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Uptake study of ClONO$_2$ and BrONO$_2$ by water droplets

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Received: 19 December 2003 – Accepted: 15 February 2004 – Published: 2 March 2004

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Abstract

The uptake kinetics of gaseous $ClONO_2$ and $BrONO_2$ on aqueous surfaces were measured, using the droplet train technique coupled to a mass spectrometer, as a function of temperature and liquid composition (pure water and NaCl or NaBr containing solutions). 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±0.001 for $ClONO_2$ and 0.063±0.009 for $BrONO_2$.

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 (Pszenny et al., 1993; Wingetener et al., 1996).

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:

$$XO + NO_2 \rightarrow XONO_2. \tag{1}$$

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 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:

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

$$ClONO_2 + KBr \rightarrow BrCl + KNO_3. \tag{3}$$
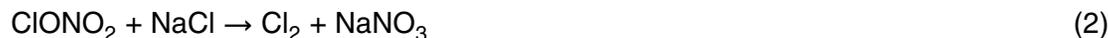
All these compounds are then rapidly photolysed to generate either Cl or Br atoms, therefore having potentially a strong impact on the oxidation capacity of the marine boundary layer. In fact, as the reaction rate constants of Cl atoms with hydrocarbons are significantly larger than those with OH radical (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 (Finlayson-Pitts and Pitts, 1986; Barrie et al., 1988; Crutzen, 1995; Wagner and Platt, 1998).

The heterogeneous reactions of $ClONO_2$ with solid NaCl and KBr have already been studied in a fast flow (Timonen et al., 1994) and a Knudsen cell (Caloz et al., 1996; Wingetener et al., 1996; Aguzzi and Rossi, 1999; Gebel and Finlayson-Pitts, 2001) and the primary reaction products on NaCl were HOCl and Cl_2 while BrCl was observed on KBr.

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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 the one depicted by Reactions (2) and (3).

However in the marine boundary layer, the relative humidity is high, eventually above the deliquescence point of sea-salt particles and rarely low enough to reach the efflorescence point. Therefore, one may argue that a significant fraction of sea-salt aerosols are wet. However, the uptake kinetics of $XONO_2$ on salt solutions have 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 273–280 K. Some reaction products have also been identified, suggesting some reaction mechanisms. In the following sections, we present our experimental methodology whereas in subsequent sections, 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 in-coming 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

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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
5 (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
10 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
15 et al. (1981).

The gas stream coming out of the flowtube was analysed using mass spectrometry with an ionisation energy of 60 eV. The signal was averaged over a second in order to increase the signal to noise ratio. $ClONO_2$ was monitored at 51 amu (ClO^+), $BrONO_2$ at 95 and 97 amu (BrO^+), Cl_2, $BrCl$, Br_2, by their parent ions (70, 116 and 160 amu, re-
20 spectively). In addition, H_2O and an inert tracer SF_6 were monitored at 18 (H_2O^+) amu and 89 (S^+F_3) amu during the experiments in order to see any potential perturbations in gas phase concentrations.

We also used FTIR spectroscopy in order to identify all the gas phase species. The system used consists of a Nicolet Protégé 460 spectrometer equipped with an IRA long
25 path White-cell (light path in the range from 2.2 to 22 m) with KBr windows. Infra-red spectra were taken in the range from 4000 to 400 cm^{-1} and were co-added in order to increase the S/N ratio.

The droplets were made from Milli-Q water (18 MΩ cm) and NaCl (Aldrich, ≥99%) or NaBr (Aldrich, ≥99%) when necessary.

2.2. Synthesis of chlorine nitrate (ClONO$_2$)

ClONO$_2$ was synthesized by reacting Cl$_2$O with an excess of N$_2$O$_5$ at low temperature, according to the following reaction (Caloz, 1997):

$$Cl_2O + N_2O_5 \rightarrow 2ClONO_2. \tag{6}$$

N$_2$O$_5$ was prepared from the oxidation of NO$_2$ by O$_3$ in the gas phase after mixing of the flows containing each reactant. To prevent any hydrolysis and the formation of HNO$_3$ both NO$_2$ and O$_3$ flows were dried by flowing the gases through traps prior to mixing. After some reaction time, N$_2$O$_5$ was collected on a cold finger kept at low temperature where it condensed as a white powdery solid.

Liquid Cl$_2$O was obtained by condensing Cl$_2$ on an excess of yellow mercury oxide (HgO) and allowing the mixture to react at a temperature of 190 K for 4 h.

