



**Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol**

S. Bleicher et al.

This discussion paper is/has been under review for the journal Atmospheric Chemistry and Physics (ACP). Please refer to the corresponding final paper in ACP if available.

# The influence of nitrogen oxides on the activation of bromide and chloride in salt aerosol

S. Bleicher<sup>1</sup>, J. C. Buxmann<sup>2,\*</sup>, R. Sander<sup>3</sup>, T. P. Riedel<sup>4</sup>, J. A. Thornton<sup>4</sup>, U. Platt<sup>2</sup>, and C. Zetzsch<sup>1</sup>

<sup>1</sup>Atmospheric Chemistry Research Unit, University of Bayreuth, Bayreuth, Germany

<sup>2</sup>Institut für Umweltphysik, University of Heidelberg, Heidelberg, Germany

<sup>3</sup>Air Chemistry Department, Max-Planck Institute for Chemistry, Mainz, Germany

<sup>4</sup>University of Washington, Seattle, USA

\* now at: Met Office, Exeter, UK

Received: 6 March 2014 – Accepted: 11 March 2014 – Published: 22 April 2014

Correspondence to: C. Zetzsch (cornelius.zetzsch@uni-bayreuth.de)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Abstract

Experiments on salt aerosol with different salt contents were performed in a Teflon chamber under tropospheric light conditions with various initial contents of nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ). A strong activation of halogens was found at high  $\text{NO}_x$  mixing ratios, even in samples with lower bromide contents such as road salts. The ozone depletion by reactive halogen species released from the aerosol, was found to be a function of the initial  $\text{NO}_x$  mixing ratio. Besides bromine, large amounts of chlorine have been released in our smog chamber. Time profiles of the halogen species  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{ClNO}_2$ ,  $\text{BrNO}_2$  and  $\text{BrO}$ ,  $\text{ClO}$ ,  $\text{OCIO}$  and  $\text{Cl}$  atoms were simultaneously measured by various techniques (chemical ionization mass spectrometry, differential optical absorption spectrometry coupled with a multi-reflection cell and gas chromatography of hydrocarbon tracers for  $\text{Cl}$  and  $\text{OH}$ , employing cryogenic preconcentration and flame ionization detection). Measurements are compared to calculations by the CAABA/MECCA 0-D box model, which was adapted to the chamber conditions and took the aerosol liquid water content and composition into account. The model results agree reasonably with the observations and provide important information about the prerequisites for halogen release, such as the time profiles of the aerosol bromide and chloride contents as well as the aerosol pH.

## 1 Introduction

Due to their high reactivity, bromine and chlorine have a strong impact on the chemistry of the atmosphere. In contrast to the situation in the stratosphere, their presence in the troposphere seems to be dominated by natural sources such as sea spray. Especially chlorinated species are difficult to measure directly, resulting in a challenge to infer a budget of total reactive chlorine in the lower atmosphere. Recent studies suggest that a significant fraction of the tropospheric  $\text{Cl}^\bullet$  source is anthropogenic (Thornton et al., 2010). Although the mechanisms of halide activation, namely the conversion of inactive

ACPD

14, 10135–10166, 2014

### Influence of $\text{NO}_x$ on the activation of $\text{BrO}$ and $\text{ClO}$ in salt aerosol

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

halides into reactive halogen species (e.g. halogen oxides), are not fully understood, it is known that the pH-value (Betts and Mackenzie, 1951; Fickert et al., 1999; da Rosa and Zetzsch, 2001) and the bromide to chloride ratio (Behnke et al., 1999) have an impact on the activation cycles. Especially the role of NO<sub>x</sub> molecules is under discussion. Recently, Lopez-Hilfiker et al. (2012) and Wren et al. (2013) found the production of gaseous chlorine and bromine molecules from NaCl/NaBr-doped and acidified ice surfaces, which was also observed in nature (Pratt et al., 2013) The acidification of such ice surfaces and aerosol droplets can be caused by nitrogen oxides, in particular by the production of N<sub>2</sub>O<sub>5</sub> during nighttime and its hydrolysis and dissociation to H<sup>+</sup> and NO<sub>3</sub><sup>-</sup> on aqueous surfaces (George et al., 1994; Schütze et al., 2002):

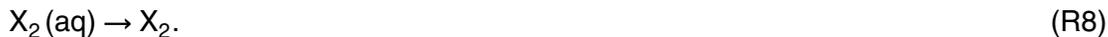


Nitric acid can also be formed during daytime by the reaction of NO<sub>2</sub> with OH (e.g. Hippler et al., 2006):



However, the first halogen molecules (indicated by X or Y = Cl, Br) can be activated by dissolved ozone (aqueous species are indicated by “aq”) even during nighttime (e.g. Hunt et al., 2004):





During the daytime the gaseous halogen molecules are photolyzed to two halogen atoms, which rapidly react with ozone:



The formed bromine oxide is known to effectively deplete ozone catalytically due to its self-reaction:



10 The branching ratio of Reactions (R11a)/(R11)(overall) is reported to be  $\sim 0.85$  and formation of OBrO and Br is considered to be unimportant (Atkinson et al., 2007). However, under the influence of light Br<sub>2</sub> is photolyzed rapidly (photolysis rates can be found in the Supplement). In the mixed case of additional activated chlorine, the depletion of ozone is even faster. Then BrO may also react with ClO to form a Br atom and an intermediate OCIO molecule. OCIO in turn reacts with chlorine atoms back to ClO:



XO radicals may also react with hydroperoxyl radicals to form hypohalide acids, which are the driver of Reaction (R7) after their uptake into the aqueous phase:



## Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

## Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

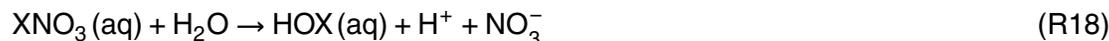
Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

The aquatic uptake of one molecule containing one halogen atom and the subsequent release of one molecule containing two halogen atoms into the gas phase results in a self-accelerating autocatalytic activation of halides and thus is called “halogen explosion” (Platt and Janssen, 1995; Hönninger et al., 2004). Under remote conditions the halogen explosion occurs rather for X = Br than for X = Cl. One reason is the faster uptake of HOBr compared to HOCl, due to the higher p*K*<sub>a</sub> value of HOBr (p*K*<sub>a</sub> = 7.8 at 273 K for HOCl, (Morris, 1966), and a p*K*<sub>a</sub> = 8.6 at 274 K for HOBr, Shilov, 1938). Additionally the release of X, Y = Br is favored over X = Cl and Y = Br or X, Y = Cl due to water phase reaction constants (Fickert et al., 1999). In polluted areas the activation can be accelerated by XNO<sub>3</sub>, which accrues in the reaction of XO and NO<sub>2</sub> (Cox and Lewis, 1979; Sander et al., 1981):



XNO<sub>3</sub> have a faster uptake to the aqueous phase than HOX (e.g. Hanson et al., 1996; Deiber et al., 2004) and its hydrolysis also provides protons needed by Reaction (R7).

