



Halogen Production from Aqueous Tropospheric Particles:

A Modelling Study

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Introduction

Halogens play an important role in chemical processes in the marine boundary layer. Halogen containing compounds are released from sea salt aerosols and then destroyed photochemically to form very reactive halogen atoms. Up to now only studies on the topic of activation of halogens from sea salt particles were used to understand the high amounts of halogen radicals in the gas phase. But there is still a large uncertainty in explaining the processes leading to halogen activation.

Within this project the production and release of halogens from cloud droplets into the gas phase is investigated. Although the concentration of halides in cloud droplets is smaller than in sea salt particles the concentration of activated halogens from cloud droplets can reach similar levels. For describing this process a very complex mechanism (RACM, CAPRAM 2.4 (MODAC-mechanism)) is used and an additional module (HALOGEN1.2) for the explicit description of halogen solution chemistry was developed.

Mechanism and parameters

Conditions of the cloud (for box modeling)

(taken from CAPRAM 2.4 (MODAC mechanism))

T=288 K p=1013 Pa
 LWC=3·10⁻⁷ m³ / (m³ (gas)) r₀=10 μm
 N_v=1·10⁷ m⁻³ RH=100 %

Input conditions were taken for marine and urban conditions. Emissions and depositions were taken into consideration to simulate exchange of some species with surrounding air.

The mechanism used in this model study consists of three parts. The basic mechanism is composed of RACM (Stockwell et al. 1997) describing reactions in the gas phase and CAPRAM 2.4 (MODAC mechanism) containing reactions in the aqueous phase. In the scheme the numbers in

brackets indicate reactions of halogen containing compounds that are already included in the basic mechanism. The additional modul for halogen containing species contains both reactions in gas and aqueous phase.

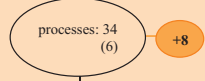
RACM/CAPRAM 2.4 (MODAC mechanism)

gas phase

RACM (Regional Atmospheric Chemistry Mechanism)

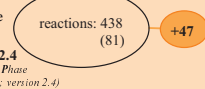


phase transfer



aqueous phase

CAPRAM 2.4 (Chemical Aqueous Phase Radical Mechanism: version 2.4)



Results

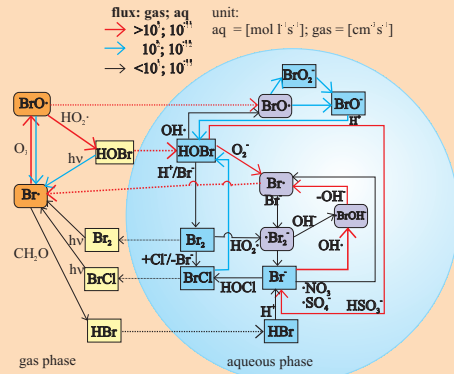


Fig. 1: Mechanism for the example of bromine species

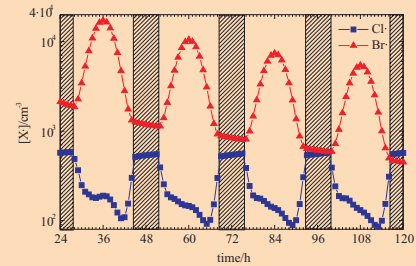


Fig. 2: Time series of concentrations of activated halogen atoms in the gas phase

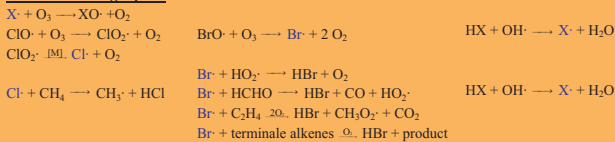
Tab. 1: Comparison of halogen atom concentrations in either phase for the maritime and polluted scenario

time	species	clean case	polluted case
t=0 h	Br _{aq} /M	8.4·10 ⁻⁷	1.5·10 ⁻⁷
	Cl _{aq} /M	5.6·10 ⁻⁴	1.0·10 ⁻⁴
t=36 h	Br _{aq} /M	1.3·10 ⁻⁷	8.8·10 ⁻⁸
	Cl _{aq} /M	6.3·10 ⁻⁴	1.3·10 ⁻⁴
	Br _{gas} /cm ⁻³	1.7·10 ⁴	5.3·10 ⁴
	Cl _{gas} /cm ⁻³	1.9·10 ²	2.0·10 ³

Apparently, especially Cl⁻ formation is enhanced in polluted air masses

Halogen Module

Reactions in the gas phase

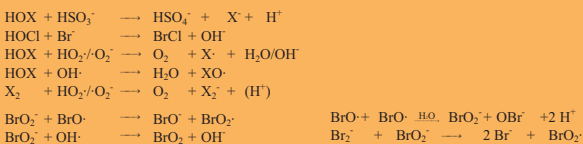


Photolysis reactions: X, HOX, XNO, ⇒ X[·]

Phase transfer processes (as proposed by Schwartz, considering K₁, D₁, α)

HCl, Cl⁻, Br⁻, ClNO, BrNO, BrCl (already included in the CAPRAM 2.4 (MODAC-mechanism))
 added species are: HBr, HOCl, HOBr, ClO⁻, BrO⁻, ClO⁻, Br⁻, Cl⁻

Aqueous phase (irreversible reactions: X=Br or Cl):



Equilibria

dissociation of HBr, HBrO₂, HOBr, HOCl
 formation of trihalide anions: Br₃Cl⁻, BrCl₂⁻
 hydrolysis of BrCl, Cl₂, Br₂
 reactions of the oxybromine compounds BrO[·], BrO₂[·], HBrO₂, and HOBr (FKN mechanism; Field et al., 1986)

Conclusion

- Although the concentration of halides in cloud droplets is lower compared to that in sea salt particles the amount of activated halogens is in the same order of magnitude.
- For the maritime case 10⁴ molecules of Br⁻ and 10⁷ molecules of Cl⁻ are activated.
- Chemistry of radicals is important for the release of halogen compounds into the gas phase.
- Direct phase transfer of Cl⁻ and Br⁻ is possibly the main source of the halogen radicals in the gas phase.
- Activation processes from cloud droplets are different between clean and polluted air masses.

Outlook

- calculations with different ionic strengths of halogen containing compounds
- development of a module considering DMS oxidation

References

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