

Reply to reviewer 1 (Authors reply is in blue)

The present work deals with the heterogeneous chemistry of HO₂ free radical with an atmospheric mineral dust proxy, namely Arizona Test Dust (ATD), and reports valuable kinetic and reaction product information on the title reaction. The work presents a coherent story, the manuscript reads well and the authors have obtained a well balanced scientific report both on experimental details and the scope and importance of the present measurements. The present is the third report by the senior author on record dealing with HO₂ free radical heterogeneous chemistry after Romanias et al. (2012) and Loukhovitskaya et al. (2009). I will take this opportunity to deplore the absence of a more detailed, perhaps observation-based, chemical-kinetic model that will provide some basic understanding of the adsorption behavior including associated chemistry. What is the model the authors have in mind to put the past experimental results on the various substrates into perspective? The authors are invited to dig a little deeper and scratch the substrate surface a little harder (no pun intended!) in order to provide additional molecular insight into this heterogeneous interaction.

We agree with both reviewers and with the statement of the reviewer 2 that "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." In fact, it is difficult and too speculative "to dig a little deeper and scratch the substrate surface a little harder in order to provide additional molecular insight into this heterogeneous interaction" in the frame of the experimental approach used in the present and in previous studies, when only the gas phase composition is monitored (and often only the reactants, but not the products of the heterogeneous reaction). It is clear that for better understanding of the reaction mechanism at the molecular level, *in situ* monitoring of the reactive surface is needed. But even in this case, problems may arise, that are specific to working with radicals, and associated with the presence of radical precursors in contact with the reactive surface.

I encourage the authors to take into account the following, mostly minor points before submission of the final manuscript:

- Pg. 8873: I propose to leave out "surface" in the title. HO₂ is a gas phase species, ATD is a solid, so it is self-evident that reaction has to at least start at the surface.

Done.

- Pg. 8875, lines 23-25: I do not understand the sentence starting with "Depending....".

The sentence is reformulated: "Considering that H₂O₂ in the atmosphere is produced via self-reaction of HO₂ radicals and H₂O₂ can photolyze to regenerate HO_x species, the HO₂ uptake on aerosols will have different effects on the concentrations of H₂O₂ and HO₂, depending on whether or not H₂O₂ is formed in the heterogeneous reaction."

- Pg. 8876, lines 18-21: Does the BET surface of ATD (probably the finest commercially available fraction) change after the treatment with ethanol? What makes the ATD particles stick to the glass support rod after evaporation of the solvent? What is the accuracy of the weight measurement of ATD after mechanically scraping off material from the glass support rod? How reproducible is this operation?

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. processed during sample preparation). In any case, BET surface area was not used in the calculations of the uptake coefficient.

The precision (and reproducibility) of mass measurements is defined by the accuracy of mass balance (0.1 mg): there is no significant mass loss when solid film is removed from the support tube.

- Pg. 8878, line 8: Why is the fractional dissociation of Cl₂ only 20-30%? Could you increase the degree of dissociation? Does undissociated Cl₂ affect the ATD coating? Is there a heterogeneous interaction of Cl₂ with ATD?

Relatively low fractional dissociation of Cl₂ is, at least partly, due to recombination of Cl atoms. The yield of Cl atoms can be somewhat increased by special treatment of the Pyrex tube in the microwave cavity or by increase of the flow rate in this tube. In this work we have not paid much attention to the interactions of radical precursors with ATD, considering that they have limited impact on the *initial* uptake of HO₂, measured on fresh (non treated) surface. Identical values of γ_0 obtained with different sources of HO₂ and with varied concentrations of excess precursors (H₂O₂, CH₃OH) seem to support this assumption.

- Pg. 8879, lines 1-7: Is there Br₂O formation in the aftermath of HOBr production? This is easily recognized by its mass spectrum (molecular ion) which should appear especially under conditions of longer gas residence time.

We have not verified for possible formation of Br₂O. However, we believe that formation of this species is unlikely in our experimental system. The only reaction - source of Br₂O that comes in mind, $\text{Br} + \text{BrO} + \text{M} = \text{Br}_2\text{O} + \text{M}$, is not operative under our experimental conditions.

- Pg. 8879, lines 18 and following: Do you observe heterogeneous Br recombination to Br₂ under your experimental conditions? Would this represent a bias in your mass balance by overpredicting Br₂ disappearance? If every product Br atom recombined you would consume half instead of one mole.

The possible impact of the heterogeneous recombination of Br atoms to Br₂ on the time scale of calibration experiments ($\leq 0.01\text{s}$) is negligible ($< 5\%$) because the rate of heterogeneous loss of Br atoms on halocarbon wax (coating the main reactor) is rather low ($< 10\text{ s}^{-1}$).

