

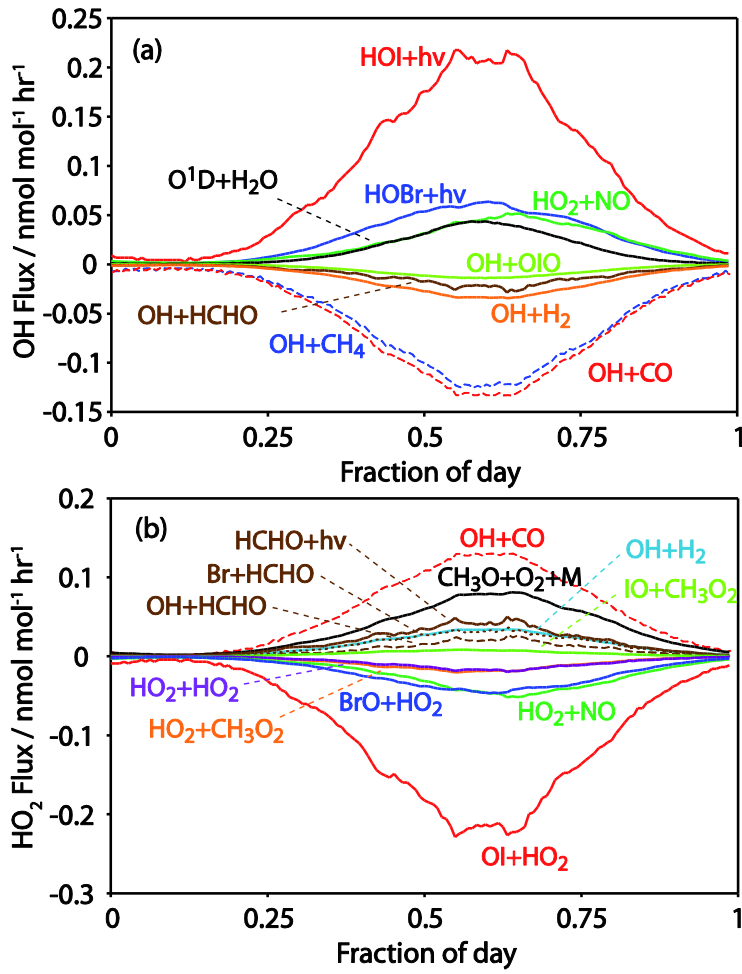
1 Coupling of HO_x, NO_x and Halogen Chemistry in the Antarctic Boundary Layer

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3 Supplementary Information

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8 Supplementary Figure 1. OH and HO₂ production / removal fluxes for the B2 scenario

1 Supplementary Table S1. Photolysis rates for halogen species

2

Reaction	Quantum Yield Note	Mean $j(x) / j(\text{NO}_2)$	Cross sections / Qm yields used	Note
$\text{I}_2 + \text{h}\nu$		20.3	Atkinson et al., 2007	
$\text{Br}_2 + \text{h}\nu$		3.45	Atkinson et al., 2007	
$\text{IBr} + \text{h}\nu$		9.10	Atkinson et al., 2007	
$\text{BrO} + \text{h}\nu$		5.41	Atkinson et al., 2007	
$\text{BrONO}_2 + \text{h}\nu$	$\Phi(\text{Br}+\text{NO}_3) = 1$	0.160	Atkinson et al., 2007	
$\text{BrONO} + \text{h}\nu$	$\Phi(\text{Br}+\text{NO}_2) = 0.5$, $\Phi(\text{BrO}+\text{NO}) = 0.5$	2.28	Atkinson et al., 2007	1
$\text{HOBr} + \text{h}\nu$		0.256	Atkinson et al., 2007	
$\text{IO} + \text{h}\nu$		18.3	Bloss et al., 2001	
$\text{OIO} + \text{h}\nu$	$\Phi(\text{I}+\text{O}_2) = 0.05$	51.6	Cox et al., 1999 / Joseph et al., 2005	2
$\text{IONO}_2 + \text{h}\nu$	$\Phi(\text{I}+\text{NO}_3) = 1$	0.556	Joseph and Plane, 2007	3
$\text{I}_2\text{O}_2 + \text{h}\nu$	$\Phi(\text{IO}) = 2$	0.556		4
$\text{I}_2\text{O}_3 + \text{h}\nu$	$\Phi(\text{IO}+\text{OIO}) = 1.0$	0.556		4
$\text{I}_2\text{O}_4 + \text{h}\nu$	$\Phi(\text{OIO}+\text{OIO}) = 1.0$	0.556		4
$\text{INO}_2 + \text{h}\nu$	$\Phi(\text{I}+\text{NO}_2) = 1$	0.319	Sander et al., 2006	
$\text{INO} + \text{h}\nu$		3.71	Sander et al., 2006	
$\text{HOI} + \text{h}\nu$		1.12	Atkinson et al., 2007	
$\text{HI} + \text{h}\nu$		6.89×10^{-3}	Atkinson et al., 2007	

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

4

5 1: Quantum yield for BrONO photolysis assumed to be 50 % for each channel (Atkinson et
6 al., 2007).

