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AMS user’s meeting @ Nanjing
IEPOX-SOA formation

**Gas Phase**

isoprene $\cdot$OH $\xrightarrow{O_2} \text{HO}_2^\cdot \xrightarrow{\cdot\text{OH}} \text{ISOPOOH} \xrightarrow{\cdot\text{OH}} \text{IEPOX}$

**Aerosol Phase**

- 2-methyltetrols
- hydroxy sulfate ester
- higher order oligomers from additional IEPOX monomers

IEPOX $\xrightarrow{H^+}$ dimer $\xrightarrow{H^+}$ hydroxy sulfate ester dimer

Surratt et al 2010
Measured IEPOX-SOA from AMS

Hayes et al., 2013; Pandolfi et al., 2014; Hu et al., 2013; Hu et al., 2016; Robinson et al., 2011; Chen et al., 2015; Xu et al., 2014, 2015; Budisulistiorini et al., 2013, 2015; Slowik et al., 2011

GEOS-Chem gas phase IEPOX for July 2013 by Fabien Paulot

Hu et al., ACP 2015
Measured IEPOX-SOA from AMS

Hayes et al., 2013; Pandolfi et al., 2014; Hu et al., 2013; Hu et al., 2016; Robinson et al., 2011; Chen et al., 2015; Xu et al., 2014, 2015; Budisulistiorini et al., 2013, 2015; Slowik et al., 2011

Hu et al., ACP 2015

GEOS-Chem gas phase IEPOX for July 2013 by Fabien Paulot
Outline:

1) Characterization of a Real-Time Tracer of IEPOX-SOA from AMS

2) Heterogeneous reaction of IEPOX-SOA
IEPOX-SOA in SOAS

Tetrols are 26% of IEPOX-SOA

IEPOX-SOA (µg/m³)

Sulfate (µg/m³)

Methyltetrol (µg/m³)

OM/OC = 1.65
O/C = 0.4
H/C = 1.46
N/C = 1.4E-3

CxHy
CxHyOz
CxHyNp
CxHyNpOz
H₂O
IEPOX-SOA mass spectra

$m/z$ 53   $m/z$ 82

Field studies

Lab studies

Mass spectra come from Budisulistiorini et al., 2013; Chen et al., 2014; Liu et al., 2014

We looked at other tracer ions in IEPOX-SOA spectra, $C_5H_6O^+$ is the best one.

$$f_{C_5H_6O} = \frac{C_5H_6O^+}{\text{IEPOX-SOA}} = 12-40 \%o$$
IEPOX-SOA from AMS

C$_5$H$_6$O$^+$ recognition

One of IEPOX-SOA species

3-MeTHF-3,4-diols (C$_5$H$_{10}$O$_3$)

Heat decomposition

Methylfuran structure C$_5$H$_6$O$^+$

Robinson et al., 2011; Lin et al., 2011; Budisulistiorini et al., 2013
Is C$_5$H$_6$O$^+$ a good tracer for IEPOX-SOA?

Reviewer in recent ACP paper:

“$m/z$ 82 is also found in SOA from biogenic monoterpene emissions… An unambiguous identification of isoprene SOA is thus not provided by the presence of $m/z$ 82 alone…”

To start: What’s the values of $f_{82}$ or $f_{C_5H_6O}$ in different OA sources?
Datasets used in this study

- Los Angeles area, US: 85%
- SE, US: 15%
- SE forest, US: 83%
- Harrow, Canada: 83%
- Bear Creek, Canada: 17%
- Atlanta, US: 94%
- Barcelona area, Spain: 67%
- Pristine Amazon forest, Brazil: 33%
- Beijing, China: 66%
- Changdao island, downwind of China: 66%
- Borneo forest, Malaysia: 76%
- NW-US: 24%
- European boreal forest (Hyytiala), Finland

Strongly influenced by:
- urban/biomass-burning emissions
- isoprene emissions
- monoterpane emissions
- SEAC4RS flight track

GEOS-Chem gas phase IEPOX for July 2013 by Fabien Paulot
Signal-to-background contrast

