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

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Uptake study of ClONO2 and BrONO2 by halide containing droplets

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Authors comments to Anonymous Referee #2

We thank the referee for his very detailed comments.

As our data are of potential interest for the halogen budget of the marine boundary layer and because these are the first experiments on the uptake and reaction of ClONO2 and BrONO2 with halide solutions, we prepared a revised version of our manuscript in which we took into accounts all comments made by referee #2.

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We hope that this revised will be accepted in ACP.

Below, is our point per point response to the comments made by referee #2. For this purpose, for each, we first list the criticism of the reviewer followed by our response (in red).

1319/26 to 1320/2: The measured kinetics is not elementary but is driven by several physical and chemical processes that have different temperature trends. The authors do not present any data that support this claim. Figure 2 presents three points over a T range of 11K which is totally insufficient to claim the above. This is mere speculation that does not belong here.

Following this remark, the text has been modified: "The temperature range which can be used with the droplet train technique is limited by several factors i.e., the properties of water and the practical design of the flowtube used during the experiments. For the current experiments, the temperature was ranging between 274 and 285 K. This is a rather narrow range which of course prevents us from any definite conclusion about temperature trends over a wider temperature range. Nevertheless, the absence (or the limited) temperature effects just illustrates the point that the measured rate of loss of ClONO2 is driven by several physical and chemical processes that may have different temperature trends. In fact, the solubility of gases increases when the temperature decreases while the chemical reactivity decreases at the same time. Even over our narrow temperature range, both the Henry's law constant and rate constant would vary sufficiently to show some temperature variations. This was not the case which is certainly an indication that the various processes are acting with the same intensity but with different temperature trends."

1320/13: The inability of the authors to observe any increase of the uptake coefficient upon adding NaCl may in fact partially have to do with the insufficient concentration of NaCl (0.1M) and/or the limited accuracy of the measurement method. It is a pity that no experiments at high [NaCl] were performed.

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Although the droplet train technique is a powerful tool to study uptake rates, its use is limited by the properties of water (freezing temperature) and the practical design of the flowtube. For exemple, high concentrations of NaCl cannot be used in our current droplet generation system because of a lack of stability in the vibrating orifice. This effect is unfortunately more pronounced for NaCl than for the other salts.

In any case, this result does NOT WARRANT the conclusion that the mechanism goes stepwise, although it is consistent with it. The only way to assert this conclusion would be to perform realtime measurements (akin to flash photolysis, relaxation or pulsed admission experiments). The present droplet experiment is a steady-state experiment and is unable to distinguish between a direct (one-step) and a sequential (two step) mechanism.

A discussion has been added to clarify our sayings: On the one hand, theoretical investigations showed that the energy barrier for the hydrolysis of ClONO2 is more than a factor of 2 lower than that of the direct reaction with Cl- : 3 kcal/mol compared to 6.4 kcal/mol, respectively. This has of course very strong impacts on the associated rate constants. On the other hand, the direct reaction of Cl- with ClONO2 has to occur on the positively charged Cl atom in ClONO2 which is favoured by a very acidic medium (as encountered in concentrated HCl / H2SO4 mixtures) or on an ice lattice, because it enhances the electropositive character of Cl and hinders hydrolysis. Such a specific environment is not present and the hydrolysis is therefore a major pathway compared to the direct reaction. Also the fact that we could not observe any increase in the uptake rate could be attributed to the concentration we used. In the real marine environment, concentrations as high as approximately 6M in NaCl can be observed for deliquescent sea-salt particle. However such high concentrations cannot be used in our current droplet generation system because of a lack of stability in the vibrating orifice. This effect is more pronounced for NaCl than for the other salts we studied. We therefore had to restrict somehow the concentrations used when doping the droplets with NaCl. Nevertheless, we are confident that our speculation on the direct reaction being a mi-

