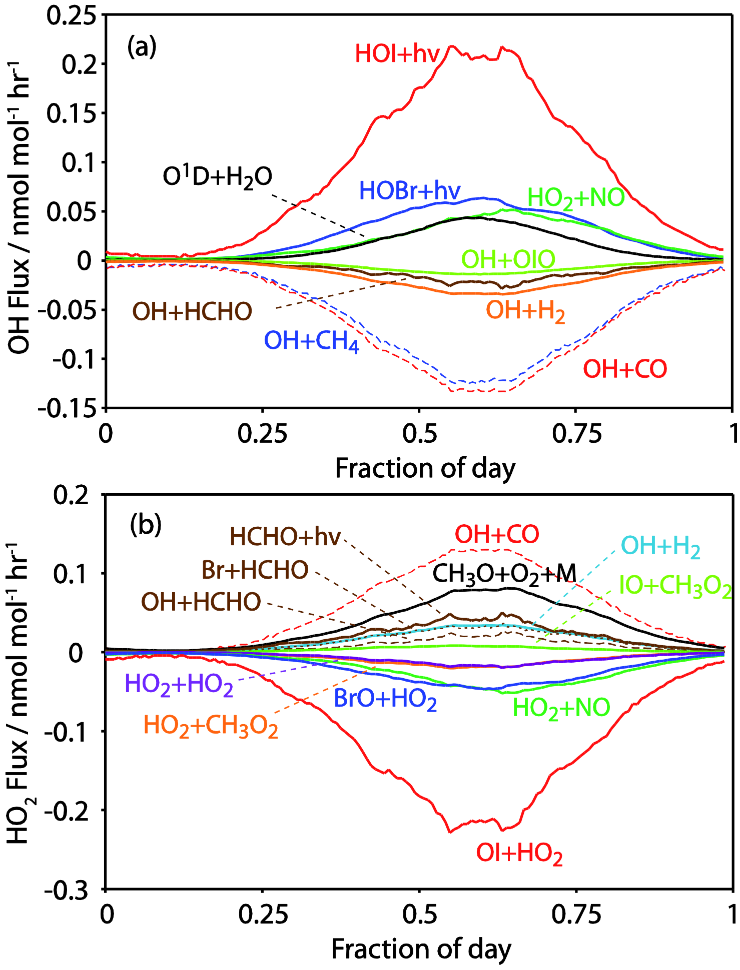
Coupling of HO_x, NO_x and Halogen Chemistry in the Antarctic Boundary Layer

Supplementary Information



Supplementary Figure 1. OH and HO_2 production / removal fluxes for the B2 scenario

Supplementary Table S1. Photolysis frequencies for halogen species

Reaction	Quantum Yield Note	Mean j(x) / j(NO_2)	Cross sections / Qm yields used	Note
I_2 + hv		20.3	Atkinson et al., 2007	
Br_2 + hv		3.45	Atkinson et al., 2007	
IBr + hv		9.10	Atkinson et al., 2007	
BrO + hv		5.41	Atkinson et al., 2007	
$BrONO_2$ + hv	Φ (Br+NO_3) = 1	0.160	Atkinson et al., 2007	
BrONO + hv	Φ (Br+NO_2) = 0.5, Φ (BrO+NO) = 0.5	2.28	Atkinson et al., 2007	1
HOBr + hv		0.256	Atkinson et al., 2007	
IO + hv		18.3	Bloss et al., 2001	
OIO + hv	Φ (I+O_2) = 0.05	51.6	Cox et al., 1999 / Joseph et al., 2005	2
$IONO_2$ + hv	Φ (I+NO_3) = 1	0.556	Joseph and Plane, 2007	3
I_2O_2 + hv	Φ (IO) = 2	0.556		4
I_2O_3 + hv	Φ (IO+OIO) = 1.0	0.556		4
I_2O_4 + hv	Φ (OIO+OIO) = 1.0	0.556		4
INO_2 + hv	Φ (I+NO_2) = 1	0.319	Sander et al., 2006	
INO + hv		3.71	Sander et al., 2006	
HOI + hv		1.12	Atkinson et al., 2007	
HI + hv		6.89×10^{-3}	Atkinson et al., 2007	

Atkinson et al., 2007 = 2007 IUPAC Evaluation; Sander et al., 2006 = NASA/JPL Evaluation 15-06.

