

## ***Interactive comment on “Uptake study of ClONO<sub>2</sub> and BrONO<sub>2</sub> by water droplets” by G. Deiber et al.***

**J. Crowley (Editor)**

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Following the authors published response to the comments of the two referees, and closing of the discussion, a further comment from referee 2 was obtained. This is published as part of this editorial comment, along with the authors replies:

Referee 2:

On page S1274 the author's claim that the reason for the absence of a measurable temperature dependence of gamma over a 11K temperature interval is proof of a complex mechanism whose individual rate-determining processes have both compensating T-dependences. This by no means constitutes a proof. The reverse might also be true given the extremely narrow T interval of 11K. Remember: experimental results never lead to a unique reaction mechanism, they only refute incorrect reaction mechanisms.

Authors:

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In the original manuscript, we admit we were probably too affirmative. Consequently, the text has been modified to be interpreted more like a possible explanation: 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 ClONO<sub>2</sub> 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 for our measured gamma values, which is probably an indication that the various processes are acting with the same intensity but with different temperature trends-

Referee 2:

From the original text I was not aware of a complicating experimental artifact in conjunction with moderately concentrated NaCl which apparently is not true for concentrated NaBr solutions. What might be the reason for this difference? The authors should honestly point out this difficulty in the text.

Authors:

First, high concentrations of either NaCl or NaBr cannot be used in our current droplet generation system because of a lack of stability in the vibrating orifice. In practice, the maximum is more or less 1M for both salts. If you attentively look at the values in the tables I and II, you will see that even for the lower concentrations of Br<sup>-</sup>, i.e. 0.01 M in our experiments, gamma increases clearly, e.g. gamma increases from 2.4

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(pure water) to 4.1 (0.01 M, NaBr) at 274 K and from 2.4 (pure water) to 3.25 (0.01 M, NaBr) at 273 K for ClONO<sub>2</sub> and BrONO<sub>2</sub>, respectively. This permits us to use Br as scavenger and derive the mass accommodation coefficient. On the other hand, the uptake coefficient did not increase when we replaced water by a solution of NaCl 0.1M, which is already ten times higher than that used for NaBr (see above). As the main objective of this work was to derive the mass accommodation of both ClONO<sub>2</sub> and BrONO<sub>2</sub>, experiments on NaCl solutions (up to 1M) appeared useless.

Referee 2:

On page S1275 a medium effect (strong acids, ice) is invoked to explain the formally positive oxidation state of Cl in ClONO<sub>2</sub>. I cannot follow the authors arguments as I believe that DFT and molecular orbital calculations are both addressing an isolated gas phase molecule and show the same, namely a partial positive charge on the Cl atom counterbalanced by a partial negative charge on N. How can the authors be confident to be able to extrapolate their speculation to real environmental conditions on the basis of what they state?

Authors:

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Referee 2:

To compare the SN<sub>2</sub> reaction of chloride between ClNO<sub>2</sub> and ClONO<sub>2</sub> as the authors do on pg. S1276 is not acceptable. The Cl in ClNO<sub>2</sub> (nitrylchloride) is formally in a (-1) formal oxidation state as ClONO<sub>2</sub> is the formal anhydride of HCl with HONO (IT IS A CHLORIDE! Consider the synthesis of ClNO<sub>2</sub> which involves passing HCl through fuming sulfuric acid!) as opposed to ClONO<sub>2</sub> where Cl is in the (+1) oxidation state. This is the reason that the SN<sub>2</sub> reaction Cl(-) + ClNO<sub>2</sub> is strongly endothermic and does not go to Cl<sub>2</sub> at ambient conditions! I strongly object to the claim that both Cl-reactions are highly analogous or that both species behave similarly toward the direct

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pathway.

Authors:

This part of the manuscript has been removed.