Additionally, heterogeneous reactions are known to influence the halogen chemistry (summarized by Rossi, 2003). E.g. the uptake of N<sub>2</sub>O<sub>5</sub> on halide aqueous phase leads to a direct transition of the halides to gaseous photolabile reservoir species (e.g. George et al., 1994):



This heterogeneous activation mechanism was originally proposed and investigated by Finlayson-Pitts et al. (1989) and confirmed in an aerosol smog chamber by Zetzsch and Behnke (1992) and Behnke et al. (1993, 1997) for chlorine and investigated in detail in a wetted-wall flow-tube by Frenzel et al. (1998), including X = Br. The production of ClNO<sub>2</sub> has been observed by Osthoff et al. (2008) in the polluted subtropical marine boundary layer. It alters. The production of ClNO<sub>2</sub> alters the NO<sub>x</sub> and Cl budgets, both

## Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

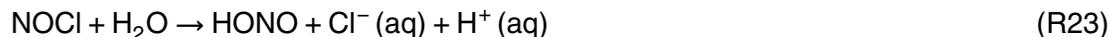
Printer-friendly Version

Interactive Discussion

of which affect the troposphere's oxidizing capacity. Recently, a few hundred ppt of ClNO<sub>2</sub> have been measured in the middle of North America (Boulder, Colorado) by Thornton et al. (2010) and over continental Europe (Phillips et al., 2012). A further important class of heterogeneous reactions provides chloride to the aqueous phase example such as the well-known conversion of molecular chlorine to bromine on halide surfaces: One example is the well-known conversion of molecular chlorine to bromine on halide surfaces:



and the formation of HONO from an uptake of NOCl into the aqueous phase (Scheer et al., 1997):



Uptake of ClNO<sub>2</sub> is possible as well (Behnke et al., 1997), but at a slower rate compared to NOCl (Frenzel et al., 1998). The most important source of NOCl is the reaction of 2 NO<sub>2</sub> + NaCl → NOCl + NaNO<sub>3</sub> (Finlayson-Pitts, 1983). A further minor source is the reaction of chlorine atoms with nitrogen monoxide ( $2.19 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ; DeMore et al., 1997).

## 2 Instrumental setup and methods

The experiments were performed in a 3.7 m<sup>3</sup> Teflon chamber (FEP 200A, DuPont) with a surface to volume ratio of 3.5 m<sup>-1</sup>. In this chamber we are able to simulate the mixed aqueous and gaseous chemistry of the tropospheric mixed boundary layer (see also Bleicher, 2012). The light of seven medium pressure arc lamps (7 × 1200 W, Osram HMI1200GS) below the chamber is filtered by glass (Schott, Tempax, 3 mm thickness)



aerosol, although not measurable, contributes to the chemistry, which results in a considerable uncertainty for the computer modeling applied in this study. A comparable chamber set-up and the wall effects on the chemistry are also discussed in a recent paper by Hoch et al. (2014).

During the experiments, the bromide concentration was varied for two reasons: (a) the influence of bromide on the activation of chloride by recombination of HOBr(aq) with chloride to BrCl instead of Br<sub>2</sub> in mechanism Reaction (R7), (b) the light loss due to the Mie-scattering by the aerosol within the light path of the differential optical absorption spectrometer (DOAS). While the efficiency of mechanism (a) is a scientific question (b) has a technical origin. The DOAS system has already been described in detail by Buxmann et al. (2012) and Buxmann (2012), and here we give a short overview. The instrument was equipped with a multi-reflection cell (White, 1976) with a base length of 2 m diagonal through the chamber using highly reflective dielectric mirrors (Layertec,  $R > 0.995$  between 335 and 360 nm) to achieve a path length of 288 m. This led to a mean BrO and OClO detection limit of 40 ppt and 150 ppt, respectively. The  $4\sigma$  statistical error of a single spectral fit was taken as an estimate of the detection limit. Optional broadband aluminum mirrors ( $R \sim 0.90$  between 300–405 nm) were used to observe a larger variety of species e.g. ClO, O<sub>3</sub> and HONO albeit at a shorter light path. For ClO the chosen light path of 32 m results in a detection limit of  $\sim 800$  ppt. The integrated output light intensity after passing the White cell is proportional to the integration time of the DOAS spectra and thus influences the sensitivity. To minimize light loss, we used low aerosol concentrations ( $lwc \sim 5 \times 10^{-10}$ ) with high bromide content ( $300 \text{ mmol L}^{-1}$ ) as compensation in all experiments where DOAS was applied. Ozone was generated by an electrical discharge (Sorbios, GSG 12) in oxygen (Rießner Gase, 99.996 %) and measured by UV absorption (Thermo Scientific, 49i). NO<sub>2</sub> was injected from gas cylinders (Rießner Gase, 101 ppm in N<sub>2</sub>) and measured by chemiluminescence (Ecophysics, CLD 88p, CLD 700) with two types of converters: a photolytic converter (Ecophysics, PLC 860, mainly sensitive to NO<sub>2</sub>) and a molybde-

## Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



num converter (used in the CLD 700 instrument), which is sensitive to a broad spectrum of NO<sub>x</sub> species.

The measurement of the ozone temporal variation allows us to estimate the BrO concentration assuming that Reaction (R10) is the dominant O<sub>3</sub> loss process and Reaction (R11a) is the rate-limiting step:

$$-\frac{d[\text{O}_3]}{dt} = 2k_1[\text{BrO}]^2 + c \quad (1)$$

where  $c$  represents other ozone sinks and  $k_1 = 2.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  is the second order rate constant of Reaction (R11a). In an empty, but humidified and illuminated chamber we observe a typical ozone loss of max.  $0.02 \text{ ppbs}^{-1}$  at ozone mixing ratios below 1 ppm. This value includes a wall loss of max.  $\sim 0.015 \text{ ppbs}^{-1}$  at typical O<sub>3</sub>-mixing ratios in the chamber and a humidity dependent loss due to the O(<sup>1</sup>D) photolysis channel of ozone. To estimate the BrO mixing ratio from Eq. (1), we eliminated the separately measured dilution rate (but not the wall loss) and removed the noise from the ozone curve by smoothing it using the Savitzky–Golay algorithm.

Hydrocarbons (HC), which can be important sinks for reactive halogens, were measured by gas chromatography (Siemens Sichromat 2, AI-PLOT column 50 m, flame ionization detector, with custom built nitrogen cold trap enrichment). By measuring the decay of a special injected HC mixture (*n*-pentane, 2,2-dimethylbutane, 2,2,4,4-tetramethylbutane, toluene) and an inert dilution standard (*n*-perfluorohexane) we could indirectly determine the concentrations of OH and Cl radicals. This method is known as the radical clock method (RCM, Zetsch and Behnke, 1992). It was used in selected experiments only since the HC species influence the halogen chemistry. The measured HC time profiles were interpolated by appropriate exponential and/or sigmoidal functions. The time derivatives of the fitted functions allow us to solve the set of  $n$  linear equations ( $n$  = count of HC species) to get the both unknowns [Cl] and [OH]

**Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol**

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



for all experimental times  $t$ :

$$\frac{d[\text{HC}]_i}{dt} = -k_{\text{OH},i}[\text{OH}][\text{HC}]_i - k_{\text{Cl},i}[\text{Cl}][\text{HC}]_i, \quad (i = 1, \dots, n) \quad (2)$$