1: Quantum yield for BrONO photolysis assumed to be 50 % for each channel (Atkinson et al., 2007).

2: OIO absorption spectrum from Cox et al. (1999) scaled to match 567 nm cross section determined by Joseph et al. (2005). Quantum yield for photolysis assumed to be 5 % yielding entirely I + O_2 following Joseph et al. (2005) and Tucceri et al. (2006); the effect of increasing the quantum yield for production of I + O_2 to unity, as recently reported by Gómez-Martin et al. (2009), was considered in the sensitivity study.

3: $IONO_2$ cross sections have been reported by Mossinger et al. (2002) and by Joseph et al. (2007). The latter data are significantly smaller at long (> 360 nm) wavelengths, corresponding to roughly one order of magnitude difference in photolysis rate. The more recent values of Joseph and Plane, taken from the table within their paper, are used here, with unit photolysis yield of I + NO_3 adopted; the magnitude of the $IONO_2$ cross sections is considered in the sensitivity study.

4: Definitive cross-sections are not available for I_2O_2, I_2O_3 or I_2O_4. Following the laboratory estimates of Bloss et al. (2001) and Gómez-Martín et al. (2005), and *ab initio* results (Kaltsoyannis and Plane, 2008) we assume the absorption spectrum is equal to that of $IONO_2$ – this corresponds to a midday photolysis frequency of 8×10^{-3} s^{-1} for these species (corresponding $j(NO_2)$ = 1.85×10^{-2} s^{-1}). The sensitivity of the model results to this assumption is evaluated in the sensitivity study section.