7 2: OIO absorption spectrum from Cox et al. (1999) scaled to match 567 nm cross section
8 determined by Joseph et al. (2005). Quantum yield for photolysis assumed to be 5 %
9 yielding entirely $\text{I} + \text{O}_2$ following Joseph et al. (2005) and Tucceri et al. (2006); the effect of
10 increasing the quantum yield for production of $\text{I} + \text{O}_2$ to unity, as recently reported by
11 Gómez-Martin et al. (2009), was considered in the sensitivity study.

12 3: IONO₂ cross sections have been reported by Mossinger et al. (2002) and by Joseph et al.
13 (2007). The latter data are significantly smaller at long (> 360 nm) wavelengths,
14 corresponding to roughly one order of magnitude difference in photolysis rate. The more
15 recent values of Joseph and Plane, taken from the table within their paper, are used here,
16 with unit photolysis yield of $\text{I} + \text{NO}_3$ adopted; the magnitude of the IONO₂ cross sections is
17 considered in the sensitivity study.

18 4: Definitive cross-sections are not available for I₂O₂, I₂O₃ or I₂O₄. Following the laboratory
19 estimates of Bloss et al. (2001) and Gómez-Martín et al. (2005), and *ab initio* results
20 (Kaltsoyannis and Plane, 2008) we assume the absorption spectrum is equal to that of IONO₂
21 – this corresponds to a midday photolysis rate of $8 \times 10^{-3} \text{ s}^{-1}$ for these species (corresponding
22 $j(\text{NO}_2) = 1.85 \times 10^{-2} \text{ s}^{-1}$). The sensitivity of the model results to this assumption is evaluated
23 in the sensitivity study section.