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nor pathway can be extrapolated to real environmental conditions due to the following reasons. First of all, in order to effectively compete with hydrolysis, the direct reaction has to be very fast which is not supported by the differences of the energy barriers for hydrolysis and direct reaction. Secondly, it has been shown for nitryl chloride that the reaction of Br- proceeds much faster and through a different mechanism than for Cl-. In fact, the direct nucleophilic attack of Cl- on the positively charged Cl atoms in ClNO2 was not observed compared to the uptake on bromide containing solutions. This is highly analogous to the observations made here. As both Cl- reactions on ClNO2 and ClONO2 would involve the same mechanism (SN2 substitution), we conclude that both species behave similarly toward the direct pathway which is a minor pathway as long as the hydrolysis is not suppressed (as it is the case on ice). As a consequence, we believe that our observations, despite being made under a limited range of conditions, can be extrapolated to the real marine environment up to deliquescent particles. Therefore, the direct nucleophic attack is expected to be a minor pathway compared to the hydrolysis. Rather, we suggest a two-step mechanism where ClONO2 is first hydrolyzed according to reaction (9) to produce HOCl which subsequently reacts with NaCl according to: HOCl + Cl- +H+ -$>$ Cl2 + H2O (11) In this case, the uptake rate is governed by the hydrolysis rate. Reaction (11) is known to be facilitated under acidic conditions (pH $<$ 4 i.e., at pH higher than those required to facilitate the hydrolysis) which may occur in our experiments for several reasons. It must be first underlined that in the droplet train technique, the reactions are taking place over short time scales (less than about 20 ms). Under such conditions, the in-coming gas cannot diffuse deeply into the droplet and the reactions are confined in a very narrow shell close to the droplet surface, at the μm level as defined by the diffuse-reactive length. This has strong impacts on the evolution of the pH at the "interface" which will be the driving force for the production of Cl2. This also introduces some restrictions in our ability to study these reactions at various pH due to the current limitations of our detection scheme. Under these conditions, the pH at the surface will be affected by HNO3 which is a product of the hydrolysis of ClONO2. In addition, even at low gas reactant concentration, the impurities present in our gas flows will affect the surface pH, as traces of HNO3 in ClONO2 are unavoidable. To minimize the influence of the impurities (less than a few % of the ClONO2 concentration), our experiments were conducted under acidic conditions (pH č 4). These observations do not allow us to convert the Cl2 production into a quantitative information as it is due to a complex reaction mechanism. Therefore this Cl2 production exhibits a highly non-linear behaviour on the experimental conditions and cannot be transposed directly into other conditions. However, this expected Cl2 generation is not a direct outcome of this study. More interestingly is the evidence that this production is due to a complex reaction mechanism rather than a direct reaction of Cl- with ClONO2.

In this study we measured for the first time, the uptake rate of both ClONO2 and BrONO2 on aqueous droplets containing either chloride or bromide anions. Simultaneously to the observation of the loss of these compounds from the gas phase, we observed the appearance of some products i.e., Cl2, Br2 and BrCl (as expected). However, we can not report any quantitative yields for these products for several reasons which are all linked to the complexity of the chemistry associated with these halogenated species. In fact, in a gas phase containing all these compounds (either as impurities or reaction products), the following (but still incomplete) reaction mechanism is occurring:

HOBr <-> H+ + Br-;

HOCl <-> H+ + Cl-;

BrCl + Br- <-> Br2Cl- ;

BrCl + Cl- <-> BrCl2- ;

Br2 + Cl- <-> Br2Cl-;

Cl2 + Br- <-> BrCl2-;

Cl- + HOCl + H+ -> Cl2 + H2O;

Br- + HOCl + H+ -> BrCl + H2O ;

Cl- + HOBr + H+ -> BrCl + H2O ;

Cl2 + H2O -> HOCl + Cl- + H+ ;

Br2 + H2O -> HOBr + Br- + H+ ;

BrCl + H2O -> HOBr + Cl- + H+ ;

This sequence of reactions (along with the others reactions listed in the text) highlights the very strong interplay between all halogenated species in the aqueous phase and the crucial role played by H+ ions. Characterising individual steps and therefore providing meaningful product yields, that can be transposed into real conditions, is far beyond the capabilities of the droplet train technique. On the same basis, working with mixed chloride Ű bromide solutions is probably useless since the product yields would have highly non linear response to the experimental conditions. However, despite the fact that our study cannot provide more insights into the chemistry occurring in the aqueous phase, subsequently to the uptake of ClONO2 and BrONO2, the droplet train technique provides a reliable approach for studying the gas phase loss rates and the associated uptake rates. Our results show that as long as the hydrolysis of ClONO2 and BrONO2 is not suppressed, only bromide can react directly with these compounds due to its higher nucleophilicity compared to chloride.

In addition, it not clear how the surface acidity will be affected by the dissolution of HOCl as it is a weak acid. What is its pKa? It may be pointed out that the reaction of ClONO2 with HCl on ice is a direct (elementary) reaction, whereas BrONO2 + HCl or HBr is not and goes through prior hydrolysis.

