**Atmospheric
Chemistry
and Physics**

Uptake study of ClONO$_2$ and BrONO$_2$ by Halide containing droplets

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Abstract. The uptake kinetics of gaseous ClONO$_2$ and BrONO$_2$ on aqueous surfaces were measured, as a function of temperature and liquid composition (pure water and NaCl or NaBr containing solutions) using the droplet train technique coupled to a mass spectrometer. The uptake kinetics are driven by the reactivity of these gases and, for both compounds, the uptake rates on pure water or on NaCl solutions (0.1 M) are comparable. The uptake coefficient γ of ClONO$_2$ does not depend on the temperature while that of BrONO$_2$ increases slightly when the temperature is raised from 272 to 280 K. For ClONO$_2$ and BrONO$_2$, the uptake rates increase on NaBr-doped droplets, enabling the estimation of the mass accommodation coefficient α. The corresponding values for α are 0.108±0.033 for ClONO$_2$ and 0.063±0.021 for BrONO$_2$ where the statistical errors correspond to ±2σ.

The reactions of ClONO$_2$ and BrONO$_2$ on NaCl solutions lead respectively to the formation of Cl$_2$ and BrCl. The uptake of ClONO$_2$ on NaBr solutions generates BrCl as primary product, which in turn can react with NaBr to produce Br$_2$. As expected, the only product of BrONO$_2$ reaction on NaBr solution is Br$_2$.

1 Introduction

During these last years, growing interest has been given to a better understanding of the oxidation capacity of the marine boundary layer. It has been recognised that heterogeneous reactions taking place on or in sea-salt containing particles may convert inert halogen reservoir species into photochemically active species leading after photolysis, to the formation of halogenated radicals which have been observed during field campaigns (Sander et al., 2003).

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These halogenated species can then have a significant impact on the rate of destruction of tropospheric ozone or of hydrocarbons. During these reactions XO type radicals (where X is a halogen) are formed. These radicals may undergo some recycling reactions (through HOX) or be trapped in reservoir compounds such as XONO$_2$.

The formation of BrONO$_2$ and ClONO$_2$ is known to occur in the atmosphere via the radical recombination reaction of XO (where X=Br, Cl.) with NO$_2$ according to the following reaction:

$$XO + NO_2 \longrightarrow XONO_2 \tag{1}$$

The potential fates of XONO$_2$ in the marine boundary layer include photolysis but also heterogeneous losses by deposition at the ocean's surface or reaction on sea-salt particles (including hydrolysis and reactive uptake driven by the halides themselves).

While reaction (1) represents a sink for XO radicals, heterogeneous reactions of XONO$_2$ on sea-salt particle (wet and dry) may recycle these reservoir species into active halogen containing gases such as HOBr, HOCl, BrCl, Cl$_2$, or Br$_2$. The primary reactions may be schematically written as:

$$ClONO_2 + NaCl \longrightarrow Cl_2 + NaNO_3 \tag{2}$$

$$ClONO_2 + NaBr \longrightarrow BrCl + NaNO_3 \tag{3}$$
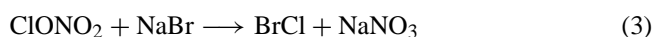
These di-halogens compounds are only poorly soluble and will first desorb into the gas phase before being rapidly photolysed to generate either Cl or Br atoms, therefore having potentially a strong impact on the oxidation capacity of the marine boundary layer. In fact, as the reaction rate constants of Cl atoms with hydrocarbons are significantly larger than those with OH radical (Mellouki, 1998; Notario et al., 1998), the increase of Cl concentration in the atmosphere may imply enhanced oxidation rates for a number of tropospheric trace gases, including DMS (dimethylsulphide) and alkanes

(Barrie et al., 1988; Crutzen, 1995; Finlayson-Pitts and Pitts, 1986; Wagner and Platt, 1998).

The heterogeneous reactions of ClONO$_2$ with solid NaCl and KBr have already been studied in a fast flow reactor (Timonen et al., 1994) and a Knudsen cell (Aguzzi and Rossi, 1999; Caloz et al., 1996; Gebel and Finlayson-Pitts, 2001; Wingenter et al., 1996) and the primary reaction products on NaCl were HOCl and Cl$_2$ while BrCl was observed on KBr.

The heterogeneous reactions of BrONO$_2$ with solid alkali halides have also been investigated in a Teflon-coated Knudsen flow reactor at ambient temperature (Aguzzi and Rossi, 1999). For solid NaCl substrates, BrCl, Br$_2$ and HCl were observed as products while for KBr both Br$_2$ and HBr were detected. This illustrates the fact that the reaction mechanism may not be as simple as a direct reaction of the halide ion on BrONO$_2$.