Average $f_{C_5H_6O}$ in IEPOX-SOA: 23 ± 9 ‰

Average $f_{C_5H_6O}$ in pollution & biomass-burning ~1.7‰

Probability density distribution

$f_{C_5H_6O}$ in pollution and biomass-burning emissions

Los Angeles area, US; Beijing, China; Changdao island, Downwind China; Barcelona area, Spain

SEAC4RS aircraft: NW US
DC3 Aircraft: western US
BB lab exhaust, emission and OH aged
SEAC4RS & DC3 aircraft: BB plumes

Std chemical species

Average $f_{C_5H_6O}$ in pollution & biomass-burning...
OH aging effect on $f_{C_5H_6O}$

Oxidation tends to decrease $f_{C5H6O}$ in aerosols
$f_{C_5H_6O}$ in isoprene influenced areas

Pollution & biomass burning

Average $f_{C_5H_6O}$ in IEPOX-SOA: $23 \pm 9 \%$

Strongly influenced by isoprene emission:
- SE forest, US
- Amazon pristine forest, Brazil
- Aircraft: SE US
- Borneo forest, Malaysia

(Robinson et al., 2011)
$f_{C_5H_6O}$ in other isoprene SOA

Pollution & biomass burning

Average $f_{C_5H_6O}$ in IEPOX-SOA: $23 \pm 9\%$

Strongly-influenced by isoprene emission:
- SE forest, US
- Amazon pristine forest, Brazil
- Aircraft: SE US
- Borneo forest, Malaysia
(Robinson et al., 2011)
Pollution & biomass burning

$f_{C_5H_6O}$ in other isoprene SOA

Average $f_{C_5H_6O}$ in IEPOX-SOA: $23 \pm 9 \%$

$f_{C_5H_6O}$
- enhanced in IEPOX-SOA
- NOT enhanced in other isoprene SOA

$C_5H_6O$ is enhanced in IEPOX-SOA but NOT enhanced in other isoprene SOA.

Strongly-influenced by isoprene emission:
- SE forest, US
- Amazon pristine forest, Brazil
- Aircraft: SE US
- Borneo forest, Malaysia (Robinson et al., 2011)

Pure lab SOA
- Isoprene derived non IEPOX-SOA

Chen et al., 2014; Kroll et al., 2006; Ng et al., 2008
$f_{C_5H_6O}$ in monoterpene emissions

Pollution & biomass burning

Average $f_{C_5H_6O}$ in IEPOX-SOA: $23 \pm 9\%$

Strongly-influenced by isoprene emission:
- SE forest, US
- Amazon pristine forest, Brazil
- Aircraft: SE US
- Borneo forest, Malaysia
  (Robinson et al., 2011)

Pure lab SOA
- Isoprene derived non IEPOX-SOA
$f_{C_5H_6O}$ in monoterpene emissions

Pollution & biomass burning

Average $f_{C_5H_6O}$ in IEPOX-SOA: 23 ± 9 %

Strongly-influenced by isoprene emission:
- SE forest, US
- Amazon pristine forest, Brazil
- Aircraft: SE US
- Borneo forest, Malaysia (Robinson et al., 2011)

Strongly-influenced by monoterpene emissions:
- Rocky mountain pine forest
- European boreal forest, Finland (Robinson et al., 2011)

Pure lab SOA
- Isoprene derived non IEPOX-SOA
$f_{C_5H_6O}$ in monoterpenes emissions

Pollution & biomass burning

Signal-to-background contrast

Average $f_{C_5H_6O}$ in IEPOX-SOA: 23 ± 9 %

Monoterpene-SOA can enhance $f_{C_5H_6O}$, but much less than IEPOX-SOA

Strongly-influenced by isoprene emission:
- SE forest, US
- Amazon pristine forest, Brazil
- Aircraft: SE US
- Borneo forest, Malaysia (Robinson et al., 2011)

Strongly-influenced by monoterpenes emissions:
- Rocky mountain pine forest
- European Boreal forest, Finland (Robinson et al., 2011)
- Isoprene derived non IEPOX-SOA
- Monoterpene SOA (Database, 2014)
Scientific questions:

- Is C$_5$H$_6$O$^+$ a good tracer for IEPOX-SOA?
  