This technique was also employed to determine the solar simulator's actinic photon flux in the UV range by chlorine actinometry. UV light below 330 nm has a high impact on the chemistry by forming excited state oxygen atoms and hence OH radicals by ozone photolysis. In this spectral region the chlorine actinometry is more precise than the NO<sub>2</sub> actinometry, since the chlorine molecule has a broad absorption maximum in the UV with its maximum at 330 nm (e.g. Maric et al., 1993). In the irradiated chamber, the behavior of chlorine atoms basically follows the equation:

$$\frac{d[\text{Cl}]}{dt} = 2j(\text{Cl}_2)[\text{Cl}_2] - \sum_i k_{\text{Cl},i}[\text{Cl}][\text{HC}]_i, \quad (i = 1, \dots, n) \quad (3)$$

where photolysis of Cl<sub>2</sub> is the source and the I reactions with hydrocarbons are the sinks of atomic Cl. Assuming that the photolytic decay of Cl<sub>2</sub> is exponential and neglecting the time dependence of HC<sub>*i*</sub> as a simplification (which is reasonable since the HC are in excess) we are able to solve Eq. (3) analytically. The solution is a bi-exponential function of time with  $j(\text{Cl}_2)$  and  $[\text{Cl}_2]_{t=0}$  as parameters. Using the obtained  $j(\text{Cl}_2) = 2.4 \times 10^{-3} \text{ s}^{-1}$  we normalize the previously measured lamp spectrum by the chlorine photolysis frequency (Fig. 1). The  $j(\text{NO}_2) = 6.7 \times 10^{-3} \text{ s}^{-1}$  values derived from Cl<sub>2</sub> photolysis were found to agree with NO<sub>2</sub> actinometry ( $j(\text{NO}_2) = 7.1 \times 10^{-3} \text{ s}^{-1}$ ) within an acceptable deviation of less than 6%.

Additionally used in a measurement campaign was a chemical ionization mass spectrometer (CIMS), which was described by Kercher et al., 2009 to observe non-radical species. All instruments, except the GC, were connected to the chamber by Teflon tubes as short as possible with (1–3 m length). Chemical conversion of highly reactive bromine compounds like BrO or HOBr on instrument and inlet surfaces is a well known

**Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol**

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

problem and can even result in a complete loss of BrO (Neuman et al., 2010). Therefore it is important to keep the inlet short, as it was demonstrated by Liao et al. (2011).

We compared our measurements to simulations with version 3.0 of the chemical box model CAABA/MECCA (Chemistry As A Boxmodel Application/Module Efficiently Calculating the Chemistry of the Atmosphere) by Sander et al. (2011). The model was run for 144 min, with output every 6 s. To represent our laboratory conditions, the “LAB” scenario in the model was set to  $T = 293\text{ K}$ ,  $p = 101\,325\text{ Pa}$ , and a RH of 60%. The modeled aerosol has a liquid water content of  $5 \times 10^{-9}\text{ m}^3\text{ m}^{-3}$  and contains particles with a radius of  $0.2\text{ }\mu\text{m}$ . In addition to the standard ozone, methane,  $\text{HO}_x$ , and  $\text{NO}_x$  chemistry, we activated chlorine and bromine multiphase chemistry in the gas phase and in the aerosol particles. A list of the chemical reactions used in this study, including rate coefficients and references, is available in the Supplement. Photolysis frequencies were calculated for the solar simulator by building a scalar product of the spectrum shown in Fig. 1 and the cross sections of the molecules weighted by the quantum efficiencies. All photolysis values are scaled with a single factor which represents the age of the lamps (a new lamp has ca. four times more intensity than an old lamp with more than 600 operating hours). The photolysis frequencies and the scaling factor were kept constant during the whole model simulation. For ozone, a constant destruction term of  $1.3 \times 10^{-5}\text{ s}^{-1}$  represents wall losses. The gas phase was initialized with  $500\text{ nmol mol}^{-1}\text{ CH}_4$ , while the ozone and  $\text{NO}_x$  mixing ratios were adapted to the conditions of individual experiments. The initial composition of the aerosol was  $6.1\text{ mol L}^{-1}$  chloride and  $0.3\text{ mol L}^{-1}$  bromide. The model in its original state overpredicts the concentrations of HOX species on the cost of the XO compared to the results gained from the DOAS and the CIMS experiments (see Sect. 3). We assume that the chamber walls act as a source of active halogens due to the deposits of HX from previous experiments. After testing various possibilities to include a simplified wall source Q, such as  $\text{HOX} + \text{Q} \rightarrow \text{X}_2$ , we found that the addition of two reactions to the model  $\text{HOX} \rightarrow \text{X} + \text{OH}$  ( $k = 0.12\text{ s}^{-1}$  for  $\text{X} = \text{Br}$  and  $0.02\text{ s}^{-1}$  for  $\text{X} = \text{Cl}$ ) results in a good agreement with the experimental data over a wide range of initial ozone and  $\text{NO}_x$  mixing ratios. Although the

## Influence of $\text{NO}_x$ on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



constants are fast, this approximation is conservative since it does not add halogens to the system.

### 3 Results and discussion

From a series of experiments with various initial  $\text{NO}_x$ -mixing ratios we discuss four experimental runs in detail: two experiments (which are quite comparable in almost all parameters except their initial  $\text{NO}_x$  mixing ratio) with the DOAS instrument and two experiments with the CIMS instrument.

#### 3.1 Low $\text{NO}_x$ experiment with DOAS

The first experiment (Fig. 3) is a low  $\text{NO}_x$ -case. Before starting the experiment, by injection of the salt aerosols, the chamber was cleaned photochemically by introducing high levels of humidity ( $> 60\%$ ) and ozone ( $\sim 700$  ppb) and UV radiation of our solar simulator. Therefore the possibility of remaining organic from former experiments and additional wall release of BrO was minimized during the actual experiment. Here we nebulized a stock solution of  $86.4 \text{ mg L}^{-1}$  NaBr and  $1 \text{ g L}^{-1}$  NaCl into a humid chamber ( $50\%$  rel. humidity at  $293 \text{ K}$ ), which should result in a bromide concentration of  $300 \text{ mmol L}^{-1}$  and  $6.1 \text{ mol L}^{-1}$  chloride in the aerosol phase according to the Köhler theory. The particle concentration reached  $1650 \text{ cm}^{-3}$ , containing  $7 \times 10^{-11} \text{ m}^3 \text{ m}^{-3}$  of liquid water. The particle size distribution is shown in Fig. 2a. The bromide concentration per  $\text{cm}^3$  could allow a maximal  $\text{Br}_x$  mixing ratio of 515 ppt in case of its entire activation. The nighttime chemistry (R1, R2 and R19) started by injection of ozone (508 ppb), which induces a complete loss of the initial  $\text{NO}_2$  mixing ratio of 500 ppt. The ozone mixing ratio was nearly constant with a (dilution-corrected) loss rate of less than  $-0.01 \text{ ppbs}^{-1}$  in the dark.

