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Discussions

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

Anonymous Referee #1

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This manuscript reports on a study of the reactivity on hydroxyl radicals in the quasi-liquid layer (QLL) above ice surfaces. The authors have developed some elegant but simple probes that indirectly monitor reactivity of OH in the condensed phase by monitoring the formation of phenol produced from the reaction of OH with benzene. The paper presents some novel tools and data and clearly addresses a relevant scientific question within the scope of ACP. I do feel however that the experimental approaches are not clearly outlined and in this type of study which is, for example, very different from a study of gas phase kinetics in which methods are well established this is important. To emphasize this I would quote from the 2007 paper of the authors.

"Measurements of the physical properties of the QLL are difficult, however, as its depth likely does not exceed 100 nm even at high temperatures and its structure almost certainly is not uniform at all depths. Therefore, different measurement techniques, which are sensitive to varying levels of disorder in the ice matrix and to different depths of the QLL, have reported quite different values of QLL depth, density, and orientational order." 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. 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.

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?

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.

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