Cl$_2$O and N$_2$O$_5$ 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. ClONO$_2$ appeared as a yellow green liquid with Cl$_2$ being the main impurity, which can be minimized by freeze-pump-thaw cycles.

2.3. Synthesis of bromine nitrate (BrONO$_2$)

Bromine nitrate was synthesized by adding Br$_2$ to ClONO$_2$, following the procedure described by Wilson and Christe (1987) and according to the reaction:

$$ClONO_2 + Br_2 \rightarrow BrONO_2 + BrCl. \tag{7}$$

ClONO$_2$ was mixed with Br$_2$ 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 BrONO$_2$ were BrCl, Cl$_2$ and unreacted ClONO$_2$ and Br$_2$. 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

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. III) 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):

$$\frac{1}{\gamma} = \frac{1}{\gamma_{\text{diff}}} + \frac{1}{\alpha} + \frac{1}{\gamma_{\text{sat}} + \gamma_{\text{rxn}}} = \frac{<c>d_{\text{eff}}}{8D_g} - \frac{1}{2} + \frac{1}{\alpha} + \frac{<c>}{4HRT\sqrt{D_a}}\left(\frac{2}{\sqrt{\pi t}} + \sqrt{k}\right)^{-1}, \qquad (8)$$

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 droplet 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. 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 (Widmann and Davis, 1997; Kolb et al., 1998), especially the diffusion correction formulation which is based on the work of Schwartz (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

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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 as discussed below.

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 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 absence of temperature effects just illustrates the point that the measured kinetic is not elementary but is driven by several physical and chemical processes that have differ-

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ent temperature trends. In fact, the solubility of gases increases when the temperature decreases while the chemical reactivity decreases at the same time. Accordingly, for a gaseous specie for which uptake is controled 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 ClONO$_2$, the chemical reaction is its hydrolysis according to:

$$ClONO_2 + H_2O \rightarrow HOCl + NaNO_3. \tag{9}$$

However, HOCl was not detected as a reaction product because it is too soluble and reactive.

It has been proposed that ClONO$_2$ reacts with NaCl according to (Timonen et al., 1994; Aguzzi and Rossi, 1999):

$$ClONO_2 + NaCl \rightarrow Cl_2 + NaNO_3 \tag{10}$$

leading to the production of Cl$_2$. However, we did not observe any increase of the uptake rate when adding NaCl into our droplets, but we observed some Cl$_2$ production. Within our experimental conditions, the same uptake rate was observed on pure water and on NaCl-doped droplets suggesting that no direct reaction is occurring with NaCl. Rather, we suggest a two-step mechanism where ClONO$_2$ is first hydrolyzed according to Reaction (9) to produce HOCl which subsequently reacts with NaCl according to:

$$HOCl + NaCl \rightarrow Cl_2 + NaOH. \tag{11}$$

This reaction is known to be facilitated under acidic conditions which may occur in our experiments due to the dissociation of HOCl at the surface (even a low concentration of in-coming gas may affect the surface pH because this region is very narrow) or due to impurities in our gas flows (some traces of HNO$_3$ in ClONO$_2$ are unavoidable).

We observed indeed Cl$_2$ 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 may underline that traces of HOCl were still present in our ClONO$_2$ source.

These traces may significantly contribute to Cl$_2$ formation (Reaction 11) and therefore we were unable to quantitatively assess the amount of Cl$_2$ formed by Reaction (10).

Very recently, Gebel and Finlayson-Pitts (2001) studied the uptake of ClONO$_2$ 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 ClONO$_2$ 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 Cl$_2$ production. These observations also strongly suggested a two-step mechanism where ClONO$_2$ is first hydrolysed leading to HOCl which is then converted into Cl$_2$. Although they have been working with solid substrates, their conclusions on a two-step mechnism can easily be applied to our own observations.

