Aerosol production from dimethyl sulfoxide and dimethyl disulfide

*Insights from chamber experiments into dimethyl sulfide chemistry*

Matthew Goss,\textsuperscript{1} Qing Ye,\textsuperscript{1*} Yaowei Li,\textsuperscript{2} Frank Keutsch,\textsuperscript{2} Jesse Kroll \textsuperscript{1}

\textsuperscript{1} Massachusetts Institute of Technology, \textsuperscript{2} Harvard University

*Now at the National Center for Atmospheric Research

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Introduction

• Dimethyl sulfide emitted by phytoplankton (DMS, CH$_3$SCH$_3$) is the largest biogenic source of sulfur to the atmosphere.

• For such a simple molecule, the oxidation scheme is surprisingly complex.
Standard DMS oxidation mechanism

Veres et al., *PNAS* (2020)
Standard DMS oxidation mechanism

Saunders et al., ACP (2003)
Barnes et al., Chem. Rev. (2006)
Veres et al., PNAS (2020)
Standard DMS oxidation mechanism

Addition and Abstraction pathways are shown with reactions involving OH, NO, and O$_3$ species. Methanesulfonic acid (MSA) and sulfate/sulfuric acid (SO$_4$) are key products and intermediates in the oxidation process.
Standard DMS oxidation mechanism

Saunders et al., ACP (2003)
Barnes et al., Chem. Rev. (2006)
Veres et al., PNAS (2020)

Addition

Abstraction

Isomerization pathway

Ye et al., Atmospheric Chem. Phys. (2022)
Jernigan et al., Geophys. Res. Lett. (2022)
Ye et al., ACS Earth Space Chem. (2021)
Standard DMS oxidation mechanism

Saunders et al., ACP (2003)
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Rapid aerosol production

Aerosol production only through SO₂??
Mechanism uncertainties

Mechanism does not describe aerosol composition

DMS
Sulfate
SO$_2$

Ye et al., *Atmospheric Chem. Phys.* (2022)
Mechanism uncertainties

Mechanism does not describe aerosol composition

Linking MSIA + OH $\rightarrow$ MSA has been used to explain high MSA yields

Lucas and Prinn (2002); von Glasow and Crutzen (2004); Wollesen de Jonge et al. (2021); Shen et al. (2022)
Mechanism uncertainties

Mechanism does not describe aerosol composition

Linking MSIA + OH → MSA has been used to explain high MSA yields

Lucas and Prinn (2002); von Glasow and Crutzen (2004); Woliesen de Jonge et al. (2021); Shen et al. (2022)
How can *isolating* parts of the mechanism inform our understanding of aerosol formation?
Isolating addition and abstraction pathways

Aerosol production only through SO₂??
Isolating addition and abstraction pathways

Dimethyl sulfoxide (DMSO)

Aerosol production only through SO$_2$??

Rapid aerosol production

See abstraction side

For all:

SO$_2$ + OH $\rightarrow$ HSO$_3$ + O$_2$

SO$_3$ + H$_2$O $\rightarrow$ HSO$_4$
Isolating addition and abstraction pathways

Past lab studies did not include online aerosol measurements

Reported DMSO oxidation products are inconsistent

- $\text{SO}_2$ (Major) $^{1,4,5}$
- $\text{SO}_2$ (Minor) $^3$
- MSIA $^{2,3}$
- DMSO $^{1,3,5}$
- MSA $^{3,5}$

1. Sørensen et al. (1996); 2. Urbanski et al. (1998); 3. Arsene et al. (2002);
DMDS and DMSO relevant on their own

• Estimated at a few percent of biogenic sulfur emissions\(^1\)
• Notable marine\(^2\) and biomass burning\(^3\) emissions

• Notable DMS oxidation product
• Observed in marine boundary layer\(^4\)

Experimental Setup

**Precursor**

- Oxidized compounds: \( \text{NH}_4^+ - \text{CIMS [PTR3]} \)
- Other gases: \( \text{SO}_2, \text{NO}_x, \text{O}_3 \) monitors

**OH source**

- HONO or \( \text{H}_2\text{O}_2 \)

**Seed Particles**

- \( \text{NaNO}_3 \)

**Dilution Tracer**

- acetonitrile

**7.5 m}^3\) Chamber**

(Dry, 293 K)

