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Atmospheric
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Discussions

Interactive comment on "Different photolysis kinetics at the surface of frozen freshwater vs. frozen salt solutions" *by* T. F. Kahan et al.

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We thank the referee for reading our manuscript and raising some valid concerns. However, many of the issues raised by Referee 3 are based on an interpretation of the term "QLL" which is different from ours. Referee 3 views the QLL as all liquid regions in ice, including liquid inclusions at grain boundaries. This interpretation is similar to the liquid-like layer (LLL), used in the Grannas et al. paper referenced by Referee 3, to describe the total liquid content of bulk ice. However, we feel that it is necessary to distinguish between the disordered region at the air-ice interface (which is our definition of the QLL), and the liquid inclusions in bulk ice, because reaction kinetics can be very different in the two regions. We have modified our Introduction slightly to make our definition of the QLL more clear, and have added a section in the Results and

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Discussion to emphasize the importance of distinguishing between the QLL at the ice surface and the liquid inclusions within ice. These changes should help to show that our results can not be interpreted in terms of aqueous phase chemistry, as the Referee would like, and as was done in the Grannas et al. paper.

Our detailed responses to the individual issues raised by Referee 3 are given below.

1. a) We have included a figure showing excitation spectra of harmine in aqueous solution and at an air-ice interface. The overlap between the two spectra shows that enhanced absorption at higher wavelengths is not responsible for the faster reaction on ice.

We have not specifically investigated the concentration dependence of harmine photolysis on ice or in aqueous solution, but we have done this for other aromatic species. We have consistently found that no concentration dependence exists. Further, the reaction kinetics for harmine photolysis on ice are first-order, indicating that bimolecular reactions are not important. We have modified the text to clarify this.

b) We have clarified our discussion of the photon flux dependence of aromatics on ice and in aqueous solution. We agree that the lack of a photon flux dependence is surprising. However, given that we have seen the same behaviour for three separate aromatic species, we believe that repeating these experiments with harmine is not necessary to make the case here.

c) We have modified Figure 1 to include a trace showing the Raman spectrum of the surface of an aqueous solution, and have added further discussion of the figure in the text. This figure is not meant to show new results, but to help explain the motivation for the current study. We have reworded the text accordingly.

d) Although further experiments could certainly be performed, we feel that the experiments discussed here are sufficient to address the question we set out to answer: Is the reaction environment at the surface of frozen salt solutions more similar to that

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of pure ice surfaces, or to liquid water? Measuring total harmine loss from the entire sample would not add to this discussion, since we are interested specifically in the air-ice interface, and not in liquid regions such as exist at grain boundaries. In the Introduction we discuss studies in which we did compare surface reaction rates to total reaction rates (in full ice samples) for unimolecular and bimolecular reactions. We feel that repeating these experiments for this reaction would not provide significantly new or interesting information.

The Grannas paper was able to be more quantitative because they were dealing with complete ice samples, where total solute concentrations were known. In our experiments we deal only with the surface region of the ice, where important pieces of information, such as the total amount of solutes excluded there (as opposed to into liquid regions at grain boundaries), and the volume of the disordered region, are not known. Until the physical nature of air-ice interfaces is better understood, it is impossible to be quantitative about processes occurring there.

With respect to adding more data points, we do not feel that this is necessary to support our major finding, which is that halide salts make the ice surface more liquid-like. The data points that we have clearly show that as [NaCl] increases, the photolysis rate at the sample surface approaches, and eventually matches, that in aqueous solution.

2. The issue raised here is based on conflicting definitions of the term QLL. As stated previously, we are defining the QLL as being only the disordered region at the air-ice interface, which has physical properties which are distinct from liquid water. Again, we feel that this distinction is necessary, and we have modified the Introduction slightly to make this more clear.

The decreased reaction rates with increased salt concentrations observed by Grannas et al. can be interpreted as being due to increased liquid content within the ice for two main reasons. First, they were monitoring the reaction in complete ice samples, and were therefore primarily sensitive to reactions occurring in liquid regions within ice,

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rather than to the QLL at the ice surface. Second, they were examining a bimolecular reaction which showed enhanced rates in ice due to freeze-concentration effects, where increasing the liquid content of the sample by adding salt diluted the reagents, thereby decreasing the second-order reaction rate. In our system, we are probing the QLL exclusively, and we are investigating a unimolecular reaction where the increased (first order) reaction rate on ice is not due to freeze-concentration effects.

Given this context, we feel that our interpretation of our results is appropriate. We observe different kinetics at ice surfaces and in aqueous solution, which we can assign, based on extensive previous research, to differences in the physical properties of the two reaction environments. Increasing the salt concentration in ice samples reduces the photolysis rate until it is the same as that measured in aqueous solution. This provides strong evidence that as salt concentration at the air-ice interface increases, the environment there becomes less like the QLL on pure air-ice interfaces, and more like the environment presented by liquid water. We do not see our interpretation as being “binary” – we describe the kinetics as a continuum between a QLL-like environment and a liquid-like environment.

Finally, we have removed references to “pure” ice in the manuscript.

3. We have removed references to “bulk ice” in the text, instead specifying that we refer to liquid inclusions within the ice, such as those found at grain boundaries. As discussed in our response to Point 2, previous work from our group (Kahan et al. 2010a,b) shows clearly that reaction rates liquid regions within ice are different from those in the QLL at ice surfaces. Therefore, we stand by our definition of the QLL as only including the disordered surfacial region.

4. We have removed the data point at 243 K in Figure 3, and all discussion about it in the text.

5. The work of Grannas et al. examined entire ice samples, and not the surface of ice where this QBL would exist.

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6. We have made it clear in our manuscript that the QLL presents a different reaction environment from aqueous solution. This is not dependent on the thickness of the QLL, as shown in previous studies from our laboratory which show no temperature dependence for a range of reactions on ice (since the QLL thickness increases with increasing temperature). Further, the Raman spectra shown in Figure 1 of the manuscript show obvious differences in the extent of hydrogen-bonding at the surface of a frozen salt solution and at the surface of a pure ice sample, indicating that the surface of a frozen salt solution is structurally distinct from a QLL. Therefore, we feel justified in claiming that the decreased photolysis rates in the presence of salt can be attributed to the formation of a true liquid solution, rather than simply to a thickening of the QLL.

7. We feel that quantifying the enhanced rates for photolysis at air-ice interfaces would be misleading, since for some compounds studied, these enhancements are due at least in part to red-shifts in absorbance spectra on ice. This table is not meant to provide an “enhancement factor” for reactions on ice; with the available data, it is unclear whether such an easy answer exists. The purpose of this table is simply to illustrate that air-ice interfaces present a unique reaction environment, and that increasing halide salt concentrations makes the reaction environment more resemble that of aqueous solution.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 12063, 2010.