

Interactive comment on “Re-evaluating the reactive uptake of HOBr in the troposphere with implications for the marine boundary layer and volcanic plumes” by T. J. Roberts et al.

Anonymous Referee #1

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The authors have performed a very detailed analysis of the fundamental kinetics of HOBr uptake kinetics into tropospheric aerosol, both as a function of acidity and halide ion (bromide, chloride) content. In some respects I like this paper, but in others I feel it needs a lot of work. Starting with the good, I agree with the basic hypothesis that under some pH conditions, the general acid assisted mechanism is a more general representation of the reaction kinetics than a simple termolecular representation. There is merit to the paper to point this issue out, which is not currently acknowledged in atmospheric models. Also, there is merit to attempting to reconcile the disparity in the laboratory reaction kinetics presented, which the paper does by illustrating that

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some of the slow HOBr/chloride kinetics of Pratte and Rossi may be due to chloride displacement at high acidity.

That being said, there are a number of weaknesses to the paper. First and foremost, it is far too long (starting with the Abstract!) and extremely hard to read. A major re-write is necessary to make the paper publishable, with a lot of the detailed mechanistic analysis shortened and going into Supplementary Information, and instead clear, major points are left in the manuscript. Currently, the paper is not approachable by an atmospheric modeler, which I see as one of the goals of this type of analysis.

Second, the paper needs to address a number of laboratory papers that looked at the kinetics of HOBr reacting with HCl and HBr in acidic sulfuric acid solutions (notably, Hanson and Ravishankara, GRL, 1995; Waschewsky and Abbatt, JPC-A, 1999) if the model is to be fully evaluated, i.e. how does the model match up against these data. Or, is the acidity too high in these experiments to make the model not appropriate (i.e. the reaction proceeds at very high acidity through protonation of HOBr initially and not via interaction of HOBr with the halide ion)?

Third, the general idea that HOBr kinetics might be so slow on small particles in the marine boundary layer because of their high acidity and subsequent halide loss that this leads to accumulation of bromide in these particles seems somewhat contradictory to me, i.e. if the bromide is building up to high levels, why is the uptake coefficient too slow to remove it? I view this suggestion as largely speculative and that a full box model needs to be implemented to test the hypothesis. Given the length of the paper, I recommend pulling out all the discussion of uptake coefficients under marine and volcanic conditions, and putting them instead into another paper with a full box model simulation, so that the ideas of HCl release and HBr uptake can be assessed.

Finally, when the halide concentrations get so low, I am not convinced that the formalism presented in Equation 2 is appropriate, i.e. this equation assumes that HOBr is the limiting reagent and that the halide ion is in excess. If that is not the case, as may occur

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if there is a lot of halide displacement and with low concentrations of bromide, the use of an HOBr uptake coefficient for atmospheric modeling is not useful, and it would be better to describe the kinetics in terms of either HCl or HBr uptake, with HOBr in a semi-steady-state in solution. The authors need to justify their decision to express all the kinetics in terms of HOBr uptake.

Small point: The diffusion coefficient listed on page 2729, line 26 has the wrong units.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 2717, 2014.