Impact of halogen monoxide chemistry upon boundary layer OH and HO_2 concentrations at a coastal site

W. J. Bloss,[1] J. D. Lee,[1] G. P. Johnson,[1] R. Sommariva,[1] D. E. Heard,[1] A. Saiz-Lopez,[2] J. M. C. Plane,[2] G. McFiggans,[3] H. Coe,[3] M. Flynn,[3] P. Williams,[3] A. R. Rickard,[4] and Z. L. Fleming[4]

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[1] The impact of iodine oxide chemistry upon OH and HO_2 concentrations in the coastal marine boundary layer has been evaluated using data from the NAMBLEX (North Atlantic Marine Boundary Layer Experiment) campaign, conducted at Mace Head, Ireland during the summer of 2002. Observationally constrained calculations show that under low NO_x conditions experienced during NAMBLEX (NO $\leq$ 50 pptv), the reaction IO + HO_2 $\rightarrow$ HOI + O_2 accounted for up to 40% of the total HO_2 radical sink, and the subsequent photolysis of HOI to form OH + I comprised up to 15% of the total midday OH production rate. The XO + HO_2 (X = Br, I) reactions may in part account for model overestimates of measured HO_2 concentrations in previous studies at Mace Head, and should be considered in model studies of HO_x chemistry at similar coastal locations.

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1. Introduction

[2] The hydroxyl radical, OH, is the principal oxidising species in the sunlit troposphere, initiating the degradation of many trace gas species emitted to the atmosphere. OH is highly reactive, and consequently has a short chemical lifetime, 0.1–1 s in the lower troposphere; OH concentrations are thus determined by local chemistry rather than transport. In the background troposphere, the principal fate of OH is reaction with CO and hydrocarbons, forming peroxy radicals. Subsequent chemical cycling may lead to regeneration of OH, depending upon levels of NO_x (NO + NO_2). The performance of chemical models of these processes can be assessed by their ability to accurately simulate measured concentrations of OH and the peroxy radicals. Several such model-measurement comparisons for HO_x (OH + HO_2) have been conducted in clean marine boundary layer (MBL) environments, characterised by low levels of NO_x (NO $\leq$ 100 pptv) and simple hydrocarbon composition dominated by C_1 - C_3 species [e.g., *Carslaw et al.*, 2002, and references therein]. The models are commonly constrained with measured concentrations of long-lived species (e.g., hydrocarbons, O_3) and intermediate oxidation products (e.g., HCHO, CH_3OH) and include HO_x, NO_x and VOC oxidation chemistry; however many such models have not considered the possible impact of halogen chemistry upon HO_x.

[3] The principal impact of halogen monoxides upon tropospheric OH and HO_2 arises through the XO (X = I, Br) + HO_2 reaction, which is followed by photolysis or heterogeneous uptake of HOX:

$$\text{(R1)} \qquad XO + HO_2 \rightarrow HOX + O_2$$

$$\text{(R2)} \qquad HOX + h\nu \rightarrow OH + X$$

$$\text{(R3)} \qquad HOX + \text{aerosol} \rightarrow \text{loss}$$

The halogen monoxide species thus provide a sink for HO_2 and (via HOX photolysis) a route for HO_2 $\rightarrow$ OH conversion. Uptake of HOX upon aerosol leads to loss of HO_x from the gas-phase system. In unpolluted conditions, if levels of IO or BrO are sufficiently high, reactions (R1)–(R3) will affect HO_x abundance and partitioning, and must be incorporated into photochemical models which attempt to simulate HO_x concentrations. Previous HO_2 model-measurement comparisons performed at Mace Head have commonly found modelled HO_2 concentrations (excluding halogen chemistry) to exceed those measured. Analysis of data from the EASE-97 (Eastern Atlantic Spring Experiment) campaign at Mace Head found modelled HO_2 concentrations exceeded those measured by a factor of *ca.* 2.8 under clean marine airmass conditions [*Carslaw et al.*, 2002]. The potential for iodine chemistry to affect tropospheric O_3, HO_x and NO_x has been considered previously [e.g., *Chameides and Davis*, 1980; *Davis et al.*, 1996; *McFiggans et al.*, 2000], and recent observations of the halogen oxides IO, OIO and BrO in MBL environments have indicated that such processes may be significant [*Alicke et al.*, 1999; *Allan et al.*, 2000, *Saiz-Lopez et al.*, 2004]; however uncertainty over the importance of this chemistry remains, owing to a scarcity of coordinated atmospheric observations of the halogen monoxides, HO_x and other related species.

