Assessment of dimethyl sulfide oxidation mechanisms through comparison with previous experiments

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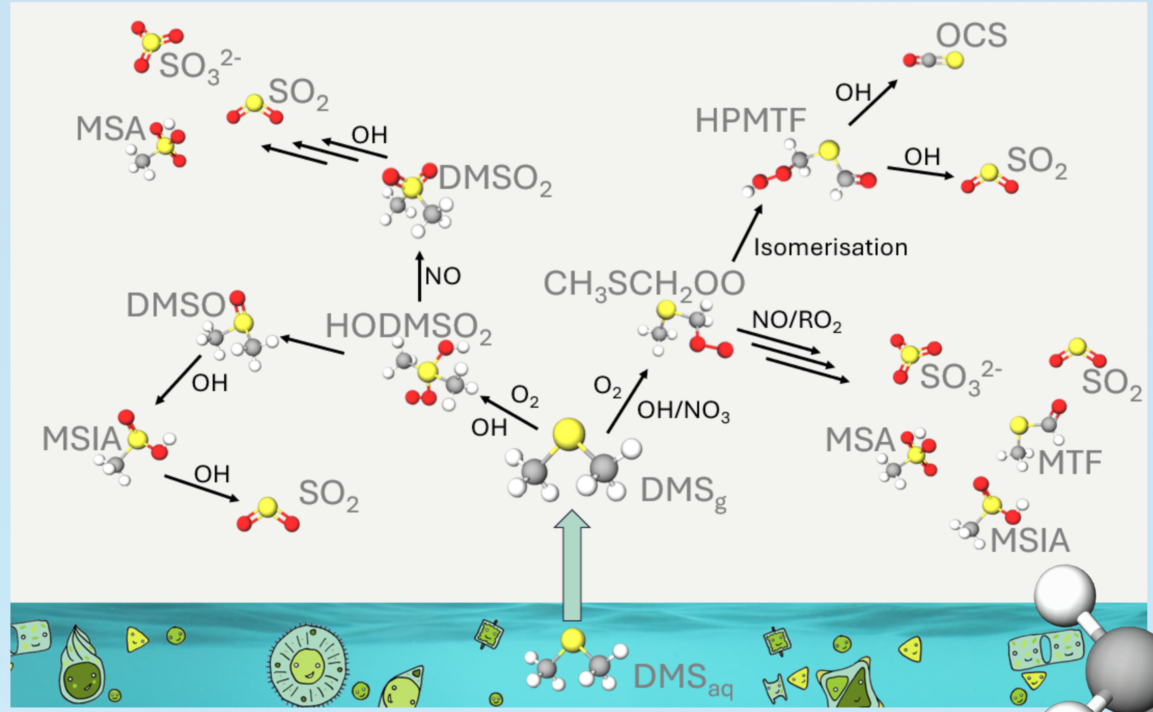
Background DMS oxidation is complex, but important

Around **28 TgS** of dimethyl sulfide (DMS) is emitted annually from phytoplankton, making DMS the **most abundant biological sulfur compound emitted**. The DMS in the atmosphere reacts to form a variety of different compounds, some of which initiate cloud formation, making them **important for rain and the radiative balance** of the planet.

Additionally, due to DMS naturally occurring above oceans, an oxidation product of DMS, **methanesulfonic acid (MSA), has been used to determine sea ice extent in ice cores** up to 300 years in the past. However, due to gaps in the oxidation pathway of DMS, there are **large uncertainties in the modelling of MSA formation.**

By comparing different experiments and mechanisms to each other, **this study allows an evaluation of the mechanisms in different conditions**, and an **assessment of the gaps in the chemical mechanisms.**



