Atmospheric chemistry of ocean organosulfur emissions

Matthew Goss, Qing Ye, Jesse Kroll

Department of Civil and Environmental Engineering, MIT

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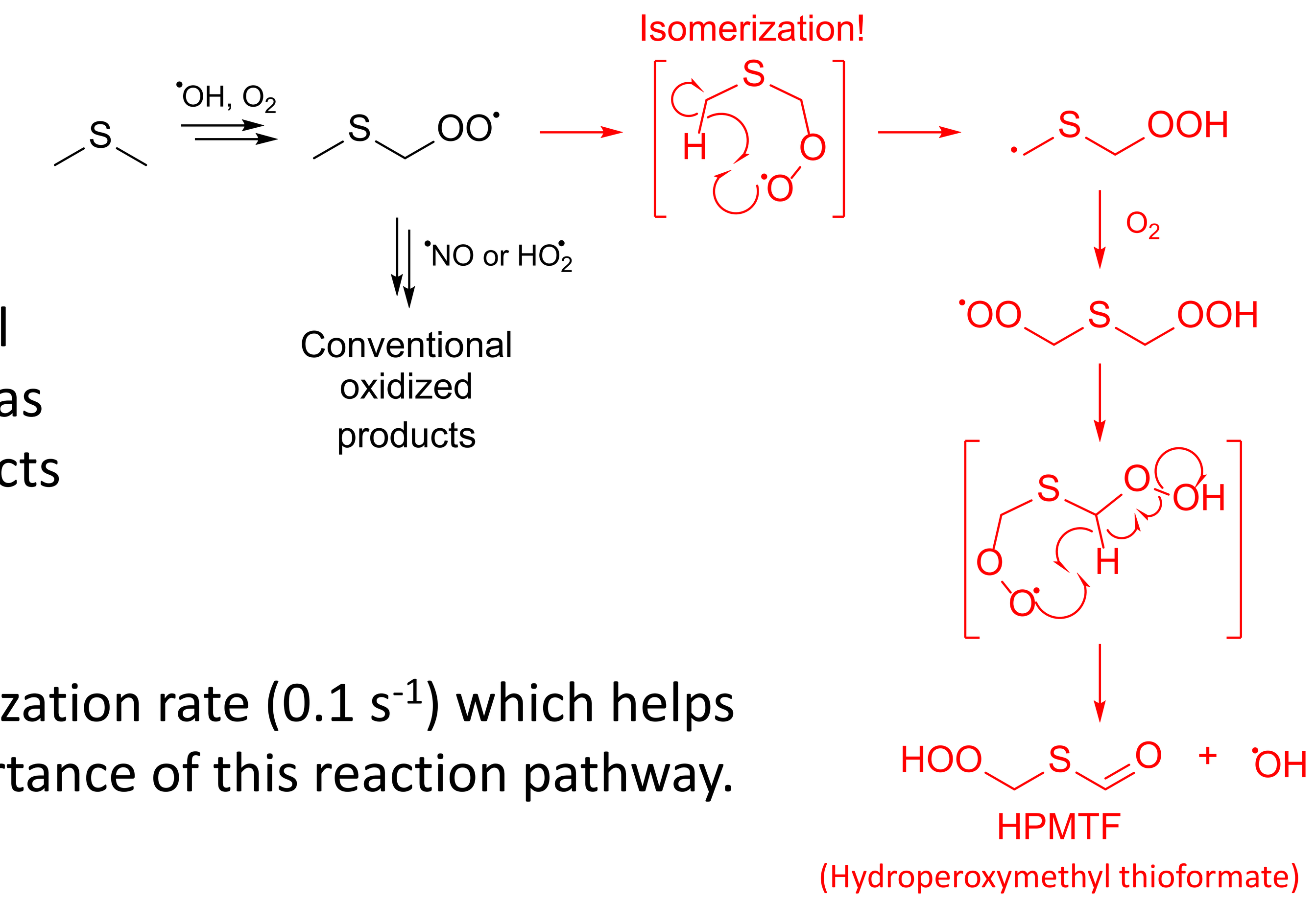
Isomerization

A recently discovered isomerization pathway[3] competes with conventional reactions and may be responsible for as much as 33% of DMS oxidation products on a global scale.[4]