We switched the solar simulator on at  $t = 0$ . The loss of ozone accelerated in the day time conditions and reached a peak value of  $-58 \text{ ppbs}^{-1}$  after 30 min of illumination. As

## Influence of $\text{NO}_x$ on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

expected, the measured BrO concentration was correlated to the O<sub>3</sub>-derivative (slope of the ozone time profile); the peak of [BrO] = 300 ± 85 ppt is coincident with the O<sub>3</sub> depletion maximum. A fraction of the observed BrO was released by the chamber walls in a previous high ozone chamber purge without aerosol and remained as a stable background level of 200 ppt of BrO in the chamber during the dark phase. Thus, from the BrO-mixing ratio an offset of 200 ppt was subtracted, since it was obviously an artefact remaining after the previous chamber purge. During the cleaning phase remaining organic, has been detected in form of formaldehyde by the DOAS-instrument. The formaldehyde signal was below the mean detection limit of ~60 ppb, once we started the salt aerosol experiment. In this experiment, the DOAS white cell was equipped with narrow band dielectric mirrors (335–360 nm) for sensitive detection of BrO. Since the absorption cross section of OCIO is within the same spectral range, this species might have been the measurable indicator for an activation of chloride. However, OCIO remained below a mean detection limit of 150 ppt, and we may follow the simple relationship in Eq. (1) to calculate the contribution of bromine to the ozone loss to a value of 12 ppts<sup>-1</sup>. The difference to the observed ozone loss of 55 ppts<sup>-1</sup> might be caused by chlorine atoms, which were not monitored during the experiment. However, reaction constants leading to ozone loss due to chlorine (e.g. Reaction R10 and R12) and are much faster compared to bromine. It is well-known that an activation of bromide directly via mechanism Reactions (R6) and (R7) needs an acidification of the aqueous phase (e.g. Fickert et al., 1999). The NO<sub>2</sub> mixing ratio of 500 ppt must have been sufficient to activate the entire bromide via Reactions (R16)–(R18) or to form enough HNO<sub>3</sub> to provide the H<sup>+</sup> ions needed by Reaction (R7) via Reactions (R2) and (R3).

To decide about the dominant activation mechanism, we show a simulation run with the same starting conditions in Fig. 4. Herein plotted are the calculated mixing ratios of important trigger species vs. the total mixing ratio of gaseous Br<sub>x</sub> species. The model plausibly reproduces the experiment in terms like the ozone decay, the BrO mixing ratio and the loss of NO<sub>2</sub>. According to the model, a large fraction of bromide was activated directly through BrNO<sub>3</sub> hydrolysis (mechanism Reactions R16–R18 and R7). After the





following this pathway and a constant mixing ratio of 3.65 ppb of  $\text{BrNO}_2$  after 100 s. Also a continued loss of chloride during nighttime by forming almost 30 ppb of  $\text{ClNO}_2$  is predicted by the model. In daytime conditions both nitril species are photolysed to X and  $\text{NO}_2$ . The halogen atoms react with ozone and  $\text{NO}_2$  and produce  $\text{XNO}_3$  according to Reaction (R16). The photodissociation of  $\text{XNO}_3$  to X and  $\text{NO}_3$  (Soller et al., 2002) leads to the photolytic steady state of  $\text{N}_2\text{O}_5$  while  $\text{NO}_2$  is available in gas phase. For X = Br, Reaction (R16) replenishes the bromide in the aerosol droplets by uptake and dissociation. In a comprehensive view, the sink for most  $\text{NO}_x$  and  $\text{XNO}_x$  species is the formation of nitrate in the droplets.

### 3.3 CIMS runs

A CIMS measurement may give information about the direct precursors of X, XO species, i.e.  $\text{X}_2$  and  $\text{XNO}_2$ . We performed two experiments to demonstrate different mechanisms of halogen activation and conversion of active halogen species. Both experiments were done on a single day, causing some remaining reaction products and a fraction of old aerosol from the first experiment to influence the second run (see Fig. 6). In these early experiments the chamber was not cleaned before the chamber runs and thus contained HC and  $\text{NO}_x$  (which was converted to HONO on the droplet surface during the aerosol injection for the first run). After the injection of ozone into the dark chamber, we observed bromine in the gas phase (both isotopes in the correct mixing ratio of 50.7%/49.3%). Since this was a nighttime formation we assume the occurrence of mechanism Reactions (R4)–(R8). Such nighttime formed gaseous bromine may trigger the auto-catalytic halide activation cycles during dawn. In daytime conditions, we observed a rapid increase of the  $\text{Br}_2$  mixing ratio, which reached its maximum of 6.1 ppb after 7 min of illumination.  $\text{Cl}_2$  reached its maximum of 11.5 ppb 6 min later. Both maxima occurred while  $\text{NO}_x$  (originating from the photolysis of HONO) was still present in high mixing ratios. This verifies the calculation of the halogen species concentrations  $\text{Cl}_2$  and  $\text{Br}_2$  by the model in Fig. 5. The slight increase of  $\text{ClNO}_2$  after the beginning of illumination is correlated with the production of  $\text{N}_2\text{O}_5$  from the  $\text{XNO}_3$

## Influence of $\text{NO}_x$ on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion







et al., 2008; Phillips et al., 2012), which do not allow a global budget. Even though, amounts of tropospheric NO<sub>2</sub> has likely decreased by 30 to 50 % in Europe and North America, it has increased by more than a factor of 2 in Asia since the mid-1990s (Hilboll et al., 2013), which might influence the total amount of reactive bromine and especially chlorine in the atmosphere, according to our findings. This should be further investigated in future studies.

Once NO<sub>x</sub> is consumed, the mechanism changes to HOX and precedes the activation cycle via the protons provided by NO<sub>x</sub> previously. The model in its current stage reasonably reproduces chamber experiments in terms of ozone loss and halogen activation and its dependence on NO<sub>x</sub>. However, the influence of the chamber walls needs to be considered as a secondary liquid phase in the model in upcoming work.

**Supplementary material related to this article is available online at <http://www.atmos-chem-phys-discuss.net/14/10135/2014/acpd-14-10135-2014-supplement.pdf>.**

*Acknowledgements.* We would like to thank R. von Glasow, F. Siekmann and J. Wittmer for detailed discussions. We also thank the Deutsche Forschungsgemeinschaft for funding research unit 763.

## References

- Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III – gas phase reactions of inorganic halogens, *Atmos. Chem. Phys.*, 7, 981–1191, doi:10.5194/acp-7-981-2007, 2007.
- Balzer, N.: Kinetische Untersuchungen der Halogen-Aktivierung einer simulierten Salzpfanne in einer Smogkammer, Ph.D. thesis, University of Bayreuth, Bayreuth, Germany, 2012.

