Tropospheric Halogen Chemistry

(A Short Presentation)

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Overview

- Introduction
- Main Reaction Mechanisms
- Tropospheric sources of reactive halogen species
- Sinks of reactive halogen species
- Iodine Chemistry looks interesting!
- Open Questions
- Summary

Introduction

- Discovery of sudden boundary layer (BL) Ozone depletion events (ODE) observed to correlate with enhanced concentrations of filterable bromine compounds after polar sunrise.

- Reactive Halogen Species (RHS) responsible for complete depletion of BL Ozone in the Arctic and Antarctic Spring.

- DOAS measurements in the BL revealed enhanced concentrations of halogen oxides, especially BrO in polar spring.

- Satellite data from GOME shows tropospheric BrO.

Main Reaction Mechanisms Destroying Ozone.

Where X = Cl, Br, or I

$$X + O_3 \rightarrow XO + O_2 \quad (1)$$

$$Y + O_3 \rightarrow YO + O_2 \quad (2)$$

$$XO + YO \rightarrow X + Y + O_2 \quad (3)$$

Net I: $2O_3 \rightarrow 3O_2$

λ<600nm

$$X_2 + h\nu \rightarrow 2X$$

$$O_3 + X \rightarrow XO + O_2$$

$$XO + HO_2 \rightarrow HOX + O_2$$

$$HOX + h\nu \rightarrow X + OH$$

$$OH + CO(\text{or VOC}) + O_2 \rightarrow CO_2 + HO_2 \text{ (or other products)}$$

Net II: $CO + O_3 \rightarrow CO_2 + O_2$

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Sources of RHS

- Emissions from organic halogen compounds e.g. CH_3Br , CH_3Cl, $CHBr_3$ & CH_3I.
- Liberation from sea salt deposits or sea salt aerosols.
- Industry and fossil fuel burning.
- Biomass burning.
- Emissions from marine algae.
- Volcanoes.

Sinks of RHS

- Reaction with hydrocarbons.

$$X + RH \rightarrow HX + R$$

- Reaction with nitrogen oxides, NO and NO_2.

$$NO + XO \rightarrow XONO$$

$$NO_2 + XO \rightarrow XONO_2$$

- Reaction with HO_2 and organic peroxy radicals RO_2

$$X + HO_2 \rightarrow HX + O_2$$

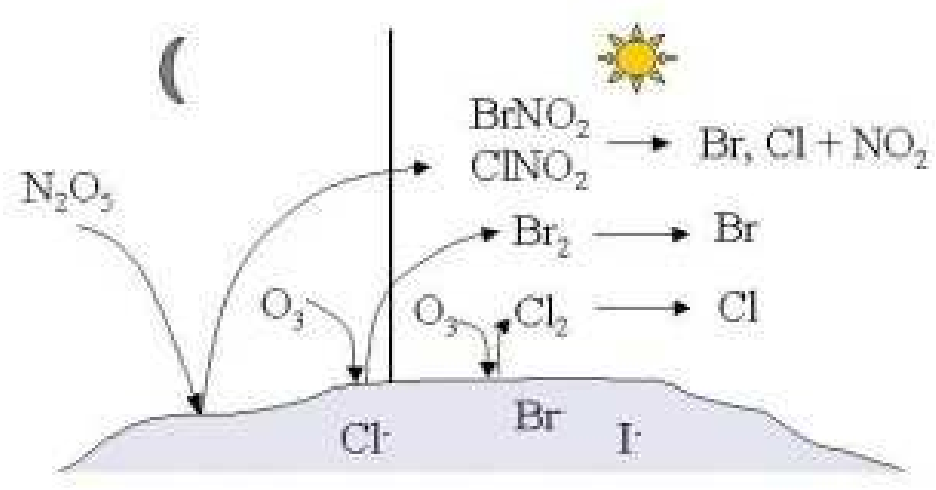

Fig 1:Heterogeneous mechanisms suspected to release RHS from sea salt

$$N_2O_5 \xrightarrow{H_2O} 2HNO_3$$

$$\xrightarrow{Br^-} BrNO_2 + NO_3^-$$

$$\xrightarrow{Cl^-} ClNO_2 + NO_3^-$$

Photolysis of XNO_2 releases halogen radicals into the gas phase.

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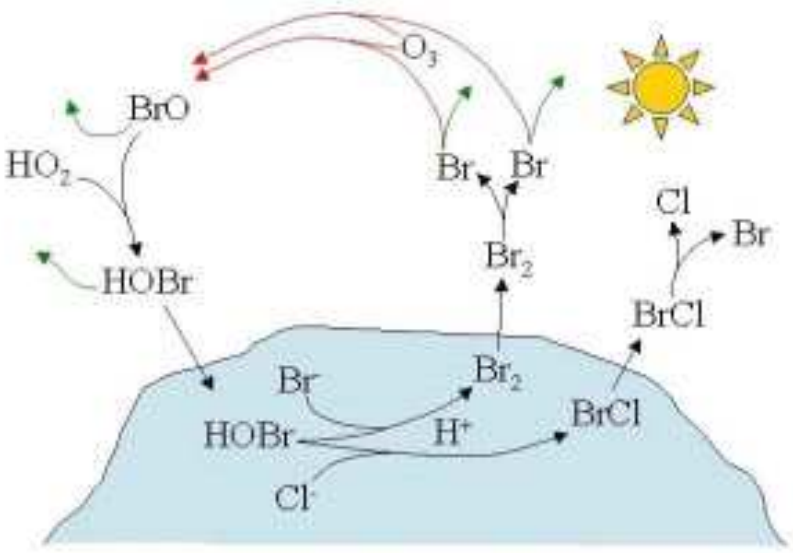

