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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Introducing the bromide/alkalinity ratio for a follow-up discussion on "Precipitation of salts in freezing seawater and ozone depletion events: a status report", by Morin et al., published in Atmos. Chem. Phys., 8, 7317–7324, 2008" *by* R. Sander and S. Morin

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I thank the authors for their response. On the way the problem is phrased, I think we understand each other and the authors can consider this if they choose to submit a revised manuscript.

However, I still don't really follow the argument about the ratio of bromide/alkalinity. Firstly, I am not convinced it is helpful to translate the values in the brine into concen-

trations in the atmosphere in considering this problem. The reaction we are interested in occurs in the brine; furthermore the volume of air containing the BrO product is not the same as the volume from which the acid has to come (nor is the timescale the same); finally the acidity does not come only from the gas phase but also from aerosol.

I think of it a different way. Again the relevant reaction is:

HOBr + Br− + H+ -> H2O + Br2

which occurs in the brine, with Br2 subsequently released to the gas phase. The instantaneous reaction rate is of course proportional to [Br-]*[H+] in the brine phase. And although it's not exact, I agree that alkalinity is related to 1/[H+], thus with quite a major approximation, the instantaneous reaction rate is proportional to [Br-]/[alkalinity]. However this alkalinity is not the initial alkalinity in the cold brine but the time varying (reducing) alkalinity as acid arrives from the atmosphere. At first the alkalinity is high and the reaction rate is very low indeed, almost no Br2 is produced and almost no BrO has accumulated. If the acidity comes in from the atmosphere, then the alkalinity reduces and the reaction gets going. But now the alkalinity in the rate equation is not the one that was calculated in the thermodynamic calculations in the Morin paper. To my mind, the alkalinity determines the time it takes for the acidity to neutralise it, and therefore for the reaction to start: but the bromide concentration plays no role in this. Once the reaction starts seriously, then the Br- concentration is important, but the initial alkalinity is now forgotten. Thus I still cannot see any point in the process at which the ratio of bromide to initial alkalinity (as determined in the Morin paper) is a parameter of interest to the eventual production of BrO. No doubt we will have another round of explanation!

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