ACPD

14, 10135–10166, 2014

## Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol**

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Behnke, W., Holländer, W., Koch, W., Nolting, F., and Zetzsch, C.: A smog chamber for studies of the photochemical degradation of chemicals in the presence of aerosols, *Atmos. Environ.*, **22**, 1113–1120, 1988.
- Behnke, W., Scheer, V., and Zetzsch, C.: Formation of ClNO<sub>2</sub> and HNO<sub>3</sub> in the presence of N<sub>2</sub>O<sub>5</sub> and wet pure NaCl and wet mixed NaCl/Na<sub>2</sub>SO<sub>4</sub>-aerosol, *J. Aerosol Sci.*, **24**, 115–116, 1993.
- Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of ClNO<sub>2</sub> from the reaction of gaseous N<sub>2</sub>O<sub>5</sub> with NaCl solution: bulk and aerosol experiments, *J. Geophys. Res.*, **102**, 3795–3804, 1997.
- Behnke, W., Elend, M., Krüger, U., and Zetzsch, C.: The influence of NaBr/NaCl ratio on the Br<sup>-</sup>-catalysed production of halogenated radicals, *J. Atmos. Chem.*, **34**, 87–99, 1999.
- Betts, R. H. and Mackenzie, A. N.: Formation and stability of hypobromous acid in perchloric acid solutions of bromine and bromate ions, *Can. J. Chem.*, **29**, 666–677, 1951.
- Bleicher, S.: Zur Halogenaktivierung im deliqueszenten Aerosol und in Salzpflanzen, Ph.D. thesis, University of Bayreuth, available at: <http://opus4.kobv.de/opus4-ubbayreuth/files/1370/Bleicher+Diss.pdf> (last access: 1 March 2014), 2012.
- Buxmann, J.: Bromine and Chlorine Explosion in a Simulated Atmosphere, Ph.D. thesis, University of Heidelberg, Heidelberg, Germany, 2012.
- Buxmann, J., Balzer, N., Bleicher, S., Platt, U., and Zetzsch, C.: Observations of bromine explosions in smog chamber experiments above a model salt pan, *Int. J. Chem. Kinet.*, **44**, 312–326, 2012.
- Cox, R. A. and Lewis, R.: Kinetics of chlorine oxide radical reactions using modulated photolysis, Part 3. – Pressure and temperature dependence of the reaction: ClO + NO<sub>2</sub>(+M) → ClONO<sub>2</sub>(+M), *J. Chem. Soc. Faraday T.*, **1**, 75, 2649–2661, 1979.
- da Rosa, M. and Zetzsch, C.: Influence of pH and halides on halogen species in the aqueous phase, *J. Aerosol Sci.*, **32**, S311–S312, 2001.
- Deiber, G., George, Ch., Le Calvé, S., Schweitzer, F., and Mirabel, Ph.: Uptake study of ClONO<sub>2</sub> and BrONO<sub>2</sub> by Halide containing droplets, *Atmos. Chem. Phys.*, **4**, 1291–1299, doi:10.5194/acp-4-1291-2004, 2004.
- DeMore, W. B., Sander, S. P., Golden, D. M., Hampson, R. F., Kurylo, M. J., Howard, C. J., Ravishankara, A. R., Kolb, C. E., and Molina, M. J.: Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation number 12, JPL Publication 97-4, Jet Propulsion Laboratory California Institute of Technology Pasadena, California, 1–266, 1997.

**Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol**

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Fickert, S., Adams, J. W., and Crowley, J. N.: Activation of Br<sub>2</sub> and BrCl via uptake of HOBr onto aqueous salt solutions, *J. Geophys. Res.*, 104, 23719–23727, 1999.
- Finlayson-Pitts, B. J.: Reaction of NO<sub>2</sub> with NaCl and atmospheric implications of NOCl formation, *Nature*, 306, 676–677, 1983.
- 5 Finlayson-Pitts, B. J., Ezell, M. J., Pitts Jr., J. N.: Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N<sub>2</sub>O<sub>5</sub> and ClONO<sub>2</sub>, *Nature*, 337, 241–244, 1989.
- Frenzel, A., Scheer, V., Sikorski, R., George, C., Behnke, W., and Zetzsch C.: Heterogeneous interconversion reactions of BrNO<sub>2</sub>, ClNO<sub>2</sub>, Br<sub>2</sub>, and Cl<sub>2</sub>, *J. Phys. Chem. A*, 102, 1329–1337, 10 1998.
- George, C., Ponche, J. L., Mirabel, P., Behnke, W., Scheer, V., and Zetzsch, C.: Study of the uptake of N<sub>2</sub>O<sub>5</sub> by water and NaCl solutions, *J. Phys. Chem.*, 98, 8780–8784, 1994.
- Hanson, D. R., Ravishankara, D. R., and Lovejoy, E. R.: Reaction of BrONO<sub>2</sub> with H<sub>2</sub>O on submicron sulfuric acid aerosol and the implications for the lower stratosphere, *J. Geophys. Res.*, 101, 9063–9069, 1996.
- 15 Hippler, H., Krasteva, N., Nasterlack, S., and Striebel, F.: Reaction of OH + NO<sub>2</sub>: high pressure experiments and falloff analysis, *J. Phys. Chem. A*, 110, 6781–6788, 2006.
- Hilboll, A., Richter, A., and Burrows, J. P.: Long-term changes of tropospheric NO<sub>2</sub> over megacities derived from multiple satellite instruments, *Atmos. Chem. Phys.*, 13, 4145–4169, doi:10.5194/acp-13-4145-2013, 2013.
- 20 Hoch, D. J., Buxmann, J., Sihler, H., Pöhler, D., Zetzsch, C., and Platt, U.: An instrument for measurements of BrO with LED-based Cavity-Enhanced Differential Optical Absorption Spectroscopy, *Atmos. Meas. Tech.*, 7, 199–214, doi:10.5194/amt-7-199-2014, 2014.
- Hunt, S. W., Roeselová, M., Wang, W., Wingen, L. M., Knipping, E. M., Tobias, D. J., Dabdub, D., and Finlayson-Pitts, B. J.: Formation of molecular bromine from the reaction of ozone with deliquesced NaBr aerosol: evidence for interface chemistry, *J. Phys. Chem. A*, 108, 11559–11572, 2004.
- 25 Kercher, J. P., Riedel, T. P., and Thornton, J. A.: Chlorine activation by N<sub>2</sub>O<sub>5</sub>: simultaneous, in situ detection of ClONO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> by chemical ionization mass spectrometry, *Atmos. Meas. Tech.*, 2, 193–204, doi:10.5194/amt-2-193-2009, 2009.
- Liao, J., Sihler, H., Huey, L. G., Neuman, J. A., Tanner, D. J., Friess, U., Platt, U., Flocke, F. M., Orlando, J. J., Shepson, P. B., Beine, H. J., Weinheimer, A. J., Sjostedt, S. J., Nowak, J. B., Knapp, D. J., Staebler, R. M., Zheng, W., Sander, R., Hall, S. R., and Ullmann, K.:

**Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol**

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

A comparison of Arctic BrO measurements by chemical ionization mass spectrometry and long path-differential optical absorption spectroscopy, *J. Geophys. Res.*, 116, D00R02, doi:10.1029/2010JD014788, 2011.

Lopez-Hilfiker, F. D., Constantin, K., Kercher, J. P., and Thornton, J. A.: Temperature dependent halogen activation by N<sub>2</sub>O<sub>5</sub> reactions on halide-doped ice surfaces, *Atmos. Chem. Phys.*, 12, 5237–5247, doi:10.5194/acp-12-5237-2012, 2012.

Madronich, S. and Flocke, S.: The role of solar radiation in atmospheric chemistry, in: *The Handbook of Environmental Chemistry*, vol. 2, Part I: Environmental Photochemistry, edited by: Boule, P., Springer, Berlin, 1–26, 1999.

