

Reply to reviewer 2. (Authors reply is in blue)

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 HO_x loss in regions of high mineral dust loading and low NO_x 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 10¹²/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.

Yes, the concentrations of HO₂ used in the present study are much higher than those in the atmosphere and additional experiments (with other more sensible to HO₂ technique) would be very useful. The values of γ_0 were found to be independent of the initial concentration of HO₂ radicals, which was varied by one order of magnitude. We believe that the surface is not saturated under the conditions of our measurements of γ_0 (initial stage of exposure) and would expect similar values for the **initial** uptake coefficient at lower concentrations of HO₂.

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.

We do not agree with the last statement. We talk about the reaction products in the gas phase and in the gas phase no H₂O₂ was detected. This is an experimental observation.

In the revised version of the manuscript we have added the information on the reference experiments on the uptake of H₂O₂ to ATD: the uptake of H₂O₂ to ATD is rather rapid ($\gamma_0 \sim 0.001$ under dry conditions) and reactive, i.e. irreversible. The products of this heterogeneous reaction are not known, however they are expected to be O₂ and H₂O. We are not sure that this information provides an additional insight into the mechanism of the HO₂ reaction with ATD. The possible partial processing of H₂O₂ (if formed in primary reaction of HO₂) in heterogeneous reaction on ATD surface was already mentioned in the manuscript. However,

in our opinion, the transformation of H_2O_2 on ATD surface is not the main reason for the absence of H_2O_2 in gaseous products of the $\text{HO}_2 + \text{ATD}$ reaction. Thus in a recent study from our group H_2O_2 was distinctly observed as a gaseous product of the interaction of OH radical with the same ATD surface, although with a relatively low yield of 10% (Bedjanian, Y., Romanias, M.N., El Zein, A., J. Phys. Chem. A 2013, 117, 393-400). The present results seem to indicate that HO_2 uptake by atmospheric aerosols does not necessarily produce H_2O_2 . In this context, in a recent paper of Mao et al. (Mao, J., Fan, S., Jacob, D.J., Travis, K.R., Atmos. Chem. Phys. 2013, 13, 509-519) a catalytic mechanism was proposed which involves a coupling of the transition metal ions Cu(I)/Cu(II) and Fe(II)/Fe(III) to rapidly convert HO_2 to H_2O in aqueous aerosols. This comment is partly added in the revised manuscript.

3. How do the authors interpret the slow rise in HO_2 signal as a function of time after initial exposure (Figure 2)? Does the amount of HO_2 lost over this period represent more than a monolayer coverage? I suspect so but have not done the calculations myself to check.

As noted in Section 3.1, the slow rise in HO_2 signal with time is a result of the surface deactivation, which may be due to its progressive saturation with the products of the heterogeneous reaction, H_2O being the most probable final reaction product partly remaining on the surface. The prolonged exposure to the compounds coming from HO_2 sources used in the study (CH_3OH , HCl , Cl_2 , H_2O_2 , HF) can also lead to modification of the surface reactivity with time, although no impact of these species on the initial uptake was observed. For the data presented in Figure 2, the total number of HO_2 radicals lost on the surface is 8×10^{15} molecule cm^{-2} (lower limit, as being calculated using total BET surface area), i.e. much higher than a monolayer coverage ($< 10^{15}$ molecule cm^{-2}).

4. I find the explanation that the inhibitory effect of H_2O 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?

No, we have not done this kind of specific experiments, but we would expect the recovery of surface reactivity upon drying.

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.

Corrected.

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.

The BET surface area of ATD powder did not change during preparation of ATD films. Similar (within 20%) specific surface areas were measured for original powder (not treated) and that removed from the support tube (i.e. deposited from ethanol slurry). In any case, BET surface area was not used in the calculations of the uptake coefficient.

We agree with this comment and we note in the paper that "the reason for the initial linear mass dependence of γ at very low masses could also be the incomplete coverage of the support tube by dust aggregates". Yes, the present data do not allow the determination of the surface area involved in the reaction with HO₂. That is why we have used the geometric surface in calculations of γ , resulting in the determination of an upper limit of the uptake coefficient.

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.

Done.

Minor points:

1. Page 8874, line 22. It is not just in the stratosphere that this reaction is important.

Yes, corrected.

2. Page 8878, line 9. Bubbler

Corrected.

3. Page 8879, line 25. How was the liquid H₂O₂ injected into the flow tube?

Using graduated syringes. This phrase is added in the text.