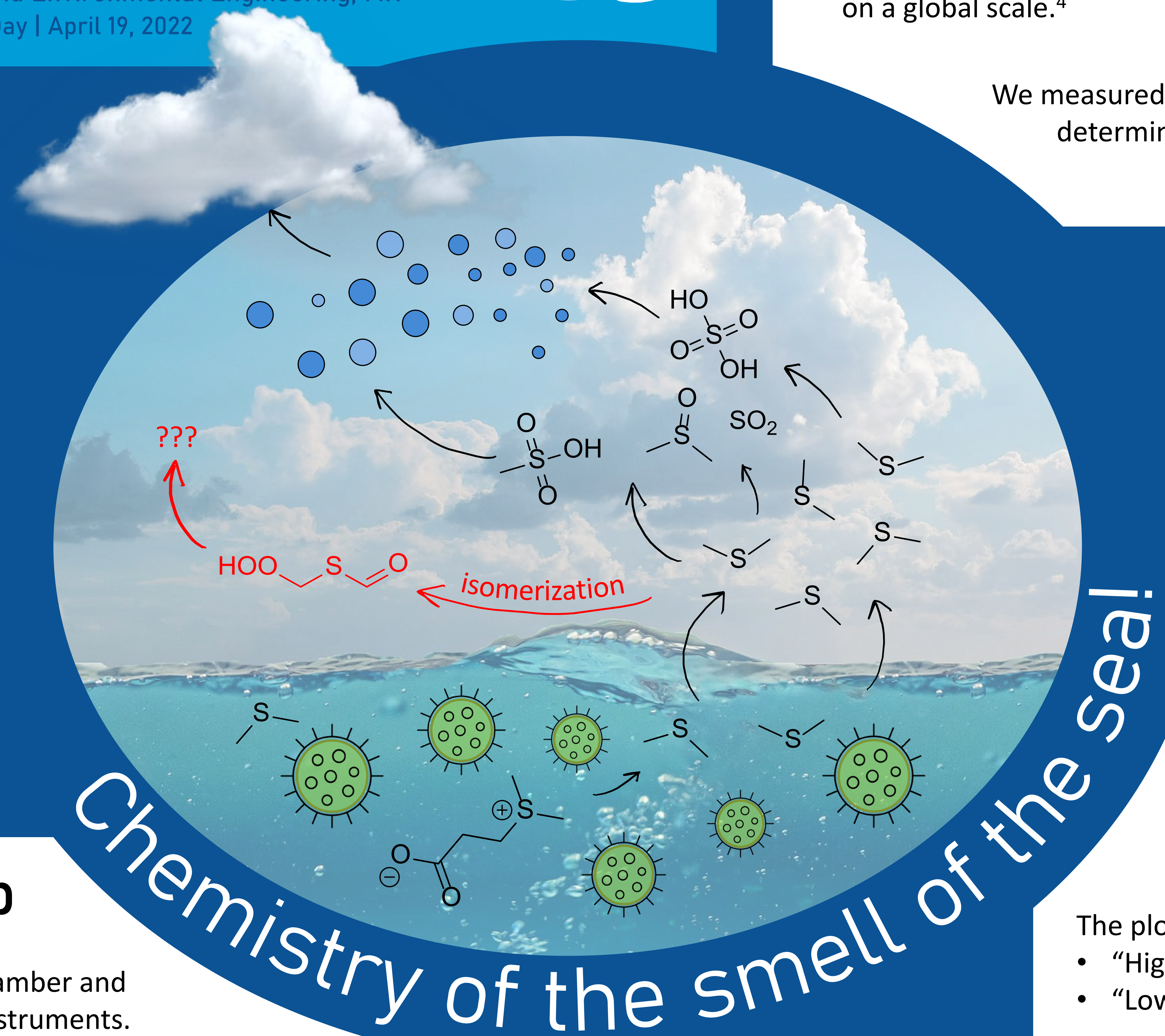


We measured the isomerization rate (0.1 s^{-1}) which helps determine the importance of this reaction pathway.