Maric, D., Burrows, J. P., Meller, R., and Moortgat, G. K.: Visible absorption spectra of molecular chlorine, *J. Photochem. Photobiol. A*, 70, 205–214, 1993.

Morris, J. C.: The acid ionization constant of HOCl from 5 to 35°, *J. Phys. Chem.*, 70, 3798–3805, 1966.

Palm, W.-U., Elend, M., Krüger, H.-U., and Zetzsch, C.: OH radical reactivity of airborne ter-butylazine adsorbed on inert aerosol, *Environ. Sci. Technol.*, 31, 3389–3396, 1997.

Neuman, J. A., Nowak, J. B., Huey, L. G., Burkholder, J. B., Dibb, J. E., Holloway, J. S., Liao, J., Peischl, J., Roberts, J. M., Ryerson, T. B., Scheuer, E., Stark, H., Stickel, R. E., Tanner, D. J., and Weinheimer, A.: Bromine measurements in ozone depleted air over the Arctic Ocean, *Atmos. Chem. Phys.*, 10, 6503–6514, doi:10.5194/acp-10-6503-2010, 2010.

Osthoff, H. D., Roberts, J. M., Ravishankara, A. R., Williams, E. J., Lerner, B. M., Sommariva, R., Bates, T. S., Derek Coffman, D., Quinn, P. K., Dibb, J. E., Stark, H., Burkholder, J. B., Talukdar, R. K., Meagher, J., Fehsenfeld, F. C., and Brown, S. S.: High levels of nitryl chloride in the polluted subtropical marine boundary layer, *Nat. Geosci.*, 1, 324–328, 2008.

Peters, C., Pechtl, S., Stutz, J., Hebestreit, K., Hönninger, G., Heumann, K. G., Schwarz, A., Winterlik, J., and Platt, U.: Reactive and organic halogen species in three different European coastal environments, *Atmos. Chem. Phys.*, 5, 3357–3375, doi:10.5194/acp-5-3357-2005, 2005.

Phillips, G. J., Tang, M. J., Thieser, J., Brickwedde, B., Schuster, G., Bohn, B., Lelieveld, J., and Crowley, J. N.: Significant concentrations of nitryl chloride observed in rural continental Europe associated with the influence of sea salt chloride and anthropogenic emissions, *Geophys. Res. Lett.*, 39, L10811, doi:10.1029/2012GL051912, 2012.

**Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol**

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

- Platt, U. and Janssen, C.: Observation and role of the free radicals NO<sub>3</sub>, ClO, BrO and IO in the troposphere, *Faraday Discuss.*, 100, 175–198, 1995.
- Pratt, K. A., Custard, K. D., Shepson, P. B., Douglas, T. A., Pöhler, D., General, S., Zielcke, J., Simpson, W. R., Platt, U., Tanner, D. J., Huey, G. L., Carlsen, M., and Stirm, B. H.: Photochemical production of molecular bromine in Arctic surface snowpacks, *Nat. Geosci.*, 6, 351–356, 2013.
- Rossi, M. J.: Heterogeneous reactions on salts, *Chem. Rev.*, 103, 4823–4882, 2003.
- Sander, R., Baumgaertner, A., Gromov, S., Harder, H., Jöckel, P., Kerkweg, A., Kubistin, D., Regelin, E., Riede, H., Sandu, A., Taraborrelli, D., Tost, H., and Xie, Z.-Q.: The atmospheric chemistry box model CAABA/MECCA-3.0, *Geosci. Model Dev.*, 4, 373–380, doi:10.5194/gmd-4-373-2011, 2011.
- Sander, S. P., Ray, G. W., and Watson, R. T.: Kinetics study of the pressure dependence of the BrO + NO<sub>2</sub> reaction at 298 Kelvin, *J. Phys. Chem.*, 85, 199–210, 1981.
- Scheer, V., Frenzel, A., Behnke, W., Zetzsch, C., Magi, L., George, C., and Mirabel, P.: Uptake of nitrosyl chloride (NOCl) by aqueous solutions, *J. Phys. Chem. A*, 101, 9359–9366, 1997.
- Schütze, M. and Herrmann, H.: Determination of phase transfer parameters for the uptake of HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> and O<sub>3</sub> on single aqueous drops, *Phys. Chem. Chem. Phys.*, 4, 60–67, 2002.
- Shilov, E. A.: On the calculation of the dissociation constants of hypohalogenous acids from kinetic data, *J. Am. Chem. Soc.*, 60, 490–491, 1938.
- Soller, R., Nicovich, J. M., and Wine, P. H.: Bromine nitrate photochemistry: quantum yields for O, Br, and BrO over the wavelength range 248–355 nm, *J. Phys. Chem.*, 106, 8378–8385, 2002.
- Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dube, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., and Brown, S. S.: A large atomic chlorine source inferred from midcontinental reactive nitrogen chemistry, *Nature*, 464, 271–274, 2010.
- Wex, H., Kiselev, A., Stratmann, F., Zoboki, J., and Brechtel, F.: Measured and modeled equilibrium sizes of NaCl and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> particles at relative humidities up to 99.1 %, *J. Geophys. Res.*, 110, D21212, doi:10.1029/2004JD005507, 2005.
- Wren, S. N., Donaldson, D. J., and Abbatt, J. P. D.: Photochemical chlorine and bromine activation from artificial saline snow, *Atmos. Chem. Phys.*, 13, 9789–9800, doi:10.5194/acp-13-9789-2013, 2013.

Zetzsch, C. and Behnke, W.: Heterogeneous photochemical sources of atomic Cl in the troposphere, Ber. Bunsen. Phys. Chem., 96, 488–493, 1992.