- Pg. 8880, line 6: What is actually monitored in Figures 2 and 3 (HOBr, NO₂)? At least the Figure captions of all Figures should say so. Regarding Figure 3: does every point represent a fresh sample? How did you perform the measurement? Please give details. The paper is short so that there is room for a little more explanation.

Figure 2: HO₂ is monitored as HOBr⁺ at $m/z = 98$ (see text).

Figure 3: HO₂ is monitored as NO₂⁺ at $m/z = 46$ (see text).

Each of the kinetics shown in Figure 3 was obtained with one mineral film in a single experiment by varying the length of the mineral film in contact with HONO. The kinetic runs were measured under quasi steady state uptake conditions on partly deactivated surface,

where decrease of the uptake with time is rather slow and could be considered as negligible during the few minutes of the acquisition time.

These comments have been added in the text.

- Pg. 8882, line 14: The linear mass dependence of the uptake coefficient “gamma” is not generally considered an indication that the entire surface area is accessible to heterogeneous interaction. The pore diffusion model has several parameters that control access of the gas to free reactive sites. When “gamma” levels off at high mass the only conclusion we may draw is that diffusion of HO₂ is rate limiting, but this does not say anything about the actual penetration depth of HO₂ within the solid sample and during the gas-lifetime of HO₂. In this respect it would have been interesting to test the coarser ATD regarding the mass dependence of “gamma”. It is difficult to reach conclusions on the basis of a single type of substrate, at least in my experience.

We agree with this comment, although continue to state that in most of the papers "the linear mass dependence of the uptake coefficient is considered as an indication that the entire surface area is accessible to heterogeneous interaction." In the present study, we could not determine the surface area involved in reaction with HO₂ (or "the penetration depth of HO₂ within the solid sample"). Therefore the geometric surface area was used in calculations of γ leading to determination of only the upper limit of the uptake coefficient.

- Pg. 8883, lines 18 to 22: These facts are indeed surprising. Are the authors prepared to say that HO₂ and H₂O₂ occupy distinctly different surface sites on ATD, or alternatively, that adsorbed H₂O₂ or CH₃OH are displaced by HO₂?

One should keep in mind that we are talking about the **initial** uptake coefficient, which is measured on non contaminated surface, where active sites (at least most of them) are not yet occupied.

- Pg. 8884, line 26 and 27: What are “similar” “gamma” values? Please give the original experimental results.

As noted in the text, we have not observed any effect of the UV irradiation on the kinetics of HO₂ loss on the ATD samples in the whole range of RH used. The measured values of γ were similar (within a few %) to those under dark conditions. Considering that the effect of UV was verified in almost all "dark" experiments, all the uptake data presented in the paper can be regarded as the original experimental results.

- Page 8886, lines 21 and 22, lines 26 and 26: Is it thermodynamically possible that HO₂ reacts with a surface hydroxyl group to form H₂O + O₂? I do not think so, but it is incumbent on the authors to specify their claim. In addition, it should be possible to monitor the extra water vapor and/or O₂ in view of the rather high values of “gamma”. Did the authors perform any reference experiments of H₂O₂ on ATD with respect to adsorption and/or reaction? ATD may be different as a substrate from TiO₂ (Loukhovitskaya et al., 2009). The results displayed in Figures 4, 5 and 6 suggest a higher value for the initial value of “gamma”.

Reaction of HO₂ radicals with surface hydroxyl groups is known to be involved in the mechanism of H₂O₂ decomposition on metal oxide surfaces, e.g.: Fe^{III}-OH + HO₂ → Fe^{II} + H₂O + O₂ (Lin S.-S., Guroi M.D., Environ. Sci. Technol. 1998, 32, 1417-1423).

Monitoring of the possible reaction products, H₂O and O₂, was impossible due to high background concentrations of these species in the flow reactor.

Yes, we have performed reference experiments on the uptake of HO₂ to ATD. It was found that the uptake of H₂O₂ to ATD is rather rapid ($\gamma_0 \sim 0.001$ under dry conditions and is decreasing upon increase of RH) and reactive, i.e. practically irreversible. The products of this heterogeneous reaction are not known, however they are expected to be O₂ and H₂O. This information has been added in the revised manuscript.

- Pg. 8888, line 3: Why did the authors take that “gamma” value (0.02) out of several possible ones (see Figure 6). What is the criterion? I question the usefulness of the “atmospheric relevance” section because you slide the rate ratios in and out of relevance by “doctoring” either “gamma” or the particle density per cm⁻³!

Neither "gamma" nor particle density were "doctoring". All the parameters used in the calculations are clearly identified: $(0.1-2) \times 10^{-5} \text{ cm}^2 \text{ cm}^{-3}$ as the range of particle surface density and $\gamma = 0.02$, the value measured at RH = 30%. Yes, the last value was chosen arbitrarily. One might as well choose the value of γ at other RH. This would lead to some changes in the results of the calculations without affecting the main conclusions.