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 increase from 0.041 to 0.073 when NaBr concentrations increase from 0.01 to 1 M, suggesting a direct reaction between ClONO$_2$ and bromide ions. The difference of reactivity of ClONO2 on 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):

$$\frac{1}{\gamma} = \frac{1}{\gamma_{\text{diff}}} + \frac{1}{\alpha} + \frac{1}{\gamma_{\text{rxn}}} = \frac{<c>d_{\text{eff}}}{8D_g} - \frac{1}{2} + \frac{1}{\alpha} + \frac{<c>}{4HRT\sqrt{D_a k}}. \tag{12}$$

Equation (12) may also be written as:

$$\frac{1}{\gamma} - \frac{1}{\gamma_{\text{diff}}} = \frac{1}{\alpha} + \frac{<c>}{4HRT\sqrt{D_a k}} \tag{13}$$

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 $(1/\gamma - 1/\gamma_{\text{diff}})$ versus $(NaBr)^{-1/2}$ as depicted in Fig. 3. The estimated value at $274.5\pm1\,K$ is $\alpha=(0.108\pm0.001)$, where the errors only reflect statistical uncertainties, without any considerations of systematic deviations. 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 controled 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, 0.1 and 0.23, respectively, are also consistent with our value.

As the uptake of $ClONO_2$ on NaBr is driven by chemical reactions, we tried to identify the possible gas phase reaction products. Figure 4 shows the evolution of $ClONO_2$ and of the reaction products (Cl_2, BrCl and Br_2) for a typical experiment conducted on a 0.1 M NaBr solution. The increased number of reaction products, illustrates that on NaBr solutions, the reaction mechanism is more complex than on NaCl solutions.

In fact on NaBr, there is a direct reaction between $ClONO_2$ and NaBr, producing BrCl:

$$ClONO_2 + NaBr \rightarrow BrCl + NaNO_3. \tag{14}$$

Note however that BrCl may also be produced by the reaction between HOCl and NaBr

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(produced from the hydrolysis of $ClONO_2$) i.e.

$HOCl + NaBr \rightarrow BrCl + NaOH$. (15)

BrCl itself is known to react with bromide anion producing Br_2, according to:

$BrCl + NaBr \rightarrow Br_2 + NaCl$. (16)

5   $ClONO_2$ reacts then with NaCl to produce Cl_2:

$ClONO_2 + NaCl \rightarrow Cl_2 + NaNO_3$. (17)

The above set of reactions can fully explains the observed trends in the reaction products. The latter are in good agreement with those observed by Aguzzi and Rossi (1999) during the interaction of $ClONO_2$ on solid KBr. BrCl is the major product gener-
10 ated. In a secondary reaction, it may react with NaBr to release Br_2.

3.2.   Uptake measurements of $BrONO_2$

The uptake of $BrONO_2$ by aqueous droplets was also studied as a function of temper-
ature 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
15 0.039 when T increased from 273 to 280 K as shown in Fig. 5. This may just reflect
different temperature trends for Henry's law constant and reactivity of $ClONO_2$ com-
pared 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
for brominated and chlorinated species (Br_2 is more soluble than Cl_2, $BrNO_2$ is more
20 soluble than $ClNO_2$, HOBr might be more soluble than HOCl 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
$ClONO_2$. 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
25 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:

$$BrONO_2 + H_2O \rightarrow HOBr + NaNO_3. \tag{18}$$

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. 5), However, it has also been proposed (Aguzzi and Rossi, 1999) that BrONO$_2$ reacts with NaCl according to:

$$BrONO_2 + NaCl \rightarrow BrCl + NaNO_3 \tag{19}$$

leading to the production of BrCl. From our experiments on NaCl doped droplets (Fig. 6), we saw indeed some BrCl production. 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$_2$, producing HOBr (Reaction 18) which subsequently reacts with NaCl according to:

$$HOBr + NaCl \rightarrow BrCl + NaOH. \tag{20}$$

The latter reaction was shown to be very efficient by Crowley and co-workers (Adams et al., 2002). As shown in Fig. 6, other minor products were observed i.e. Cl$_2$ and Br$_2$. These may be formed on or in the droplets by subsequent reaction of both HOBr and BrCl and therefore are not directly linked to the primary uptake of BrONO$_2$.

This two-step mechanism for the reaction of BrONO$_2$ on NaCl doped droplets differs slightly from the mechanism proposed by Aguzzi and Rossi (1999) who studied the uptake of BrONO$_2$ on solid NaCl particles with a Knudsen cell reactor. To explain their observations, they consider that there exist a competition between the hydrolysis of BrONO$_2$ (Reaction 18) and the direct reaction between BrONO$_2$ and NaCl producing BrCl (Reaction 19).