[4] In this paper we present an analysis of recent simultaneous measurements of OH, HO_2, IO and BrO in the coastal MBL, obtained at Mace Head Atmospheric Research Station (MHARS), Co. Galway, Ireland in the course of the UK NAMBLEX campaign, which ran from 20th July–3rd Sept. 2002. The data allow the impact of halogen oxide chemistry (as represented by reactions (R1)–

[1]Department of Chemistry, University of Leeds, Leeds, UK.
[2]School of Environmental Science, University of East Anglia, Norwich, UK.
[3]Physics Department, Institute of Science and Technology, University of Manchester, Manchester, UK.
[4]Department of Chemistry, University of Leicester, Leicester, UK.

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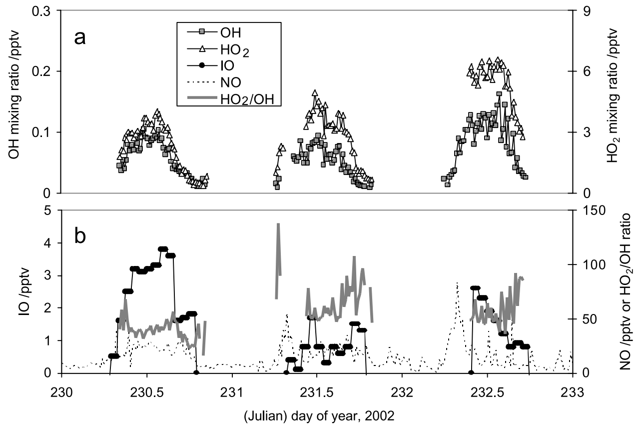

Figure 1. Measured volume mixing ratios (pptv) of OH, HO_2, IO and NO, plus HO_2:OH ratio. Values measured as zero are shown; gaps indicate values not measured.

(R3)) upon HO_x levels at Mace Head to be quantified, and indicate that the XO + HO_2 reactions may account for the model-measurement discrepancies previously observed.

2. Measurements: Techniques

[5] MHARS is located on the western coast of Ireland, and experiences prevailing westerly air masses from the North Atlantic Ocean. A range of instrumentation was deployed during NAMBLEX to study the chemical and dynamic MBL environment; however this work focuses upon measurements of OH, HO_2 and IO. OH radicals were measured via on-resonance LIF (laser-induced fluorescence) at 308 nm; HO_2 was detected following conversion to OH by added NO. The LIF system [*Bloss et al.*, 2003] was calibrated through the water photolysis/ozone actinometry method, with a systematic uncertainty of 13% (1σ) and detection limits of 0.012/0.03 pptv (OH/HO_2). IO was measured using a long-path DOAS (Differential Optical Absorption Spectroscopy) instrument [*Saiz-Lopez et al.*, 2004], located at MHARS, with the analysis light beam directed to Croaghnakeela Island (4.2 km offshore to the west) and folded back by a retro-reflector array, providing a total light path of 8.4 km, *ca*. 10 m above sea level. IO radicals were detected by spectral fitting between 425 and 448 nm [*Saiz-Lopez and Plane*, 2004] using reference IO absorption cross sections with an uncertainty of 13%, and a detection limit of 0.5 pptv. Additional measurements pertinent to this work were O_3, NO_x (NO detection limit 6 pptv), $\sum RO_2 + HO_2$ (sum of peroxy radicals, measured via a peroxy radical chemical amplifier – PERCA, uncertainty 35% [*Salisbury et al.*, 2002]), photolysis rates (spectral radiometer) and meteorological parameters. The HO_x, RO_2, NO_x and O_3 measurements were co-located approximately 50 m from the high tide mark, with inlets 10 m above mean sea level. Total aerosol size distributions from 3 nm to 30 μm were assembled from a combination of mobility, backscatter and forward scattering measurements. Aerosol uptake rates were then derived from the ambient humidity aerosol size distributions considering mass transfer in the transition regime, as opposed to the more conventional but erroneous assumption that mass transfer to the aerosol distribution proceeds according to free molecular uptake on the available surface area. Typical aerosol total surface area was 535 $\mu m^2\ cm^{-3}$ (noon, day 230).

