

# MODELING STUDY ON CHEMISTRY OF HALOGENS IN MARINE AEROSOLS

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Keywords: MULTIPHASE MODELLING, HALOGEN ACTIVATION, CLOUDS.

## INTRODUCTION

Up to now modelling studies have only been performed to explain the high amounts of activated halogens in the marine boundary layer. However, still a large uncertainty in explaining the chemical processes of halogen containing compounds in marine regions exists (Spicer et al., 1998).

Within this study the contribution of clouds on halogen activation processes is analysed by the use of a box model. The chemistry in both the gas and the aqueous phase is described by a very complex mechanism consisting of three parts (RACM, CAPRAM 2.4, HALOGEN 1.2). The gas phase reactions are characterised by RACM (Stockwell et al., 1997; regional atmospheric chemistry mechanism), and the aqueous phase reactions are taken from CAPRAM 2.4 (MODAC mechanism, Ervens et al., 2001), which is a further development of CAPRAM 2.3 (chemical aqueous phase radical mechanism; Herrmann et al., 2000). To describe the reactions of halogen containing compounds a special module was developed (HALOGEN2.1). This module contains reactions of halogen species in both the gas and the aqueous phase and also includes phase transfer of the species.

## MODEL PARAMETERS

A box model is applied to treat this complex multiphase chemistry system. Additional, to consider exchange of surrounding air, emissions and depositions are introduced to the box. The model runs were performed for a cloud ( $LWC = 0.3 \text{ g m}^{-3}$ ,  $r_{\text{drop}} = 10 \text{ }\mu\text{m}$ ,  $N_{\text{dr}} = 1 \cdot 10^8 \text{ m}^{-3}$  and  $RH = 100 \%$ ) under marine boundary layer conditions ( $T = 288 \text{ K}$ ,  $p = 1013 \text{ hPa}$ ). The two regimes for the input parameters, and emission and deposition datasets were mainly taken from the EC-funded project MODAC. This leads to initial concentrations of  $[\text{Br}^-] = 1.8 \cdot 10^{-6} \text{ M}$  and  $[\text{Cl}^-] = 5.6 \cdot 10^{-4} \text{ M}$  for the clean (marine) case and of  $[\text{Br}^-] = 3.0 \cdot 10^{-6} \text{ M}$  and  $[\text{Cl}^-] = 1.0 \cdot 10^{-4} \text{ M}$  for the polluted (urban) case.

## HALOGEN MODULE

Reactions of halogens in the gas phase are not included in the basic mechanism RACM. The photolysis reactions of  $\text{X}_2$ , HOX, and  $\text{XNO}_2$  (where  $\text{X} = \text{Cl}$  or  $\text{Br}$ ) have now been included and establish the sources of reactive halogens in the gas phase. The generated radicals are able to react with ozone in a catalytic cycle. The result of this cycle is a depletion of ozone to  $\text{O}_2$  and the recycled radical. The reaction of  $\text{XO}\cdot + \text{HO}_2\cdot \rightarrow \text{HOX} + \text{O}_2$  leads to another, more important way of degradation of  $\text{XO}\cdot$ . This reaction is a pathway to form HOX which can be transferred into the aqueous phase. Phase transfer takes place with the halogen containing compounds  $\text{X}_2$ ,  $\text{HX}$ , HOX,  $\text{XNO}_2$ ,  $\text{XO}\cdot$ ,  $\text{X}\cdot$ . Whereas only HBr, HOCl, HOBr,  $\text{ClO}\cdot$ ,  $\text{BrO}\cdot$ ,  $\text{Cl}\cdot$  and  $\text{Br}\cdot$  are added because the other species are already included in the basic mechanism.

For the aqueous phase the basic mechanism CAPRAM 2.4 (MODAC mechanism) already characterizes various reactions of the radicals  $\text{X}_2\cdot^-$ , and  $\text{X}\cdot$ . The additional halogen module contains 47 reactions in the aqueous phase. Irreversible reactions are HOX with sulphur(IV), and the radicals  $\text{HO}_2\cdot$ ,  $\cdot\text{O}_2^-$ , and  $\text{OH}\cdot$ . The reaction of  $\text{X}_2$  with  $\text{HO}_2\cdot$ ,  $\cdot\text{O}_2^-$  is another part of the developed module. The formation of  $\text{BrCl}$  couples the mechanisms of bromine species with chlorine species. Some irreversible reactions of the species  $\text{BrO}_2^-$  and  $\text{BrO}$  are also added. Further reactions rates of the oxybromine compounds  $\text{BrO}_3^-$ ,  $\text{BrO}_2$ ,  $\text{HBrO}_2$ , and  $\text{HOBr}$  were available from the Field-Körös-Noyes mechanism where the equilibrium

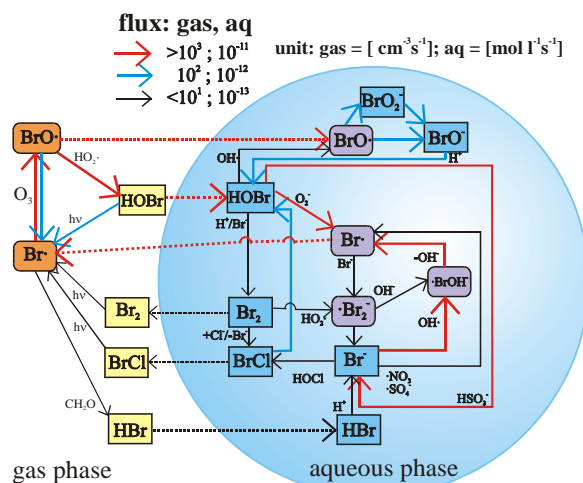
reactions in the aqueous phase are specified (Field and Försterling, 1986). Additional equilibria of halogen compounds in the aqueous phase contain dissociation of HBr, HOX, whereas the basic mechanism already includes the dissociation of HCl. The formation of the trihalogenide anions  $\text{Br}_2\text{Cl}^-$  and  $\text{BrCl}_2^-$  are as well a part of the halogen module as is the hydrolysis of  $\text{X}_2$ .

## RESULTS

Although cloud droplets contain lower concentrations of halides than sea salt particles the amount of activated halogens is in the same order of magnitude. For the maritime case  $10^4$  molecules per  $\text{cm}^3$  of  $\text{Br}\cdot$  and  $10^3$  molecules per  $\text{cm}^3$   $\text{Cl}\cdot$  are formed in the gas phase.

Chemistry of radicals in the aqueous phase is important for the release of halogen compounds into the gas phase. Direct phase transfer of these radicals is probably the main contributor to the high concentrations of the species.

The mechanism of halogen activation depends on the condition of the investigated aerosol. One example is for instance the difference between halogen activation under clean and polluted conditions.



**Fig 1.:** Mechanism of bromine compounds under clean (marine) conditions

## CONCLUSIONS

The release of halogen containing species from cloud droplets into the gas phase is strongly influenced by chemistry of radicals. Within this study it is shown, that the amount of halogen atoms in the gas phase can reach the same order of magnitude like it is shown for aerosol particles (Vogt et al., 1996).

## ACKNOWLEDGEMENTS

This study has been supported within the BMBF-funded project 07 AF 212 within the German AFS. Part of the study has been performed within the EC-funded project MODAC under contract ENV4-CT97-0388.

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