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Atmospheric
Chemistry
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Discussions

Interactive comment on “Uptake study of $ClONO_2$ and $BrONO_2$ by water droplets” *by* G. Deiber et al.

Anonymous Referee #1

Received and published: 10 March 2004

This is an experimental study of reactions that are of potential interest for the halogen budget of the marine boundary layer. They are the first experiments on the uptake and reaction of $ClONO_2$ and $BrONO_2$ with halide solutions. The experimental data looks to be of good quality, though limited in scope.

Unfortunately, the data is presented in a very sloppy manner. The authors appear to be reluctant to be quantitative, and do not calculate or use errors properly. The impact of this study is severely diminished by the fact that the authors did not conduct experiments using salt solutions with mixed chlorine and bromine content. The gas phase products leaving the droplets after $ClONO_2$ or $BrONO_2$ have been taken up depend on the relative concentration of bromine and chloride. This study does not provide this information. The data set deserves better interpretation and more thought invested than the authors have done so far. Major revision is necessary. See below:

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Title:

Why are halide solutions not mentioned in the title. Most experiments appear to have been conducted on halide solutions, not water droplets.

Abstract.

The 1 % statistical errors given for α-$ClONO_2$ are wrong (see later)

Page 1313, Line 14 and equations (2) and (3)

"all these compounds are then rapidly photolysed" This is rather ambiguous. In which phase are these species, aqueous- or gas-phase ? Do the authors include the nitrates in this statement or are they referring only to the di-halogens ? Are they photolysed in the aqueous-phase, or are they transferred to the gas-phase beforehand ? Clarify and expand the text.

Page 1313, Line 22 (also 1314, Line 1) and Page 1322 Line 4

What exactly is solid NaCl and NaBr. Are these experiments on single crystal surfaces, or powder samples. What was the relative humidity. Describe the salt surfaces with which you compare your results more thoroughly.

Page 1314, Line 5

[For $BrONO_2$] "the reaction may not be as simple as the one depicted by reactions (2) and (3)." This is certainly true as reactions (2) and (3) do not contain any bromine nitrate at all ! The equivalent reactions for bromine nitrate should be added.

Page 1314, Line 7

What does "eventually" mean here ? "inevitably" or "usually" or "maybe" ? "one may argue that a significant fraction of sea-salt aerosols are wet". Rather than giving such qualitative statements why not be quantitative and say what the typical RH is in the MBL, and compare this to the deliquescence point of sea-salt particles is.

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Page 1316, Line 16-27.

Only qualitative information about the detection systems is given. What were the detection limits. What concentrations were used ? What molecules were detected with which system ?

Page 1318, Line 3

Why cite Caloz 1997 here. Was this the first time $ClONO_2$ was made by this reaction ?

P1318, equation (8)

The terms γ(diff), γ(sat) and γ(rxn) are not defined. In the part of the equation in parentheses: Should the "root" symbol not include the "t" ?

Page 1319, Line 27-28

"The measured kinetic is not elementary kinetic" Perhaps "the measured rate of loss of $ClONO_2$ is driven by several..... would be better.

Page 1320, equation (9)

The reaction does not balance. Na should be H

Page 1320, Line 14

"we did not observe any increase of the uptake coefficient when adding NaCl to the droplets, but we observed some Cl_2 production." Once again, this needs to be quantitative: how much NaCl was added ? (presumably to an aqueous sample that was used to generate the droplets, and not to the droplets themselves): How much Cl_2 was formed ?

Page 1320, Line 19

As the authors mention in the next line, this reaction involves H^+ in the aqueous phase, i.e. $HOCl + H^+ + Cl^- = Cl_2 + H_2O$. i.e. the rate of Cl_2 production depends both on H^+ and Cl^-. If the authors wish to claim that the HOCl itself is the source of H^+, then the dependence of the Cl_2 production rate will be very non-linear in HOCl or $ClONO_2$. Was this observed ? Exactly how is this self-acidification mechanism proposed to operate? In what form is HOCl in aqueous solution at high pH (i.e. what is the pKa ?) Aqueous-phase studies show that the yield of Cl_2 must depend on pH. As this is an important parameter, why did the authors not make a systematic investigation of pH ?

The authors might consider the other product of the $ClONO_2$ hydrolysis, which is HNO_3. Could this provide the acidity ? If so, what are the characteristic times for reaction versus diffusion out of the droplet for HOCl ? Some quantitative discussion is necessary here.!

