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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.

J. W. Adams et al.

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General comment 1: As the referee already indicates in his comment, this study does not include experimental (spectroscopic or microscopic) investigations of the surfaces involved, but concentrates on the changes in gas-phase composition that occur upon exposure to HOBr. We concede that surface sensitive measurements would have been desirable, but note that the ice surfaces we used were designed not only to mimic those found in the polar ice pack, but were of systematically varied composition, temperature and pH that enabled certain fundamental aspects of the uptake and reaction to be examined under laboratory conditions. A new section, in which we make a coarse estimate of the number of reactive sites per area of frozen substrate will be added to the revised manuscript. Frozen surfaces formed by the relatively slow freezing of aqueous solutions of similar chloride / bromide ratio as found in sea water are not expected to be vastly dissimilar in surface chloride / bromide /

H^+ concentrations to those formed on the ice-pack, and should provide a reasonable basis for atmospheric modelling of the chemistry taking place on such surfaces.

General Comment 2: The uptake coefficient provides an overall measure of the efficiency of removal of HOBr from the gas-phase. As the referee states, this comprises various elements including rate of reaction at the surface, which will depend on the (unknown) concentration of surface reactants, and (unknown) rate coefficients. However, as we indicate in the discussion, the rate of reaction of HOBr with frozen sea-salt on the polar ice pack will most likely be limited by its deposition velocity rather than any physico-chemical parameters that influence reaction at the surface.

Specific Comments:

p6 (now 114). The calibration of the HOBr signal is performed by assuming 100 % yield of Br_2 in the reaction of HOBr with aqueous, acidified, bromide containing surfaces. The validity of this assumption was tested in the Fickert et al. paper that is cited, and is supported by observations of HOBr to Br_2 conversion on dry bromide salts that are also cited by Fickert et al. Some text describing this will be added to the revised manuscript.

p6 (now 114). The bromide /chloride solutions were prepared from de-ionised (but not degassed) water. The pH of the un-buffered, non-acidified solution was $\sim$ 5.5. This will be mentioned in the revised version of the manuscript.

p8 (now 116). The relevant literature (Hanson et al., 1992) will be cited in the revised version of the manuscript.

p8 (now 116). Theoretical values for the diffusion coefficient of HOBr in bath gases have been calculated using average collision diameters and Lennard-Jones potentials (Wachsmuth et al., 2002) and have been found to agree with our previous experimental determination. This will be mentioned in the revised version.

p10 (now 118). A coarse estimate of the capacity of the surface to remove HOBr can be derived from the data in e.g. Figures 3 and 4. In Figure 4, (NaCl = 2M, NaBr = 3×10^{-4}M), during the exposure phase (t $\sim$ 450 -1500 s) approximately 1×10^{16} HOBr have been lost from the gas-phase due to contact with $\sim$ 80 cm^2 of the frozen surface, yielding a lower limit to the capacity of the frozen surface to remove HOBr of 1×10^{14} per cm^2. In contrast, in Figure 3a (NaCl = 2M, NaBr = $3 \times 10^{-3} M) \sim 5 \times 10^{14}$ HOBr are taken up per cm^2 (and converted to Br_2) with no significant change in the rate of reaction over the exposure period. Again, this is different to the result in 3b in which much higher fluxes of HOBr to the same surface result in a deactivation of the surface after just 50 s in which $\sim 1.5 \times 10^{14}$ HOBr were taken up. This indicates that the capacity of the surface to support reaction can depend on the concentration of HOBr and the rate of reactivation, perhaps due to surface reorganisation. Note that reactivation of the surfaces, which are quite dynamic at these temperatures, has previously been documented in studies of HOI and $IONO_2$ uptake (Holmes et al., 2001). Some text will be added to the revised version to include this.

p11 (now 119). The less than unity yield of gas-phase BrCl per gas-phase HOBr taken up in experiments on frozen surfaces made from chloride containing solutions is taken to indicate that HOBr can be physi-absorbed to some non-reactive surface sites. Evidence for this is provided in the experiments with dry surfaces, in which HOBr was seen to desorb from the surface when the injector was re-inserted (see Figure 8 and text in section 3.5). Again the yield of BrCl was significantly less than unity. Some text will be added to the revised version to include this.

p12 (now 119). The reason for not including protons in reactions (4) and (5) is apparent when we later discuss the results at pH 10, where average H^+ concentrations are very low yet the results we obtained are the same as those obtained at pH = 4. The term "on the surface" refers to the location of the reaction between HOBr and halide ions. "we expect HOBr to react on the surface with either Cl^- or Br^-" is grammatically more precise, and shall be used in the revised version.

p13 (now 120). In the experimental study of Zangmeister et al. (2001), the measured surface enhancement in the Br^- to Cl^- ratio in mixed crystals formed from aqueous solutions is attributed to the factor 2.5 greater solubility of Br^- compared to Cl^-.

p22 (now 128). We present data that show that variation of the pH (of the aqueous solution) between 4 and 10 had no significant influence on the efficiency of the reaction, or on the yield or identity of the products. If the surface reactions are pH driven, it is difficult to understand how variation of the H^+ concentration by six orders of magnitude could have no measurable effect on either product yield or uptake coefficient. Note also that the amount of HOBr converted to Br_2 (or BrCl) exceeds the initial concentration of protons in the entire ice film by several orders of magnitude at high pH. Additional text will be added to the revised manuscript to clarify this.

typos on pages 14 (now 121), 13 now (120). Page 121, "greater THAT", replaced with "greater THAN". Page 120, "IN via formation" replaced with "via formation".

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