ozone in the Arctic are placed in doubt, as are predictions of future ozone trends and climate impacts in the Arctic.

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^[48] Acknowledgments. Funding for this project was via the UK Natural Environment Research Council (NERC) COBRA grant (NE/ D005914/1 and NE/E007880/1). We would also like to thank Claude Tremblay of Centre d'études Nordiques, Laval University, for his logistical support in Kuujjuarapik.

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