All these experiments were conducted over different solid substrates corresponding to powders (Timonen et al., 1994; Caloz et al., 1996; Gebel et al., 2001), spray deposited films, grains of various sizes and also single crystals (Caloz et al., 1996 ; Aguzzi and Rossi, 1999). Most of these experiments were also performed at low pressure (e.g. needed to achieve molecular transport in the Knudsen cell regime) which means that the gas phase humidity was very low. Nevertheless, even at such low pressures a certain amount of water is adsorbed on the salt surface and can only be (partially) pumped off when heated above 100°C. Such treatment was used in the studies on solid substrates which were accordingly performed on "dry" solids.

However in the marine boundary layer (MBL), the relative humidity is high, reaching often more than 90%. As the deliquescence and efflorescence points of NaCl are 75% and 43% respectively, a very large fraction of sea-salt aerosols is wet. As the relative humidity is controlled by the temperature gradient, only under specifically cold situations or during a rapid up-lifting of an air mass, the humidity might get low enough to dry locally the sea-salts. Therefore, one may argue that a significant fraction of sea-salt aerosols in the MBL is wet. However, the uptake kinetics of XONO$_2$ on liquid salt solutions has not been reported yet.

In this work, we report the first measurements of uptake coefficients, using the droplet train technique, for ClONO$_2$ and BrONO$_2$ on pure water droplets or on aqueous solutions containing NaCl or NaBr (in order to mimic sea-salt particles) over the temperatures range 273–285 K. Some reaction products have also been identified, suggesting some reaction mechanisms. In the following sections, we present our experimental methodology whereas in the subsequent section, we present and discuss the results of the uptake rate measurements.

2 Experimental Section

2.1 Uptake experiments

The uptake rate of a trace gas by a liquid is a multi-step process that can be related to fundamental properties of the incoming gas, interface and condensed phase such as the mass accommodation coefficient (α), solubility and reactivity. The rate at which a trace gas molecule may be transferred into the condensed phase can be obtained from the kinetic theory of gases. This allows the calculation of the net flux Φ_{net} that crosses the interface:

$$\Phi_{net} = \frac{1}{4} <c> n\gamma \tag{4}$$

where $<c>$ is the trace gas average thermal speed, γ the uptake coefficient (taking into account all processes potentially affecting the uptake rate) and n the number density of the trace gas.

Uptake rates were measured using the droplet train technique already described elsewhere (Magi et al., 1997; Schweitzer et al., 1998). We will therefore provide only a brief summary of its principle of operation. The uptake coefficient was determined by measuring the decrease of the gas phase concentration of the trace species, due to their exposure to a monodispersed train of droplets. This latter was generated by a vibrating orifice (100 μm diameter) leading to droplet diameters of about 200 μm. The apparatus, where the contact between both phases takes place, is a vertically aligned low pressure flowtube. Its length can be varied up to 20 cm, in order to change the gas/liquid interaction time (0–20 ms) or the surface exposed by the droplet train (0–0.2 cm^2). Since the uptake process is directly related to the total surface S exposed by the droplets, any change ΔS in this surface results in a change of the trace gas density Δn at the exit ports of the flowtube. The uptake coefficient was calculated by considering the kinetic gas theory and the integrated signal during the transit time due to changes in the exposed surface (Worsnop et al., 1989):

$$\gamma = \frac{4F_g}{<c> \Delta S} ln\left(\frac{n}{n - \Delta n}\right) \tag{5}$$

where F_g is the carrier gas volume flow rate, n and $(n-\Delta n)$ are respectively the trace gas density at the inlet and outlet port of the interaction chamber. The overall uptake coefficient γ was derived from the measurement of the fractional changes in concentration $ln(n/(n-\Delta n))$ as a function of $<c>\Delta S/4F_g$. This parameter can be measured as a function of the total pressure, gas/liquid contact time or composition of the liquid used to produce the droplets. These measurements are necessary in order to decouple the overall process into individual steps (see results section). An important aspect of this technique is the careful control of the partial pressure of water in the flowtube since it controls the surface temperature of the droplets through evaporative

cooling (Worsnop et al., 1989). Therefore, the carrier gas (helium) was always saturated, at a given temperature, with water vapour before entering the flow tube.

The extraction of kinetic information from the droplet train technique may be affected by the high speed of the droplets which favours convective transport into the droplets. However, several facts demonstrate that, given the accuracy of the experiments, this effect does not represent a significant source of error. The time scale of the experiment was short (typically less than 20 ms) which do not allow a massive influence of convective transport. Using the description given by Pruppacher and Klett (1978), some calculations have shown that this influence on the uptake process is less than 5% for times below 20 ms (George, 1993), in agreement with the results of Baboobal et al. (1981).

