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Atmospheric
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Discussions

Interactive comment on "Hydroxyl radical reactivity at the air-ice interface" *by* T. F. Kahan et al.

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We thank the reviewer for the very careful reading of our manuscript. We have addressed almost all the points raised in the review. Our response is detailed below.

- pp. 20883: lines 3-7: The link between hydroxyl photoproduction within snowpack and organics in snow packs (cited in brackets, after citation of Domine and Shepson 2002 and Grannas et al., 2002) should be explained.

We have clarified this section of the manuscript.

- pp. 20883: line 16: it seems that an expression is missing after "handful"

This has been corrected in the manuscript.

- pp. 20884: lines 10-22: previous works concerning direct photolysis of aromatic compounds are cited. If is it so, the link between this paragraph and the following one (lines 23-29), where the same papers are cited concerning indirect photolysis of the same compounds, is not clear.

The papers that were cited twice report both direct and indirect photolysis kinetics.

- pp. 20885: lines 6-9: the last sentence should not be placed in the introduction

We believe this sentence helps guide the reader through the manuscript; it has not been removed.

- pp. 20885: line 16: replace “Several types of experiments were performed:” by “Several types of complementary experiments were performed:”

This change has been made.

- pp. 20885: lines 22- 26 and pp. 20886 lines 1- 8: recall each type of experiments cited.

This section has been clarified.

- pp. 20886: line 23: Table 1 is cited where the LIF is cited whereas it has not yet been described in the text. This should be rewritten.

The acronym LIF has been defined at this point, although the experimental technique has not been discussed in detail. We have not changed the table.

- pp. 20887: line 2: “The lamp’s output”: is it the 75 W Xenon arc lamp described earlier ?

Yes.

- pp. 20887: line 6: When the samples were melted, was there any evaporation of the VOCs?

We have included the following paragraph in the Discussion regarding the possible melting of benzene. We conclude that loss of benzene through pathways other than phenol formation does not affect our results. "The second artefact that we consider is that benzene could evaporate from ice surfaces and ice granules before reaction with OH can occur. This would explain the lack of phenol formation observed in these experiments. However, we do not believe this to be the case. Using glancing-angle LIF, we have monitored benzene at air-ice interfaces (Kahan and Donaldson in preparation), and have observed minimal loss in the dark. Under illumination conditions similar to those in this work (irradiation by a 100 W xenon arc lamp with a longpass 295 nm cutoff filter), we measure a photolysis rate constant on ice of 3 x 10(-4) s-1. This is much slower than the rate constants for phenol fluorescence growth measured in aqueous solution in the presence of nitrite and hydrogen peroxide, and is of similar magnitude (but generally lower) than the rate constants for phenol fluorescence growth in the presence of nitrate. These results, as well as the fact that we can observe phenol formation from the direct photolysis of benzene at air-ice interfaces (both when benzene is frozen from solution and deposited from the gas phase), indicate that the loss of benzene through processes other than phenol formation is not likely affecting our results. We are therefore confident that the lack of reactivity observed at air-ice interfaces is a real phenomenon, and is not due to an experimental artefact.

- pp. 20887: lines 9-10: specify that the further reactivity of phenol towards OH was taken into account in the results

We have done this in the manuscript.

- pp. 20887: lines 10-15: it should be mentioned that the concentrations of phenol used in Fig. 1 are 5 times lower than that of benzene, and thus, its excitation and emission spectra are 5 times more intense than that of benzene, and thus, at the chosen wavelengths, the interferences due to benzene must have been of negligible importance.

The spectra shown here are normalized to maximum intensity. That said, it is clear

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from the figure that benzene absorption is minimal at 271 nm.

- Section 2.3: recall the type of experiment with a longer title than (b), (c), (d) or (e).

We have not made the suggested change, as we do not believe it would increase the clarity of the manuscript.

- pp. 20888: specify how the initial concentrations of reactants were chosen.

We have added a brief statement in the Results section to the effect that we varied the reagent concentrations to ensure that the lack of observed reactivity was not due to concentration effects.

- pp. 20888: line 17: specify what is SLPM

We have changed the notation to L min-1.

- pp. 20890: line 11: a 100 W Xenon arc lamp is cited while a 75 W Xenon arc lamp is previously mentioned in the manuscript.

We have clarified that it is a different lamp.

- pp. 20890: lines 26-29: what is the surface thickness? How is possible to differentiate between surface and bulk reactions?

