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Atmospheric Chemistry and Physics 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 pointing out some unclear parts of the manuscript. We have addressed all the comments as detailed below.

Comment 1: "My confusion with this manuscript relates to understanding how well they monitor the QLL as opposed to the bulk ice and liquid phases. For example giving normalized fluorescence intensities without showing relative magnitudes and explaining the magnitude of the observations does not help."

We have added the following discussion in the Methods Section about our ability to probe the QLL selectively: "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

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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."

Comment 2: "Experiments in part a) observe phenol formation after irradiation of bulk ice mixtures containing an H2O2 as an OH precursor and benzene. After crushing the ice to increase surface area no phenol formation is observed. However, while this may have increased the area of the surface QLL most of the ice is still present in the bulk phase. The authors suggest that the reagent must have partitioned into the QLL but they provide no evidence for this. Fig 3 suggests that no phenol has formed presumably requiring that all of the peroxide and benzene partition into the QLL."

We have added the following statement in the Section 3.1: "Based on the uncertainty in the data, we can ascribe an upper limit to the phenol formation rate in the ice granules of 9 x 10(-11) M/s."

And this discussion in 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 detection limits."

Comment 3: "For b) it's unclear to me that the ice observations involve a surface layer. Is there no phenol signal in the absence of gas phase oxygen?"

We do not observe phenol formation in the absence of gas-phase oxygen. This was stated in the original manuscript and we have emphasized this in the revised version.

Comment 4: "For c), d) and e) my problem is again the absence of any observation of reactivity in the ice surface experiments. Observations of reduced activity and an ability to relate it in some systematic way to concentration and quantify the reduction in rate would be convincing. However from my perspective what we have here are some interesting observations but no way to assess whether these are real or merely some artifact of the experimental approach, especially since the detection schemes for phenol on ice and liquid surfaces are different. Hence I feel that, as written, the results do not support the conclusions."

We have included this paragraph in the manuscript, explaining why we are confident that the lack of reactivity we observe at air-ice interfaces is real, and not an artefact of our experimental approach: "There are several possible explanations for a reduction in reactivity between OH and an organic compound at the air-ice interface. The first possibility which must be addressed is that the lack of observed reaction could be due to an experimental artefact. Here we consider two types of artefacts which could affect our measurements. The first possibility is that the glancing-angle LIF technique used may not accurately follow reactions at air-ice interfaces. We are confident that this is not the case, as we have observed the same result (a lack of reactivity of OH with organics at ice surfaces) using two very different techniques (in situ glancing-angle LIF measurements and offline spectroscopy of melted ice cubes and granules). Further, using the same two complementary techniques, we have measured increased anthracene photolysis rates at ice surfaces (Kahan and Donaldson 2007; Kahan et al. accepted). We would not expect an experimental artefact to have the opposite effect on two systems."

One argument against an experimental artefact is that we have obtained the same results using two very different techniques. A second point is that glancing-angle LIF measurements show enhanced PAH photolysis kinetics at air-ice interfaces compared to in aqueous solution or at air-water interfaces, whereas reaction of OH with aromatics is observed to be suppressed using the same technique. An experimental artefact would not likely result in observations of increased reaction rates in one system and suppressed rates in another. We believe that this discussion shows that our observations are due to actual occurrences at air-ice interfaces rather than to experimental artefacts.

We have quantified the reduction in rate as much as possible, in that we say that kinetics at the ice surface are unmeasurably slow. We have added a sentence in the manuscript stating that the lowest phenol formation rate we can measure, based on the uncertainty in our ice granule data, is ∼9 x 10(-11) M/s (see response to comment above).

The detection methods for phenol on ice and on liquid surfaces are the same in that both use glancing-angle LIF to monitor phenol emission at the substrate surface. The only difference is the excitation and emission wavelengths used to monitor phenol. In experiment set (b) we show that we can measure phenol growth both in aqueous solution and at air-ice interfaces from the direct photolysis of benzene using this in situ technique, and that the kinetics are the same. And again, the agreement in kinetics measured at air-ice interfaces using glancing-angle LIF and in high surface-area-to-volume ice granules, both in this work and in a previous study (Kahan and Donaldson, Environ. Sci. Technol., accepted), provide confirmation that the in situ LIF technique provides reliable data.

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

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