The gas stream coming out of the flowtube was analysed using a quadrupole mass spectrometer operated with an ionisation energy of 60 eV. The signal was averaged over a second in order to increase the signal to noise ratio. ClONO₂ was monitored at 51 amu (ClO⁺), BrONO₂ at 95 and 97 amu (BrO⁺), Cl₂, BrCl, Br₂, by their parent ions (70, 116 and 160 amu respectively). In addition, H₂O and an inert tracer SF_6 were monitored at 18 (H₂O⁺) amu and 89 (S⁺F₃) amu during the experiments in order to see any potential perturbations in gas phase concentrations. All these masses were chosen in order to minimize potential cross contributions to the signal which might result in incorrect interpretations.

As only the relative decay of the gas phase reactants has to be known in order to derive uptake coefficients, the MS data listed below are given in arbitrary units. 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 10^{12} molecule cm^{-3}. The gas phase concentrations were estimated to range from 10^{13} to 10^{15} molecule cm^{-3}.

The droplets were made from Milli-Q water (18 MΩ cm) and NaCl (Aldrich, ≥99%) or NaBr (Aldrich, ≥99%) when necessary, leading to an initial droplet pH of about 6.

2.2 Synthesis of chlorine nitrate (ClONO₂)

ClONO₂ was synthesized by reacting Cl₂O with an excess of N₂O₅ at low temperature, according to the following reaction (Caloz, 1997):

$$Cl_2O + N_2O_5 \longrightarrow 2ClONO_2 \qquad (6)$$
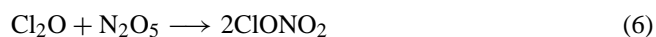
N₂O₅ was prepared from the oxidation of NO₂ by O₃ in the gas phase after mixing of the flows containing each reactant. To prevent any hydrolysis and the formation of HNO₃ both NO₂ and O₃ flows were dried by flowing the gases through traps prior to mixing. After some reaction time, N₂O₅ was collected on a cold finger kept at low temperature where it condensed as a white powdery solid.

Liquid Cl₂O was obtained by condensing Cl₂ on an excess of yellow mercury oxide (HgO) and allowing the mixture to react at a temperature of 190 K for 4 h.

Cl₂O and N₂O₅ were then mixed at low temperature. This mixture underwent several heating and cooling cycles from 190 K (storage temperature) to 230 K in order to accelerate the reaction. ClONO₂ appeared as a yellow green liquid with Cl₂ being the main impurity, which can be minimized by freeze-pump-thaw cycles.

2.3 Synthesis of bromine nitrate (BrONO₂)

Bromine nitrate was synthesized by adding Br₂ to ClONO₂, following the procedure described by Wilson and Christe (1987) and according to the reaction:

$$ClONO_2 + Br_2 \longrightarrow BrONO_2 + BrCl \qquad (7)$$
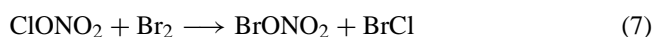
ClONO₂ was mixed with Br₂ in a trap kept at 77 K. The mixture was allowed to warm up slowly from 190 to 260 K and was subsequently kept at the latter temperature for several hours. Then, the mixture was condensed in a cold trap at 190 K. The observed impurities in BrONO₂ were BrCl, Cl₂ and unreacted ClONO₂ and Br₂. These impurities were removed by pumping on the mixtures for 2–3 h at 210 K. The remaining fraction consisted of a yellow solid which was stored at 190 K.

3 Results and discussion

As already mentioned, uptake coefficients are measured from the fractional changes in trace gas concentration due to a modification in the exposed droplets surface (Eq. 5) which is function of diffusion rates in both phases, mass accommodation process and solubility and reactivity in the liquid phase. To each of these processes, one can attribute a specific "conductance or resistance" and the overall uptake coefficient is calculated by summing up the individual resistances (defined as the inverse of the specific uptake coefficient) according to Kolb et al. (1994):

$$\frac{1}{\gamma} = \frac{1}{\gamma_{diff}} + \frac{1}{\alpha} + \frac{1}{\gamma_{sat} + \gamma_{rxn}}$$

$$= \frac{<c> d_{eff}}{8 D_g} - \frac{1}{2} + \frac{1}{\alpha} + \frac{<c>}{4 H R T \sqrt{D_a}} \left(\frac{2}{\sqrt{\pi t}} + \sqrt{k} \right)^{-1} \qquad (8)$$

where d_{eff} is the effective droplet diameter (which takes into account the fact that a droplet train may not be considered as a sum of individual droplets; note however that its value is very close to the real diameter) (Worsnop et al., 1989), H the Henry's law constant, R the perfect gas constant, T the droplets temperature, D_g and D_a the gas and aqueous phase diffusion coefficients, t the gas/liquid contact time and k the first order rate constant for a given reaction in the liquid phase. The term $-1/2$ accounts for the distortion of the Boltzmann collision rate and the terms denoted

Table 1. Results and experimental conditions of ClONO$_2$ uptake kinetics.