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

2

Reaction	Rate Expression	Reference	Note
Br + O ₃ → BrO + O ₂	$k = 1.7 \times 10^{-11} \exp(-800/T)$	Atkinson et al., 2007	
Br + HO ₂ → HBr + O ₂	$k = 7.7 \times 10^{-12} \exp(-450/T)$	Atkinson et al., 2007	
OH + HBr → Br + H ₂ O	$k = 6.7 \times 10^{-12} \exp(155/T)$	Atkinson et al., 2007	
OH + Br ₂ → HOBr + Br	$k = 2.0 \times 10^{-11} \exp(240/T)$	Atkinson et al., 2007	
Br + HCHO → HBr + HCO	$k = 7.7 \times 10^{-12} \exp(-580/T)$	Atkinson et al., 2007	
Br + CH ₃ CHO → HBr + CH ₃ CO	$k = 1.8 \times 10^{-11} \exp(-460/T)$	Atkinson et al., 2007	
Br + NO ₂ → BrONO	$k_0 = 4.2 \times 10^{-31} (T/300)^{-2.4}$ $k_\infty = 2.7 \times 10^{-11}$, $F_c = 0.6$	Sander et al., 2006	
BrO + BrO → Br + Br + O ₂	$k = 2.7 \times 10^{-12}$	Atkinson et al., 2007	
BrO + BrO → Br ₂ + O ₂	$k = 2.9 \times 10^{-14} \exp(840/T)$	Atkinson et al., 2007	
BrO + HO ₂ → HOBr + O ₂	$k = 4.5 \times 10^{-12} \exp(500/T)$	Atkinson et al., 2007	
OH + HOBr → H ₂ O + BrO	$k = 5.0 \times 10^{-11}$		1
BrO + CH ₂ O ₂ → HOBr + CH ₂ O ₂	$k = 4.6 \times 10^{-13} \exp(798/T)$	Enami et al., 2007 / Aranda et al., 1997	2
BrO + NO → Br + NO ₂	$k = 8.7 \times 10^{-12} \exp(260/T)$	Atkinson et al., 2007	
BrO + NO ₂ → BrONO ₂	$k_0 = 5.2 \times 10^{-31} (T/300)^{-3.2}$ $k_\infty = 6.9 \times 10^{-12} (T/300)^{-2.9}$, $F_c = 0.6$	Sander et al., 2006	
BrONO ₂ → BrO + NO ₂	$k = 2.8 \times 10^{13} \exp(-12360/T)$	Orlando and Tyndall, 1996	
I + O ₃ → IO + O ₂	$k = 2.1 \times 10^{-11} \exp(-830/T)$	Atkinson et al., 2007	
I + HO ₂ → HI + O ₂	$k = 1.5 \times 10^{-11} \exp(-1090/T)$	Atkinson et al., 2007	
OH + HI → I + H ₂ O	$k = 1.6 \times 10^{-11} \exp(440/T)$	Atkinson et al., 2007	
OH + I ₂ → HOI + I	$k = 2.1 \times 10^{-10}$	Atkinson et al., 2007	
NO ₃ + I ₂ → I + IONO ₂	$k = 1.5 \times 10^{-12}$	Atkinson et al., 2007	3
NO ₃ + HI → HNO ₃ + I	$k = 1.3 \times 10^{-12} \exp(-1830/T)$	Atkinson et al., 2007	
I + NO ₂ → INO ₂	$k_0 = 3.0 \times 10^{-31} (T/300)^{-1.0}$ $k_\infty = 6.6 \times 10^{-11}$, $F_c = 0.6$	Sander et al., 2006	
INO ₂ → I + NO ₂	$k = 0.14 \text{ s}^{-1}$ (at 268 K)	Van den Bergh and Troe, 1976	4
INO ₂ + INO ₂ → I ₂ + 2NO ₂	$k = 4.7 \times 10^{-13} \exp(-1670/T)$	Atkinson et al., 2007	
I + NO → INO	$k_0 = 1.8 \times 10^{-32} (T/300)^{-1.0}$ $k_\infty = 1.7 \times 10^{-11}$, $F_c = 0.6$	Sander et al., 2006	
INO → I + NO	$k = 0.087 \text{ s}^{-1}$ (at 268 K)	Van den Bergh and Troe, 1976	4
INO + INO → I ₂ + NO + NO	$k = 8.4 \times 10^{-11} \exp(-2620/T)$	Atkinson et al., 2007 or JPL	
IO + IO → 2I + O ₂	$k = 0.11 \times 5.4 \times 10^{-11} \exp(180/T)$	Atkinson et al., 2007	5
IO + IO → I + OIO	$k = 0.38 \times 5.4 \times 10^{-11} \exp(180/T)$	Atkinson et al., 2007	5
IO + IO → I ₂ O ₂	$k = 0.51 \times 5.4 \times 10^{-11} \exp(180/T)$	Atkinson et al., 2007	5
IO + HO ₂ → HOI + O ₂	$k = 1.4 \times 10^{-11} \exp(540/T)$	Atkinson et al., 2007	
OH + HOI → IO + H ₂ O	$k = 1.0 \times 10^{-10}$		6
IO + CH ₃ O ₂ → CH ₃ O + IOO	$k = 2.0 \times 10^{-12}$	Dillon et al., 2006	7
IO + NO → I + NO ₂	$k = 7.15 \times 10^{-12} \exp(300/T)$	Atkinson et al., 2007	
IO + NO ₂ → IONO ₂	$k_0 = 6.5 \times 10^{-31} (T/300)^{-3.5}$ $k_\infty = 7.6 \times 10^{-12} (T/300)^{-1.5}$, $F_c = 0.6$	Sander et al., 2006	
IONO ₂ → IO + NO ₂	$k = 2.1 \times 10^{15} \exp(-13670/T)$	Kaltsoyannis and Plane, 2008	8
IO + NO ₃ → OIO + NO ₂	$k = 9 \times 10^{-12}$	Dillon et al., 2008	
I + NO ₃ → IO + NO ₂	$k = 1 \times 10^{-12}$	Dillon et al., 2008	
IO + BrO → I + Br + O ₂	$k = 0.2 \times 1.5 \times 10^{-11} \exp(510/T)$	Atkinson et al., 2007	9
IO + BrO → Br + OIO	$k = 0.8 \times 1.5 \times 10^{-11} \exp(510/T)$	Atkinson et al., 2007	
IO + OIO → I ₂ O ₃	$k = 5 \times 10^{-11}$	Gomez-Martin et al., 2007	10
OIO + OIO → I ₂ O ₄	$k = 1.5 \times 10^{-10}$	Gomez-Martin et al., 2007	10.1
OIO + I ₂ O ₃ → PI ₁	$k = 1.5 \times 10^{-10}$	Gomez-Martin et al., 2007	10.1
OIO + I ₂ O ₄ → PI ₂	$k = 1.5 \times 10^{-10}$	Gomez-Martin et al., 2007	10.1
I ₂ O ₂ + O ₃ → I ₂ O ₃ + O ₂	$k = 1.0 \times 10^{-12}$	Saunders and Plane, 2005	10.2
I ₂ O ₃ + O ₃ → I ₂ O ₄ + O ₂	$k = 1.0 \times 10^{-12}$	Saunders and Plane, 2005	10.2
I ₂ O ₄ + O ₃ → PI ₃	$k = 1.0 \times 10^{-12}$	Saunders and Plane, 2005	10.2
I ₂ O ₂ → IO + IO	$k = 10 \text{ s}^{-1}$	Kaltsoyannis and Plane, 2008	10.3
I ₂ O ₄ → OIO + OIO	$k = 0.1 \text{ s}^{-1}$	Kaltsoyannis and Plane, 2008	10.3
NO + OIO → IO + NO ₂	$k = 1.1 \times 10^{-12} \exp(542/T)$	Plane et al., 2006	
OH + OIO → PI ₄ (HIO ₃)	$k = 2.2 \times 10^{-10} \exp(243/T)$	Plane et al., 2006	11
BrO + DMS → Br + DMSO	$k = 1.4 \times 10^{-14} \exp(950/T)$	Sander et al., 2006	
Br + DMS → HBr + CH ₃ SCH ₂	$k = 9.0 \times 10^{-11} \exp(-2390/T)$	Sander et al., 2006	12
IO + DMS → I + DMSO	$k = 1.2 \times 10^{-14}$	Sander et al., 2006	