Set up 5 experiments, 4 mechanisms

Experiment	Arsene2001	Albu2008	Ye2022 exp. 1	Ye2022 exp. 2a	Jernigan2022
Temp (K)	295	290	295	295	298
Chamber (m^3)	1.08	0.37	7.5	7.5	0.6
OH Source	H_2O_2 photolysis	H_2O_2 photolysis	HONO photolysis	H_2O_2 photolysis	TME ozonolysis
Avg. OH (cm^{-3})	1.6×10^8	2.5×10^7	8.2×10^6	1.5×10^6	1.3×10^6
Avg. RO_2 (cm^{-3})	3.4×10^{10}	2.0×10^{11}	2.0×10^7	4.0×10^8	1.8×10^9
DMS (ppb)	7000	15000	72.8	82	10
NO (ppb)	1070	-	50	-	-
NO_2 (ppb)	505	-	90	-	-
H_2O_2 (ppb)	25000	25000	-	1500	-
HONO (ppb)	-	-	90	-	-
O_3 (ppb)	-	-	-	-	23
VOC photolysis?	Yes (320-480 nm)	No	Yes (300-400 nm)	Yes (300-400 nm)	No
Length (hrs)	0.5	0.5	2	5	20

Master Chemical Mechanism (MCM)

Near explicit mechanism