Solution	T (K)	P (Torr)	$10^2 \times \gamma$ (2σ)	$1/\gamma - 1/\gamma_{diff}$ (2σ)
Water	274.6	20.0	2.41±0.20	38.0±3.4
	278.4	20.2	2.60±0.34	34.6±5.0
	285.0	19.3	2.30±0.23	38.9±4.3
NaCl 0.1 M	274.6	21.3	2.44±0.23	37.3±3.9
NaBr 0.01 M	274.1	21.0	4.10±0.67	20.8±4.0
	277	21.7	4.60±0.19	17.8± 0.9
	280.8	20.3	4.70±0.11	17.1±0.5
NaBr 0.025 M	274.3	20–26	4.40±0.27	18.8±1.4
	276.2	21.1	4.10±0.43	20.6±2.6
NaBr 0.05 M	274	20.0	5.50±0.60	14.7±2.0
	277	20.4	5.40±0.39	14.7±1.3
	281	20.7	5.30±0.28	14.6±1.0
NaBr 0.1 M	274.9	20.0	5.70±0.48	14.0±1.5
	276.2	19.3	4.90±0.24	16.8±1.0
	279.9	18.9	5.60±0.08	14.0±0.3
NaBr 0.5 M	274.4	22.0	6.55±0.15	11.5±0.4
	276.5	22.6	6.63±0.11	11.0±0.3
NaBr 1 M	274.6	20.6	7.30±1.06	10.3±4.0

Table 2. Results and experimental conditions of BrONO$_2$ uptake kinetics.

Solution	T (K)	P (Torr)	$10^2 \times \gamma$ (2σ)	$1/\gamma - 1/\gamma_{diff}$ (2σ)
Water	272.5	20.3	2.4±0.08	38.1±1.4
	275.0	20.2	3.0±0.15	29.7±1.7
	277.5	20.7	3.6±0.16	23.9±1.2
	279.7	21.6	3.9±0.12	21.4±0.8
NaCl 0.1 M	277.4	21.2	3.55±0.62	24.2±4.9
	279.6	21.7	4.00±0.24	20.8±1.5
NaBr 0.01 M	272.9	18.4	3.25±0.20	27.6±1.9
NaBr 0.05 M	272.5	18.8	4.89±0.36	17.2±1.5
	278.0	20.3	6.14±0.35	12.4±0.9
	280.4	20.3	6.22±0.28	12.0±0.7
NaBr 1 M	274.3	21.0	6.74±0.37	11.2±0.8
	277.6	19.5	5.58±0.37	14.2±1.2
	280.4	19.1	6.16±0.34	12.3±0.9

γ_{diff}, γ_{sat} and γ_{rxn} correspond to the incoming flux driven respectively by gas phase diffusion, saturation and diffusion in the liquid phase and existing chemical aqueous phase reactions. Equation (8) clearly shows that the uptake coefficient is a function of different fundamental properties of the gas molecule such as its solubility, diffusion, etc. One can note also that the treatment used to obtain Eq. (8) is very similar to the one used for the calculation of deposition velocities on an ocean surface (Liss and Slater, 1974). The application of Eq. (8) was recently the subject of some discussion (Kolb et al., 1998; Widmann and Davis, 1997), especially the diffusion correction formulation which is based on the work of Schwartz (1986) who derived in a "simple but effective" manner the background leading to Eq. (8). As already underlined by several authors, most of the expressions describing the kinetics of mass transport are subject to some criticisms because of the assumptions made in their derivation. Therefore, the expressions used to correct the measured uptake coefficients for gas phase diffusion limitations are only approximate.