3. Measurements: Results

[6] Figure 1 shows mixing ratios of OH, HO_2, IO and NO, together with the HO_2/OH ratio, measured over the 18th–20th August 2002 (Julian days 230–232). This period was characterised by light westerly winds bringing marine air to MHARS; back-trajectory analyses confirmed that the sampled air was of mid-Atlantic origin, and had not encountered land during the previous 5 days. NO_x levels were correspondingly low during this period – the mean NO mixing ratio was 20 pptv. The OH, HO_2, IO and NO levels shown were typical of those observed during clean westerlies throughout NAMBLEX – the daily maximum IO levels recorded, on days when observations were made, ranged from 0.8 to 4.0 pptv.

[7] The impact of the IO + HO_2 reaction upon HO_2 radical concentrations was assessed by comparing the rates of the principal HO_2 radical loss reactions:

(R4) $HO_2 + HO_2(+M) \rightarrow H_2O_2 + O_2(+M)$

(R5) $HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2$

(R6) $HO_2 + NO \rightarrow OH + NO_2$

(R7) $HO_2 + O_3 \rightarrow OH + 2O_2$

(R8) $HO_2 + IO \rightarrow HOI + O_2$

(R9) $HO_2 + \text{aerosol} \rightarrow \text{loss}$

HO_2, NO, O_3 and IO concentrations, and aerosol uptake rate, were measured as described above. CH_3O_2 concentrations were determined as the total peroxy radical measurement ($\sum RO_2 + HO_2$, from the PERCA instrument) minus HO_2 (as determined by LIF), i.e., assuming all measured RO_2 was CH_3O_2. Rate constants were taken from *Sander et al.* [2003] with the exception of reaction (R8), for which $k_8 = 1.4 \times 10^{-11} \times \exp(554/T)$ was used [*Knight and Crowley*, 2001]. A reaction probability (γ) of 0.2 was used for reaction (R9) [*Jacob*, 2000].

[8] Under the conditions experienced, reaction with NO (R6) and heterogeneous loss (R9) dominate the removal of HO_2, if halogen chemistry is disregarded. Figure 2 shows the pseudo-first-order rate coefficients (k') for HO_2 loss through each of the reactions listed above (R4)–(R9) for days 230–232 (k' for reaction (R4) was defined as $2k_4[HO_2]$). Figure 2 shows that the IO + HO_2 reaction made a significant contribution to the total HO_2 sink throughout the measured period, comparable to or greater than heterogeneous loss. Reaction with IO dominated HO_2 loss on day 230 (when IO levels were highest), accounting for up to 40% of the total HO_2 removal rate. Also shown in Figure 2 is the HO_2 uptake rate calculated using the free molecular approach (discounting the gas to particle diffusion limitation) – adoption of this method would lead to the HO_2 loss rate to aerosol being overestimated by up to a factor of 2. Propagation of the uncertainties in the rates of reactions (R4)–(R8) leads to an overall uncertainty of 30% in the relative importance of the calculated HO_2 + IO

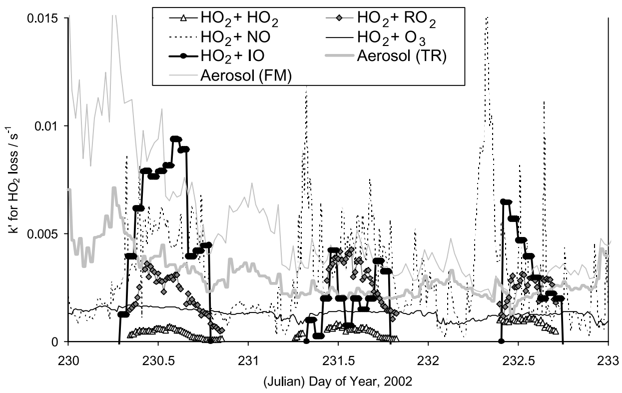

Figure 2. Pseudo-first order rate coefficients for HO_2 loss over days 230–232, by removal reaction. Aerosol (TR) indicates transition regime approach (used in this work); Aerosol (FM) indicates free molecular approach.

reaction flux. Figure 3a compares the cumulative contribution of reactions (R4)–(R9) to the removal of HO_2 over the days 230–232; the HO_2 + IO reaction makes the largest contribution, followed by reaction with NO and heterogeneous loss.