Referee 2:

On page 1277 and the following the authors claim not to be able to evaluate the Cl<sub>2</sub> yield because of complexities of the reaction mechanism. Despite the less than ideal experimental conditions (HNO<sub>3</sub> impurity) the evaluation of the Cl<sub>2</sub> yield will give useful overall information but may not help in the identification of the elementary reactions. The inability to report quantitative yields of reaction products (probable absence of MS signal calibration) has in my view nothing to do with the complexity of the chemistry which is connected to the interpretation of experimental data. I would accept a statement that in view of the preliminary nature of the present experiments no attempt has been made at quantifying the product yields. In this case the title should reflect this.

Authors:

Following the editor's advice, we focused only on the uptake kinetics in this second revised manuscript. Consequently, any detailed concerning reaction mechanism has been removed.

Referee 2:

The last three reactions of Cl<sub>2</sub>, Br<sub>2</sub> and BrCl are slow in aqueous solution (pH=7) compared to the other reactions displayed involving halide ions.

Authors:

This set of reactions has been removed (see above).

Referee 2:

I strongly object to the statement -working with mixed chloride/bromide solutions is

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probably useless-. How can the authors tell if they have not tried? The issue here is the competition between chloride and bromide despite the complexities of the reaction mechanism.

Authors:

In our experimental conditions, we are not definitely convinced by the fact that a chloride/bromide solution could give such information. Indeed, with our droplet train flow-tube, the ratio of droplet to glass surface is very small i.e., mainly glass or wax coated glass is exposed to the gas phase. This is resulting in unwanted wall reactions (already with either Cl- or Br- in aqueous phase) so that we cannot fairly quantify the product yields.

Referee 2:

The authors rule out the direct reaction (10) in favor of the stepwise hydrolysis (9) followed by (11) for ClONO<sub>2</sub>/chloride aqueous solution owing to the fact that hydrolysis is faster than the direct reaction. In this case they should also have seen HOCl in view of the stated HNO<sub>3</sub> impurities as HOCl is a weak acid whose solubility is low. Comparing BrONO<sub>2</sub> with ClONO<sub>2</sub> reactions the authors state on pg. 1283 that the hydrolysis rate of BrONO<sub>2</sub> is lower than that of ClONO<sub>2</sub> owing to a larger reaction barrier, and that moreover it is lower than the direct reaction (19). Why is it then that uptake experiments of BrONO<sub>2</sub> on bromide-containing solutions show such a strong concentration effect as displayed in Figure 7 when they claim that hydrolysis is the rate-determining step in the uptake? This is a contradiction that the authors have failed to respond to as one expects the uptake rate constant to be independent of the bromide concentration. In addition, the slower hydrolysis rate of BrONO<sub>2</sub> vs. ClONO<sub>2</sub> goes against all experimental evidence.

Authors:

We have here some difficulties to understand the referee remarks. We stated in the

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original version: -The uptake rate of BrONO<sub>2</sub> was strongly affected by the concentration of NaBr in the droplet. The values of the uptake coefficients  $\gamma$  varied from 0.032 to 0.062 when the NaBr concentrations increased from 0.01 to 1 M. suggesting again a direct reaction between BrONO<sub>2</sub> 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 BrONO<sub>2</sub> in the liquid phase-. Therefore we never claimed that hydrolysis is the rate determining step in this case. This is again stated in the conclusion: -a direct reaction was observed between ClONO<sub>2</sub> and BrONO<sub>2</sub> with NaBr, which then acted as a scavenger. This allowed the estimation of the mass accommodation coefficient (original article). In the revised version, this has been slightly modified, but the conclusion remains the same: only bromide can react directly with these compounds (ClONO<sub>2</sub> and BrONO<sub>2</sub>) due to its higher nucleophilicity compared to chloride.

Referee 2:

The case of the lower accommodation coefficient of BrONO<sub>2</sub> compared to ClONO<sub>2</sub> has not been explained satisfactorily. I am not sure if it helps to compare it with the one for molecules such as HBr and BrNO<sub>2</sub> whose reactivities are very different.

Authors:

Unfortunately, we have no better explanation or comparison for the moment, but any suggestion will be welcome.

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

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