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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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Report on ŞUptake Study of ClONO2 and BrONO2 by water dropletsŤ published in Atmospheric Chemistry and Physics Discussions 4, 1311-1337, 2004. By G. Deiber, Ch. George, S. Le Calvé, F. Schweitzer and Ph. Mirabel This work deals with the heterogeneous kinetics of two trace gas molecules of atmospheric interest with aqueous salt solutions and pure water in a fairly narrow temperature range. The authors use the now well-established droplet train technique coupled to residual gas electron-impact mass spectrometry, a combination the authors were the first to use. This is the first report on the uptake of the title molecules on pure water droplets and on droplets containing NaCl and NaBr and should therefore be of interest to many active in the field of marine atmospheric chemistry. The authors put their study in the context of marine boundary layer chemistry in order to justify the choice of the trace gases and the condensed phase substrate. However, the design of the study leaves wanting because the NaCl concentration never exceeds 0.1M, whereas the NaBr concentration goes up to 1M. The authors should at least have gone to 0.6M or higher for NaCl in order to mimick

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sea water and/or deliquescent sea salt aerosols whereas they could have emphasized the mM concentration regime for NaBr. This shortfall in [NaCl] leads to a significant uncertainty with respect to the corresponding reaction mechanism in chloride solution (see below). One gets the impression that the environmental/marine context is just an afterthought, especially so because mixtures of chlorides and bromides have not been considered. The presentation is ambiguous at times, there are several Şnon-sequitursŤ (conclusions that are not supported by arguments presented in the text, see below) and often there is a missing argument that makes it impossible for the interested reader to follow the authorŠs line of thinking. In addition, the presented amount and quality of data are not exactly a treasure trove of information because this study deserved the collection of a lot more systematic data as a function of concentration, temperature, pH, time (saturation), etc. On behalf of the atmospheric chemist interested in the chemistry of the marine boundary layer I will support the publication of these data in ACP only after major revision of the manuscript, knowing that additional data are most probably not forthcoming at this point as the projects have ended a long time ago. However, I expect the authors to do a much better job in presenting and critically discussing the available data. This referee has had knowledge of the points made by one referee. Therefore, I will focus on points not raised by the other referee. However, a certain overlap is unavoidable. 1319/26 to 1320/2: ŞĚthat the measured kinetics is not elementary but is driven by several physical and chemical processes that have different temperature trends.Ť 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. 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. 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

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(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 ŞdirectŤ (one-step) and a sequential (two step) mechanism. 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. 1320/26: Ştraces of HOCl..ŤHere a semiquantitative estimate of the HOCl impurity in ClONO2 is imperative in order to support the statement: How can ŞtracesŤ of HOCl lead to significant Cl2 formation? 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 Şat short reaction timesŤ 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. 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? 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 (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! 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. 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 HenryŠs 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). 1324/11: In relation to Figure 6: what does ŞĚsome BrCl production Ş mean? 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! 1325/2-5: ŞFrom these observations we concludeĚŤ This is a non-sequitur! There must be a missing argument here! How can the fact that  increases with [NaBr] be responsible for the conclusions cited in this sentence? 1325/15-16: What is Şthe correction level between 1/alpha and 1/gamma compared to ClONO2Ť? Please explain. 1325/17: Ş...less hindered thanĚŤ Why then is alpha smaller for BrONO2 compared to ClONO2? Please explain. It appears that

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the authors are confusing thermodynamic with kinetic arguments, i. e. solubility with uptake kinetics of accommodation. 1326/8: The ŞlatterŤ needs two subjects that are to be compared. What are they?

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