Bromine explosion in smog chamber experiments above a model salt pan

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Fig. 1.1 Geographical distribution of major areas with salt lakes. Note: salt lakes occur outside these areas, but not as frequently.

[Williams, 2002]
Bromine chemistry on salt surfaces

- Bromine (Br) reacts with ozone ($O_3$) to form BrO.
- HO$_2$ reacts with Br to form HOBr.
- HOBr is converted to BrCl under UV light (hv).
- BrCl is oxidized to Br$_2$.
- Br$_2$ is converted to HBr under UV light.
- HBr is converted to Br$^-$ under UV light.
- Br$^-$ reacts with Cl$^-$ to form BrCl.
- BrCl is converted to HOBr under UV light.

[Aldehydes, alkenes]
Bromine chemistry on salt surfaces

BrONO₂ → BrO
Br → BrONO₂
NO₂ → BrONO₂

BrCl → HBr
Cl → BrCl

Br₂ → HBr
H⁺ → BrONO₂

[Simpson 2007]
Experimental setup

Analytical instruments:

- Multireflection system for DOAS detection of Br
- O₃ analyzer
- NOₓ analyzer
- GC-FID with preconcentrator for toluene, n-butane, n-pentane, 2,2-dimethylbutane, 2,2,3,3-tetramethylbutane, and n-perfluorohexane
  → indirect determination of OH and Cl
Experimental preparation

- Preparation of salt sample:
  artificial salt samples
  NaCl/NaBr = 300/1 (similar to sea water)
  internal mixture
  (dissolved in water, dried overnight, milled)

- Flush chamber overnight with zero air by distilled water to "adjust" relative humidity

- T = 20°C (temperature controlled)

- Add O₃ (O₂ + UV light) and hydrocarbons
- Switch solar simulator on
DOAS spectra

- **RH = 37%**

- **BrO**: 498 ±70 ppt

- **O₃**: 585 ppb  (below detection limit)

- **HCHO**: 52 ppb  (below detection limit)
Experimental conditions: RH=2%, NaCl/NaBr=300/1

\[
\text{BrO} + \text{BrO} \rightarrow \text{Br} + \text{Br} + \text{O}_2 \quad \text{(rate determining)}
\]

\[
2 (\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2)
\]

\[
\text{net: } 2 \text{O}_3 \rightarrow 3 \text{O}_2
\]

\[
\frac{-d}{dt} \left[\text{O}_3\right] \text{ (“simple model“)} = 2 k [\text{BrO}][\text{BrO}]
\]

\[
\frac{dt}{dt} = 0.005 \text{ ppb/s}
\]

\[
\frac{-d}{dt} \left[\text{O}_3\right]\text{(measured)} = 0.005 \text{ ppb/s}
\]

with:

\[
k = 2.7 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \quad \text{[Atkinson, 2007]}
\]

and [BrO]=200 ppt
Experimental conditions: RH=2%, NaCl/NaBr=300/1

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\text{BrO} + \text{BrO} \rightarrow \text{Br} + \text{Br} + \text{O}_2 \text{(rate determining)}
\]

\[
2 (\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2)
\]

net: \[2 \text{O}_3 \rightarrow 3 \text{O}_2\]

\[
-\frac{d}{dt}[\text{O}_3] \text{ (“simple model“)} = 2k[\text{BrO}][\text{BrO}]
\]
\[
\frac{dt}{dt} = 0.005 \text{ ppb/s}
\]

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-\frac{d}{dt}[\text{O}_3] \text{(measured)} = 0.005 \text{ ppb/s}
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with:

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k = 2.7 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \text{ [Atkinson, 2007]}
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\text{net: } 2 \text{O}_3 \rightarrow 3 \text{O}_2

\[ -d \left[ \text{O}_3 \right] \text{ (“simple model”) } = 2 \, k \left[ \text{BrO} \right] \left[ \text{BrO} \right] \]

\[ \frac{dt}{dt} = 0.005 \text{ ppb/s} \]

\[ -\frac{d}{dt} \left[ \text{O}_3 \right] \text{(measured)} = 0.005 \text{ ppb/s} \]

with:

\[ k = 2.7 \times 10^{-12} \, \text{cm}^3 \text{molec}^{-1} \text{s}^{-1} \, [\text{Atkinson, 2007}] \]

and \([\text{BrO}]=200 \text{ ppt}\)
Experimental conditions: RH=37%, NaCl/NaBr=300/1

\[ \text{BrO} + \text{BrO} \rightarrow \text{Br} + \text{Br} + \text{O}_2 \text{(rate determining)} \]

\[ 2 \left( \text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \right) \]

net: \[ 2 \text{O}_3 \rightarrow 3 \text{O}_2 \]

\[ \frac{-d}{dt} [\text{O}_3] \text{ ("simple model") = } 2 k [\text{BrO}][\text{BrO}] \]

\[ \frac{dt}{0.04} = 0.04 \text{ppb/s} \]

\[ \frac{-d}{dt} [\text{O}_3] \text{(measured)} = 0.03 \text{ppb/s} \]

with:

\[ k = 2.7 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ [Atkinson, 2007]} \]

and [BrO]=500 ppt
Experimental conditions: RH=37%, NaCl/NaBr=300/1

BrO + BrO → Br + Br + O₂ (rate determining)