Fig 2: Bromine release mechanism by Vogt et al 1996
(Uptake of HOBr on acidic salt surfaces)

$$BrCl + h\nu \rightarrow Br + Cl \qquad \lambda<560nm$$

$$Br + O_3 \rightarrow BrO + O_2$$

$$BrO + HO_2 \rightarrow HOBr + O_2$$

$$HOBr \rightarrow HOBr_{aq}$$

$$HOBr_{aq} + H^+ + Cl^- \rightarrow BrCl_{aq} + H_2O$$

$$BrCl_{aq} + Br^- \leftrightarrow Br_2Cl^-$$

$$Br_2Cl^- \leftrightarrow Br_{2aq} + Cl^-$$

$$Br_{2aq} \leftrightarrow Br_2$$

Net: $BrCl + O_3 + HO_2 + Br^- + H^+ \rightarrow Cl + Br_2 + H_2O + 2O_2$

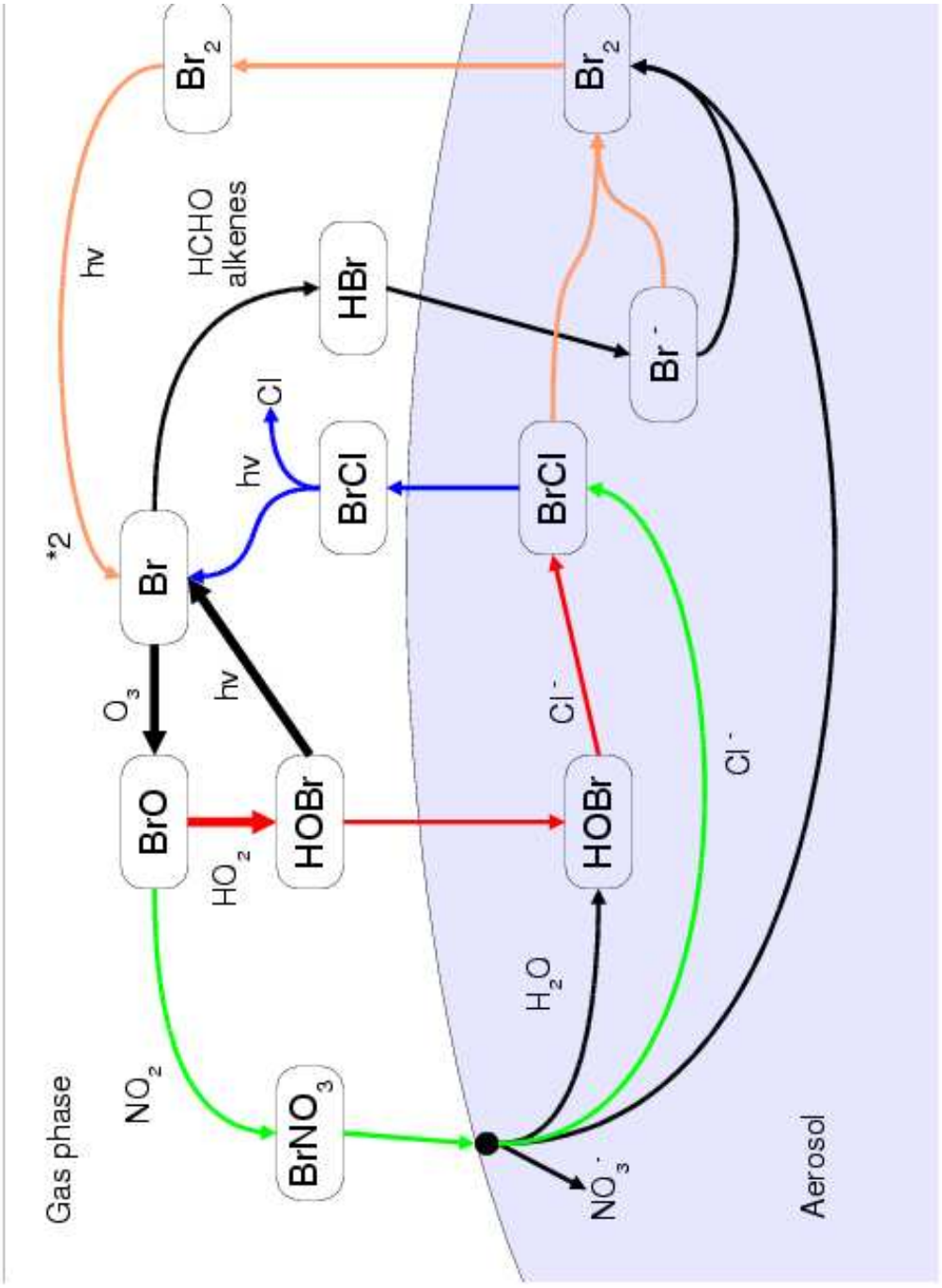

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Figure courtesy Rolf Sander et al

Iodine Chemistry looks Interesting!

