Atmos. Chem. Phys. Discuss., 13, C2563–C2565, 2013
www.atmos-chem-phys-discuss.net/13/C2563/2013/

Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Uptake of HO_2 radicals on Arizona test dust surface" *by* Y. Bedjanian et al.

Anonymous Referee #2

Received and published: 21 May 2013

The authors present a coated-injector flow tube study of the uptake of HO2 by a mineral dust sample, Arizona Test Dust. This chemistry is of importance to HOx loss in regions of high mineral dust loading and low NOx pollution levels. Given that this is the first study to examine the loss of HO2 on dust, there is merit to its eventual publication. In general, the paper is clearly written, the experiments appear to have been performed with excellent precision, and many of the standard parameters have been varied to test the applicability of the results. In particular, the initial uptake coefficient was studied as a function of temperature, relative humidity, HO2 concentration, HO2 source and ATD thickness. Only the ATD film thickness and the RH had any large effect. It is very challenging to make measurements of this nature and to be confident of their atmospheric significance, and so this paper is a good start in that regard. It does not, however, close the door on the subject, leaving quite a few open questions. For example,

1. The HO2 concentrations used are high, on the order of 10ˆ12/cm3 or so. This does affect the relevance of this work because different uptake rates may be observed with lower, more atmospherically relevant values. For example, the authors show that there is no dependence on HO2 concentration under the range studied, but it may be the case that the surface is saturated under these conditions. Perhaps the authors could make a caveat in the paper on this topic. 2. The mechanism of the HO2 loss is mysterious but not unique to this paper, i.e. other studies of HO2 loss have also not definitively identified the loss mechanism. Normally, one does not think of HO2 as an oxidant, especially of a material such as ATD that is made of feldspars and clays. Instead, at high HO2 concentrations my hunch would have been that HO2 would recombine to form H2O2 but the results from the paper suggest this is not the case. However, a missing control experiment is the uptake of H2O2 by ATD under the conditions of this experiment. Is it possible that H2O2 is the product of the reaction, and that it is strongly adsorbed, the way that H2O is to a clay, to the ATD? Without this control experiment, the value of one of the main conclusions of the paper, i.e. that the reaction goes not form H2O2, is questionable. 3. How do the authors interpret the slow rise in HO2 signal as a function of time after initial exposure (Figure 2)? Does the amount of HO2 lost over this period represent more than a monolayer coverage? I suspect so but have not done the calculations myself to check. 4. I find the explanation that the inhibitory effect of H2O on the reaction, i.e. that there is some blocking of surface sites, to be reasonable. However, it does not help us to interpret the mechanism. Were any experiments done on films that were first humidified and then dried? Did the reactivity return to its value before humidification? 5. On page 8888, line 3, I don't think it is appropriate to say that the value of 0.02 was measured. Rather, it is an upper limit for one set of conditions. 6. The relationship between surface area and uptake coefficients is not an easy one, and sometimes best resolved by doing an aerosol uptake experiment. However, that is beyond the scope of the present work. At issue is whether the BET specific surface area is the same as that of the ATD deposited on the insert from an ethanol slurry. It has never been clear to me that the two quantities are the same.

This is particularly important for interpreting the linear portion of an uptake coefficient versus particle mass plot. It is possible that the plot is linear because uptake goes up when additional surface area is available for reaction (in a proportionate amount) but whether all the surface area on the rod is available for reaction is hard to know, i.e. there may be clumps of ATD on the insert for which only the surfaces are accessible, and by adding more mass one is only adding more clumps. 7. In the Abstract, it should be mentioned that the uptake coefficients are upper limits. Otherwise, a modeler might take the uptake coefficient equation and put it in a model, not realizing its limitations.

Minor points: 1. Page 8874, line 22. It is not just in the stratosphere that this reaction is important. 2. Page 8878, line 9. Bubbler 3. Page 8879, line 25. How was the liquid H2O2 injected into the flow tube?

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 8873, 2013.