2 (Br + O₃ → BrO + O₂)

net: 2 O₃ → 3 O₂

\[-d\frac{[O_3]}{dt}\] ("simple model") = 2 k [BrO][BrO]
\[dt = 0.04 \text{ppb/s}\]

\[-d\frac{[O_3]}{dt}\] (measured) = 0.03 ppb/s

with:
\[k=2.7 \times 10^{-12} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \text{ [Atkinson, 2007]}\]
and [BrO]=500 ppt
Experimental conditions: RH=37%, NaCl/NaBr=300/1

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\text{BrO} + \text{BrO} \rightarrow \text{Br} + \text{Br} + \text{O}_2 \text{(rate determining)}
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2 (\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2)
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net: \(2 \text{O}_3 \rightarrow 3 \text{O}_2\)

\[
\frac{-d}{dt} [\text{O}_3] \text{ (“simple model“)} = 2 k [\text{BrO}][\text{BrO}]
\]

\[
\frac{dt}{= 0.04 \text{ppb/s}}
\]

\[
\frac{-d}{dt} [\text{O}_3] \text{(measured)} = 0.03 \text{ppb/s}
\]

with:

\[
k = 2.7 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \text{ [Atkinson, 2007]}
\]

and [BrO]=500 ppt
**Role of H\textsubscript{2}O\textsubscript{2} and NO\textsubscript{2}**

Very fast release of Br-source
d \[ \frac{d[BrO]}{dt} = 40 \text{ppt/s} \]

Rate coefficient \( R = \frac{1}{4} \cdot \gamma \cdot v \cdot A \), \( v \sim 220 \text{m/s} \), \( A = \text{effective surface} \sim 1 \text{m}^2/3.5 \text{m}^3 \)

\[ \text{Rate} = 5 \text{ s}^{-1} \rightarrow \tau = 200 \text{ms} \]

\[ \text{Rate} = 0.09 \text{ s}^{-1} \rightarrow \tau = 11 \text{s} \]

\( \text{RH} = 60\% \), \( \text{NaCl/NaBr} = 300/1 \)

\( \text{BrO}_{\text{max}} = 6420 \text{ ppt} \)

\[ \text{Rate coefficient } R = \frac{1}{4} \cdot \gamma \cdot v \cdot A \text{, } v \sim 220 \text{m/s, } A = \text{effective surface} \sim 1 \text{m}^2/3.5 \text{m}^3 \]

[Mochida et al., 1998], [Aguzzi and Rossi 1999]
at 37% RH:

\[[\text{Cl}]_0 \approx 3.5 \times 10^4 \text{ cm}^{-3}\]

\Rightarrow \ [\text{ClO}] \approx 3.3 \times 10^6 \text{ cm}^{-3}
Repeated exposure of salt pan at 60% RH: $O_3$
Repeated exposure of salt san at 60% RH: Br
Repeated exposure of salt pan at 60% RH: BrO
Three “bromine explosions”: Comparison

Graph showing the comparison of O₃ and BrO concentrations over time at different relative humidities (2%, 30%, and 60%). The graphs plot O₃ and BrO concentrations in ppb and ppt, respectively, against time in hh:mm.

- O₃:
  - 2% relative humidity: Concentration decreases over time, reaching a peak at approximately 03:00.
  - 30% relative humidity: Concentration decreases more gradually, reaching a peak at approximately 02:00.
  - 60% relative humidity: Concentration decreases at a slower rate, reaching a peak at approximately 01:00.

- BrO:
  - 2% relative humidity: Concentration increases sharply at the beginning, reaching a peak at approximately 00:00.
  - 30% relative humidity: Concentration increases more gradually, reaching a peak at approximately 01:00.
  - 60% relative humidity: Concentration increases at a slower rate, reaching a peak at approximately 02:00.

The graphs illustrate the different responses of O₃ and BrO to varying relative humidities, with BrO showing a more pronounced increase at 2% relative humidity.
Discussion of humidity dependence: $[\text{BrO}]_{\text{max}}$
Discussion of humidity dependence: $\text{d}[\text{BrO}] / \text{d}t$
First direct observation of “bromine explosion” in laboratory

BrO up to 6000ppt

Strong dependence on relative humidity

Controlled by thickness of quasi liquid microlayer?

Fast Br-release for 60%rh is not explained by reaction with HO$_2$ alone.

NO$_2$ might play a key role in „bromine explosion“
Scattering by aerosol in the light path
Thank you for your attention!