In the same context: "dissociation of HOCl at the surface may affect the surface pH because this region is very narrow". What region are the authors referring to ? Presumably the region close to the surface, in which the reaction takes place and which is defined by the diffuso-reactive length ? Could the authors please state what "very narrow" means in more quantitative terms. There are kinetic data describing the aqueous phase reaction of HOCl with Cl^- that enable calculation of this length.

Page 1320, Line 26

How much HOCl are "traces" of HOCl present in the $ClONO_2$ source ? Can you at least make en estimate based on the relative strengths of mass spectrometer signals.

Page 1322, Line 4

A glance at the data in Figure 3 shows that the error limits on alpha are underestimated. Based on the data in Table 1, I got errors of close to 10 % in the intercept (without weighting), and slightly smaller with weighting. In addition, the data point at 1 M NaBr (Figure 3) is missing from the Table. The authors state that the errors presented are statistical only, and do not include systematic errors. As they quote exactly the same number and error in the abstract, they clearly do not believe that they have any systematic errors, or do not care to think about them. This is sloppy, and especially regrettable when comparisons are made with other datasets. On line 17 they state that a value of 0.23 is consistent with their value of 0.1. How can this be consistent when neither value appear to have any associated errors ?

Is the value obtained for alpha consistent with expectations of the uptake coefficient to an aqueous surface. What is the corresponding value for H_2SO_4 ?

Page 1323, Line 1-6

"The above set of reactions fully explains the observed trends in reaction products" This is a purely qualitative statement, showing that the authors have found some reactions that are known to generate the same products as they observe. The "fully explains" is rather optimistic. These equations certainly do not quantitatively explain why Cl2 is the dominant product as it appears to be from Figure 4. This would imply that the rate of release of BrCl from the droplet is much smaller that its rate of reaction with Br^-. This will be dependent on the concentration of Br^-, which was varied. Do the authors see a dependence on the yield of BrCl and thus also Cl_2 on the concentration of Br^- ? I do not see why the fact that Aguzzi and Rossi observe BrCl from the reaction of $ClONO_2$ with KBr provides any confirmation of the present results (line 10).

The Figures 4 and 6 have y-axes that are scaled with "arbitrary units". Does this imply that the authors have made no attempt to calibrate the sensitivity of their detectors. Surely this has to be done for species such as Cl_2 and BrCl and Br_2.

Page 1323, Line 20

"HOBr might be more soluble than HOCl". Might it also be less soluble ? What is the purpose of this statement ?

Page 1324, Line 15

The reaction between $BrONO_2$ and NaCl is said to proceed via initial HOBr formation, followed by the reaction between HOBr and NaCl to form BrCl, which is however acid catalyzed (see comment for $ClONO_2$). It has been shown that the BrCl product is only

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formed at low pH. The same arguments apply as for HOCl. Why does this reaction proceed in the present experiments ?. It would have been useful to conduct experiments at different pH to test for changes in the yields of e.g. BrCl. Can the authors really rule out that there is a direct (but not rate limiting) reaction between $BrONO_2$ and NaBr ? This may have important repercussions (see Sander, Geophys. Res. Lett. 26, 2857 (1999).

Page 1325, Line 9

The accommodation coefficient of $BrONO_2$ on these aqueous surfaces appears to be lower than the uptake coefficient on aqueous sulfuric acid surfaces (values as high as 0.8 have been measured) and also with uptake to "dry" NaCl or NaBr (Line 20). This would appear to be counter-intuitive. Could the authors speculate some more about this. The sentence "...this could be linked to the nature of their solid surfaces and of its water content....." is inadequate.

P1328, Line 3,4

The reference to the work of Sander appears to be incomplete

P1328, Line 3,4

The reference to the work of Timonen et al. contains chemical formula which require attention.

P1328, Line 3,4

The first author is Wingenter not Wingetener. Also, I do not understand why this reference is used on page 1313, Line 24 as a citation for Knudsen reactor work.

Figures 3 and 7 contain information not only about the accommodation coefficient, but also about lifetimes of $ClONO_2$ and $BrONO_2$ in halide solutions. Could the authors not use this data to provide a more quantitative description of reactions of $ClONO_2$ and $BrONO_2$ in sea-salt. Will these molecules react with Br- in real sea-salt, or will reaction be dominated by Cl^- ?

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 1311, 2004.

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