Photoproduction of singlet oxygen from aqueous organic aerosols

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Why do we care about reactive oxygen species (ROS)?

Importance of oxidants in atmospheric chemistry:
• Oxidative capacity of the atmosphere
• Fate of pollutants
• Aerosol-cloud interactions
4 ingredients necessary for the production of $^1\text{O}_2$

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Can $^{1}\text{O}_2$ also be formed in organic aerosols?

Research questions on $^1\text{O}_2$ in organic aerosols:

1. Is $^1\text{O}_2$ formed?

2. Does $^1\text{O}_2$ matter in the atmosphere?

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Making secondary organic aerosols (SOA) in the lab

UVB lamps

5 m³ chamber with Teflon bag

H₂O₂ + hν \rightarrow 2 \text{OH}

toluene

diphenyl

naphthalene
dimethyl naphthalene

α-pinene + O₃ = control

Brown carbon

Prof. Sergey Nizkorodov

Kurtis Malecha
Quantifying $^{1}\text{O}_2$ steady-state concentrations

- **Experimental setup**

- **Data analysis**

Rate of disappearance:
\[
\ln\left(\frac{\text{[FFA]}_t}{\text{[FFA]}_0}\right) = -k \cdot [^{1}\text{O}_2]_{ss} \cdot \text{[furfuryl alcohol]}
\]


$[^{1}\text{O}_2]_{ss(aq)} = 2.0 - 6.8 \times 10^{-14}$ M

$[\text{OH}]_{ss(aq)} \sim 10^{-17}$ M
Steady state concentrations of $^{1}\text{O}_2$ are highly variable

$^{1}\text{O}_2$ production depends on:
1. Photons of light absorb
2. Concentration of chromophores

- Necessary to normalize $\Rightarrow$ quantum yield values

$^{1}\text{O}_2$ quantum yield:
- In SOA: $\Phi^{1}\text{O}_2 = 0.029 \pm 0.009$
- In aquatic environments: $\Phi^{1}\text{O}_2 = 0.01-0.05$

[Diagram showing perinaphthenone quantum yield = 0.98 and SOA with furfuryl alcohol, showing liquid chromatography UV/Vis spectroscopy in aquatic environments.]
Research questions on $^1\text{O}_2$ in organic aerosols:

1. Is $^1\text{O}_2$ formed?
   - How much is formed?
   
   $[^1\text{O}_2]_{ss(aq)} = 2.0 - 6.8 \times 10^{-14} \text{ M}$
   $\Phi[^1\text{O}_2] = 0.029 \pm 0.009$

2. Does $^1\text{O}_2$ matter in the atmosphere?
   - Compared to other oxidants?
   - Present in ambient aerosols?
   - For the degradation of compounds within aerosols?
   - For aerosol-cloud interactions?
Quantum yields of ROS within lab-generated SOA

$^1O_2$ is produced in high concentrations relative to other ROS

- $^1O_2$ quantum yields $\gg$ H$_2$O$_2$ quantum yields (100x)
- $^1O_2$ quantum yields $\gg\gg$ OH radical quantum yields (1000x)
- $\alpha$-pinene is not a sensitizer

Can $^1O_2$ also be formed in ambient organic aerosols?
Field collected particulate matter sensitize $^{1}\text{O}_2$

- In Roveredo, Switzerland
- November 17, 2017 & March 18, 2018

Both naphthalene and $\alpha$-pinene SOA became better cloud condensation nuclei after UVB photooxidation.

Likely negligible role of $^{1}$O$_2$ in atmospheric aging for SOA.

Research questions on $^{1}\text{O}_2$ in organic aerosols:

1. Is $^{1}\text{O}_2$ formed?
   • How much is formed?
   \[ [^{1}\text{O}_2]_{\text{ss(aq)}} = 2.0 \times 10^{-14} \text{ M} \]
   \[ \Phi^{^{1}\text{O}_2} = 0.029 \pm 0.009 \]

2. Does $^{1}\text{O}_2$ matter in the atmosphere?
   • Compared to other oxidants?
   • Present in ambient aerosols?
   • For the degradation of compounds within aerosols?
   • For aerosol-cloud interactions?
   • For indoor air chemistry? Check out Sebastian Zala’s lightning talk!

It depends… … and still much to learn!
Summary: Relevance of $^1$O$_2$ as a reactive oxygen specie in organic aerosols