- 17,000 reactions

In the DMS mechanism:
- 31 sulfur species
- 81 sulfur reactions

Shen Mechanism

Based on MCM v3.3.1 with the addition of Hoffmann2016 reactions, along with the addition of the HPMTF pathway and formation of CH_3SOH
- 25 sulfur reactions added
- 5 sulfur reactions adjusted
- 19 non-sulfur reactions adjusted, added or removed

Ye Mechanism

Based on MCM v3.3.1 with the addition of the HPMTF pathway
- 12 sulfur reactions added

Jernigan Mechanism

Based on MCM v3.3.1 along with a (simplified) HPMTF pathway
- 5 reactions added
- 4 reactions adjusted
- 2 non-sulfur reactions added

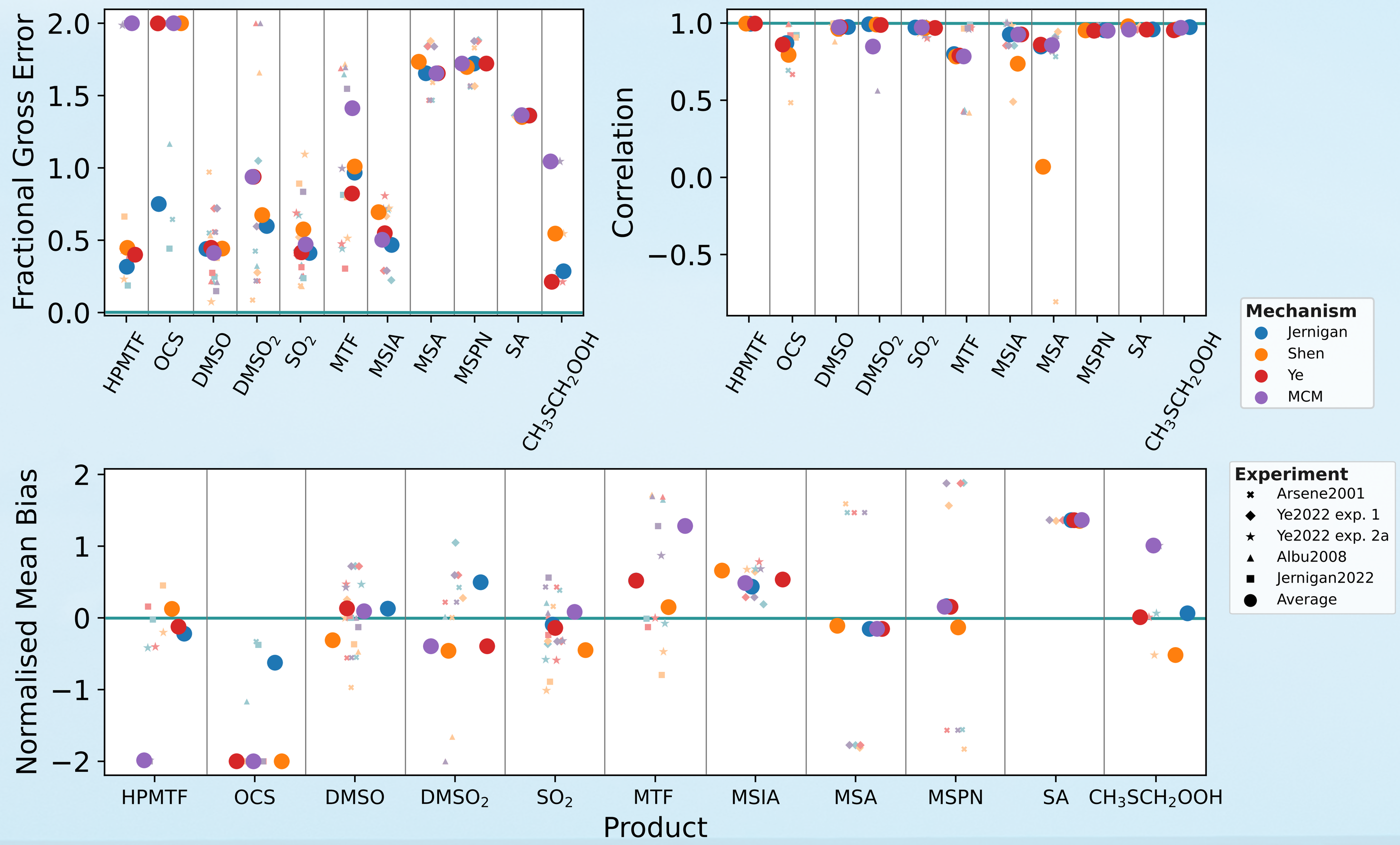
Overview The mechanisms all deviate from the experiments