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

1 Supplementary Table S3. Heterogeneous reaction probabilities

2

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 ₂ O ₅	0.04	JPL 15-06
HO ₂	0.2	Jacob, 2000
CH ₃ O 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 ₂ O ₂ , I ₂ O ₃ , I ₂ O ₄	1	Assumed
PI _n	1	Assumed

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

2

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

5

6 -Termolecular I atom recombination

7 -Halogen atom / molecule reactions (I + Br₂, Br + I₂, I + IBr, Br + IBr)

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

9 -Oxygen atom / halogen reactions (O + I₂, O + Br₂, O + IO, O + BrO)

10 -Halogen monoxide / ozone reactions (IO + O₃, BrO + O₃)

11

12 **Specific Notes**

13

14 1: OH + HOBr – Rate constant estimated with reference to OH + HOCl, O + HOCl and O +
15 HOBr.

16

17 2: Temperature-dependent kinetics for BrO + CH₃O₂ taken from Enami et al. (2007);
18 products assumed to be HOBr + CH₂O₂ following Aranda et al. (1997). Within the model
19 CH₂O₂ dissociates to CO + H₂O (Mariq et al., 1994).

20

21 3: I₂+NO₃. Products assumed to be I+IONO₂ following Atkinson et al. (2007) on enthalpy
22 arguments. Effect of alternative product channel (IO + INO₂, as adopted by Saiz-Lopez et
23 al., 2008) considered in sensitivity study.

24

25 4: INO and INO₂ thermal decomposition calculated via the formation rate constants given,
26 plus temperature-dependent equilibrium constant expressions from van den Burgh and Troe,
27 1976: $K_{eq}(I + NO \leftrightarrow INO) = 10^{-5.70} \times \exp(9160/T)$ and $K_{eq}(I + NO_2 \leftrightarrow INO_2) = 10^{-$
28 $6.43} \times \exp(9560/T)$, both in atm⁻¹.

1

2 5: IO + IO: Overall rate constant and OIO+I channel from Atkinson et al. (2007); branching
3 ratio for 2I + O₂ / I₂O₂ channels from Bloss et al. (2001). See also comments below (note
4 10.3).

5

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

8

9 7: Base-case for the IO + CH₃O₂ reaction is “slow” kinetics ($k = 2 \times 10^{-12}$; Dillon et al., 2006)
10 and formation of CH₃O + IOO (i.e. the CH₃OOOI intermediate, likely decomposing to
11 CH₃O + IOO and hence HCHO + HO₂ + I + O₂ in the atmospheric boundary layer) with unit
12 yield. Sensitivity studies described in the text consider the potential impact of a higher rate
13 constant (e.g. Bale et al., 2005; Enami et al., 2007) and alternative product channels, e.g. via
14 the CH₃OOIO channel to CH₃O + OIO (Drougas and Kosmas, 2007).

