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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Hydroxyl Radical in/on Illuminated Polar Snow: Formation Rates, Lifetimes, and Steady-State Concentrations" *by* Zeyuan Chen et al.

Anonymous Referee #1

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In this paper, Chen et al. use kinetic analysis of OH p-HBA formation in illuminated snow samples to infer OH photochemical formation rates and steady-state concentrations in (assumed) pristine snow taken from Arctic regions. This work is important and timely: in a rapidly changing and increasingly human-impacted Arctic environment, understanding the contributions to local atmospheric reactivity and oxidation state due to chemistry associated with "pristine" snow and firn air will give a yardstick against which to measure any changes due to human activities.

Although the concentrations of OH determined here are certainly in line with expectations, I do have some concerns about some of the methods and assumptions used to derive these. I outline these below.

First, as noted by the authors on page 15 of the MS (in the "Implications and Uncertainties" section), the experiments were all carried out by first melting the snow sample, then adding the benzoic acid, then re-freezing, carrying out the illumination, then melting again for analysis. What we know about snow reactivity (Bartels-Rausch et al. ACP (2014); Dominé et al., JPCA (2013)) indicates that morphology may indeed play a significant role in chemistry, so it could well be important here as well. As well, Kahan et al. (ACP (2010), ES&T (2010)) have shown that OH reactivity on ice surfaces may be orders of magnitude different from that within the matrix. These considerations suggest that care should be taken in trying to infer OH concentrations within a disordered layer.

Second, also as noted in the same section by the authors, the re-freezing not only alters the "natural" morphology, but could also alter the partitioning of the HOOH and organics within the sample. I think it is fair to say that we do not yet have any quantitative understanding about how different solutes distribute themselves as an aqueous solution freezes.

Third, I do worry a bit that the bulk of the MS discusses laboratory kinetic results which the authors conclude to have been significantly impacted by an unknown contaminant. What are the implications of this for the general results?

On a more technical note, I am not convinced that the slopes and intercepts obtained from 4-point fits (such as those displayed in Figure 2) are as well constrained as the authors imply. Perhaps some discussion is warranted along these lines.

Also on a technical note, I find the presentation in Section 2.7, concerning how the data were treated, to be quite confusing.

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