Reaction (11) and the text have been modified: "Rather, we suggest a two-step mechanism where ClONO2 is first hydrolyzed according to reaction (9) to produce HOCl which subsequently reacts with NaCl according to: HOCl + Cl- +H+ -> Cl2 + H2O (11) In this case, the uptake rate is governed by the hydrolysis rate. Reaction (11) is known to be facilitated under acidic conditions (pH $<$ 4 i.e., at pH higher than those required to facilitate the hydrolysis) which may occur in our experiments for several reasons. It must be first underlined that in the droplet train technique, the reactions are taking place over short time scales (less than about 20 ms). Under such conditions, the in-coming gas cannot diffuse deeply into the droplet and the reactions are confined in a very narrow shell close to the droplet surface, at the μm level as defined by the diffuse-reactive length. This has strong impacts on the evolution of the pH at the "interface" which will be the driving force for the production of Cl2. This also introduces some restrictions in our ability to study these reactions at various pH due to the current limitations of our detection scheme. Under these conditions, the pH at the surface will be affected by HNO3 which is a product of the hydrolysis of ClONO2. In addition, even at low gas reactant concentration, the impurities present in our gas flows will affect the surface pH, as traces of HNO3 in ClONO2 are unavoidable. To minimize the influence of the impurities (less than a few % of the ClONO2 concentration), our experiments were conducted under acidic conditions (pH č 4). These observations do not allow us to convert the Cl2 production into a quantitative information as it is due to a complex reaction mechanism. Therefore this Cl2 production exhibits a highly non-linear behaviour on the experimental conditions and cannot be transposed directly into other conditions. However, this expected Cl2 generation is not a direct outcome of this study. More interestingly is the evidence that this production is due to a complex reaction mechanism rather than a direct reaction of Cl- with ClONO2."

1320/26: ÿtraces of HOClĚ There a semi quantitative estimate of the HOCl impurity in ClONO2 is imperative in order to support the statement: How can traces of HOCl lead to significant Cl2 formation?

The text was modified: "We observed indeed Cl2 as a unique product. Similar observations have already been made by Timonen et al. (1994) or Aguzzi and Rossi (1999) on solid NaCl. However, we have to underline that traces of HOCl in the ClONO2 source may significantly contribute to Cl2 formation (reaction 11). We did not observe any

HOCl in our ClONO2 source. However if HOCl was present, even at concentrations below our detection limit, its presence may drastically change the quantitative conclusion about the Cl2 yield. Such an observation prevents us from giving any quantitative assessment on the amount of Cl2 formed by reaction 10."

1321/3-15: Gebel et al. observe the formation of HOCl, Caloz et al. do not! Both groups are using the Knudsen reactor technique. My suspicion is that Gebel et al. saw HOCl resulting from wall-catalyzed hydrolysis at short reaction times whereas Caloz did not observe HOCl at even shorter reaction times (pulsed admission technique). The latter study also provides for a mass balance of 100% Cl2 that does not leave room for significant amounts of HOCl.

Reference to work of Caloz et al. was added as follows: "It must however be underlined, that Caloz et al. (1996) did not observe any HOCl formation but a 100% yield of Cl2, despite using also a Knudsen cell reactor. This difference may highlight the crucial role played by adsorbed water and by the corresponding ionic environment offered to in-coming ClONO2 which may affect the importance of the hydrolysis."

1322/3-7: The error bar for the mass accommodation coefficient "alpha" must be similar to the uncertainty of the point closest to the origin of Figure 3. This leads to an upper and lower limit for "alpha" of 0.20 and 0.07, respectively, leading to a factor of three uncertainty in "alpha". Do the authors really suspect "alpha" to change significantly over a six degree temperature range?

The evaluation of errors has been revised (this appears in the abstract and in the text, p 12 and 15 of the present version). They correspond now to 2s + 20% (systematic errors).

1322/20-25: Is there any chance of calibration of the Cl2, Br2 and BrCl MS signal? Without a calibration the discussion of the mechanism which admittedly is the charted way the authors wanted to go remains inconclusive. The Cl2 product should be formed at a later stage because it is a ŞlateŤ secondary reaction product according to reaction

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(17). Figure 4 conveys this feature as the Cl2 signal increases with time, that is the number of exposures of ClONO2 to NaBr solution. A little bit more effort would have brought a lot more insight and certainty!

