EFFECT OF NO\textsubscript{x} IN THE PHOTOCHEMICAL SYSTEM OF \textalpha-PINENE

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1. **MOTIVATION**

Peroxy Radical and Highly Oxidized Molecule (HOM)

1. Monomer HOM pattern change
2. Fragmentation
3. Dimer suppression
4. Alkoxy-peroxy pathway

Iida Pullinen thesis
Ehn et al 2014
2. EXPERIMENTS: JÜLICH PLANT ATMOSPHERE CHAMBER

**Experimental procedure**

- Continuously stirred tank reactor (1450l), residence time: ≈ 50-60 min.
- Bring system into steady state
- UV on: photolyze O$_3$ and produce OH, range $0.1 - 8 \cdot 10^7$ cm$^{-3}$
- Black lights on: photolyze NO$_2$ -> NO (0.3-100 ppb)
3.1 RESULT: MONOMER HOM PATTERN CHANGE

Reaction: $\text{RO}_2+\text{HO}_2$, $\text{RO}_2+\text{RO}_2$

$\text{RO}_2+\text{NO}$, $\text{RO}_2+\text{NO}_2$
3.1 RESULT: MONOMER HOM PATTERN CHANGE

No dependency on termination functional group: Similar functionality (multiple hydroperoxyl groups)

\[ c(HOM) = \frac{P(HOM)}{L(HOM)} \]

\[ \frac{c(HOM)^0}{c(HOM)} = \frac{L_W(HOM) + L_P(HOM)}{L_W(HOM)} \]

\[ L_P(HOM) = \gamma_{eff} \cdot \frac{\bar{u}}{4} \cdot S_P \]

Fuchs-Sutugin!
3.2 RESULT: FRAGMENTATION

Fragmentation of Monomer and Dimer formation

Alkoxy radical: \( \text{ROO}^+ + \text{NO} \rightarrow \text{RO}^+ + \text{NO}_2 \)

Increase of smaller compounds in monomer and dimer range
\( \rightarrow \) More volatile compounds
3.3 RESULT: DIMER SUPPRESSION

Dimer intensity decreased (16 times)

1. $\text{RO}_2 + \text{NO/NO}_2$  
   $\rightarrow$ Organic Nitrate

2. Smaller dimer ($\text{C}<20$)  
   $\text{C}_{15-19}/\text{C}_{20}$ (2 $\rightarrow$ 9.5)
3.3 RESULT: DIMER SUPPRESSSION

Effect on SOA?

Dimer $\rightarrow$ involving one relative volatile compound $=$ lose mass of dimer

(Dimer formation involves less functionalized per oxy radical, SVOC)
3.4 RESULT: ALKOXY-PEROXY PATHWAY

Correction for NPF, factors 1 - 1.17, correction for turnover, factors of 0.8 - 1.2
Reference for normalization: $(9.1 \cdot 10^7 \pm 5.8 \cdot 10^6 \text{ cm}^{-3} \text{ s}^{-1} \text{ at } \sim 0.3 \text{ ppb NO}_X)$

a) If HOM-alkoxy radical decompose to small fragments
   $\rightarrow \Sigma \text{HOM number concentration decrease}$

b) If HOM-alkoxy rearrange, keeping the C-number (observable with NO$_3^-$ CIMS)
   $\rightarrow \Sigma \text{HOM number concentration } \approx \text{constant}$
3.4 RESULT: ALKOXY-PEROXY PATHWAY

Alkoxy-peroxy pathway keeps $RO_2$ up
3.4 RESULT: ALKOXY-PEROXY PATHWAY

Mass Defect plot

Kendrick-mass = IUPAC-mass × \frac{16.00000}{15.99492}

C: 12.00000 Da
H: 1.00783 Da
O: 15.99492 Da
N: 14.00307 Da

1. No NOx has only dimer in this middle mass range

2. Monomer only appear when there is NOx → oxidation degree increased
4. SUMMARY

Effect of NOx in photochemical system of α-pinene

a. Monomer HOM pattern change
   Ketone, Hydroperoxide, Alcohol → Organic Nitrate
   → Not much effect on SOA mass ($\gamma_{\text{eff}}$)

b. Fragmentation increased
   Major C10 compounds → Increase of C$_5$ to C$_9$ compound
   → SOA mass suppression (Less condensable compound)

c. Dimer suppression of HOM-SVOC dimers
   Lose chance for SVOC to condense on SOA (Dimer-O$_2$ lose)
   Smaller dimers because of fragmentation → higher vapor pressure
   → SOA mass suppression (main reason)

However:

d. Alkoxy-Peroxy Pathway
   Produce more peroxy radical (even with lower [OH])
   → SOA mass gain (Compensate suppression)
Back up slides
HOM in photochemical systems

HOM are *efficiently* formed with OH by α-pinene (and β-pinene)

Berndt et al., 2016
NO\textsubscript{x} „controls“ photochemical OH / HO\textsubscript{2} system

- **low NO\textsubscript{x}**
  \[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]
  radical sink

- **medium NO\textsubscript{x}**
  \[ \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \]
  radical recycling

- **high NO\textsubscript{x}**
  \[ \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 \]
  radical sink

\[ \begin{align*}
\text{CO} & \quad \text{CH}_4 \\
\text{VOC} & \quad \text{O}_2 \\
\text{CO}_2 & \quad \text{OVOC}
\end{align*} \]
Starting point: $\beta$-pinene SOA yield as $f[NO_x]$
increase of $[\text{OH}]$: $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$
lower [OH]: OH + NO₂ → HNO₃
HOM-ON, HOM-PP -> SOA: condensation

- Photochemistry in JPAC into ss
- Add seed aerosol increase surface sink, decrease HOM lifetime
- Apply gas-phase kinetics

\[ L_P(HOM) = \gamma_{eff} \cdot \frac{\bar{U}}{4} \cdot S_P \]
Apply:
Correction for NPF, factors 1 - 1.17.
Correction for OH, factors of 0.8 - 1.2
reference for normalization: \((9.1 \cdot 10^7 \pm 5.8 \cdot 10^6 \text{ cm}^{-3} \text{ s}^{-1} \text{ at } \sim 0.3 \text{ ppb } \text{NO}_X)\)

Black:
HOM concentration fairly constant
Mass decreases: HOM lower with lower molecular weight

Red:
Hydrolysis of type HOM-RONO2 → HOM-ROH will affect the HOM mass