**Particle-Phase Products**

- AMS & SMPS

**Gas-Phase Products**

- Precursor (GC-FID or PTR3)
- Oxidized compounds (\( \text{NH}_4^+ - \text{CIMS [PTR3]} \))
- Other gases (\( \text{SO}_2, \text{NO}_x, \text{O}_3 \) monitors)
Experiment conditions

Low $NO_x$

$H_2O_2$ added

$\bullet$

0 hrs

NO or HONO added

3 hrs

High $NO_x$

HONO added

$\bullet$

0 hrs

SO$_2$ + OH lifetime is > 100 hrs under these conditions
• AMS measures particle-phase MSIA
• Product spectra are linear combination of MSA, MSIA, and SO$_4$
DMDS oxidation results (abstraction pathway)

Mostly $\text{SO}_2$ formed under low $\text{NO}_x$ oxidation...
DMDS oxidation results (*abstraction pathway*)

Mostly SO$_2$ formed under low NO$_x$ oxidation...

... the addition of NO increases [OH] and [NO$_x$]

- increased aerosol
Is this just due to increase in [OH]?

• Under low NO\textsubscript{X} conditions, SO\textsubscript{2} is the major product
Is this just due to increase in [OH]?

- Under low NO\textsubscript{X} conditions, SO\textsubscript{2} is the major product.
- Shift in yield suggests direct involvement of NO\textsubscript{X}.
• Under low NO$_x$ conditions, SO$_2$ is the major product
• Shift in yield suggests direct involvement of NO$_x$
Back to the mechanism

Addition

Abstraction

Dimethyl disulfide (DMDS)

For all:

SO₂ → OH → HSO₂ → O₂ → SO₃ → H₂O → H₂SO₄

see abstraction side
Back to the mechanism

Dimethyl disulfide (DMDS)

Addition

Abstraction

For all:

SO₂ + OH → H₂SO₃ + O₂ → SO₃ + H₂O → H₂SO₄
Back to the mechanism

**Back to the mechanism**

**Addition**

- **DMS**

**Abstraction**

- **Methanesulfonic acid (MSA)**
  - **SO$_4$**
  - **Sulfate / Sulfuric acid (SO$_4$)**

**Dimethyl disulfide (DMDS)**

- **Slow!**
  - **Fast!**

- **see abstraction side**

**For all:**

- **SO$_2$**
  - **OH**
  - **H$_2$SO$_3$**
  - **O$_2$**
  - **SO$_3$**
  - **H$_2$O**
  - **H$_2$SO$_4$**
Back to the mechanism

Back to the mechanism

Dimethyl sulfoxide (DMSO)

Dimethyl disulfide (DMDS)

For all:

SO₂ + OH → HSO₃⁻ + O₂ → SO₃²⁻ + H₂O → H₂SO₄

see abstraction side
MSIA formed under low NO\textsubscript{x} oxidation...

DMSO oxidation results (*addition pathway*)
DMSO oxidation results (addition pathway)

MSIA formed under low NO\textsubscript{x} oxidation...

… the addition of HONO increases [OH] and [NO\textsubscript{x}] 
- increased aerosol
Is this just due to increase in [OH]?

• Under low NO$_x$ conditions, MSIA is the only product
Is this just due to increase in [OH]?

- Under low NO\textsubscript{\(x\)} conditions, MSIA is the only product
- Shift in yield suggests direct involvement of NO\textsubscript{\(x\)}
DMSO mechanism

- $O_2$ addition explains MSA and sulfate
- OH addition can explain only MSA
- Neither explain the high $NO_x$ formation of $SO_2$

**Diagram:**

MCM/JPL

$O_2$ addition

$OH$ addition

Burkholder et al., *NASA JPL* (2020)

Returning to DMS

Barnes et al., Chem. Rev. (2006)
Wolfe et al., Geosci. Model Dev. (2016)
Veres et al., PNAS (2020)

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Rapid aerosol production
Returning to DMS

Barnes et al., Chem. Rev. (2006)
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Veres et al., PNAS (2020)

DMS

Rapid aerosol production!

For all:
SO₂ + OH → HSO₃⁻ + O₂
SO₃ + H₂O → H₂SO₄

see abstraction side
Returning to DMS

Rapid aerosol production!
Conclusions

• Develop a method for quantifying MSIA in the AMS
• Rapid aerosol production from DMSO and DMDS
  • Particularly under high $\text{NO}_x$
• Insight into DMS mechanism
  • $\text{NO}_x$-dependent aerosol composition and yield from the abstraction channel
  • Intermediates DMSO and MSIA lead to MSA and sulfate aerosol formation from addition channel

Questions?