Supplementary Table S2. Halogen Scheme: Gas-Phase Kinetic Parameters

Reaction	*Rate Expression*	*Reference*	*Note*
$Br + O_3 \rightarrow BrO + O_2$	$k = 1.7\times10^{-11}exp(-800/T)$	Atkinson et al., 2007	
$Br + HO_2 \rightarrow HBr + O_2$	$k = 7.7\times10^{-12}exp(-450/T)$	Atkinson et al., 2007	
$OH + HBr \rightarrow Br + H_2O$	$k = 6.7\times10^{-12}exp(155/T)$	Atkinson et al., 2007	
$OH + Br_2 \rightarrow HOBr + Br$	$k = 2.0\times10^{-11}exp(240/T)$	Atkinson et al., 2007	
$Br + HCHO \rightarrow HBr + HCO$	$k = 7.7\times10^{-12}exp(-580/T)$	Atkinson et al., 2007	
$Br + CH_3CHO \rightarrow HBr + CH_3CO$	$k = 1.8\times10^{-11}exp(-460/T)$	Atkinson et al., 2007	
$Br + NO_2 \rightarrow BrONO$	$k_0 = 4.2\times10^{-31}(T/300)^{-2.4}$ $k_\infty = 2.7\times10^{-11}$, $F_c = 0.6$	Sander et al., 2006	
$BrO + BrO \rightarrow Br + Br + O_2$	$k = 2.7\times10^{-12}$	Atkinson et al., 2007	
$BrO + BrO \rightarrow Br_2 + O_2$	$k = 2.9\times10^{-14}exp(840/T)$	Atkinson et al., 2007	
$BrO + HO_2 \rightarrow HOBr + O_2$	$k = 4.5\times10^{-12}exp(500/T)$	Atkinson et al., 2007	
$OH + HOBr \rightarrow H_2O + BrO$	$k = 5.0\times10^{-11}$		1
$BrO + CH_3O_2 \rightarrow HOBr + CH_2O_2$	$k = 4.6\times10^{-13}exp(798/T)$	Enami et al., 2007 / Aranda et al., 1997	2
$BrO + NO \rightarrow Br + NO_2$	$k = 8.7\times10^{-12}exp(260/T)$	Atkinson et al., 2007	
$BrO + NO_2 \rightarrow BrONO_2$	$k_0 = 5.2\times10^{-31}(T/300)^{-3.2}$ $k_\infty = 6.9\times10^{-12}(T/300)^{-2.9}$, $F_c = 0.6$	Sander et al., 2006	
$BrONO_2 \rightarrow BrO + NO_2$	$k = 2.8\times10^{13}exp(-12360/T)$	Orlando and Tyndall , 1996	
$I + O_3 \rightarrow IO + O_2$	$k = 2.1\times10^{-11}exp(-830/T)$	Atkinson et al., 2007	
$I + HO_2 \rightarrow HI + O_2$	$k = 1.5\times10^{-11}exp(-1090/T)$	Atkinson et al., 2007	
$OH + HI \rightarrow I + H_2O$	$k = 1.6\times10^{-11}exp(440/T)$	Atkinson et al., 2007	
$OH + I_2 \rightarrow HOI + I$	$k = 2.1\times10^{-10}$	Atkinson et al., 2007	
$NO_3 + I_2 \rightarrow I + IONO_2$	$k = 1.5\times10^{-12}$	Atkinson et al., 2007	3
$NO_3 + HI \rightarrow HNO_3 + I$	$k = 1.3\times10^{-12}exp(-1830/T)$	Atkinson et al., 2007	
$I + NO_2 \rightarrow INO_2$	$k_0 = 3.0\times10^{-31}(T/300)^{-1.0}$ $k_\infty = 6.6\times10^{-11}$, $F_c = 0.6$	Sander et al., 2006	
$INO_2 \rightarrow I + NO_2$	$k = 0.14\ s^{-1}$ (at 268 K)	Van den Bergh and Troe, 1976	4
$INO_2 + INO_2 \rightarrow I_2 + 2NO_2$	$k = 4.7\times10^{-13}exp(-1670/T)$	Atkinson et al., 2007	
$I + NO \rightarrow INO$	$k_0 = 1.8\times10^{-32}(T/300)^{-1.0}$ $k_\infty = 1.7\times10^{-11}$, $F_c = 0.6$	Sander et al., 2006	
$INO \rightarrow I + NO$	$k = 0.087\ s^{-1}$ (at 268 K)	Van den Bergh and Troe, 1976	4
$INO + INO \rightarrow I_2 + NO + NO$	$k = 8.4\times10^{-11}exp(-2620/T)$	Atkinson et al., 2007 or JPL	
$IO + IO \rightarrow 2I + O_2$	$k = 0.11 \times 5.4\times10^{-11}exp(180/T)$	Atkinson et al., 2007	5
$IO + IO \rightarrow I + OIO$	$k = 0.38 \times 5.4\times10^{-11}exp(180/T)$	Atkinson et al., 2007	5
$IO + IO \rightarrow I_2O_2$	$k = 0.51 \times 5.4\times10^{-11}exp(180/T)$	Atkinson et al., 2007	5
$IO + HO_2 \rightarrow HOI + O_2$	$k = 1.4\times10^{-11}exp(540/T)$	Atkinson et al., 2007	
$OH + HOI \rightarrow IO + H_2O$	$k = 1.0\times10^{-10}$		6
$IO + CH_3O_2 \rightarrow CH_3O + IOO$	$k = 2.0\times10^{-12}$	Dillon et al., 2006	7
$IO + NO \rightarrow I + NO_2$	$k = 7.15\times10^{-12}exp(300/T)$	Atkinson et al., 2007	
$IO + NO_2 \rightarrow IONO_2$	$k_0 = 6.5\times10^{-31}(T/300)^{-3.5}$ $k_\infty = 7.6\times10^{-12}(T/300)^{-1.5}$, $F_c = 0.6$	Sander et al., 2006	
$IONO_2 \rightarrow IO + NO_2$	$k = 2.1\times10^{15}exp(-13670/T)$	Kaltsoyannis and Plane, 2008	8
$IO + NO_3 \rightarrow OIO + NO_2$	$k = 9\times10^{-12}$	Dillon et al., 2008	
$I + NO_3 \rightarrow IO + NO_2$	$k = 1\times10^{-12}$	Dillon et al., 2008	
$IO + BrO \rightarrow I + Br + O_2$	$k = 0.2 \times 1.5\times10^{-11}exp(510/T)$	Atkinson et al., 2007	9
$IO + BrO \rightarrow Br + OIO$	$k = 0.8 \times 1.5\times10^{-11}exp(510/T)$	Atkinson et al., 2007	
$IO + OIO \rightarrow I_2O_3$	$k = 5\times10^{-11}$	Gomez-Martin et al., 2007	10
$OIO + OIO \rightarrow I_2O_4$	$k = 1.5\times10^{-10}$	Gomez-Martin et al., 2007	10.1
$OIO + I_2O_3 \rightarrow PI_1$	$k = 1.5\times10^{-10}$	Gomez-Martin et al., 2007	10.1
$OIO + I_2O_4 \rightarrow PI_2$	$k = 1.5\times10^{-10}$	Gomez-Martin et al., 2007	10.1
$I_2O_2 + O_3 \rightarrow I_2O_3 + O_2$	$k = 1.0\times10^{-12}$	Saunders and Plane, 2005	10.2
$I_2O_3 + O_3 \rightarrow I_2O_4 + O_2$	$k = 1.0\times10^{-12}$	Saunders and Plane, 2005	10.2
$I_2O_4 + O_3 \rightarrow PI_3$	$k = 1.0\times10^{-12}$	Saunders and Plane, 2005	10.2
$I_2O_2 \rightarrow IO + IO$	$k = 10\ s^{-1}$	Kaltsoyannis and Plane, 2008	10.3
$I_2O_4 \rightarrow OIO + OIO$	$k = 0.1\ s^{-1}$	Kaltsoyannis and Plane, 2008	10.3
$NO + OIO \rightarrow IO + NO_2$	$k = 1.1\times10^{-12}exp(542/T)$	Plane et al., 2006	
$OH + OIO \rightarrow PI_4$ (HIO_3)	$k = 2.2\times10^{-10}exp(243/T)$	Plane et al., 2006	11

