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Atmospheric Chemistry and Physics Discussions

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.

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Scope The heterogenous oxidation of halide ions in atmospheric aerosols is complex chemically and despite efforts over past years a number of outstanding questions remain. It is nevertheless an important aspect of atmospheric chemistry which needs attention This paper presents a new analysis of available data from laboratory and field experiments, which significantly improves our understanding of the heterogeneous chemistry as it relates to the atmospheric chemistry of bromine compounds and to the oxidising capacity of the troposphere. The analysis shows that revised kinetics of the aqueous phase HOBr + X- reaction that includes acid saturation effects indicates cur-

rent numerical models substantially overestimate the rate of HOBr uptake on acidic halogen-rich particles. Scientific quality The paper is comprehensive, extends previous conceptions of the heterogenous chemistry, and reaches important new quantitative conclusions on the kinetics and mechanisms of the reactions, as investigated in laboratory and field experiments. It also discusses the significance of the results for atmospheric chemistry in the marine boundary layer and in volcanic plumes, where halogen chemistry plays an important role. The analysis is thorough and makes good use of existing up-to-date literature on kinetics and thermochemical data pertaining to the gas-aerosol reactions, to obtain fundamental parameters allowing representation in models of the rates of overall chemical processes involving Br- and Cl-containing species in the atmosphere. A weak point in calculating uptake coefficients is the reliance on the accommodation coefficient of 0.6 from Wachsmuth et al. in the analysis. This is a reasonable assumption, as is the reliance on the E-AIM model for electrolyte concentrations in the aerosol. On this basis I recommend publication of the work. Presentation Although the presentation is well structured, mostly clear, it is hardly concise. The abstract contains all the achievements but includes too much detail and hence is inappropriately long. A summary giving the novel mechanistic aspects, the key numerical results and the main conclusions relating to the marine BL chemistry and volcanic would suffice. The structure of the paper is good overall, but the arguments tend to be obscured by too many caveats and too much repetition. This makes the paper more like a tutorial and could be improved by simplification and less qualification of the important points and conclusions. Personally I prefer use of the passive tense rather than the use of active first person for general description. The background material in the introduction (section 2) and the methodology (section 3) seems to be up-to-date and error free. I particularly like the use of the e-AIM model for calculation of aerosol composition, crucial for quantifying the rate of uptake controlled by reaction of HOBr in solutions containing X- ion. Both these sections which are based on material in contemporary literature, could be presented more concisely, with emphasis on details which are specific to the present study. In section 4 the results of the kinetic analysis are presented. In section 4.1 the key equations are (11) and (15)-(18). The derivation could be omitted in the main text – case for supplementary material. In section 4.4 the explanation of the discrepancy between the earlier results for gamma(HOBr) is dealt with. The reconciliation is not perfect but considering the assumptions and uncertainty in both studies the results are convincing. However the argument is hard to pull together because of repetition (eg on p2742 to p2743) and qualification (p2744) – could be improved. In section 5 - atmospheric implications – Generally the material demonstrates new information regarding the release of BrOx in marine BL and Volcanic plume environment. The conclusions drawn are reasonable. However the text contains superfluous material (eg l. 16 – l.18, p 2747; l.14 – l.19, p 2748). ; l.7 – l.12, p 2750), and would benefit from emphasizing the key conclusions

Queries and Corrections p. 2734 l.6 in conventional kinetics jargon equation 12 results from steady state for [HOBrX-] in eq 11 not equilibrium p. 2736 l.4: a definition of relative stability constants' would be helpful here p. 2738 l.13 and l.19: units of k0 should be s-1, not M-1s-1; R19 is first order! p. 2741 l.22 and p2742 l.8 harmonise assumed radius and diameter for these particles p.2744 l.8 - 9:|Do you mean 'an HOBr diffusion coefficient'? If so give units (cm2s-1 I presume)

Comments on Figures Figure 1: annotation of Br- and Cl- together with more contrasting color distinction would make clearer; Figure 2: Graphs are too small for easy registration of content Figure 3 Dotted line too faint; caption too long – move some of comment material into main text (eg last sentence) Figure 4. Needs clear labelling of C- data and Br- data on figure; misspelt 'grey' on line 2 of caption. Graphs would be clearer if bigger Figure 5. Graphs altogether too small; cannot see lines, colours, labels or axis numerals! Figure 6. Graphs altogether too small; cannot see lines, labels or axis numerals; 4 graphs of larger size would be sufficient to give the message.

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