The Fuchs-Sutugin equation (Fuchs and Sutugin, 1971) is certainly the most widely employed equation for the description of mass transport in the Knudsen regime i.e. in the transition region from the continuum to the free-molecular regime. It is also valid for a wide range of experimental conditions. However, its derivation is less simple than the one made by Schwartz and therefore Schwartz's formulation is often preferred (such as in the present work). Using the expression for γ_{diff} derived by Hanson et al. (1996) from

the Fuchs-Sutugin treatment, one can easily show that, under our experimental conditions, Eq. (8) is still valid. In our case (i.e. for pressures in the range 14–25 torr) the deviation from the Fuchs-Sutugin formulation is less than 5% and for most experiments even less then 3%. This conclusion is similar to the one reached by Kolb et al. (1998). Therefore, we are confident that, under our experimental conditions, Eq. (8) can be adequately used in order to correct our raw data for potential mass transport limitations (see Tables 1 and 2). Of more concern is the (unknown) value of the diffusion coefficient, which may introduce severe uncertainties. Diffusion coefficients have been estimated using methods presented by Reid et al. (1977). Especially, the semi-empirical calculations by Fuller et al. (1969) was applied to estimate the binary diffusion coefficients of the trace gases in water and helium respectively i.e. D_{g-H_2O} and D_{g-He}. These diffusion coefficients are respectively 0.16 and 0.45 cm^2 s^{-1} for ClONO$_2$ and 0.15 and 0.44 cm^2 s^{-1} for BrONO$_2$. The employed estimation method has an average absolute error of about 5% but shows deviation in excess to 20% (Reid et al., 1977) which will, under our experimental conditions, introduce an additional error of less than 15% in the measured mass accommodation coefficients.

In all the experiments presented below, no saturation of the droplet surface was observed i.e. the uptake is driven by the chemical reaction within the aqueous phase in which both ClONO$_2$ and BrONO$_2$ are involved.

3.1 Uptake measurements of ClONO$_2$

The uptake coefficient of ClONO$_2$ was measured on water and on aqueous solutions containing NaCl and NaBr in the temperature range 274–285 K. The uptake coefficients were derived according to Eq. (5) as depicted in Fig. 1, where the slope of the fitted line is directly related to the uptake
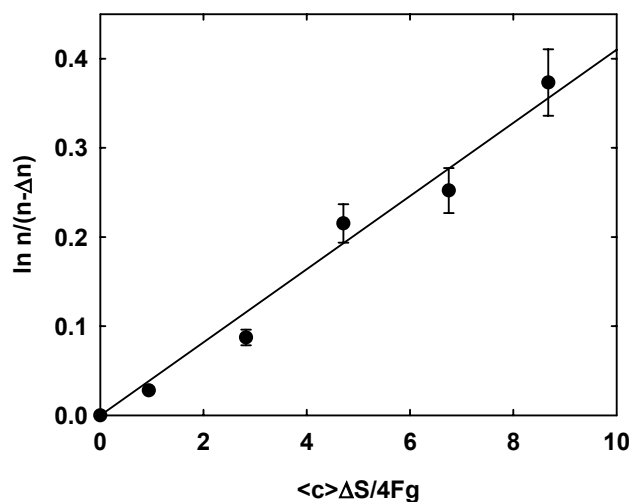
Fig. 1. Typical plots of $\ln(n/n - \Delta n)$ versus $<c>\Delta S/4F_g$ for ClONO₂ on a 0.05 M NaBr solution at 277 K. The slope is γ according to Eq. (5).

Fig. 2. ClONO₂ uptake coefficient as a function of temperature. The error bars are given at 1σ level. (• water; △ NaBr 0.01 M; ▲ NaBr 0.05 M; □ NaCl 0.1 M).

coefficient γ. For the example given in Fig. 1, the slope is 0.054 ± 0.004 and is temperature independent for all solutions studied (Fig. 2). In all cases, the uptake rates were shown to be independent of the contact time meaning that no saturation of the droplets or more exactly of their surface occurred within our experimental conditions.

The measured uptake coefficient on pure water is of the order of 2×10^{-2} at all temperatures, and once corrected for diffusion limitations raises to about 3×10^{-2}. 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 for our measured γ values, which is probably an indication that the various processes are acting with the same intensity but with different temperature trends. Accordingly, for a gaseous specie for which uptake is controlled by chemical reactions, it is not surprising that the uptake appears to be temperature independent since it can be described by the product $H\sqrt{k}$. In the particular case of ClONO₂, the chemical reaction is its
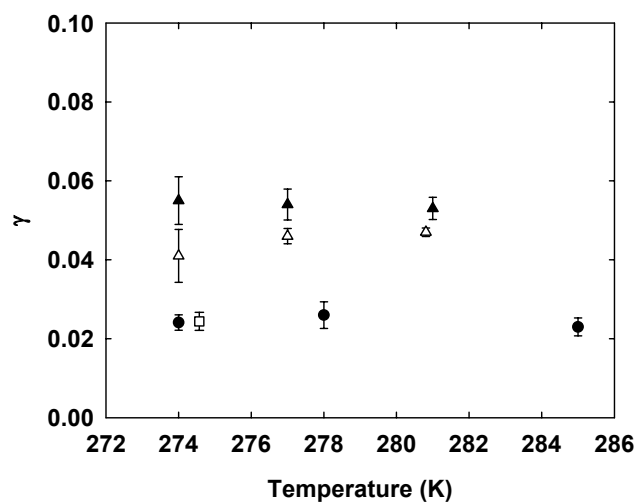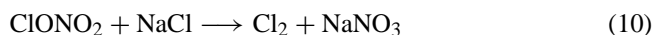
hydrolysis according to:

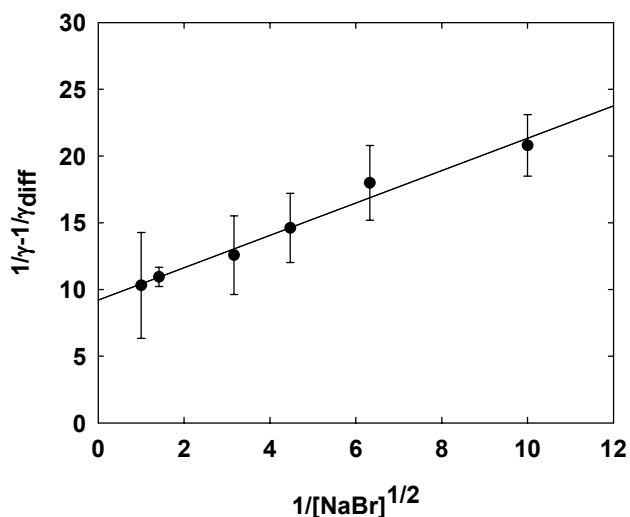$$ClONO_2 + H_2O \longrightarrow HOCl + HNO_3 \qquad (9)$$
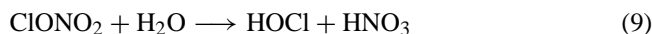
However, HOCl was not detected as a reaction product because it is too soluble and reactive. It has been proposed that ClONO₂ reacts with NaCl according to Aguzzi and Rossi (1999) and Timonen et al. (1994):

$$ClONO_2 + NaCl \longrightarrow Cl_2 + NaNO_3 \qquad (10)$$

leading to the production of Cl₂. However, we did not observe any increase of the uptake rate on 0.1 M NaCl droplets. Within our experimental conditions, the same uptake rate was observed on pure water and on NaCl-doped droplets. We observed here Cl₂ as a unique product. Similar observations have already been made by Timonen et al. (1994) or Aguzzi and Rossi (1999) on solid NaCl.

Very recently, Gebel and Finlayson-Pitts (2001) studied the uptake of ClONO₂ on solid NaCl and synthetic sea-salt using a Knudsen cell reactor. They observed first large initial uptake rates with uptake coefficient as large as 0.1 (consistent with the upper limit of our uptake coefficient, see below), followed by a smaller and declining uptake rate at longer reaction times. They concluded from their study that the initial uptake is driven by the water adsorbed on the solid sample, even at the low pressure used in their Knudsen cell reactor, meaning that ClONO₂ is primarily taken up by the water adsorbed on the salt surface, where it reacts. They also observed from the reaction products that HOCl is produced first (at very short reaction times) followed by some Cl₂ production. These observations also strongly suggested a two-step mechanism where ClONO₂ is first hydrolysed leading to HOCl which is then converted into Cl₂. Although they

Fig. 3. Plot of uptake coefficients for ClONO$_2$ according to equation 12. The intercept is the inverse of the mass accommodation coefficient α. T=274.5±1 K. The error bars are given at the 1σ level.

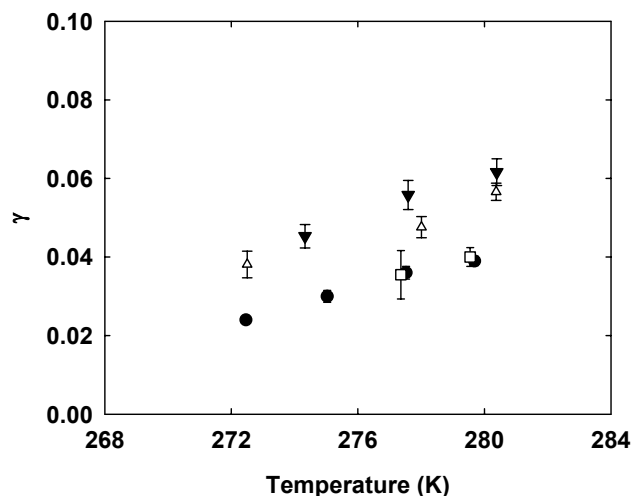$$= \frac{<c> d_{eff}}{8 D_g} - \frac{1}{2} + \frac{1}{\alpha} + \frac{<c>}{4 H R T \sqrt{D_a k}} \qquad (11)$$