The uptake rate of BrONO$_2$ was strongly affected by the concentration of NaBr in the droplet (see Fig. 7). The values of the uptake coefficients γ varied from 0.032 to 0.062

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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:

$$BrONO_2 + NaBr \rightarrow Br_2 + NaNO_3. \tag{21}$$

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. 7. The estimated value is 0.063±0.009 at 273 K where again the errors only reflects statistical uncertainties without any considerations of systematic deviations. 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 for ClONO$_2$, as it was already observed for HBr compared to HCl (where the same trend in solubility would apply). Consequently, we can observe that the correction level between $1/\gamma$ and $1/\alpha$ is reduced in this case compared to ClONO$_2$. According to Eq. (8), the uptake is intrinsically less hindered due to the higher solubility of the brominated species.

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 but could be linked to the nature of their solid surface and of its water content.

4. Conclusions

We reported here first measurements of the uptake rate of ClONO$_2$ and BrONO$_2$ on pure water and NaCl or NaBr-doped droplets using the droplet train technique. From

the reaction products, we identified for both compounds that there was no direct reaction (at least within our experimental conditions) with NaCl but a secondary reaction with the hydrolysis product i.e. the hypohalogeneous acid HOX (where X= Cl, Br). However, a direct reaction was observed between ClONO$_2$ and BrONO$_2$ and NaBr, which

5 then acted as a scavenger. This allowed the estimation of the mass accommodation coefficient. The hydrolysis reaction has direct implication for the simulation of the activation of halogenated radicals in the marine environment where it has been thought that only the latter is of any significance.

Edited by: J. Crowley

References

15 Adams, J. W., Holmes, N. S., and Crowley, J. N.: Uptake and reaction of HOBr on frozen and dry NaCl/NaBr surfaces betwen 253 and 233 K, Atmos. Chem. Phys., 2, 79–91, 2002.
Aguzzi, A. and Rossi, M. J.: The Kinetics of the Heterogeneous Reaction of BrONO$_2$ with Solid Alkali Halides at Ambient Temperature. A Comparison with the Interaction of ClONO$_2$ on NaCl and KBr, Phys. Chem. Chem. Phys., 1, 4337–4346, 1999.
20 Baboobal, L. B., Pruppacher, H. R., and Topalian, J.H.: A sensitivity study of a theoretical model of SO$_2$ scavenging by water drops in air, J. Atmos. Sci., 38, 856–870, 1981.
Barrie, L. A., Bottenheim, J. W., Schnell, R. C., Crutzen, P. J., and Rasmussen, R. A.: Ozone destruction and photochemical reactions at polar sunrise in the lower Arctic atmosphere, Nature, 334, 138–141, 1988.
25 Caloz, F.: Labory kinetic studies of heterogeneous processes relevant to the marine troposphere, Thesis, Ecole Polytechnique de Lausanne, 1997.
Caloz, F., Fenter, F. F., and Rossi, M. J.: Heterogeneous Kinetics of the Uptake of ClONO$_2$ on NaCl and KBr, J. Phys. Chem. 100, 18, 7494–7501, 1996.

Crutzen, P. J.: Overview of Tropospheric Chemistry – Developments During the Past Quarter-Century and a Look-Ahead, J. Faraday Discussion, 100, 1–21, 1995.

Finlayson-Pitts, B. J. and Pitts, J. N.: Atmospheric chemistry : fundamentals and experimental techniques, Wiley, New York, xxviii, 1098, 1986.

5 Fuchs, N. A. and Sutugin, A. G.: Highly dispersed aerosols, International Reviews of aerosol Physics and Chemistry, edited by Hidy, G. M. and Brock, J. R., New York, 1–60, 1971.

Gebel, M. E. and Finlayson-Pitts, B. J.: Uptake and Reaction of $ClONO_2$ on NaCl and Synthetic Sea Salt, J. Phys. Chem. A., 105, 21, 5178–5187, 2001.

George, C.: Physico-chimie Hétérogène de l'Atmosphère: Etude Expérimentale et
10 Modélisation des Processus de Transfert Gaz/Liquide. Thèse de doctorat, Université Louis Pasteur de Strasbourg, 1993.

Hanson, D. R., Ravishankara, A. R., and Lovejoy, E. R.: Reaction of $BrONO_2$ with H_2O on Sub-micron Sulfuric-Acid Aerosol and the Implications for the Lower Stratosphere, J. Geophys. Res. - Atmos., 101, D4, 9063–9069, 1996.

15 Kolb, C. E., Worsnop, D. R., Jayne, J. T., and Davidovits, P.: Comment on Mathematical-Models of the Uptake of $ClONO_2$ and Other Cases by Atmospheric Aerosols, J. Aerosol Sci., 29, 7, 893–897, 1998.