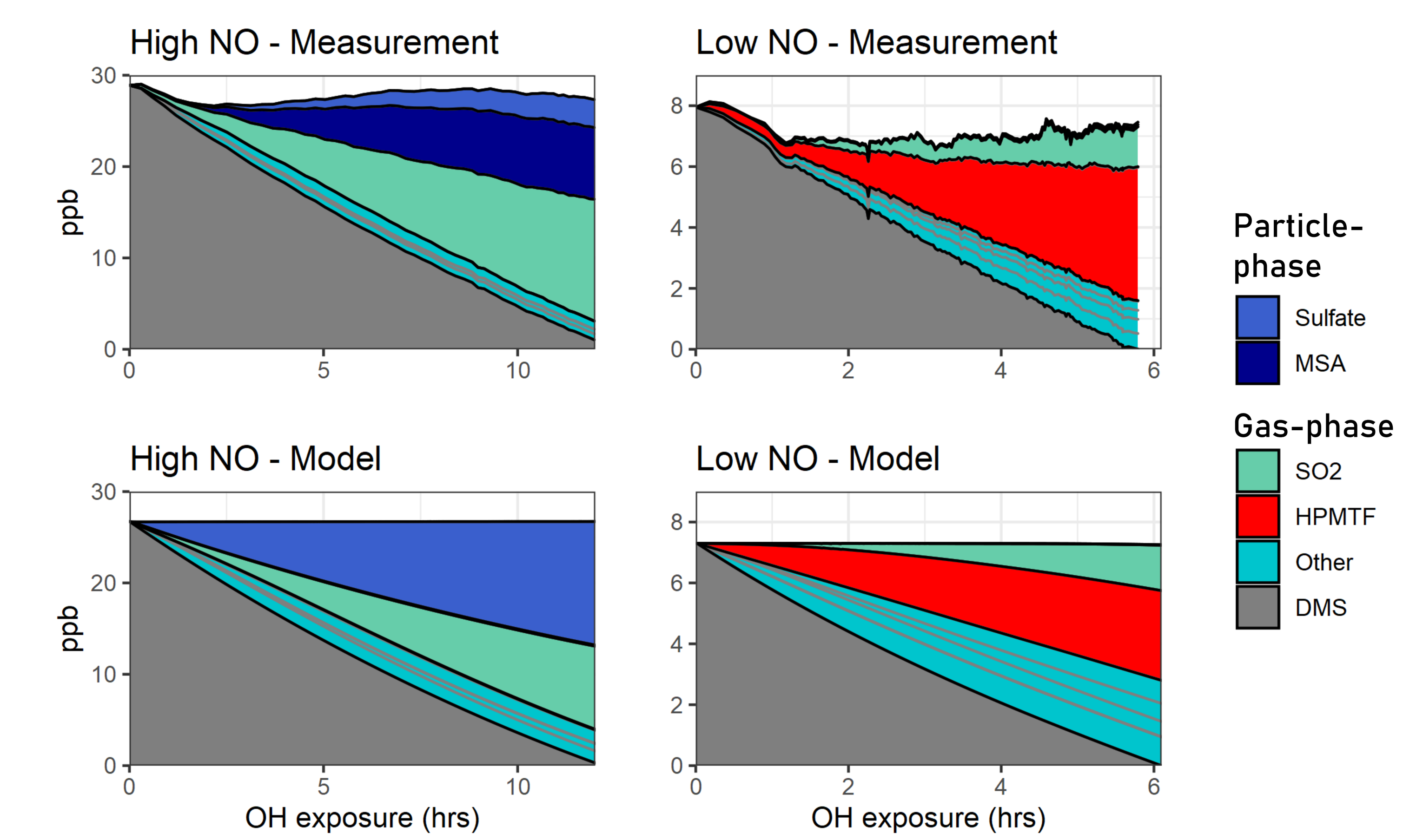
Background

Dimethyl sulfide (CH_3SCH_3, DMS) emitted by phytoplankton is the largest natural source of sulfur to the atmosphere.[1,2] In the air, it oxidizes to form dozens of products and fine aerosol particles. Understanding the formation of these particles is important since they can reflect sunlight or impact cloud formation, both affecting the climate.

We quantify these oxidation processes under controlled conditions in the lab to identify reaction rates and patterns in product formation that can help improve chemical transport and climate models.