Equation (11) may also be written as:

$$\frac{1}{\gamma} - \frac{1}{\gamma_{diff}} = \frac{1}{\alpha} + \frac{<c>}{4 H R T \sqrt{D_a k}} \qquad (12)$$

After correction due to diffusion processes in the gas phase, we were able to estimate the mass accommodation coefficient α from the intercept of plots of $(1/\gamma - 1/\gamma_{diff})$ versus (NaBr)$^{-1/2}$ as depicted in Fig. 3. The estimated value at 274.5±1 K is α=(0.108±0.011) where the errors only reflect statistical uncertainties (2σ), without any considerations of systematic deviations. Systematic deviations may arise from uncertainties in diffusion coefficients (as discussed above, within a 15% error limit), in the water vapour pressure (leading to uncertainties in the flowrates and temperature which are known better than 5%). Altogether, we estimate our uncertainty to 20%. As we were not able to observe any temperature trend in the explored range, we estimate that the above value can be applied to a temperature range of 274–280 K. To our knowledge, this is first reported value for the mass accommodation coefficient of ClONO$_2$ on aqueous solutions. As already underlined, the mass accommodation coefficient is directly related to the maximum mass flux that can be transported across the air/water interface and corresponds therefore to the uptake rate that could hypothetically be observed at very short gas/liquid contact times. We can therefore compare our value of α to the initial uptake rates reported by Gebel and Finlayson-Pitts on solid NaCl as they state that it is controlled by water on the surface. As mentioned, they do report values larger than 0.1 which is in quite good agreement with the present determination of the mass accommodation value of ClONO$_2$ on water. Other determinations on solid NaCl have also been conducted by Caloz et al. (1996) and by Aguzzi and Rossi (1999). The reported values, 0.23±0.06 and 0.10±0.05 respectively, are also in fair agreement with our value. A larger dataset can be found for the reactive uptake of ClONO$_2$ on surfaces found under stratospheric conditions. It is however difficult to compare those data with our results as the temperature but also the substrates are totally different. Nevertheless, large uptake coefficient for the loss of ClONO$_2$ were also found.

3.2 Uptake measurements of BrONO$_2$

The uptake of BrONO$_2$ 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 ClONO$_2$, the uptake rate increased with temperature, from 0.024 to 0.039 when T increased from 273 to 280 K as shown in Fig. 4. This may just reflect different temperature trends for Henry's law constant and reactivity of ClONO$_2$ compared to BrONO$_2$ and therefore different trends for the products $H\sqrt{k}$. Basically, we would expect BrONO$_2$ to be more soluble than ClONO$_2$, as this is generally the case

have been working with solid substrates, their conclusions on a two-step mechnism can easily be applied to our own observations. It must however be underlined, that Caloz et al. (1996) did not observe any HOCl formation but a 100% yield of Cl$_2$, 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 ClONO$_2$ which may affect the importance of the hydrolysis.

Contrarily to the uptake of ClONO$_2$ on NaCl, its uptake on NaBr is dependant on the concentration of the salt (Fig. 3). The values of γ increases from 0.041 to 0.073 when NaBr concentrations increases from 0.01 to 1 M, suggesting a direct reaction between ClONO$_2$ and bromide ions.

This increase in the uptake rate may highlight an additional reaction pathway in the case of bromide compared to chloride. Accordingly, any increase in the gas phase loss rate of that compound can be attributed to a direct reaction on ClONO$_2$. This increase which was not observed in the case of chloride suggests that in bromide containing solutions, ClONO$_2$ reacts directly with Br$^-$ while with chloride containing solutions it first dissociates. The difference of reactivity of ClONO$_2$ towards Cl$^-$ and Br$^-$ can be explained by the stronger nucleophilic character of Br$^-$ compared to Cl$^-$. From these observations, we conclude that saturation effects in the droplets were absent and that the uptake process was driven by the reactivity of ClONO$_2$ and limited by its diffusion in the gas phase. Accordingly, Eq. (8) simplifies to (Worsnop et al., 1989):

$$\frac{1}{\gamma} = \frac{1}{\gamma_{diff}} + \frac{1}{\alpha} + \frac{1}{\gamma_{rxn}}$$

Fig. 4. BrONO$_2$ uptake coefficient as a function of temperature. The error bars are given at the 1σ level. (● water; △ NaBr 0.05 M; ▼ NaBr 1 M; □ NaCl 0.1 M).

