

SUPPORTING INFORMATION

Photochemical Chlorine and Bromine Activation from Artificial Saline Snow

Sumi N. Wren, D. J. Donaldson*, J. P. D. Abbatt*

Department of Chemistry, University of Toronto, 80 St. George St., Toronto, ON, M5S 3H6

* Corresponding Authors: jdonalds@chem.utoronto.ca, jabbatt@chem.utoronto.ca

Additional Results

Ozone concentration

Since the dark ozonation of frozen NaCl/NaBr solutions is known to exhibit a (non-linear) $[O_3]$ dependence (Oldridge and Abbatt, 2011), and the observed photochemical dihalogen production may be sensitive to the extent of bromide ion depletion and the gas phase concentration of the dihalogens themselves, the effect of $[O_3]$ on the photochemical dihalogen production was investigated in experiments in which the samples were illuminated first, and then subsequently exposed to ozone. No halogen production was observed prior to ozone exposure.

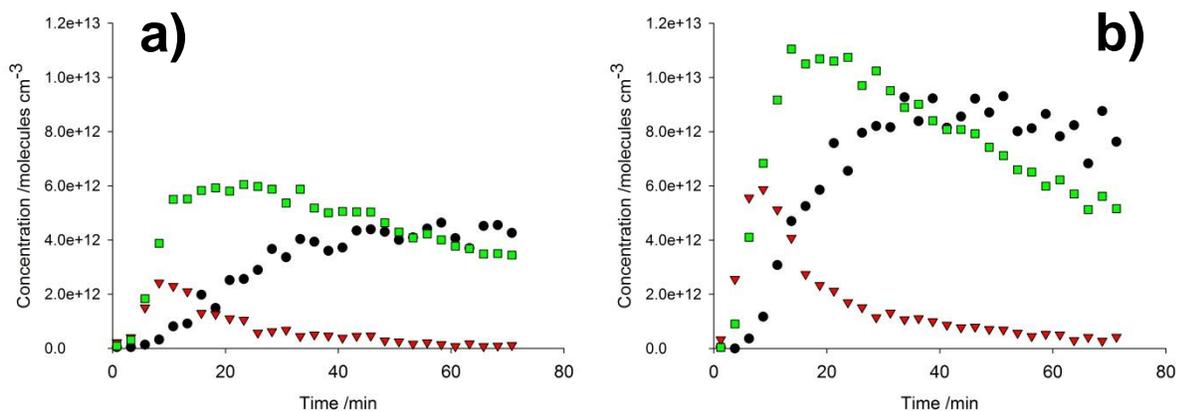


Figure S1. Time evolution of dihalogen concentrations: Br₂ (red triangles), Cl₂ (black circles) and BrCl (green squares) for the BASE scenario conditions with $[O_3]$ of **a)** 3×10^{13} molecules cm⁻³ and **b)** 9×10^{13} molecules cm⁻³. Each point represents the average of a 2.5 minute time bin (77 data points). In these experiments the samples were illuminated ($\lambda > 310$ nm) prior to turning on the ozone generator (at $t = 0$).