We have added the following discussion about the thickness of the QLL and our ability to probe it selectively to the Methods Section: "The surface thickness of the QLL is a subject of much debate. It is likely no greater than 100 nm in thickness, although it could be as shallow as a few Angstroms. In this work, we are not concerned with its thickness, but solely with the fact that it appears to present a reaction environment that is different from bulk ice or aqueous solution. We have previously (Kahan and Donaldson 2007) measured identical anthracene photolysis kinetics on ice surfaces whether anthracene was introduced to the ice surface from the gas phase (in which case all anthracene is expected to react at the ice surface) or whether it was frozen from solution (in which case reactions are expected to occur at the ice surface and in the ice bulk). The identical kinetics suggest that we do not measure significant contributions from the ice bulk using this technique. In the current work, for some experiments we introduced one or both reagents to ice samples from the gas phase, thus ensuring that they were present – and reacted – at the surface. Ensuring that reactions are occurring at aqueous surfaces is more difficult, as diffusion into the bulk is possible. We have previously demonstrated (Mmereki and Donaldson 2003) that anthracene partitions extensively to aqueous surfaces, and that reactions with gas-phase compounds occur at the surface, as opposed to in the bulk. Therefore, we are satisfied that anthracene reacted with OH at the water surface. We have not performed experiments to determine the extent to which benzene partitions to aqueous surfaces. Therefore, it is possible that at least some of the phenol formation we observed during the reaction with gas-phase OH occurred in the bulk. However, we do not feel this affects our conclusions, as we have confidence that the reaction with anthracene does occur primarily at the air-water interface."

- pp. 20892: lines 5-15: The results obtained with ice granules should be emphasized with tests performed on different ice granule diameters.

The large uncertainty associated with these measurements suggest that it will be difficult to obtain meaningful results by doing this. We have added the following discussion to Section 3.4: "To further test our hypothesis that the kinetics measured in ice granules contain contributions from reactions occurring both in bulk ice and at air-ice interfaces (with different kinetics), we estimated the relative phenol formation rates expected in our ice granules and ice cubes, using the rate constant measured in aqueous solution (4.2 x 10(-10) M/s) to describe the rate in liquid regions within bulk ice, and a rate constant at air-ice interfaces of zero. Assuming spherical granules, the rate constant associated with the surface reaction should be inversely related to the relative increase in surface area compared to that of the ice cubes. For our samples, that means that the rate in the ice granules should be approximately 6 times lower than in the ice cubes. This would result in a phenol formation rate of 7 x 10(-11) M/s, which is beneath our

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detection limits."

- pp. 20892: line 21 and pp. 20893: lines 2-5: specify the reaction between benzene and O2

We have described the proposed mechanism in the manuscript.

- pp. 20893: lines 20-29 and pp. 20894: lines 1-7: add a discussion on the different slopes obtained in fig 6 using different OH precursors, and compare with literature (see for example : Minero C., Serge Chiron, Gianpaolo Falletti, Valter Maurino, Ezio Pelizzetti, Roberto Ajassa, Maria Eugenia Carlotti and Davide Vione: chemincal processes involving nitrite in surface water samples, Aquatic Sciences - Research Across Boundaries, Volume 69 (1), 71-85, 2007.)

Since we do not have an independent method of measuring the photon flux from our lamp, we cannot compare our measured kinetics with literature values. Instead, we used our measured kinetics to determine the photon flux. Since the OH formation kinetics from each precursor predicted similar photon fluxes, and since the predicted fluxes were in reasonable agreement with the manufacturer's specifications, we are satisfied that our in situ OH-trap yields accurate kinetics. These actinometry experiments are fully described in the Supplementary Information.

- pp. 20896: lines 2-6. The temperature argument is not clear.

We have rephrased this argument.

- Throughout the manuscript: the pH of the solutions should be stated and a discussion may be useful concerning this parameter.

We have stated in the Methods section that we did not adjust the pH of any of the solutions. They were likely around pH 5.5, except for samples containing acids, which would have been more acidic.

- All figures: recall the type of experiments

We have made the suggested changes.

- Figure 6: specify the concentrations of benzene, and the pH.

We have added the benzene concentrations to the figure caption. Since we did not adjust the pH, it was likely ∼pH 5.5 for nitrite and hydrogen peroxide samples, but was much lower (and variable) for nitrate samples, as they were prepared from nitric acid. We have not stated the solution pH in the figure caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 20881, 2009.