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Atmospheric
Chemistry
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Discussions

Interactive comment on "Uptake and reaction of HOBr on frozen and dry NaCl / NaBr surfaces between 253 and 233 K" *by* J. W. Adams et al.

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This paper gives interesting new insights into the kinetics and mechanisms of the reactivity of HOBr with surfaces of relevance to the arctic troposphere. It nicely adds to the surprisingly low number of laboratory studies in this field, even though the issue of the low ozone events in the polar boundary layer has received substantial attention in the recent years. This study addresses ice surfaces containing sea salt components and is motivated by the notion (supported by field observations) that these sea salt rich ices are more likely to be the source of photolabile bromine than the relatively low mass of sea salt aerosol, especially in absence of an acidifying process under clean conditions. The frozen salt surfaces used in these experiments were meant to mimic such ices. The results obtained clearly illustrate the effect of the surface on the rate of the reactions involved and also on the overall yield of products to the gas-phase.

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Overall, the paper is well written, the results are clearly presented and discussed, and therefore I would recommend it for publication in ACP, once a few further issues are addressed, which are detailed below.

General comments

The reader might wish to know more about the detailed nature of these "frozen salt surfaces". Once it is mentioned that the phase diagram indicates a water ice phase and a chloride/bromide mixed phase. This would mean that the surface is quite heterogeneous in composition, but on what spatial scale? Could an inspection with an electron microscope, or even an optical microscope, help to identify the relevant scales? For instance it is difficult to estimate the amount of chloride or bromide exposed to the gas-phase as long as nothing is known about how these phases arrange in bulk and at the surface. An additional point is the few experiments where the pH of the solutions before freezing was varied. Is it known what happens with the excess protons after freezing, ev sitting within grain boundaries (surface or bulk) in an extremely acidic environment? These issues are all strongly linked to the way these "frozen salt films" grow, and there is also some chance that some key property is significantly different in the real environment.

The kinetics of the reactions going on was simply discussed in terms of the uptake coefficient. However, without an appropriate parameterisation of the processes beyond uptake it might be difficult to compare uptake coefficients with those obtained in other studies. The concentration dependence addressed in the text is only one example. I know well that a parameterisation for such a complex system is not available, but the transfer of the numbers obtained to the modelling community should occur with some caveats in the discussion.

Specific comments

Section 2.2

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p6: For the sake of completeness it might be useful to tell more (than simply a reference) about the detection and calibration of HOBr, as the quantitative relation between HOBr loss and products formed is an important point in this study.

p6: What was the pH of the bromide /chloride solutions? Were they prepared with degassed water? this might be different to sea-water.

section 3.1

p8: equation (iii): no reference is given for this formula

p8: paragraph below: what would be the theoretical estimates be for the diffusion coefficients determined experimentally?

section 3.2

p10: A relation between the amount of HOBr dosed to the surface and the surface area should be given, maybe that is giving an estimate of surface bromide available for reaction.

p11: It was not clear to me why at low HOBr concentration, the BrCl yield was 0.5, so if possible, this could be clarified here. Also what the consequence of the $>$100s response time precisely is (forming a reactant reservoir, probably related to the above), how much does the HOBr coverage increase within this time?

p12: reactions (4) and (5): Often this mechanism is written as third order reaction with the protons as third partner. Preceding sentence: Chloride and bromide are stated as "on the surface": what could that mean more precisely?

p13: same paragraph: the enhanced surface concentration of bromide within solid NaBr/NaCl crystals is not a solubility effect but a solid state segregation, and might lead to enhanced bromide in all individual salt crystals at the surface.

section 3.7

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p22: I think this study does not tell whether the mechanism is driven by protons or not. So it might well be necessary to provide acidity also to the frozen sea salt for efficient bromine activation?

Technical comments

Is the numbering of equations according to the journals format ?

p14: 3rd line: typo: "at a pH greater than about 7"

p13: first paragraph: typo: "an indirect mechanism via formation of"

p13: last paragraph: typos: "considerably rougher than" and "less porous than those"

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 109, 2002.

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