Total sulfur



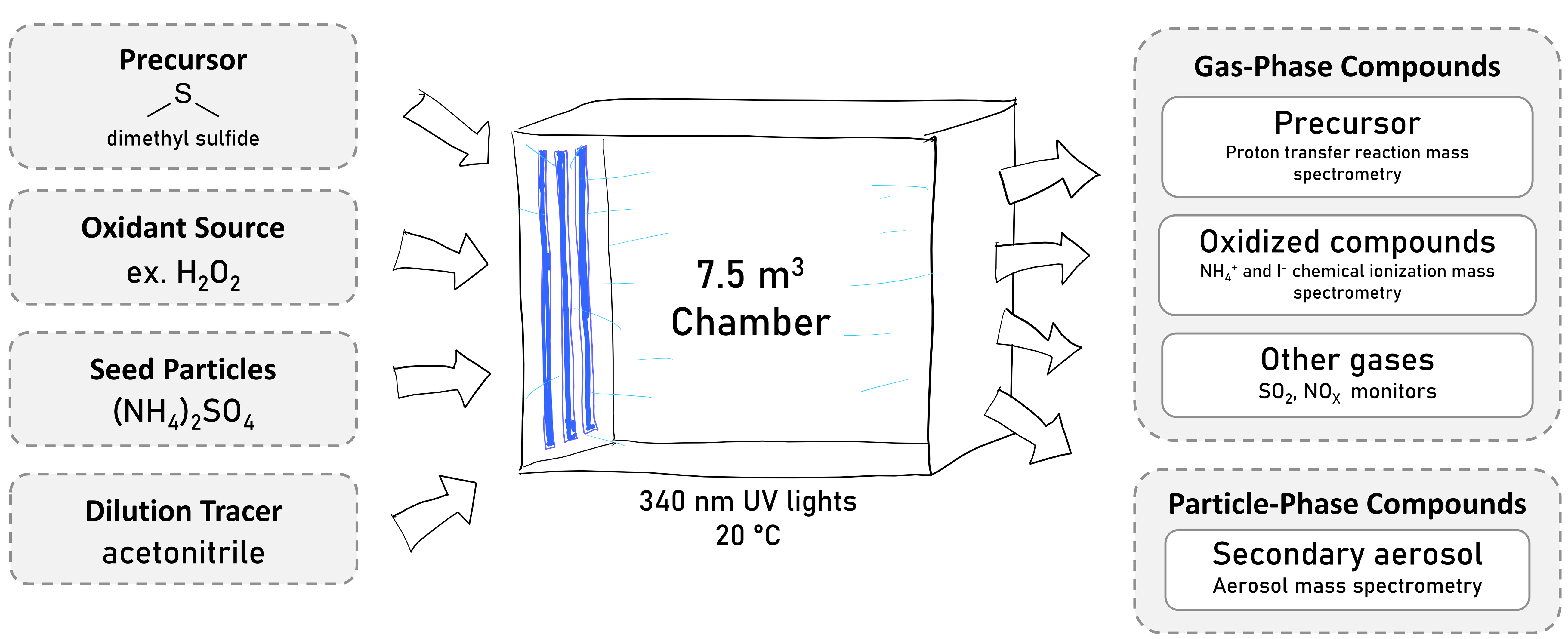
The plots above show all products of DMS oxidation over time. Note:

- "High NO" (polluted) → rapid formation of particle-phase products
- "Low NO" (pristine) → lots of isomerization-product HPMTF

The modeled[5] results reproduce measurements well, with the exception of the formation of particle-phase methane sulfonic acid (MSA).

Experimental setup

Dimethyl sulfide is oxidized in a Teflon chamber and all products are monitored by assorted instruments.



Applications and implications

Measurements of chemical rate constants and product distributions are essential for improving climate models. Our measurements show that:

1. Isomerization is fast enough to compete with other known RO_2 channels.
2. Current models may incorrectly predict particle formation, potentially impacting their predictions of cloud formation.

Citations 1. Kilgour, et al., *Atmos. Chem. Phys.*, 2022. 2. Andreae, *Mar. Chem.*, 1990. 3. Veres, et al., *PNAS*, 2020. 4. Fung, et al., *Atmos. Chem. Phys.*, 2022. 5. Saunders, et al., *Atmos. Chem. Phys.*, 2003.