Kolb, C. E., Worsnop, D. R., Zahniser, M. S., Davidovits, P., Hanson, D. R., Ravishankara, A. R., Keyser, L. F., Leu, M. T., Williams, L. R., Molina, M. J., and Tolbert, M. A.: Laboratory Studies
20 of Atmospheric Heterogeneous Chemistry. In: J.R. Barker (Editor), Advances in Physical Chemistry Series, World scientific, Singapore, 771–875, 1994.

Liss, P. S. and Slater, P. G.: Flux of Gases across the Air-Sea Interface, Nature, 247, 181–184, 1974.

Magi, L., Schweitzer, F., Pallares, C., Cherif, S., Mirabel, P., and George, C.: Investigation of
25 the Uptake Rate of Ozone and Methyl Hydroperoxide by Water Surfaces, J. Phys. Chem. A, 101, 27, 4943–4949, 1997.

Mellouki, A.: Kinetic studies of Cl atom reactions with a series of alkanes using the pulsed laser photolysis-resonance fluorescence method, J. Chim. Phys., 95, 513–522, 1998.

Notario, A., Le Bras, G., and Mellouki, A.: Absolute rate constants for the reactions of Cl Atoms
30 with a series of esters, J. Phys.Chem., 102, 3112–3117, 1998.

Pruppacher, H. R. and Klett, J. D.: Microphysics of Clouds and Precipitation, Reidel Publishing Co., Dordrecht, The Netherlands, 1978.

Pszenny, A. A. P., Keene, W. C., Jacob, D. J., Fan, S., Maben, J. R., Zetwo, M. P., Springer-

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Young, M., and Galloway, J. N.: Evidence of inorganic chlorine gases other than hydrogen chloride in marine surface air, Geophys. Res. Lett. 20, 699–702, 1993.

Sander, R.: Compilation of Henry's Law Constants for norganic and Organic Species of Potential Importance in Environmental Chemistry (Version 3), 1999.

5   Schwartz, S. E.: Chemistry of Multiphase Atmospheric Systems, 4, NATO ASI Ser., edited by Jaeschke, W., Springer-Verlag, Berlin Heidelberg, 415, 1986.

Schweitzer, F., Mirabel, P., and George, C.: Multiphase Chemistry of N_2O_5, $ClNO_2$, and $BrNO_2$, J. Phys. Chem. A, 102, 22, 3942–3952, 1998.

Timonen, R. S., Chu, L. T., Leu, M. T., and Keyser, L. F.: Heterogeneous Reaction of

10    $Clono_2(G)+nacl(S)-)Cl^{-2}(G)+nano_3(S)$, J. Phys. Chem. A. 98, 38, 9509–9517, 1994.

Wagner, T. and Platt, U.: Satellite Mapping of Enhanced Bro Concentrations in the Troposphere, Nature 395, 6701, 486–490, 1998.

Widmann, J. F. and Davis, E. J.: Mathematical models of the uptake of $ClONO_2$ and other gases by atmospheric aerosols, J. Aerosol. Sci., 28, 1, 87–106, 1997.

15   Wilson, W. W. and Christe, K. O.: Bromine Nitrates, Inorg. Chem., 26, 1573–1580, 1987.

Wingetener, O. W., Kubo, M. K., Blake, N. J., Smith Jr., T. W., Blake, D. R., and Rowland, F. S.: Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, vertical mixing obtained during Lagrangian flights, J. Geophys. Res., 101, 4331–4340, 1996.

20   Worsnop, D. R., Zahniser, M. S., Kolb, C. E., Gardner, J. A., Jayne, J. T., Watson, L. R., Van Doren, J. M., and Davidovits, P.: Temperature dependence of mass accommodation of SO_2 and H_2O_2 on aqueous surfaces. J. Phys. Chem. A, 93, 1159–1172, 1989.

