

### **Response to Anonymous Referee #1**

We would like to thank Anonymous Referee #1 for his/her careful reading of this manuscript and constructive suggestions. We have addressed all of his/her comments in the revised manuscript, and describe in detail changes made below in the order in which they were raised by the reviewer. All page numbers and line numbers are in reference to those in the revised version of the manuscript, except where indicated otherwise. For clarity, the text of the reviewer's comments is in **black**, while the authors' responses are in blue.

**The manuscript by Halfacre et al. describes a number of laboratory experiments conducted to better elucidate the nature of halogen activation from halide-containing ices. This is an important topic in polar boundary layer chemistry, and only a couple of lab studies have been performed on this system before. So there is inherent merit to the work in that regard.**

**The halogen release is driven either by exposure to ozone or by illumination when an OH radical precursor, such as nitrite or hydrogen peroxide, is incorporated into the frozen solution. The experiments are performed using a flow tube that is coupled to a chemical ionization mass spectrometer operated with an iodide reagent ion. The solutions also contain a buffer to maintain the acidity of the solution, given that protons are required for some of these activation processes. I have a few questions concerning the experimental approach (see below) but my major comments are related to the presentation of the experimental results, although I am in general agreement with their interpretations. Some of the results themselves are new and interesting (e.g. I<sub>2</sub> release in the dark) but others have been showed before, albeit with different approaches (e.g. Br<sub>2</sub> release with light).**

**I'll start by saying that I found this paper very challenging to read, especially the Results and Discussion sections which were excessively wordy. The Introduction and Conclusions are fine. Given that there are only a few figures of data, I believe that the experimental results and their discussion could be much more succinctly described, perhaps cut in length by a factor of two. As opposed to describing every observation, could the major findings be emphasized? Indeed, I recommend that the authors rewrite the paper so that the results and associated discussion are united, i.e. the results are discussed as they are presented. I found myself moving back and forth many times between the two sections as I was reading the paper.**

Thank you for your comments and suggestions. We have been diligent in working to improve the readability of the manuscript. The Results and Discussion sections have been combined into Section 3, discussing results as presented, which we believe improved readability, as you suggested. An effort was made to make the new section more concise.

**The Abstract, too, could be improved. For example, the authors should explain what they mean when they state that photochemical production of Br<sub>2</sub> was observed (line 33). What were the conditions that led to Br<sub>2</sub> production?**

We have amended this sentence to clarify that photochemical production of Br<sub>2</sub> at low pH requires an OH precursor (lines 32-33).

**Another example is that the mechanism of the heterogeneous recycling should be mentioned (line 35).**

We have reworded this sentence to clarify that the gas phase HOX compounds would diffuse into our frozen sample solution to oxidize  $X^-$  (line 36)

**Finally, the last sentence should point out that these mechanisms, even if slow, may be important as the initiation of halogen release to the atmosphere, even if it is found they do not ultimately constitute the major source.**

We have included this statement at the end of our abstract (lines ~ 40-43), as suggested.

**Another weakness of the paper is the attempt to connect the laboratory results to those measured in the field. There are so many factors that come into play in this chemistry, I don't think we can plan to quantitatively relate the lab and the field in the manner attempted. For example, is the spatial distribution of the salts, protons, and OH precursors the same in the field snow samples as those in the lab? I believe the answer is no, given the totally different manner by which the ice samples are prepared. For example, how might the buffer materials (such as acetate) interact with OH in the ice? Is the surface segregation of these species the same? My advice would be to give up on the goal of making that comparison, except in the most qualitative manner. My advice would be to give up on the goal of making that comparison, except in the most qualitative manner.**

We have reevaluated our discussion points as a result of this comment and have removed, most notably, the calculation of relative production rates for the field based on our calculated relative reactivities. While we feel the calculation of relative reactivities represents an important empirical result, it is less defensible to apply them quantitatively to field observations derived from samples very different from ours, as the reviewer suggests.

Interactions between buffers and OH are discussed in more detail below under the more specific question from the reviewer. We have also incorporated discussion to this end in the Supplemental Information, lines 3-28.

The reviewer is also correct in implying vast differences in the spatial distribution of ions between our lab samples and field samples. We acknowledge and discuss this point in the paragraph that spans lines 386-407 in the revised manuscript.

**That said, I do believe that the relative rate approach for interpreting the kinetics of oxidation of different halides has merit. There could be more done interpreting these reactivity ratios in terms of the (much better) known bulk aqueous reaction rate constants.**

A comparison of our calculated relative reactivities with the bulk aqueous OH-halide rate constants, along with a discussion of the implications of the differences, has been included and begins on line 372.

### **Experimental questions-**

#### **Will the acetic acid/acetate buffer be affected by volatilization of acetic acid from the ice?**

pH measurements were recorded before and after each experiment, but no statistically significant difference was observed. We have now clarified that this suggests no significant loss of the buffering capacity over the course of the experiment on lines 146-148.

#### **I found line 128 confusing – i.e. was no iodide observed by IC? If so, what LOD was prevalent for the IC method?**

Iodide was not observed above the observed limit of detection by IC. We have clarified this point and added the limit of detection for the method used (90 nM), line 327.

#### **For the bisulfate buffer, will OH react with bisulfate to form the sulfate radical anion, rather than react with the halide ions?**

This reaction pathway will indeed occur, potentially followed by reaction with the halides.



However, the OH reactions rates with the halides are >10,000 faster ( $k_{\text{Cl}^-} = 3 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ ,  $k_{\text{Br}^-} = k_{\text{I}^-} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ ). We calculate that the sulfate radical would contribute less than 0.1% to halide oxidation, compared that from OH-halide oxidation. Because this is only believed to influence the results to a minor degree, we have included this discussion in the Supplemental Information, lines 3-28.

#### **Line 150: Was it room air that went through the flow tube? If so, what contamination may result?**

The flow tube was cleaned in between experiments with three rinses of ultrapure water with a final rinse of acetone. It was then dried with a > 99.99% purity nitrogen cylinder before being capped. Likely a small amount of room air that contains small amounts of ozone and nitrogen oxides diffuses into the flow tube during the addition of sample to the tube. However, this air would be quickly flushed from the flow tube by zero air on connection with the CIMS, and experimental data are only obtained after signals stabilize. We thank the reviewer for raising this point, and now discuss it on lines 154 as well as detail our cleaning procedure on lines ~181-185.

#### **Line 170: What is the spectrum of the solar simulator bulbs?**

We have included the solar spectrum of the solar simulator bulbs in Figure S1.

**Line 177: typo**

“Ion” was corrected to “Ions”

**Line 189: Where is the Cl<sub>2</sub> background coming from? Just from chloride on flow tube or plumbing surfaces?**

The signal at  $m/z$  197 during ozone addition is not due to Cl<sub>2</sub> because corresponding isotopic signals at  $m/z$  199 and 201 did not rise in concert. This has been clarified in Sect. 2.3, lines 201-203.

**Line 203: I am nervous of how the HOBr sensitivity is estimated, given that the CIMS instrument is not the same as used in the referenced work by Liao et al. Wouldn't it be wiser to just call this signal uncalibrated?**

On line 203-206 of the revisions, we have indicated that the HOBr signal is uncalibrated, and only discuss the relative changes in HOBr signal. Figures 3 and 4 have been adjusted to present the IHOB<sup>-</sup> signals instead of the estimated mole fractions.