BrO + DMS → Br + DMSO	$k = 1.4\times10^{-14}\exp(950/T)$	Sander et al., 2006	
Br + DMS → HBr + CH_3SCH_2	$k = 9.0\times10^{-11}\exp(-2390/T)$	Sander et al., 2006	12
IO + DMS → I + DMSO	$k = 1.2\times10^{-14}$	Sander et al., 2006	

Atkinson et al., 2007 = 2007 IUPAC Evaluation; Sander et al., 2006 = NASA/JPL Evaluation 15-06.

Supplementary Table S3. Heterogeneous reaction probabilities

Species	Reaction Probability γ	Reference
HONO	0.04	JPL 15-06
PNA	0.1	JPL 15-06
HNO_3	0.1	JPL 15-06
N_2O_5	0.04	JPL 15-06
HO_2	0.2	Jacob, 2000
CH_3O_2	0.04	Jacob, 2000
HI	0.2	JPL 15-06
HBr	0.2	JPL 15-06
HOI	0.5	Mossinger and Cox, 2001 / Braban et al. (2007) / JPL 15-06
HOBr	0.6	JPL 15-06
$BrONO_2$	0.2	JPL 15-06
$IONO_2$	0.2	Assumed as $BrONO_2$
INO_2	0.1	Assumed
$BrNO_2$	0.1	Assumed
IO	0.5	Assumed
OIO, I_2O_2, I_2O_3, I_2O_4	1	Assumed
PI_n	1	Assumed