ACPD

14, 10135–10166, 2014

**Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol**

S. Bleicher et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

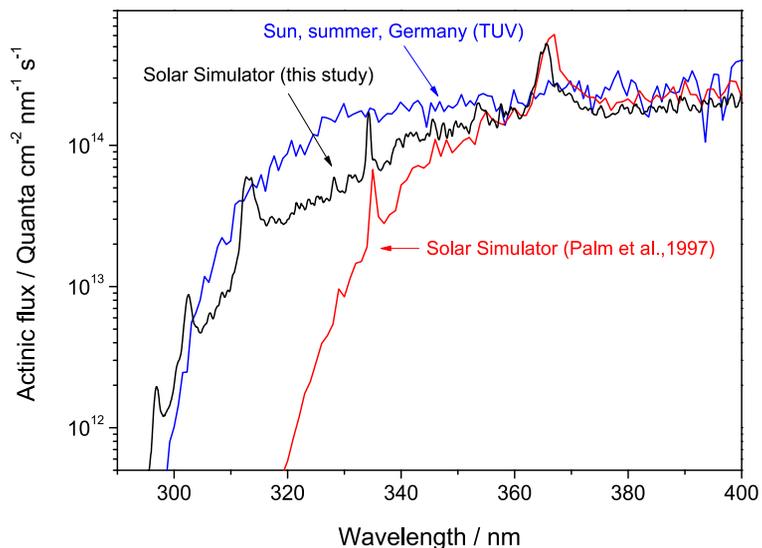
Interactive Discussion

10158



## Influence of $\text{NO}_x$ on the activation of $\text{BrO}$ and $\text{ClO}$ in salt aerosol

S. Bleicher et al.



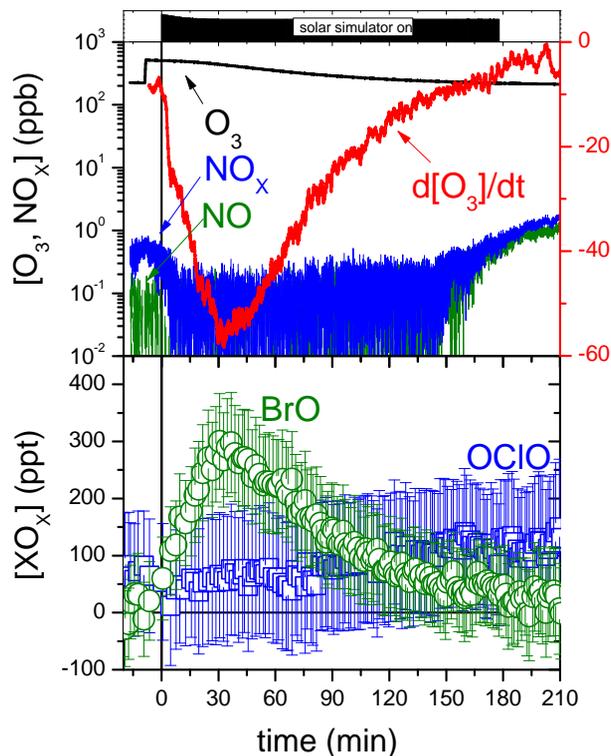
**Fig. 1.** Measured actinic photon flux in comparison to the sun in mid summer in Germany, calculated by Tropospheric Ultraviolet & Visible Radiation Model (TUV, Madronich and Flocke, 1999) and to a previous publication (Palm et al., 1997) with a glass filter that had been in use for 15 years. The glass filter is subject to solarization, which moves the UV-cutoff to red.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)



Influence of  $\text{NO}_x$  on the activation of BrO and ClO in salt aerosol

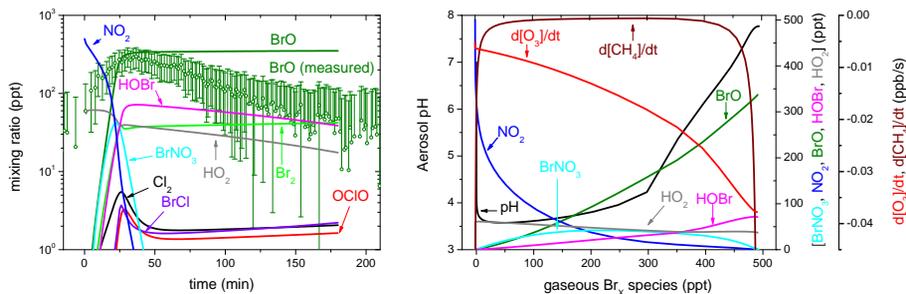
S. Bleicher et al.



**Fig. 3.** Activation of bromide and its impact on ozone in a low  $\text{NO}_x$  scenario. A part of the BrO mixing ratio (200 ppt) was subtracted as an artifact from the previous chamber purge, since it was stable under night time conditions.

## Influence of $\text{NO}_x$ on the activation of $\text{BrO}$ and $\text{ClO}$ in salt aerosol

S. Bleicher et al.



**Fig. 4.** Model calculation of the experiment shown in Fig. 3. Time profiles are plotted in the left figure, while in the right figure the data of the first 30 min is plotted against the gained gaseous  $\text{Br}_x$  species coming from the loss of bromide of the liquid phase. The modeled  $\text{BrO}$  reaches a stationary state at 350 ppt after 35 min with a slower decrease than the experiment and confirms a low level of  $\text{OCIO}$  of 3 ppt, well below the detection limit of the DOAS instrument. The change of the activation regime during “day time” from  $\text{BrNO}_3$  to  $\text{HOBr}$  after the  $\text{NO}_2$  has almost completely been consumed and is indicated by a fast consumption of protons as it can be seen in the right figure.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

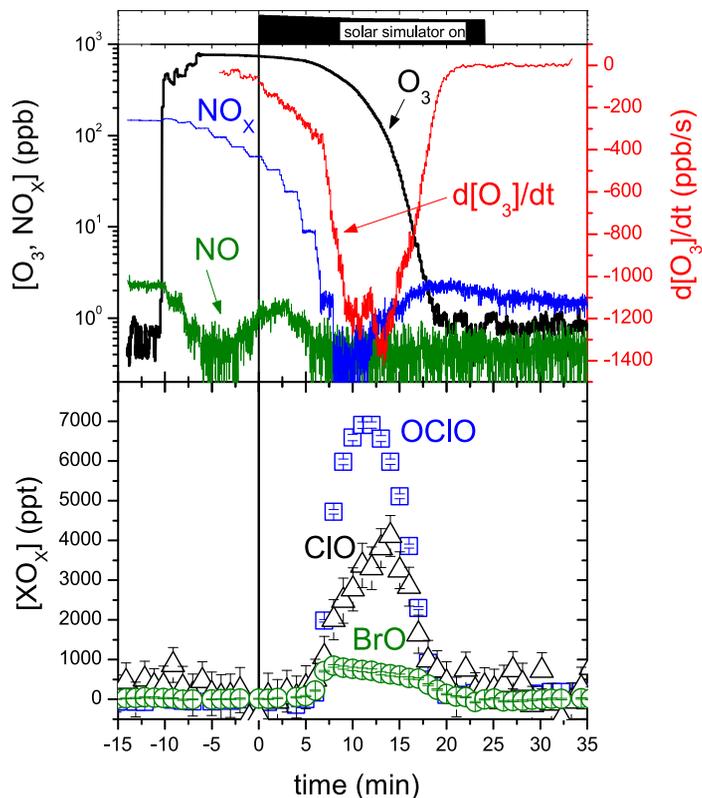
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Influence of $\text{NO}_x$ on the activation of $\text{BrO}$ and $\text{ClO}$ in salt aerosol