[9] Occurrence of the IO + HO_2 reaction leads to formation of HOI, the principal fates of which are photolysis and heterogeneous loss. The midday photolysis rates for HOI measured over days 230–232 ranged from (8–10) $\times$ 10^{-3} s^{-1} (spectral radiometer). Heterogeneous loss rate coefficients for HOI (calculated using a reaction probability of γ = 0.6) varied from (2.2–6.9) $\times$ 10^{-3} s^{-1}, with a mean value of 3.3 $\times$ 10^{-3} s^{-1} over the same period; photolysis to form OH + I is thus the major fate of HOI. The uptake coefficient for HOI loss on wet sea salt aerosol is uncertain: While a value of γ = 0.061 has been measured in a wetted-wall flow-tube experiment [*Mössinger and Cox*, 2001], some studies indicate that values an order of magnitude larger may be applicable to MBL aerosol [*Abbatt and Waschewsky*, 1998; *Wachsmuth et al.*, 2002]. In this work the higher value (0.6) was used, corresponding to the more conservative analysis of the impact of HOI formation upon OH production. If the value of 0.061 were adopted for γ, the heterogeneous loss rate for HOI would range from (2.1–9.2) $\times$ 10^{-4} s^{-1}, and the rate of production of OH from HOI photolysis would increase by *ca.* 30%.

[10] The magnitude of the HO_x sink resulting from HOI uptake may be compared with the rates of the peroxy radical termination reactions (R4) and (R5), and the OH + NO_2 reaction. Over the period shown in Figure 1, representative of clean marine conditions, HOI uptake comprised 16% of the HO_x loss, with the bulk (33% / 31%) arising from the HO_2 + RO_2 reaction and HO_2 uptake respectively, with OH + NO_2 contributing 3%. Under more polluted conditions (NO_x $\approx$ 500 pptv), with equal IO present, the contribution to HO_x loss due to HOI uptake would fall to 11%, while the importance of the OH + NO_2 reaction increases to 31% of the total radical loss rate.

[11] The contribution of HOI photolysis to the OH concentration was investigated by comparing the rate of production of OH radicals from HOI photolysis with that from other major OH production mechanisms (O_3 + $h\nu$; HO_2 + NO; HO_2 + O_3). $j(O^1D)$, O_3, H_2O, NO and HO_2 were measured as described above. HOI was assumed to be in photochemical steady state (PSS) as described by reactions (R1)–(R3). Ozone photolysis / reaction of $O(^1D)$ with H_2O was the dominant OH source (reflecting the clean marine - low NO_x - conditions encountered); however photolysis of HOI made a contribution of *ca.* 15% of the total flux into OH at midday on days 230 and 232, comparable to that from the HO_2 + NO reaction (13%). Figure 3b shows the relative cumulative contribution to the production of OH, over the days 230–232. Simple PSS calculation of OH levels determined average ratios for calculated/measured OH of 1.22 and 1.08 with the inclusion/omission of the IO + HO_2 chemistry respectively, i.e., the PSS overestimates OH, to a greater extent with the inclusion of the iodine-mediated HO_2 to OH conversion. The values are, however, in agreement within the (2σ) measurement uncertainty; and the PSS overestimate of OH levels may indicate an incomplete accounting for all hydrocarbon species which form OH sinks.

4. Discussion

[12] The above analysis neglects the possibility of non-uniform spatial distributions – local concentrations of IO at MHARS may be substantially higher than the mean value along the DOAS beampath, if shoreline emissions of halocarbons and/or molecular halogens comprise a significant fraction of the total iodine source [*Alicke et al.*, 1999; *Saiz-Lopez and Plane*, 2004]. In this case the effects in the shoreline, littoral zone are increased, while those through the rest of the beampath are diminished. In this instance, if the interlittoral region of the DOAS beampath is representative of the open ocean, the impact of halogen chemistry on a global scale will be much less than at MHARS, and hence less than calculated in this work; however the impact upon HO_x concentrations specifically at the MHARS shoreline measurement site will be greater than indicated in Figure 3.

[13] BrO radicals were also observed by DOAS during NAMBLEX, at levels up to 6.5 pptv [*Saiz-Lopez et al.*, 2004], and will have a qualitatively similar effect upon HO_x to that of IO. Due to instrumental limitations the BrO and IO data are mutually exclusive, however qualitative conclusions regarding their likely combined impact may be drawn: The rate constant for the BrO + HO_2 reaction is a factor of 3.8 lower than that for IO + HO_2 (at 298 K), and the photolysis rate of HOBr is 4.5 times lower than that of HOI; consequently both formation and photolysis of HOBr