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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

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

Solution	T (K)	P (Torr)	$10^2 \times \gamma$ (2σ)	$1/\gamma - 1/\gamma_{\text{diff}}$ (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
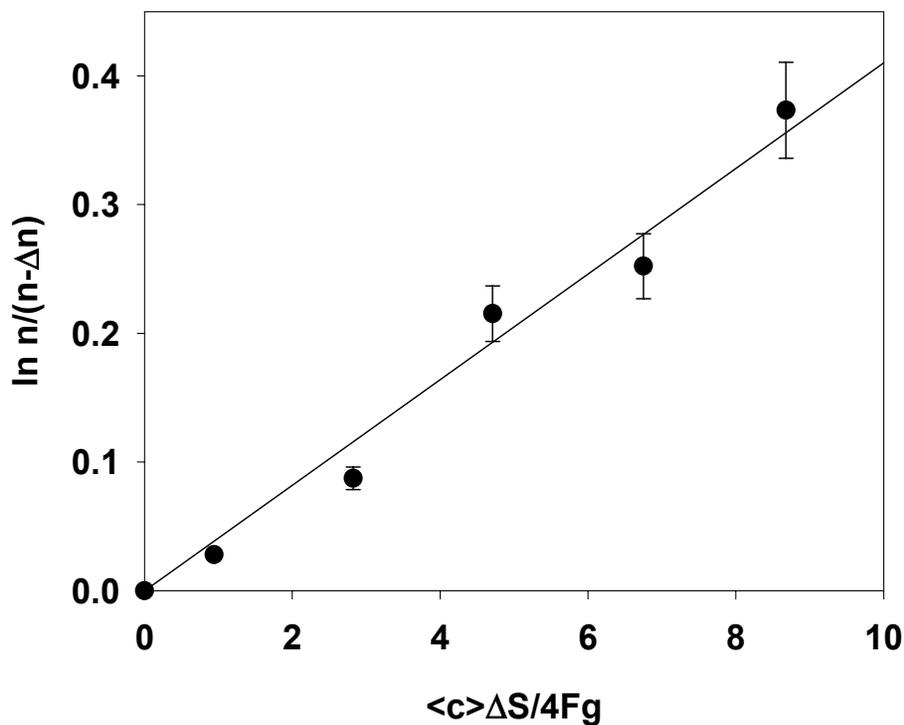
Fig. 1. Typical plots of $\ln(n/n - \Delta n)$ versus $<c>\Delta S/4F_g$ for ClONO$_2$ on a 0.05 M NaBr solution at 277 K. The slope is γ according to Eq. (5).