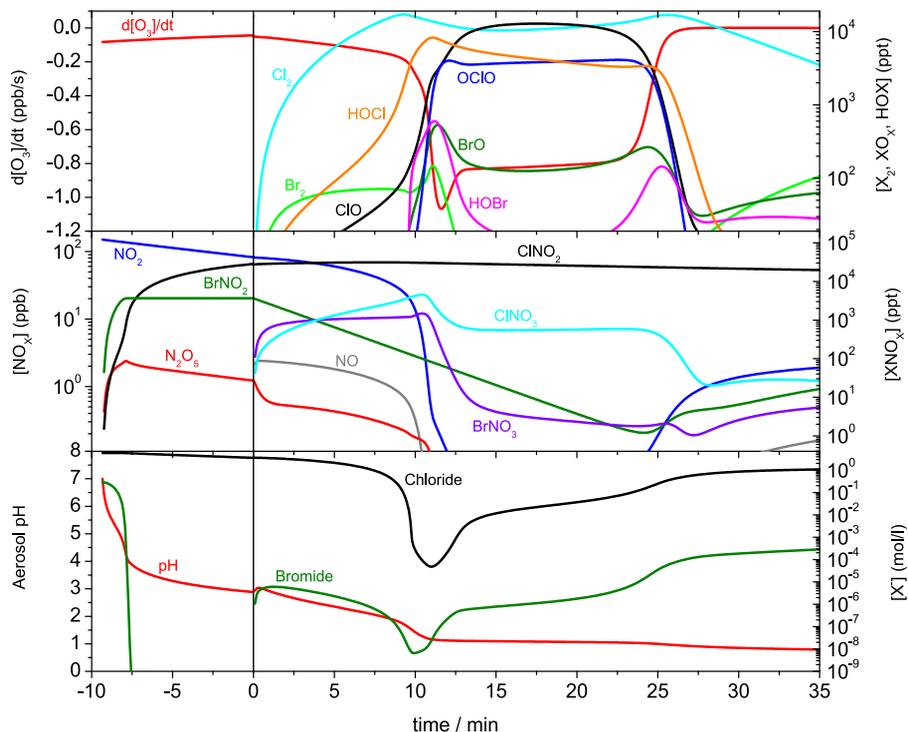
S. Bleicher et al.



**Fig. 5.** High  $\text{NO}_x$  scenario with a large activation of chloride. The loss of  $\text{NO}_2$  begins in the dark and can be explained by the production of  $\text{N}_2\text{O}_5$  and  $\text{XNO}_2$ . A rapid loss of ozone was observed after the consumption of  $\text{NO}_2$  under light conditions, thus forming the observable  $\text{XO}_x$  species. The remarkable round shape of  $\text{OCIO}$  can be explained by the time profiles of its precursors  $\text{BrO}$  and  $\text{ClO}$ , which are both trapezoids.

## Influence of NO<sub>x</sub> on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.

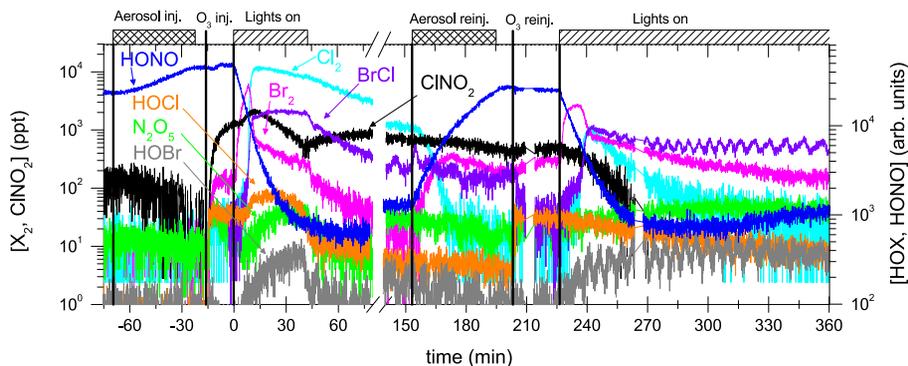


**Fig. 6.** Model calculation of halogen activation in a high NO<sub>x</sub> scenario. Although the values of ozone depletion are comparable to the experiment, the simulation is 3–5 min delayed. This can be explained with wall sources from previous experiments. A higher simulated content of bromide in the liquid phase would explain a faster consumption of ozone and higher OCIO mixing ratios as observed. In the logarithmic scale is the photolysis of ClNO<sub>2</sub> almost imperceptible: the ClNO<sub>2</sub> mixing ratio raises right after the day time conditions are switched on while NO<sub>x</sub> is still available and declines after with its photolytic life time of  $3 \times 10^{-4} \text{ s}^{-1}$ .

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)

## Influence of $\text{NO}_x$ on the activation of $\text{BrO}$ and $\text{ClO}$ in salt aerosol

S. Bleicher et al.



**Fig. 7.** CIMS measurement of HONO and the direct precursors of  $\text{BrO}$  ( $\text{Br}_2$  and  $\text{HOBr}$ ) and  $\text{ClO}$  ( $\text{Cl}_2$ ,  $\text{ClNO}_2$  and  $\text{HOCl}$ ). The chamber contained a sum of 25 ppb of HONO and  $\text{NO}_x$  from ambient air impurities. During the aerosol injection,  $\text{NO}_x$  was heterogeneously converted to HONO. Its decay during daytime conditions suits the measured photolysis frequency of  $j(\text{HONO}) = 2 \times 10^{-3} \text{ s}^{-1}$ . The maximum values of  $\text{Br}_2$  and  $\text{Cl}_2$  were reached while  $\text{NO}_x$  as a product of HONO.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

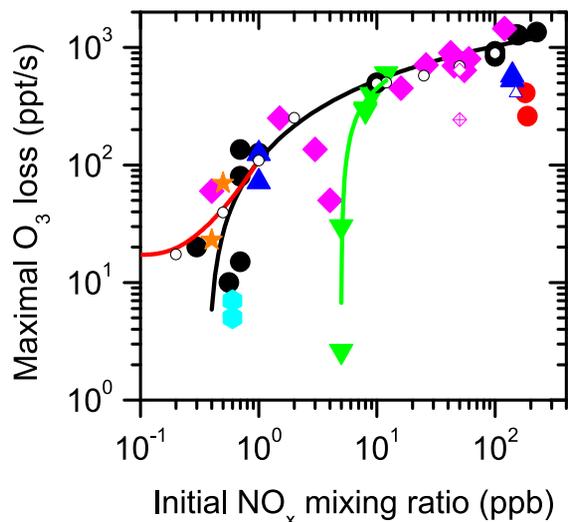
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Influence of $\text{NO}_x$ on the activation of BrO and ClO in salt aerosol

S. Bleicher et al.



**Fig. 8.** Dependence of the maximum ozone loss on the initial  $\text{NO}_x$  concentration for  $1 \text{ g L}^{-1}$  NaCl aerosol with different bromide contents and variations of other parameters. The full symbols are experiments: black circles –  $0.3 \text{ mol L}^{-1}$  bromide and  $\text{lwc } 5 \times 10^{-10}$ , red circles –  $0.3 \text{ mol L}^{-1}$  bromide and  $\text{lwc } 5 \times 10^{-10}$  and additional VOC injected, blue triangles –  $1.5 \text{ mmol L}^{-1}$  (road salt) bromide and  $\text{lwc } 5 \times 10^{-10}$ , green triangles – salt pan experiments from Buxmann et al., 2012, pink diamonds –  $0.03 \text{ mol L}^{-1}$  bromide and  $\text{lwc } 5 \times 10^{-9}$ , cyan dots –  $5.2 \text{ mmol L}^{-1}$  bromide and  $\text{lwc } 5 \times 10^{-9}$ , orange asterisks –  $52 \text{ mmol L}^{-1}$  bromide and  $\text{lwc } 5 \times 10^{-9}$ . The open symbols are model runs with initial parameters corresponding to the experiments. The black curve was fitted to the full black circles, while the red curve was fitted to the open black circles. In the low range the model differs from the experiment due to VOC impurities in the zero air which slow down the halogen chemistry. The salt pan experiments are slowed down due to low rel. humidity.

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[◀](#)
[▶](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)