- **Main source of reactive Iodine in the MBL is emission of biogenic alkyl iodides (BAI) produced in the ocean by various types of microalgae & phytoplankton.**
- **In sea salt aerosols, Iodine is strongly enriched (100-1000) times the seawater ratio hence aerosols appear to be a SINK rather than source in MBL.**
- **Biogenic alkyl iodides are rapidly destroyed by photolysis or degradation with OH to form (I, IO) which potentially has a strong impact on BL Ozone chemistry.**
- **Short lifetimes make estimates of fluxes difficult.**

Biog. alkyl Iodide	*Lifetimes***	*Typ.mix ratio*
CH_2I_2*	*~5mins*	*0.5pmol mol^{-1}*
CH_2ClI	*~4.5hrs*	*<1pmol mol^{-1}*
CH_3I	*~ 5days*	*UL 43 pmol mol^{-1}*
C_3H_7I	*~40hrs*	*0.2-2 pmol mol^{-1}*

Mixing ratios compiled by Vogt et al 1999.
** By Pruvost et al of up to 57 pmol mol^{-1} during a phytoplankton bloom.*
*** Lifetime measurements taken at mid-latitudes.*

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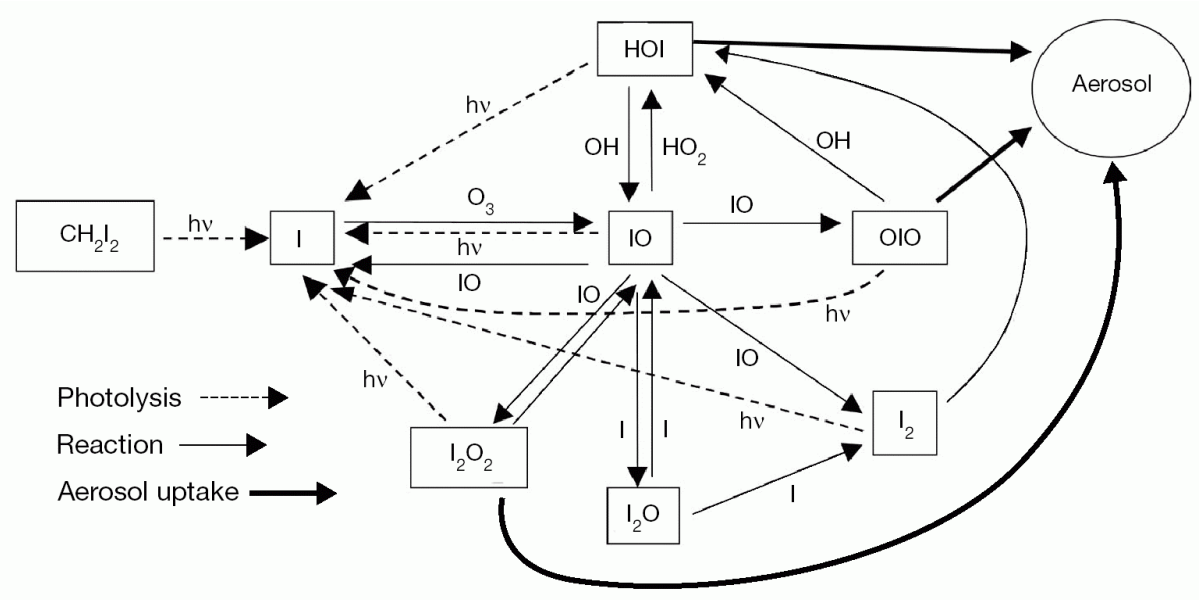
- *Detection of IO and OIO by DOAS technique in the coastal MBL and IO in the polar regions.*

Fate of reactive Iodine.



Chemical pathway from CH_2I_2 to aerosol production, on the basis of current state of the Knowledge of the gas-phase chemistry. Adapted from Colin O´Dowd et al 2002.

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Open Questions!

- *What is the global distribution of RHS in the BL?*
- *What are the release processes for the RHS observed at different locations?*
- *What are the levels of RHS in the free troposphere?*
- *How can RHS influence the Ozone budget on a global scale? What are the conditions (meteorology, tide, biology) necessary for a release of reactive Iodine? What are the exact sources?*
- *How frequent and where can elevated levels of reactive Iodine be found?*
- *What are the deposition rates of the different Iodine compounds?*
- *What are the consequences for the oxidizing capacity of the atmosphere and the global radiation budget?*