Fractional Gross Error $= \frac{2}{n}\sum_i \left|\frac{M_i - O_i}{M_i + O_i}\right|$ **Ideal = 0**

Normalised Mean Bias $= \frac{2}{n}\sum_i \frac{M_i - O_i}{M_i + O_i}$ **Ideal = 0**

Correlation $= \frac{cov(O,M)}{\sigma_O \sigma_M} = \frac{\sum_i (O_i - \overline{O})(M_i - \overline{M})}{\sqrt{\sum_i (O_i - \overline{O})^2}\sqrt{\sum_i (M_i - \overline{M})^2}}$ **Ideal = 1**

where:
$M = (M_i)_{0 \le i \le n}$ = Modelled values
$O = (O_i)_{0 \le i \le n}$ = Observed values

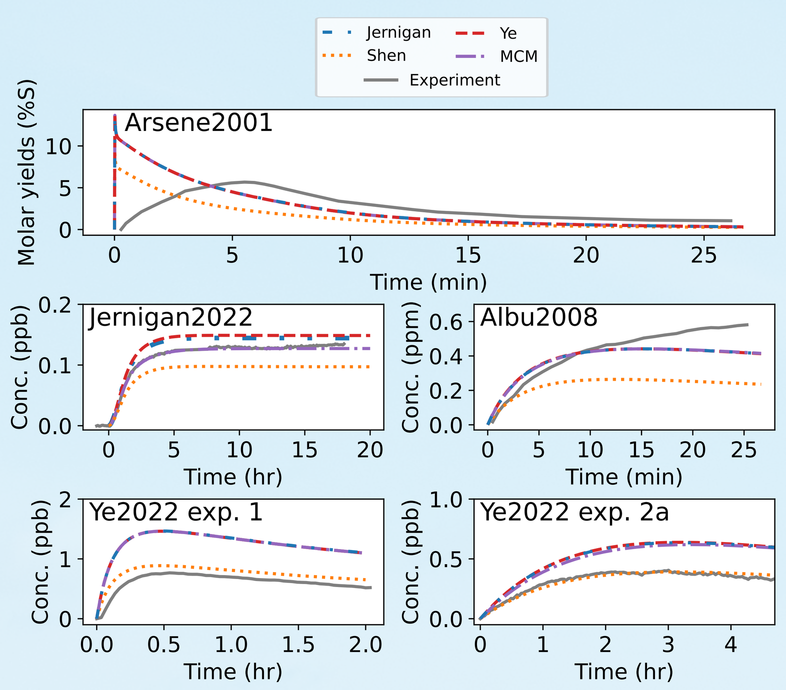


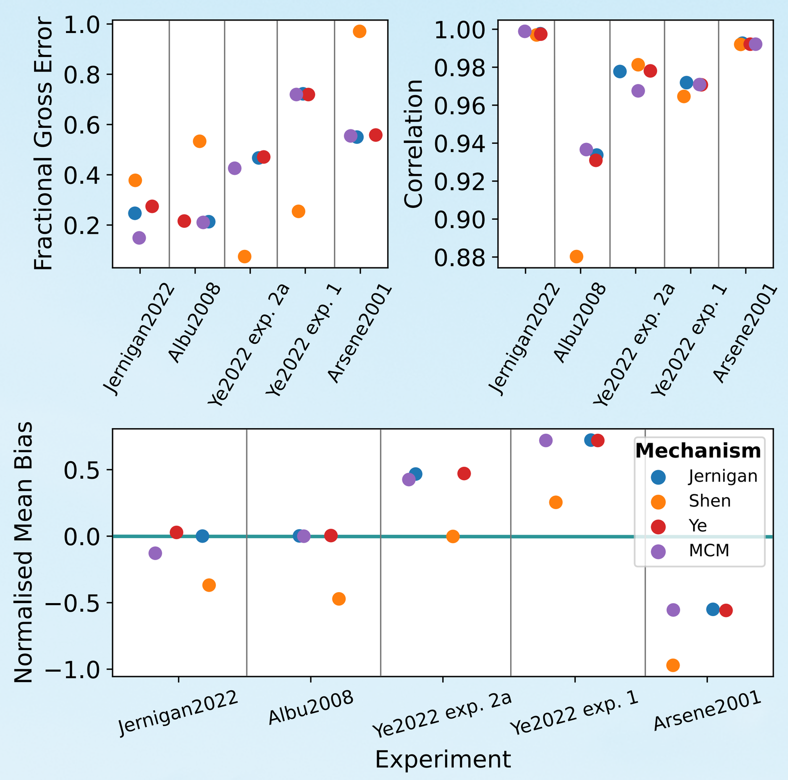
Conclusion and future work

The mechanisms deviate from each other, and the experiments; more work is needed to improve these mechanisms.
- By looking into where the deviations in the mechanisms come from, there can be insight into which reactions should be adjusted. This investigation has been performed for DMSO and OCS in the following two 'Spotlight' boxes, however more compounds can be explored.
- Focusing on where the mechanisms underperform (such as for MSA, MSPN and SA) allows an exploration of reactions that may be missing, or have inaccurate rate constants.

Spotlight Less DMSO is formed by the Shen mechanism

Time dependent formation of DMSO in the experiments, and how they are modelled:





What is causing the differences in the mechanisms?

DMSO comes from OH addition to DMS. The initial OH addition reaction to $CH_3SCH_2O_2$ is reversible, however, the addition of oxygen to $CH_3SCH_2O_2$ to form $HODMSO_2$ is irreversible. The Shen mechanism includes these two addition reactions separately, whereas the other mechanisms combine them into one reaction. Although both methods are correct (with the Shen mechanism being more explicit), **the Shen mechanism uses the combined rate constant for the initial OH + DMS addition reaction instead of the recommended rate constant for that reaction.** This rate constant lowers the amount of DMSO formed from the Shen mechanism.

MCM, Jernigan and Ye Mechanisms:

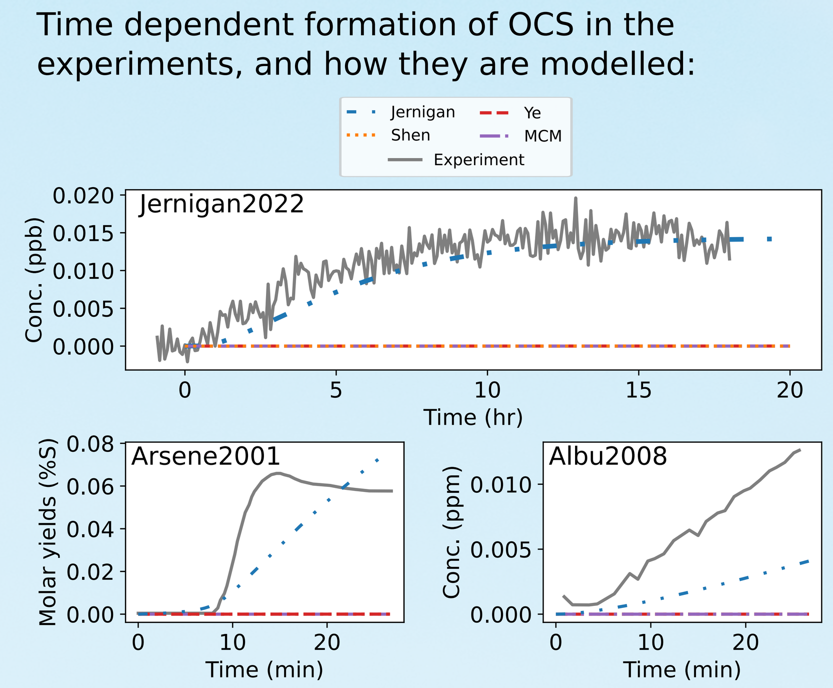
$DMS + OH \rightarrow CH_3SCH_2O_2$	$k_{298\,K} = 4.8\times10^{-12}$
$DMS + OH \rightarrow HODMSO_2$	$k_{298\,K}^{1\,atm} = 2.2\times10^{-12}$
$HODMSO_2 + NO \rightarrow DMSO_2 + HO_2 + NO_2$	$k_{298\,K} = 9.0\times10^{-12}$
$HODMSO_2 \rightarrow DMSO + HO_2$	$k_{298\,K} = 140$

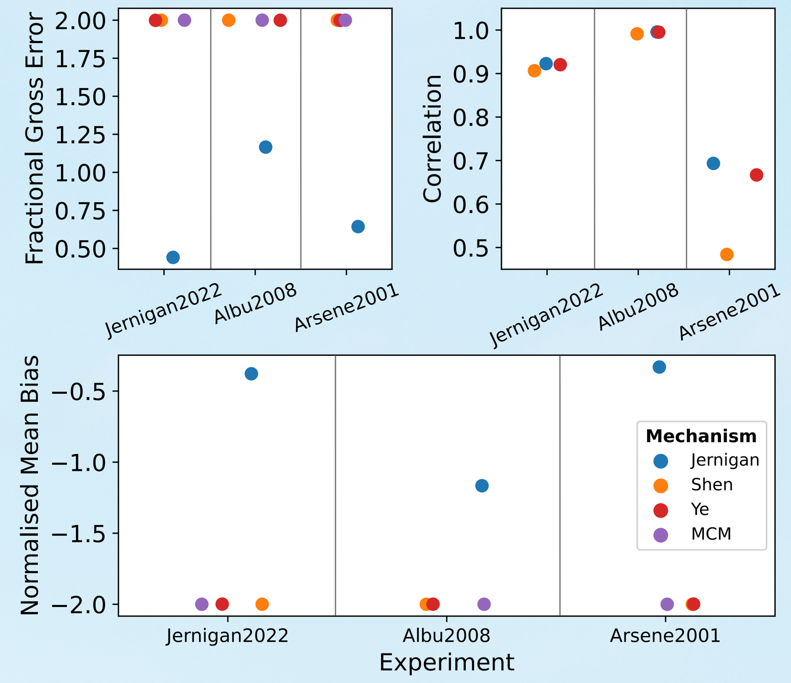
Shen Mechanism:

$DMS + OH \rightarrow CH_3SCH_2O_2$	$k_{298\,K} = 4.8\times10^{-12}$
$DMS + OH \rightarrow CH_3SOHCH_3$	$k_{298\,K}^{1\,atm} = 2.2\times10^{-12}$
$CH_3SOHCH_3 \rightarrow DMS + OH$	$k_{298\,K} = 2.3\times10^6$
$CH_3SOHCH_3 \rightarrow CH_3SOH + CH_3O_2$	$k = 5.0\times10^5$
$CH_3SOHCH_3 \rightarrow HODMSO_2$	$k_{1\,atm} = 4.4\times10^6$
$HODMSO_2 + NO \rightarrow DMSO_2 + HO_2 + NO_2$	$k_{298\,K} = 9.0\times10^{-12}$
$HODMSO_2 \rightarrow DMSO + HO_2$	$k_{298\,K} = 140$

Spotlight The Jernigan mechanism models OCS the best

Time dependent formation of OCS in the experiments, and how they are modelled:





What are causing the differences in the mechanisms?