Such information is far beyond the capacity of the droplet train technique. In fact, the only quantitative information we can deliver concern the uptake coefficients., We can however, from our experimental results, discuss in a qualitative way a few aspects of the chemistry of both ClONO2 and BrONO2. We have tried in the revised manuscript to make a more distinct difference between both quantitative and qualitative aspects of our study. Both analytical devices were operated in uncalibrated mode as only the relative decay of the gas phase reactants has to be known in order to derive uptake coefficients. However, the linear response of the detector was routinely verified. For halogen containing compounds the masses were unambiguous markers for the gas phase reactants and were associated with detection limits of the order of 1012 molecule cm-3. The gas phase concentrations were estimated to range from 1013 to 1015 molecule cm-3.

1323/15-25: The positive T-dependence of the uptake coefficient of BrONO2 on pure H2O, NaCl and NaBr solutions is indeed noteworthy as displayed in Figure 5 despite the very small T-range of 8K which normally prohibits every serious kineticist to draw any firm conclusions.

Although the droplet train technique is a powerful tool to study uptake rates, its use is limited by the properties of water (freezing temperature) and the practical design of the flowtube. The temperature range (273 - 285 K) is rather narrow and prevents us from any definite conclusion about temperature trends over a wider temperature range.

The argument of the coincidence of the pure H2O and NaCl solution results for ClONO2 have been taken as evidence for a two-step hydrolysis-halogen exchange reaction, thus hydrolysis (reaction (9)) is not the rate-limiting step compared to the halogen-exchange reaction (10). For BrONO2 the experimental results are the same (Figure

5, see the two NaCl-solution points that coincide with the pure water results). However, the authors claim in this case that the hydrolysis, reaction (18), is rate-controlling and therefore the slow step because of the positive T-dependence, that is the presence of an activation energy. This is inconsistent and seems contradictory. In both cases the addition of NaCl to water droplets does not change the uptake coefficient "gamma" of ClONO2 and BrONO2, respectively. However, the authors seem to claim rapid hydrolysis, reaction (9) for ClONO2, and slow (compared to ClONO2) hydrolysis for BrONO2, reaction (18). The authors do not make a clear distinction between the concentration and T-dependence of "gamma" when comparing both cases. Please explain as I am unable to understand the given explanation. By the way, the authors may put the guesses at the solubility on a firm basis by using numerical values of Henrys law constants! As alluded to above the authors may be reminded that the hydrolysis of BrONO2 is much faster on ice that is laced with HCl compared to the analogous reaction of ClONO2. Second, the used droplet train technique is unable to distinguish between a rapid sequential hydrolysis/halogen exchange reaction compared with a direct reaction of BrONO + NaBr, reaction (19).

From our understating the main difference between the uptake rate of ClONO2 and BrONO2 may be due to their respectively solubility. In fact, the uptake rate on water for these gases is driven by Hk1/2, where H is the Henry's law constant and k the first order rate constant for the hydrolysis. If the respective ratio between these two parameters is changed, this can introduce an observed different temperature trend. This is what is discussed in the manuscript as:

The uptake of BrONO2 by aqueous droplets was also studied as a function of temperature between 273 and 280 K. However in this case and contrarily to what has been observed with ClONO2, the uptake rate increased with temperature, from 0.024 to 0.039 when T increased from 273 to 280 K as shown in Figure 5. This may just reflect different temperature trends for Henry's law constant and reactivity of ClONO2 compared to BrONO2 and therefore different trends for the products . Basically, we

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would expect BrONO2 to be more soluble than ClONO2, as this is generally the case for brominated and chlorinated species (Br2 is more soluble than Cl2, BrNO2 is more soluble than ClNO2, etc.) (Sander, 1999). The uptake rates g of both components being of the same order of magnitude, one can assume that the hydrolysis of BrONO2 has to proceed at a reduced rate, compared to ClONO2. But in both cases, the hydrolysis governs the uptake rate in water and also Cl- containing droplets. Therefore, the observed temperature dependence of g can be attributed to a higher activation energy for the hydrolysis of BrONO2. Such considerations may indeed explain the difference in temperature trends in the uptake coefficients for BrONO2 and ClONO2.

1324/11: In relation to Figure 6: what does ÿ Şsome BrCl productionŤ ÿmean? Figure 6 conveys the message that BrCl is the main product with Cl2 and Br2 being minor products. Here calibration would indeed be very useful. I think without calibration the authors will be unable to say something definitive about the reaction mechanism. By the way, I cannot see any significant Br2 formation!