Fig. 5. Plot of uptake coefficients for BrONO$_2$ according to equation 12. The intercept is the inverse of the mass accommodation coefficient α. T=273±1 K. The error bars are given at the 1σ level.

for brominated and chlorinated species (Br$_2$ is more soluble than Cl$_2$, BrNO$_2$ is more soluble than ClNO$_2$, etc.) (Sander, 1999). The uptake rates γ of both components being of the same order of magnitude, one can assume that the hydrolysis of BrONO$_2$ has to proceed at a reduced rate, compared to ClONO$_2$. But in both cases, the hydrolysis governs the uptake rate in water and also Cl$^-$ containing droplets. Therefore, the observed temperature dependence of γ can be attributed to a higher activation energy for the hydrolysis of BrONO$_2$. Such considerations may indeed explain the difference in temperature trends in the uptake coefficients for BrONO$_2$ and ClONO$_2$. These observations show that the temperature dependence is mainly governed by that of the hydrolysis reaction which proceeds according to:

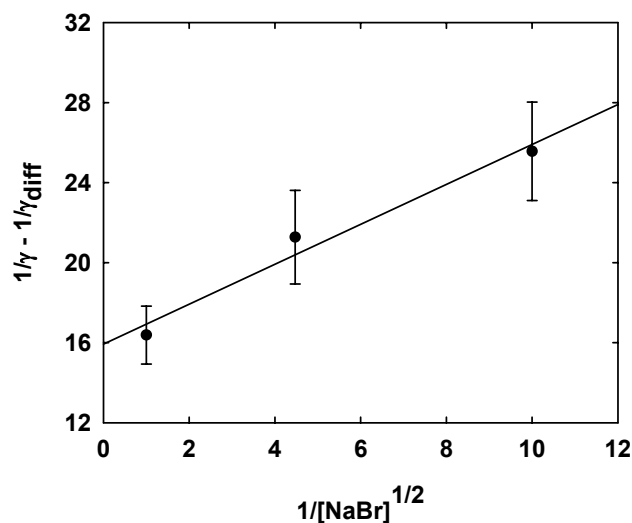$$BrONO_2 + H_2O \longrightarrow HOBr + NaNO_3 \qquad (13)$$
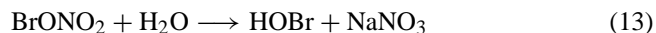
HOBr was not detected as a reaction product on pure water droplets (similarly to HOCl in ClONO$_2$ experiments), because it is too soluble and reactive. The introduction of NaCl in the droplets has no influence on the uptake coefficient (Fig. 4). It has also been proposed (Aguzzi and Rossi, 1999) that BrONO$_2$ reacts with NaCl according to:

$$BrONO_2 + NaCl \longrightarrow BrCl + NaNO_3 \qquad (14)$$
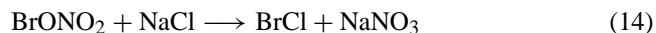
This reaction leads to the production of BrCl. From our experiments on NaCl doped droplets, we saw indeed some BrCl production. However, the uptake kinetics were not affected by the presence of NaCl.

The uptake rate of BrONO$_2$ was strongly affected by the concentration of NaBr in the droplet (see Fig. 5). The values of the uptake coefficients γ 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$_2$ 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$_2$ in the liquid phase. Br$_2$ was the only product observed, according to the following reaction:

$$BrONO_2 + NaBr \longrightarrow Br_2 + NaNO_3 \qquad (15)$$

After correction due to slow diffusion process in the gas phase, the mass accommodation coefficient α was estimated from the intercept of plots of $(1/\gamma - 1/\gamma_{diff})$ versus $(NaBr)^{-1/2}$ as depicted in Fig. 5. The estimated value is 0.063±0.009 at 273 K where again the errors only reflects statistical uncertainties (2σ) without any considerations of systematic deviations which can be again estimated to 20%. To our knowledge, this is the first reported value for the mass accommodation coefficient of BrONO$_2$ on water surfaces. Concerning the accommodation step, the accommodation coefficient of BrONO$_2$ is lower than ClONO$_2$ 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. No reaction in the aqueous phase does not provide any pathway producing BrONO$_2$ 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 BrONO$_2$ highlighting a sequential reaction pathway.

As already performed for $ClONO_2$, 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 $BrONO_2$ 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 $BrONO_2$ on water. We can first compare to previous studies on nitryl type compounds. It was shown that the uptake coefficient of $ClNO_2$ on water was larger than that of $BrNO_2$. 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 $BrONO_2$ 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.

4   Conclusions

In this study we measured for the first time, the uptake rate of both $ClONO_2$ and $BrONO_2$ 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. Cl_2, Br_2 and BrCl (as expected). Our results show that as long as the hydrolysis of $ClONO_2$ and $BrONO_2$ is not suppressed, only bromide can react directly with these compounds due to its higher nucleophilicity compared to chloride.

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