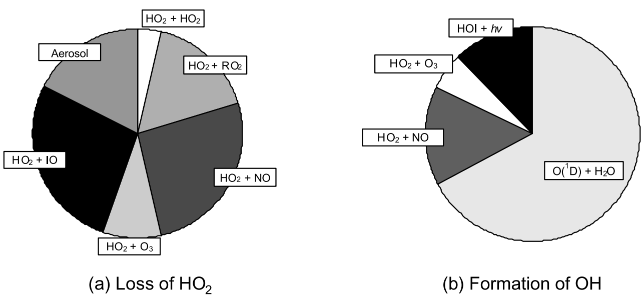

Figure 3. Fractional importance of each process for (a) removal of HO_2 and (b) production of OH, summed over the days 230–232.

will have a smaller direct effect upon HO_2 and OH than the equivalent processes for HOI. For equal XO levels, the $BrO + HO_2$ reaction represents only 19% of the HO_2 to OH flux of its IO equivalent. However, the slower photolysis rate of HOBr allows uptake to compete effectively with HOBr photolysis, thus the rate of loss of HO_x increases significantly in the presence of BrO, by nearly 60%.

[14] The HO_x dependence upon halogen levels is complex – as Figure 1a shows, HO_2 levels are comparable between days 230 and 231, while the IO level has approximately halved. The day-to-day variation in the HO_2:OH ratio (Figure 1b) does however correlate well with the mean IO levels. The total radical level depends upon the balance between the OH production rate, NO_x levels and hydrocarbon loading, and cannot be simply related to a single factor over the period considered. BrO levels were not measured, however bromine chemistry probably affected the observed HO_x also - recent measurements have suggested that the bromine source is oceanic in nature, and thus is not correlated with the coastal iodine activity at MHARS [*Saiz-Lopez and Plane*, 2004]. Other iodine-related chemistry which will affect HO_x levels include ozone destruction, changes in NO_x partitioning and possibly new particle formation. Many aspects of the iodine chemistry are currently poorly understood (e.g., HOI reaction probability and the properties of reservoirs such as $IONO_2$, OIO and I_2O_2), while the biogenic iodine source is likely to respond to temperature, tide, and solar intensity in a complex manner. Further understanding of these parameters through laboratory studies, and field measurements to constrain the spatial distribution of halogen species (coastline vs. open ocean) at the Mace Head site are required to fully quantify the coupled MBL HO_x-halogen chemistry.

[15] During the SOAPEX-2 (Southern Ocean Atmospheric Photochemistry Experiment) campaign conducted at Cape Grim, Tasmania, modelled HO_2 concentrations exceeded those measured by a factor of 1.4 during unpolluted conditions [*Sommariva et al.*, 2004]. Concurrent observations of IO [*Allan et al.*, 2000] suggested that halogen chemistry could be occurring, although the levels observed ($IO \approx 0.3$ pptv) were much lower than those detected during NAMBLEX. HO_x concentrations were measured at a coastal site on Rishiri Island, Japan during June 2000, and compared with the results of constrained model simulations; the model underestimated [OH] whilst overestimating [HO_2], the latter by a factor of 1.7 [*Kanaya et al.*, 2002]. Volatile iodocarbon species were measured at the same site the following year suggesting that iodine chemistry may have been responsible for the model overestimate: Kanaya et al. estimated that IO concentrations of 12–25 pptv could explain the model-measurement discrepancy for HO_2.

5. Conclusion

[16] The HO_2 + XO (X = I, Br) reactions have a significant impact upon HO_x concentrations at Mace Head under low NO_x conditions: The HO_2 + IO reaction accounted for up to (40 ± 12) % of the removal rate of HO_2 during the NAMBLEX campaign, and the subsequent photolysis of HOI comprised up to 15% of the production of OH. Model studies of MBL HO_x levels at Mace Head and similar coastal sites should incorporate the XO + HO_2 reactions, and consider diffusion limitations in the treatment of heterogeneous loss.

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W. J. Bloss, D. E. Heard, G. P. Johnson, J. D. Lee, and R. Sommariva, Department of Chemistry, University of Leeds, Leeds LS2 9JT, UK. (w.bloss@chemistry.leeds.ac.uk)

H. Coe, M. Flynn, G. McFiggans, and P. Williams, Physics Department, Institute of Science and Technology, University of Manchester, Manchester M6O 1QD, UK.

Z. L. Fleming and A. R. Rickard, Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK.

J. M. C. Plane and A. Saiz-Lopez, School of Environmental Science, University of East Anglia, Norwich NR4 7TJ, UK.