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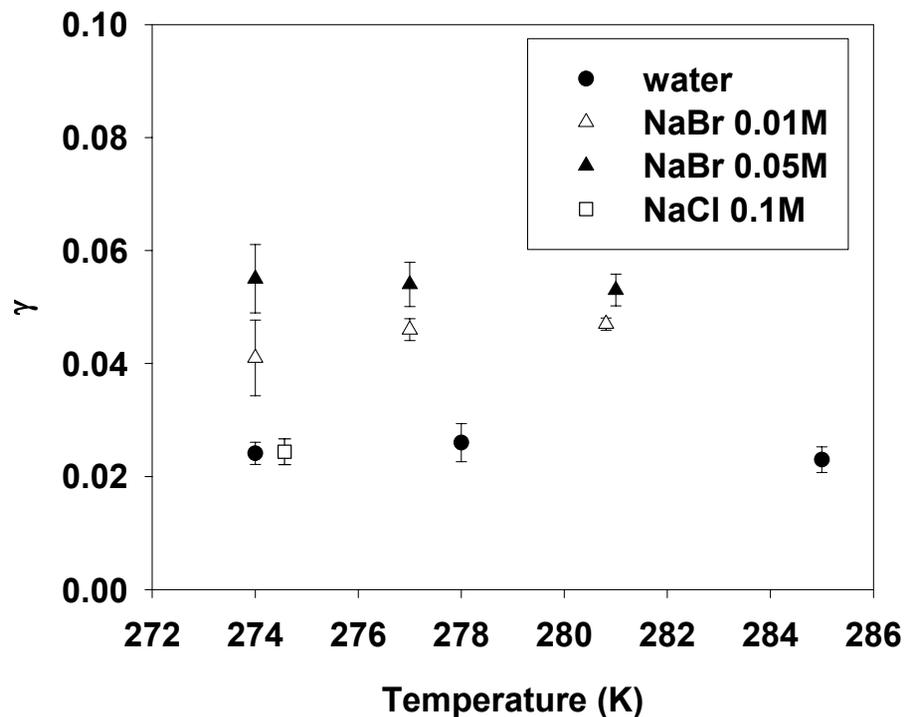
Fig. 2. ClONO$_2$ uptake coefficient as a function of temperature. The error bars are given at 1σ level. (black dot: water; triange: NaBr 0.01M ; black triangle: NaBr 0.05M; square: NaCl 0.1M).
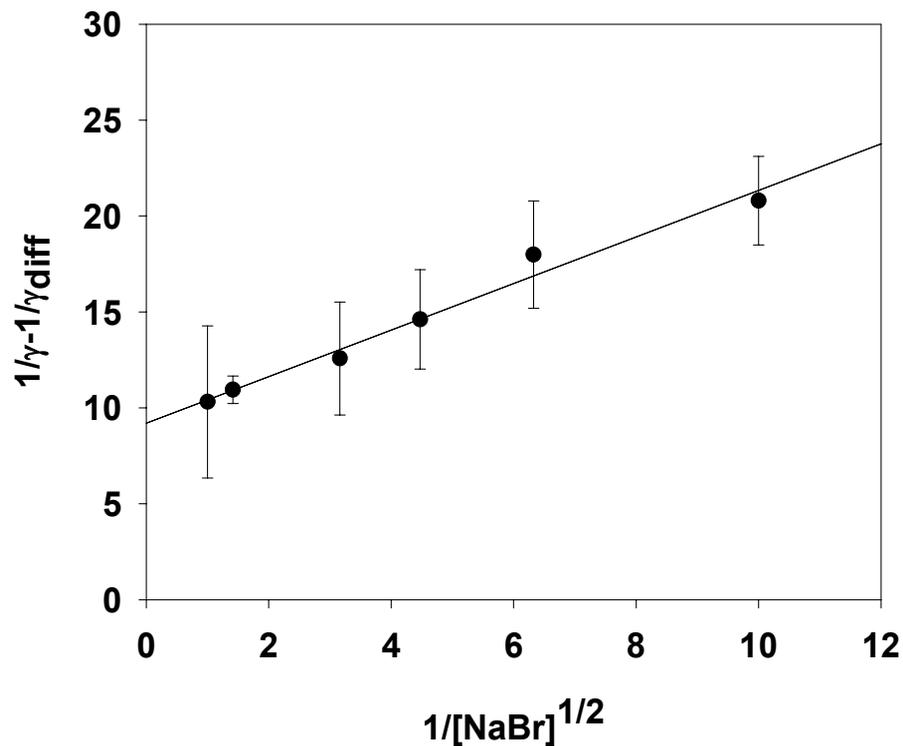
Fig. 3. Plot of uptake coefficients for ClONO$_2$ according to Eq. (13). The intercept is the inverse of the mass accommodation coefficient α. T=274.5±1 K. The error bars are given at the 1σ level.
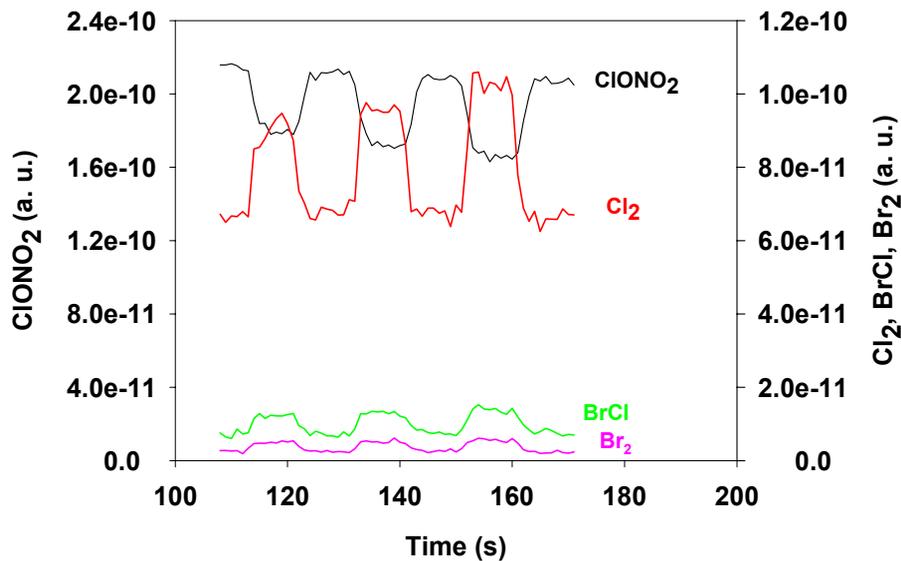