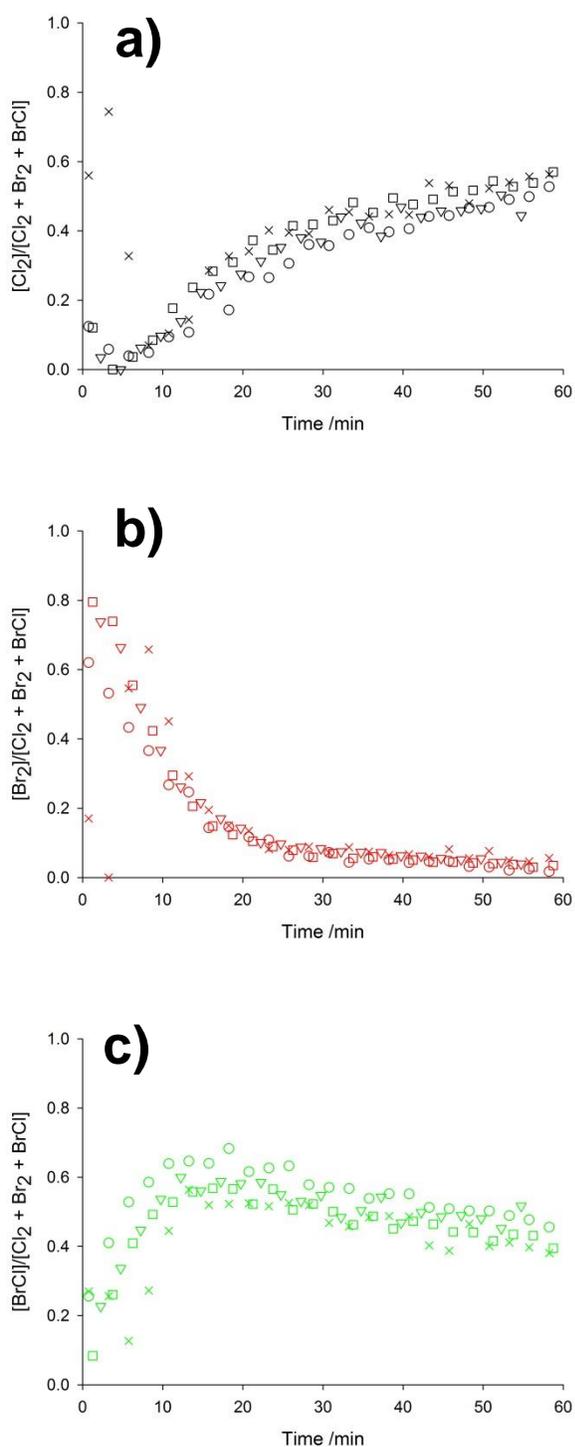


Figure S2. Time evolution of a given dihalogen concentration as a fraction of the total dihalogen concentration for the BASE scenario conditions and varying $[O_3]$ of 3×10^{13} molecules cm^{-3} (circle), 6×10^{13} molecules cm^{-3} (triangle), 9×10^{13} molecules cm^{-3} (square) and 1.3×10^{15} molecules cm^{-3} at 252 K (crosses). Samples were illuminated ($\lambda > 310$ nm) prior to turning on the ozone generator (at $t = 0$). Panel a) Cl_2 (black symbols); b) Br_2 (red symbols) and c) $BrCl$ (green symbols).

Temperature dependence

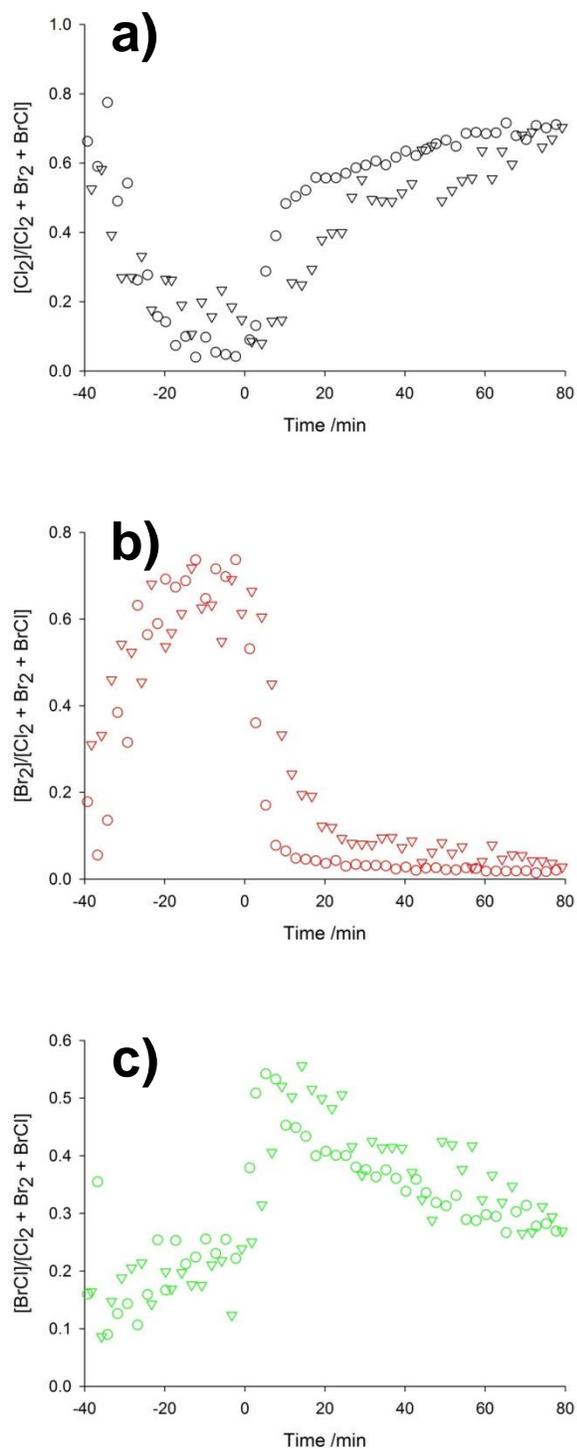


Figure S3. Time evolution of a given dihalogen concentration as a fraction of the total dihalogen concentration for the BASE scenario conditions and snow sample temperature of 252 K (triangles) and 257 K (circles). Samples were illuminated at $t = 0$. Panel a) Cl_2 (black symbols); b) Br_2 (red symbols) and c) BrCl (green symbols).