Notes to Halogen Reaction Scheme (Supplementary Tables 2, 3)

Other reactions considered, but discounted as their effects were found to be negligible for this environment, were :

-Termolecular I atom recombination

-Halogen atom / molecule reactions (I + Br_2, Br + I_2, I + IBr, Br + IBr)

-Halogen atom / halogen monoxide reactions (I + BrO, Br + IO)

-Oxygen atom / halogen reactions (O + I_2, O + Br_2, O + IO, O + BrO)

-Halogen monoxide / ozone reactions (IO + O_3, BrO + O_3)

Specific Notes

1: OH + HOBr – Rate constant estimated with reference to OH + HOCl, O + HOCl and O + HOBr.

2: Temperature-dependent kinetics for BrO + CH_3O_2 taken from Enami et al. (2007); products assumed to be HOBr + CH_2O_2 following Aranda et al. (1997). Within the model CH_2O_2 dissociates to CO + H_2O (Mariq et al., 1994).

3: I_2+NO_3. Products assumed to be I+$IONO_2$ following Atkinson et al. (2007) on enthalpy arguments. Effect of alternative product channel (IO + INO_2, as adopted by Saiz-Lopez et al., 2008) considered in sensitivity study.

4: INO and INO_2 thermal decomposition calculated via the formation rate constants given, plus temperature-dependent equilibrium constant expressions from van den Burgh and Troe, 1976: $K_{eq}(\mathrm{I + NO \leftrightarrow INO}) = 10^{-5.70} \times \exp(9160/T)$ and $K_{eq}(\mathrm{I + NO_2 \leftrightarrow INO_2}) = 10^{-6.43} \times \exp(9560/T)$, both in atm^{-1}.

5: IO + IO: Overall rate constant and OIO+I channel from Atkinson et al. (2007); branching ratio for 2I + O_2 / I_2O_2 channels from Bloss et al. (2001). See also comments below (note 10.3).

6: OH + HOI – Rate constant estimated with reference to OH + HOCl, O + HOCl and O + HOBr.

7: Base-case for the IO + CH_3O_2 reaction is “slow” kinetics ($k = 2\times10^{-12}$; Dillon et al., 2006) and formation of CH_3O + IOO (i.e. the CH_3OOOI intermediate, likely decomposing to CH_3O + IOO and hence HCHO + HO_2 + I + O_2 in the atmospheric boundary layer) with unit yield. Sensitivity studies described in the text consider the potential impact of a higher rate constant (e.g. Bale et al., 2005; Enami et al., 2007) and alternative product channels, e.g. via the CH_3OOIO channel to CH_3O + OIO (Drougas and Kosmas, 2007).

8 Thermal decomposition rate reported by Kaltsoyannis and Plane (2008) adopted; this is based upon revised RRKM analysis coupled to laboratory kinetic data for the forward reaction obtained by Allen and Plane (2002), and supersedes the decomposition rate determined in a similar manner in the earlier paper.

9: Branching ratio for IO + BrO from Atkinson et al. (2007) in combination with Rowley et al. (2001); note approach adopted neglects possible increase in atomic channels at reduced temperature.

10: *Higher Iodine Oxides*

In addition to thermal reactions with other chemical families (NO_x, BrO_x *etc.*) , iodine oxides are thought to polymerise through a series of addition reactions potentially involving IO, OIO, I_2O_2 and higher iodine oxides. Considerable laboratory evidence exists for the near-gas kinetic removal of OIO in fast iodine kinetics studies (e.g. Bloss et al., 2001; Ingham et al., 2000), and also for the formation of particles of bulk composition I_2O_5 / I_4O_9 (e.g.