OCS is formed through the reaction of HPMTF with OH radicals. **As the MCM does not include the HPMTF pathway, it does not have a way to produce OCS** (hence no correlation). The other mechanisms include OCS formation, but each uses different rate constants, and Jernigan uses different branching ratios.

Shen Mechanism:

$HPMTF + OH \rightarrow HOOCH_2SCO$	$k = 1.4\times10^{-12}$
$HOOCH_2SCO \rightarrow HOOCH_2S + CO$	$k_{298\,K} = 1.7\times10^9$
$HOOCH_2SCO \rightarrow OH + HCHO + OCS$	$k_{298\,K} = 1.2\times10^5$

Ye Mechanism:

$HPMTF + OH \rightarrow HOOCH_2SCO$	$k = 1\times10^{-11}$
$HOOCH_2SCO \rightarrow HOOCH_2S + CO$	$k_{298\,K} = 1.7\times10^9$
$HOOCH_2SCO \rightarrow OH + HCHO + OCS$	$k_{298\,K} = 1.2\times10^5$

Jernigan Mechanism:

$HPMTF + OH \rightarrow OCS$	$k = 1.4\times10^{-11}*0.14$
$HPMTF + OH \rightarrow SO_2 + CO$	$k = 1.4\times10^{-11}*0.86$

The three mechanisms have different rate constants for the reaction of HPMTF with OH (1.4×10^{-12}-1.4×10^{-11} cm^3 $molecules^{-1}$ s^{-1}), however, the largest source of deviation is from the branching ratio of the decomposition of the intermediate. **In the Shen and Ye mechanisms, the OCS pathway accounts for 0.007% of the decomposition, however, in the Jernigan mechanism it is 14%.** The Jernigan mechanism branching ratio, along with the higher rate constant, seems to fit OCS production better across the experiments.

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References

1. Albu, M.; Barnes, I.; Becker, K. H.; Patroescu-Klotz, I.; Benter, T.; Mocanu, R. In *Simulation and Assessment of Chemical Processes in a Multiphase Environment*, Barnes, I., Kharytonov, M. M., Eds.; Springer Science: Dortdrecht, 2008, pp 501–513.
2. Arsene, C.; Barnes, I.; Becker, K. H.; Mocanu, R. *Atmos. Environ.* **2001**, 35, 3769–3780
3. Ye, Q.; Goss, M. B.; Krechmer, J. E.; Majluf, F.; Zaytsev, A.; Li, Y.; Roscioli, J. R.; Canagaratna, M.; Keutsch, F. N.; Heald, C. L.; Kroll, J. H. *Atmos. Chem. Phys.*, **2022,** 22, 16003–16015
4. Jernigan, C. M.; Fite, C. H.; Vereecken, L; Berkelhammer, M. B.; Rollins, A. W.; Rickly, P. S.; Novelli, A.; Taraborrelli, D.; Holmes, C. D.; Bertram, T. H. *Geophys. Res. Lett.* **2022**, 49, e2021GL096838
5. Shen, J. *et al. Environ. Sci. Technol.* **2022**, 56, 13931-13944
6. Hoffmann, E. H.; Tilgner, A.; Schrödner, R.; Bräuer, P.; Wolke, R.; Herrmann, H. *PNAS* **2016**, 113, 11776-11781
7. Saunders, S. M.; Jenkin, M. E.; Derwent, R. G.; Pilling, M. *J. Atmos. Chem. Phys.* **2003**, 3, 161–180.

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