Pre-freezing [NaCl] dependence

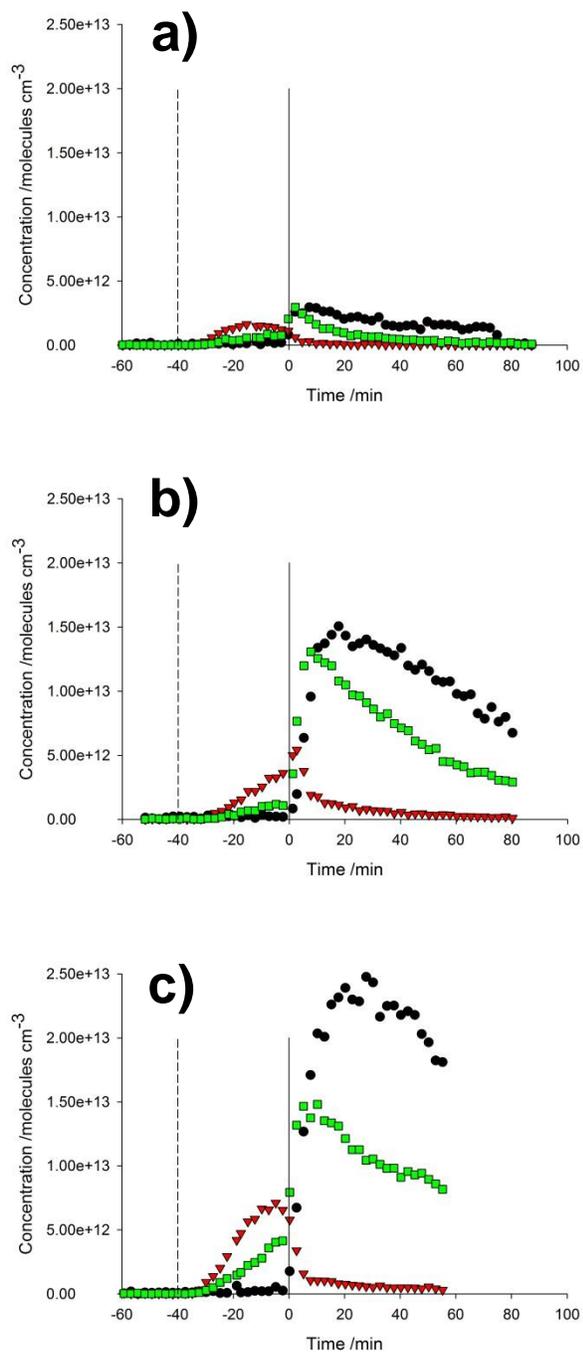


Figure S4. Representative time evolution of dihalogen concentrations: Br₂ (red triangles), Cl₂ (black circles) and BrCl (green squares) for BASE scenario conditions but different pre-freezing NaCl concentrations a) 0.1 M, b) 0.5 M (BASE) and c) 1.0 M. Each point represents the average of a 2.5 minute time bin (77 data points). The dashed line indicates the time at which the ozone generator was turned on and the solid line (t = 0) indicates the time at which the samples were illuminated.