Fig. 4. ClONO$_2$ and products profiles in gas phase versus time (T= 6.8°C, (NaBr)=0.1 M).
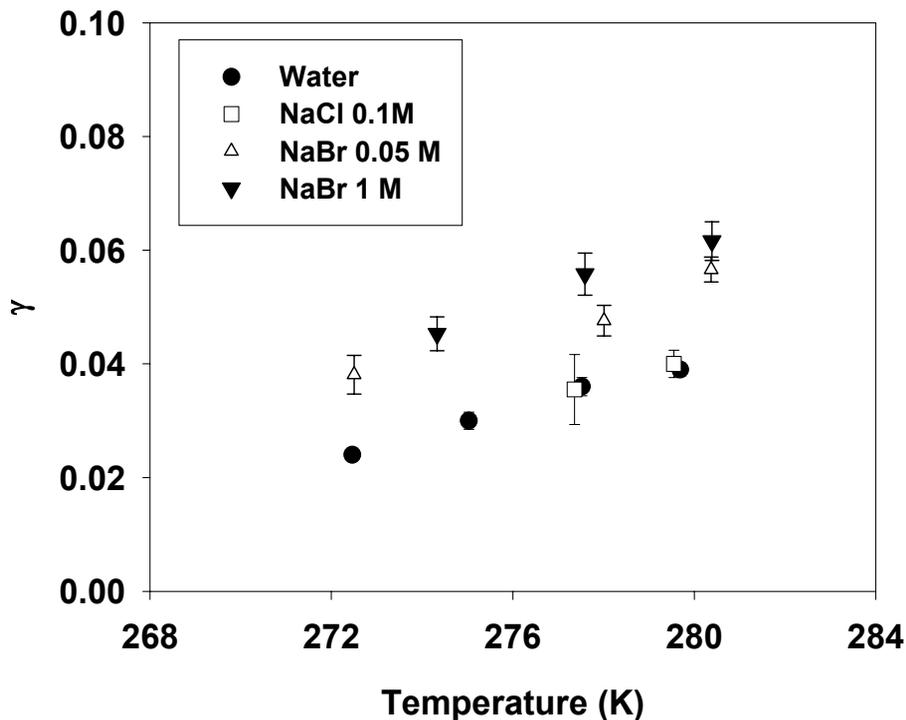
Fig. 5. BrONO$_2$ uptake coefficient as a function of temperature. The error bars are given at the 1σ level. (black dot: water; triangle: NaBr 0.05M; black triangle: NaBr 1M; square: NaCl 0.1M).
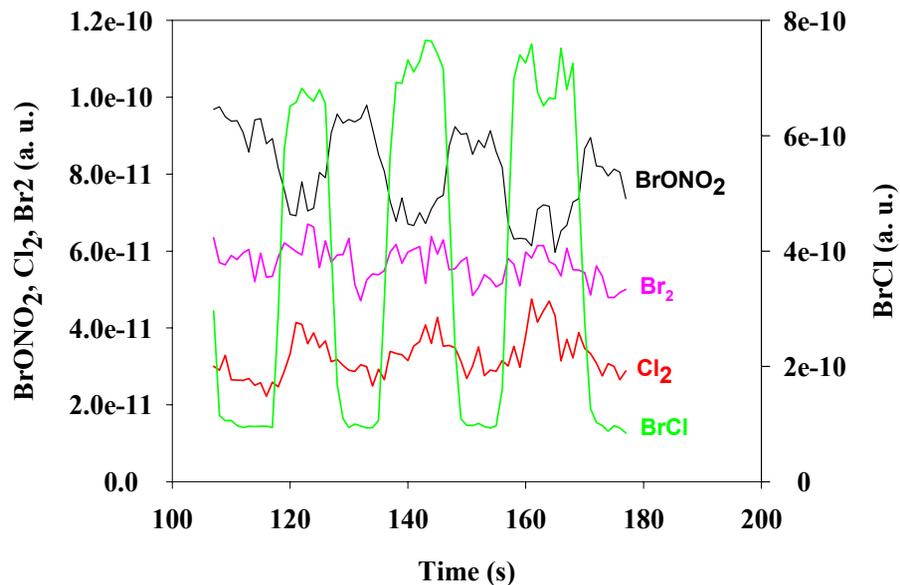
**Fig. 6.** BrONO$_2$ and products profiles in gas phase versus time (T= 6.4°C, (NaCl)=0.1 M).

Fig. 7. Plot of uptake coefficients for BrONO$_2$ according to Eq. (13). The intercept is the inverse of the mass accommodation coefficient α. T=273±1 K. The error bars are given at the 1σ level.