Burkholder et al., 2004; McFiggans et al., 2004), but details of the nucleation process are far from understood. In this paper, we adopt an iodine source selected to replicate the observed levels of IO subject to the chemical mechanism, which must therefore include a representation of the process for the removal of active iodine into the condensed phase. Whilst given our current level of understanding any specific mechanism is unlikely to be totally correct, the modelled effects of iodine chemistry upon HO_x and NO_x (the focus of the paper) should be robust as the levels of IO (which effectively constrains most of the other iodine-inorganic chemistry interactions) match those observed. The details of the mechanism adopted for removal of active iodine into the condensed phase will however impact upon the iodine source required to generate a given level of IO; this is considered further in the sensitivity studies.

Here we adopt a mechanism drawn from recent laboratory and theoretical studies, in which two routes to higher iodine oxides are considered: Sequential addition of ozone to $I_2O_2/I_2O_3/I_2O_4$ (Saunders and Plane, 2005), and polymerisation of OIO (Gomez-Martin et al., 2007). We consider any species above I_2O_4 to be thermally and photolytically stable on the timescale of these simulations, i.e. to irreversibly incorporate into particulate iodine: PI_1,PI_2 and PI_3, which may in reality be identified with I_3O_5 or I_2O_5 + I, I_3O_6 or I_2O_5 + IO, and I_2O_5+O_2 respectively. We also consider the thermal stability of I_2O_2, I_2O_3 and I_2O_4, based upon the calculations of Kaltsoyannis and Plane (2008), and the photolysis of OIO, I_2O_2, I_2O_3 and I_2O_4 as described above. (These assumptions are explored further in the sensitivity study).

10.1 Gomez-Martin et al. (2007) infer limits for an association reaction between OIO and small (n = 1 - 4) OIO polymers of (1.2 – 3) × 10^{-10} $molec^{-1}cm^3s^{-1}$. Here we choose a mid-range value of 1.5 × 10^{-10} $molec^{-1}cm^3s^{-1}$, and apply this to the reaction of OIO with itself, I_2O_3 and I_2O_4.

10.2 : Oxidation of I_2O_2, I_2O_3 and I_2O_4 by ozone. The rate constant adopted (1×10^{-12} $molec^{-1}cm^3s^{-1}$) is based upon the analysis of Saunders and Plane (2005), although recent calculations (Kaltsoyannis and Plane, 2008) indicate that the reaction may be slower, and the calculated short thermal lifetime for I_2O_2 indicates that IO/OIO recombination is probably the dominant route to I_2O_3 / I_2O_4 in the atmosphere).

10.3 Kaltsoyannis and Plane calculate the lifetimes of I_2O_2, I_2O_3 and I_2O_4 with respect to thermal decomposition to be of the order of 0.1, 10^8 and 10 seconds respectively (293 K); appropriate (temperature-independent) decomposition rates for I_2O_2 and I_2O_4 are therefore included. I_2O_2 is assumed to be IOIO; IOOI is found to dissociate promptly.

11: The reaction of OIO with OH is assumed to form HIO_3, which is stable (Plane et al., 2006), and is assumed to contribute to particulate iodine: PI_4.

12: DMS-Br adduct channel neglected.

In addition to the halogen and DMS scheme, the MCM (version 3.1) kinetics describing the fate of $O(^1D)$ atoms were updated to the JPL (Sander et al., 2006) rate constants :

$O(^1D) + O_2 \rightarrow O(^3P) + O_2$	$k = 3.3\times10^{-11}\exp(55/T)$	Sander et al., 2006
$O(^1D) + N_2 \rightarrow O(^3P) + N_2$	$k = 2.15\times10^{-11}\exp(110/T)$	Sander et al., 2006
$O(^1D) + H_2O \rightarrow OH + OH$	$k = 1.63\times10^{-10}\exp(60/T)$	Sander et al., 2006