The text has been completed: "From our experiments on NaCl doped droplets (figure 6), we saw indeed some BrCl production. However, due to the high complexity of the reaction scheme (see below) we can not assess any quantitative yields as those are far from being accessible with the uptake rate measurements. However, as the kinetic is not affected by the presence of NaCl, and as BrCl is formed as a new product, we suggest again a two-step reaction i.e., first the hydrolysis of BrONO, producing HOBr (reaction 18) which subsequently reacts with NaCl according to: HOBr + NaCl ő BrCl + NaOH (20)"

1325/2-5: ŞFrom these observations we conclude ŞThere must be a missing argument here! How can the fact that gamma increases with [NaBr] be responsible for the conclusions cited in this sentence?

The uptake rate of BrONO2 was strongly affected by the concentration of NaBr in the droplet (see figure 7). The values of the uptake coefficients g varied from 0.032 to

0.062 when the NaBr concentrations increased from 0.01 to 1 M. suggesting again a direct reaction between BrONO2 and bromide ions. From these observations, we conclude that the uptake process was limited by diffusion in the gas phase and controlled by the reactivity of BrONO2 in the liquid phase. Br2 was the only product observed, according to the following reaction: BrONO2 + NaBr ő Br2 + NaNO3 (21) After correction due to slow diffusion process in the gas phase, the mass accommodation coefficient a was estimated from the intercept of plots of (1/g-1/gdiff) versus (NaBr)-1/2 as depicted in figure 7. The estimated value is 0.063 ś 0.009 at 273 K where again the errors only reflects statistical uncertainties (2s) without any considerations of systematic deviations which can be estimated to 20%. To our knowledge, this is the first reported value for the mass accommodation coefficient of BrONO2 on water surfaces. Concerning the accommodation step, the accommodation coefficient of BrONO2 is lower than ClONO2 one as it was already observed for HBr compared to HCl (where the same trend in solubility would apply). This increase in uptake rate is a clear indication that an additional reaction pathway exists in the case of bromide compared to chloride. As discussed below, a detailed reaction mechanism in the aqueous phase does not provide any pathway producing BrONO2 in the aqueous phase nor the involvement of an equilibrium. Accordingly, any increase in the gas phase loss rate of that compounds can be attributed to a direct reaction on BrONO2 highlighting a sequential reaction pathway. As already performed for ClONO2, we can compare our values with those reported on solid NaCl or NaBr. Aguzzi and Rossi (1999) reported initial uptake coefficients larger than 0.3 and therefore inconsistent with our estimated mass accommodation coefficient. This discrepancy remains unresolved at this time. The uptake coefficient of BrONO2 on sulphuric acid surfaces has also been measured to be relatively large, reaching values of 0.5-0.8 (Hanson et al., 1996). It may therefore be counter intuitive to have an order of magnitude lower values for its uptake on water. To explain this observed trend we can only speculate as there is no other data for the uptake of BrONO2 on water. We can first compare to previous studies on nitryl type compounds. It was shown that the uptake coefficient of ClNO2 on water was larger than that of BrNO2.

As already mentioned we also observed that the mass accommodation coefficient of HBr was smaller than that of HCl (Schweitzer et al., 2000). The data on BrONO2 is therefore following these trends which might be related to the Br atom. Although it is difficult to present any quantitative attempt to explain these observations, we can speculate that they are linked to the ability of Br atoms to interact with water molecules at the interface. It is known that bromide ions (and even more strongly iodide anions) present concentration enhancement at the air/water interface, reflecting their capacity to have non-complete solvation shells at the interface. If we extend these observations to the brominated compounds considered here, we can speculate that only a fraction of the in-coming gas will be fully solvated and therefore counted in the calculation of the mass accommodation coefficient which is the probability for a complete phase transfer. If such a surface storage capacity exist, a lowering of the overall measured uptake rate may result.

1325/15-16: What is Ťthe correction level between 1/alpha and 1/gamma compared to ClONO2Ť ? Please explain.

This sentence has been deleted.

1325/17: ÿ Şless hindered than Ě" Why then is alpha smaller for BrONO2 compared to ClONO2? Please explain. It appears that the authors are confusing thermodynamic with kinetic arguments, i. e. solubility with uptake kinetics of accommodation.

This part of the manuscript was modified: "This increase in uptake rate is a clear indication that an additional reaction pathway exists in the case of bromide compared to chloride. As discussed below, a detailed reaction mechanism in the aqueous phase does not provide any pathway producing BrONO2 in the aqueous phase nor the involvement of an equilibrium. Accordingly, any increase in the gas phase loss rate of that compounds can be attributed to a direct reaction on BrONO2 highlighting a sequential reaction pathway."

1326/8: The Şlatter ąT needs two subjects that are to be compared. What are they?

This part of the sentence was deleted.

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