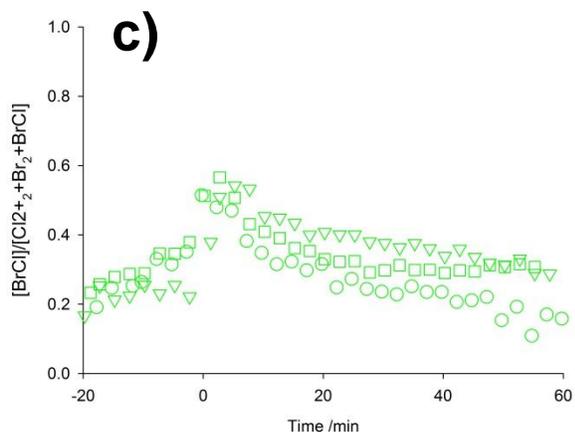
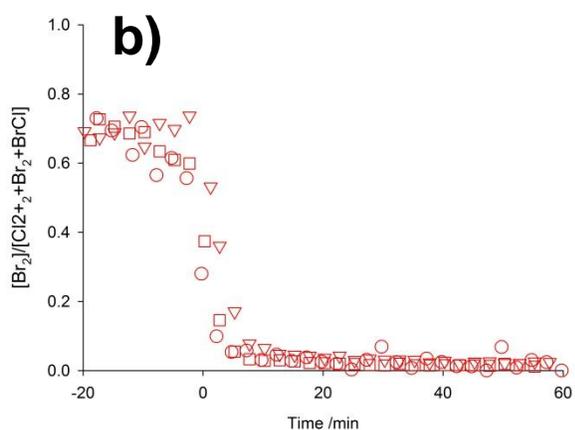
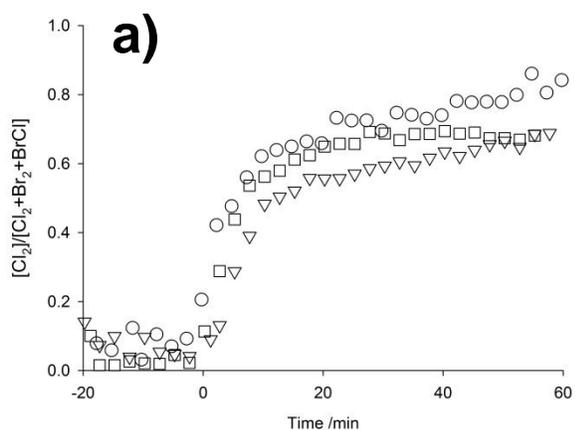


Figure S5. Time evolution of a given dihalogen concentration as a fraction of the total dihalogen concentration for the BASE scenario conditions and pre-freezing NaCl of 0.1 M (circle), 0.5 M (triangle), 1.0 M (square) (the same data as in S4). Samples were illuminated at $t = 0$. Panel a) Cl_2 (black symbols); b) Br_2 (red symbols) and c) BrCl (green symbols).

Other possible HO_x sources

Here we discuss possibilities for OH formation. These could represent possible HO_x sources or could act as oxidants themselves. Direct halide oxidation by OH radical could be responsible for some of the observed halogen release, if a route to OH formation (in the condensed or gas phase) exists. The mechanism for OH oxidation of halide solutions is described in greater detail in (Sjostedt and Abbatt, 2008; Frinak and Abbatt, 2006). One possibility is OH formation from impurities within the snowpack, as mentioned in the main text. Another possibility is that OH or HO₂ are formed during the photolysis of surface-adsorbed ozone. The products of the photodissociation of ozone adsorbed to an ice surface at relatively warm temperatures are not well known. Ignatov et al. (Ignatov et al., 2003) studied the photolysis of ozone ($\lambda = 320$ nm) adsorbed to water ice films at 80 K (which are bare compared to the ‘brine-covered’ snow grains in this experiment) and found evidence (using reflection-absorption FTIR) for an H₂O₂ complex with the ice surface; they also suggest the possibility of HO₂ and OH complexes with the ice surface. Another possibility for OH production is that translationally-excited O(³P) from O₃ photolysis at longer wavelengths could react with H₂O (either in the gas phase or at the ice surface) to form OH. This reaction has an activation energy ~ 17 kcal mol⁻¹ and Braunstein et al. (Braunstein et al., 2005) have shown that the cross-section for OH formation is non-zero for collision energies $> \sim 20$ kcal mol⁻¹. Thus photolysis of ozone in the visible Chappuis band could lead to O(³P) with sufficient energy to form OH (although such a route would require the collision with H₂O to occur without prior energy dissipation).

Oxidation by O(³P)

Finally, an alternative route to OCl⁻ formation could be the oxidation of Cl⁻ by O(³P) formed via the photolysis of surface adsorbed or dissolved O₃. Very little is known about reactions of O(³P)_{aq} under the cold, briny conditions of our experiment. However one study suggests that O(³P)_{aq} efficiently scavenges halides in solution to form OCl⁻ or OBr⁻ (Amichai and Treinin, 1969). The authors report a relative scavenging rate for Cl⁻ only two orders of magnitude smaller than that for Br⁻ (the difference is over six order of magnitude for the ozonation reaction, (Finlayson-Pitts, 2003)). This could imply a route to form OCl⁻ which could go on to release Cl₂.

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