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Interactive comment on "Uptake of hypobromous acid (HOBr) by aqueous sulfuric acid solutions: low-temperature solubility and reaction" *by* L. T. Iraci et al.

Anonymous Referee #1

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Review of Iraci et al., Uptake of HOBr by sulfuric acid solutions

This paper presents measurements of the time dependent uptake of gas-phase HOBr by cold sulfuric acid solutions, where most of the uptake is solubility driven. With estimates of the liquid phase diffusion coefficient of HOBr, the Henry's Law constant for HOBr in these solutions can be determined from these data. The importance of this quantity is that it is used in estimates of the rates of halogen activation in the lower stratosphere and, perhaps, in the cold Arctic boundary layer as well.

A Knudsen cell technique has been used and the overall result is that the measure-

ments are in fairly good agreement with one other study, performed using a coated-wall flow tube, and in not so-good-agreement with a second flow tube measurements conducted at somewhat different temperature and acid concentration conditions. My recommendation is that the paper be published after the authors address the comments below. Overall, the manuscript is clearly written with good experimental details.

1. One general comment is the HOBr concentrations are relatively high, about 10ˆ-4 to 10ˆ-5 torr (if it is true that the HBr and HOBr EI-MS sensitivities are indeed equal to each other). I wonder how this affects the uptake measurements, particularly those in the more concentrated acid solutions and at low temperatures, where Br2O is observed to form? On p1223, it is claimed that this gives rise to only a 25% uncertainty but it is not clear to me how well this effect can be estimated. 2. p1219. How did the variations in the relative humidity match between the input water and the vapour pressure of the acid solution affect the uptake? Could they have given rise to some of the scatter in the data in Figure 2? 3. p1220. It is said that stirring of the solutions was done between runs "to regenerate a fresh surface". If this is truly reversible uptake (and in the absence of changes of sulfuric acid concentration at the surface due to water evaporation/uptake), such stirring should not have been necessary. Was there any evidence that stirring was necessary? If so, this could indicate interesting, unaccounted-for chemistry. 4. p1222. Coming back to Point #1 above, was there any dependence on the yields of Br2O on the input partial pressure of HOBr? If the reaction really does proceed via HOBr reacting with itself, this dependence might arise. 5. p1227, first sentence. The authors should be careful in drawing a conclusion about the possible non-saturation of the uptake of HOBr, via the production of Br2O for example, given their high HOBr concentrations. Would Br2O be produced under atmospheric conditions? 6. p1227 bottom and p1228 top. I think the authors have not made good assumptions about the rate constants of the three reactions which are compared to each other. There is some data in the solution literature that says the HOBr/HBr reaction is very fast, going at the diffusion limit. Also, given that both HOBr/HBr and HOBr/HCl proceed via ionic mechanisms in all likelihood, it is unlikely that they will have the same rate constant

ACPD

5, S472–S474, 2005

Interactive Comment

as the HOBr/HOBr reaction that probably does not have an ionic mechanism. I think the discussion in this section should reflect the assumptions made that all three rate constants are equal. Also, the statement that the rate = k [HOBr][HX] is not necessarily true if the reaction is one that occurs close to the surface instead of through the bulk of the particle. 7. In Figure 2, it would be useful to put in the sulfuric acid concentrations used by the three investigators, perhaps in the Figure caption.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 1213, 2005.