  Yes

- Can C$_5$H$_6$O$^+$ be used to estimate IEPOX-SOA?
Estimate IEPOX-SOA

$$IEPOX\text{-SOA}=\frac{C_5H_6O_{total}}{f_{C_5H_6O_{IEPOX-SOA}}} - \frac{C_5H_6O_{background}}{f_{C_5H_6O_{background}}}$$

- **Measured by AMS**
- **Background from MT-influenced regions**
- **Background from pollution & biomass burning emissions strongly influenced areas**
- **f_{C_5H_6O} in fresh IEPOX-SOA = 21\%**

- **Background from monoterpane emissions**
- **Average f_{C_5H_6O} in IEPOX-SOA: 23 \pm 9 \%**

- **Background from pollution and biomass burning emissions**
Estimated IEPOX-SOA in SOAS

Estimated IEPOX-SOA:
- using background from monoterpane emissions.

IEPOX-SOA (μg/m³)

Local time

Outline:

1) Characterization of a Real-Time Tracer of IEPOX-SOA from AMS

2) Heterogeneous reaction of IEPOX-SOA
Scientific question: IEPOX-SOA fate

IEPOX-SOA account for 6-36% of OA in forest areas

1) Volatility of IEPOX-SOA?

2) Aging quickly to form more oxidized OA?

Hu et al., ACP, 2016
Setup of Thermodenuder

Time resolution: 4 min
Temperature range: 35-260 °C
Residence time: 21 s

Hu et al., ACP 2016;
Huffman et al., 2008, 2009a, b
Volatile of IEPOX-SOA—partially exist as oligomers

Consistent with multiple other studies: Lopez-Hilfiker et al., 2016; Isaacman-VanWertz et al., 2016; Lin et al., 2014

Faulhaber et al., 2009; Huffman et al., 2009; Hu et al., ACP, 2016
Scientific question: IEPOX-SOA fate

1) Volatility of IEPOX-SOA?
   Low volatility

2) Aging quickly to form more oxidized OA?

Hu et al., ACP, 2016
Setup of Oxidation flow reactor

- **OH Production:**
  
  - $O_2 + hv(185\text{nm}) \rightarrow O_3$
  - $O_3 + hv(254\text{nm}) + H_2O \rightarrow 2\ OH$
  - $H_2O+hv(185\text{nm}) \rightarrow OH$

- Estimated OH conc. in reactor: $0-7 \times 10^{10}$ (molec. cm$^{-3}$)

- Photochemical aging: several hours to a few months
Simulated gas-phase IEPOX fate

Negligible IEPOX-SOA formation in OFR

Hu et al., ACP, 2016
OH Heterogeneous lifetime of IEPOX-SOA

$\leftarrow_{\text{Equivalent aging time (days)}}$

$0.1 \quad 1 \quad 10 \quad 100$

$1.4$

$1.2$

$1.0$

$0.8$

$0.6$

$0.4$

$0.2$

$0.0$

$10^{10}$

$10^{11}$

$10^{12}$

$10^{13}$

MFR of IEPOX-SOA in OFR

OH exposure in OFR (molec. cm$^{-3}$ s$^{-1}$)

$\leftarrow_{\text{Quantile SE, US}}$

$\leftarrow_{\text{Quantile Amazon}}$

$\leftarrow_{\text{RH range:}}$

$<60$

$60-80$

$80-90$

$90-100$

$k_{OH} = 4.0 \pm 2.0 \times 10^{-13}$ cm$^3$ molec.$^{-1}$ s$^{-1}$

Lifetime is $> 2$ weeks

(19$\pm$9 days)

Assuming the ambient OH conc. is

$\sim 1.5 \times 10^6$ molec. cm$^{-3}$

Hu et al., ACP, 2016
OH Heterogeneous lifetime of IEPOX-SOA

-RH dependent

Hu et al., ACP, 2016
Conclusions

• Heterogeneous oxidation of IEPOX-SOA
  ✓ Low volatility
  ✓ Lifetime ~ > two weeks

• $f_{C_5H_6O}$ is a good tracer for IEPOX-SOA
  • Low background levels in OA:
    ✓ pollution and biomass-burning emissions:
      0.02 - 3.5‰ with an average of 1.7‰
    ✓ monoterpene emissions.
      2.5 - 6‰

• Simplified method to estimate IEPOX-SOA from tracer
  ✓ Performs well compared to PMF