Review of manuscript acp-2013-169 „Uptake of HO_2 Radicals by Arizona Test Dust Surface“ by Y. Bedjanian, M.N. Romanias, A. El Zein

The present work deals with the heterogeneous chemistry of HO_2 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 HO_2 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. 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. HO_2 is a gas phase species, ATD is a solid, so it is self-evident that reaction has to at least start at the surface.
- Pg. 8875, lines 23-25: I do not understand the sentence starting with “Depending….”.
- 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?
- Pg. 8878, line 8: Why is the fractional dissociation of Cl_2 only 20-30%? Could you increase the degree of dissociation? Does undissociated Cl_2 affect the ATD coating? Is there a heterogeneous interaction of Cl_2 with ATD?
- Pg. 8879, lines 1-7: Is there Br_2O 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.
- Pg. 8879, lines 18 and following: Do you observe heterogeneous Br recombination to Br_2 under your experimental conditions? Would this represent a bias in your mass balance by overpredicting Br_2 disappearance? If every product Br atom recombined you would consume half instead of one mole.
- Pg. 8880, line 6: What is actually monitored in Figures 2 and 3 (HOBr, NO_2)? 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.

- 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 HO_2 is rate-limiting, but this does not say anything about the actual penetration depth of HO_2 within the solid sample and during the gas-lifetime of HO_2. 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.
- Pg. 8883, lines18 to 22: These facts are indeed surprising. Are the authors prepared to say that HO_2 and H_2O_2 occupy distinctly different surface sites on ATD, or alternatively, that adsorbed H_2O_2 or CH_3OH are displaced by HO_2?
- Pg. 8884, line 26 and 27: What are “similar” “gamma” values? Please give the original experimental results.
- Page 8886, lines 21 and 22, lines 26 and 26: Is it thermodynamically possible that HO_2 reacts with a surface hydroxyl group to form $H_2O + O_2$? 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 O_2 in view of the rather high values of “gamma”. Did the authors perform any reference experiments of H_2O_2 on ATD with respect to adsorption and/or reaction? ATD may be different as a substrate from TiO_2 (Loukhovitskaya et al., 2009). The results displayed in Figures 4, 5 and 6 suggest a higher value for the initial value of “gamma”.
- 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}!