15

16 8 Thermal decomposition rate reported by Kaltsoyannis and Plane (2008) adopted; this is
17 based upon revised RRKM analysis coupled to laboratory kinetic data for the forward
18 reaction obtained by Allen and Plane (2002), and supersedes the decomposition rate
19 determined in a similar manner in the earlier paper.

20

21 9: Branching ratio for IO + BrO from Atkinson et al. (2007) in combination with Rowley et
22 al. (2001); note approach adopted neglects possible increase in atomic channels at reduced
23 temperature.

24

25 10: *Higher Iodine Oxides*

26 In addition to thermal reactions with other chemical families (NO_x, BrO_x etc.), iodine oxides
27 are thought to polymerise through a series of addition reactions potentially involving IO,
28 OIO, I₂O₂ and higher iodine oxides. Considerable laboratory evidence exists for the near-
29 gas kinetic removal of OIO in fast iodine kinetics studies (e.g. Bloss et al., 2001; Ingham et
30 al., 2000), and also for the formation of particles of bulk composition I₂O₅ / I₄O₉ (e.g.

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

12

13 Here we adopt a mechanism drawn from recent laboratory and theoretical studies, in which
14 two routes to higher iodine oxides are considered: Sequential addition of ozone to
15 I₂O₂/I₂O₃/I₂O₄ (Saunders and Plane, 2005), and polymerisation of OIO (Gomez-Martin et al.,
16 2007). We consider any species above I₂O₄ to be thermally and photolytically stable on the
17 timescale of these simulations, i.e. to irreversibly incorporate into particulate iodine: PI₁, PI₂
18 and PI₃, which may in reality be identified with I₃O₅ or I₂O₅ + I, I₃O₆ or I₂O₅ + IO, and
19 I₂O₅+O₂ respectively. We also consider the thermal stability of I₂O₂, I₂O₃ and I₂O₄, based
20 upon the calculations of Kaltsoyannis and Plane (2008), and the photolysis of OIO, I₂O₂,
21 I₂O₃ and I₂O₄ as described above. (These assumptions are explored further in the sensitivity
22 study).

23

24 10.1 Gomez-Martin et al. (2007) infer limits for an association reaction between OIO and
25 small (n = 1 - 4) OIO polymers of $(1.2 - 3) \times 10^{-10} \text{ molec}^{-1}\text{cm}^3\text{s}^{-1}$. Here we choose a mid-
26 range value of $1.5 \times 10^{-10} \text{ molec}^{-1}\text{cm}^3\text{s}^{-1}$, and apply this to the reaction of OIO with itself,
27 I₂O₃ and I₂O₄.

28

29 10.2 : Oxidation of I₂O₂, I₂O₃ and I₂O₄ by ozone. The rate constant adopted ($1 \times 10^{-12} \text{ molec}^{-1}$
30 cm^3s^{-1}) is based upon the analysis of Saunders and Plane (2005), although recent
31 calculations (Kaltsoyannis and Plane, 2008) indicate that the reaction may be slower, and the

1 calculated short thermal lifetime for I₂O₂ indicates that IO/OIO recombination is probably
2 the dominant route to I₂O₃ / I₂O₄ in the atmosphere).

3

4 10.3 Kaltsoyannis and Plane calculate the lifetimes of I₂O₂, I₂O₃ and I₂O₄ with respect to
5 thermal decomposition to be of the order of 0.1, 10⁸ and 10 seconds respectively (293 K);
6 appropriate (temperature-independent) decomposition rates for I₂O₂ and I₂O₄ are therefore
7 included. I₂O₂ is assumed to be IOIO; IOOI is found to dissociate promptly.

8

9 11: The reaction of OIO with OH is assumed to form HIO₃, which is stable (Plane et al.,
10 2006), and is assumed to contribute to particulate iodine: PI₄.

11

12 12: DMS-Br adduct channel neglected.

13

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

O(¹ D) + O ₂ → O(³ P) + O ₂	$k = 3.3 \times 10^{-11} \exp(55/T)$	Sander et al., 2006
O(¹ D) + N ₂ → O(³ P) + N ₂	$k = 2.15 \times 10^{-11} \exp(110/T)$	Sander et al., 2006
O(¹ D) + H ₂ O → OH + OH	$k = 1.63 \times 10^{-10} \exp(60/T)$	Sander et al., 2006

16