

Comment on acp-2022-566

Anonymous Referee #2

Referee comment on "Product distribution, kinetics, and aerosol formation from the OH oxidation of dimethyl sulfide under different RO₂ regimes" by Qing Ye et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-566-RC2>, 2022

Ye et al present new laboratory measurements of the OH-oxidation of DMS at high and low NO and high and low RH. The measurements are used to provide better constraints on the isomerization rate of CH₃SCH₂O₂ as well as the bimolecular rate for HPMTF+OH. Both of these rates have been reported previously in the literature, but the uncertainty in the prior measurements is much larger than that reported here. One of the more interesting results of the manuscript is the apparent difference in the MSA-sulfate ratio measured at high NO compared to that expected from the model. The paper is well written and is an important contribution to the literature. I recommend that paper be published and that the authors consider the following comments and suggestions:

Line 77: Just confirming that tau(bi) includes reactions of RO₂ with RO₂ (and HO₂) and not just NO.

Section 2: What is the chamber temperature and how constant is it over an experiment. Or more interestingly, what fraction of DMS oxidized proceeds down the H-abstraction pathway.

Line 105: The authors state that: "*The quantification of MSA was determined from the AMS tracer ion CH₃SO₂⁺ + 105 (see SI); this ion is unique to MSA/methylsulfonate, with negligible contributions from other sulfur-containing species (Hodshire et al., 2019; Huang et al., 2015).*" I agree in the context of previous experiments and known other S-containing species, but this work (and other recent work) is highlighting that we don't fully understand DMS oxidation and the variety of S-containing species that are produced under atmospheric conditions. It seems possible that this non-specific ion (CH₃SO₂⁺) could be from molecules other than MSA as we learn about DMS oxidation. Perhaps there is a way to state this in the manuscript?

Figure 2: Sulfur closure over the first 1hr (OH exposure) in the low NO, low RH experiment is not very good. It is exceptional after 1 hr. What is happening in this first

hour where you are losing 2ppb of DMS, but there is no indication of any sulfur products being formed? Is this a mixing issue?

Line 175: I would suggest citing Jernigan et al 2022 (JPC-A) where they show that HPMTF uptake to dry aerosol particles is small, consistent with the idea that reactive uptake to seed aerosol is insignificant.

Line 190: The MSA-sulfate part of this story is very interesting. I am curious if among the many experiments you have run if there are sufficient experiment-to-experiment differences in HO₂ to test the branching between R4 and R5.

Line 226: The asymptote of the yield curve of 1.5 is an interesting constraint on the CIMS sensitivity to HPMTF. Is this still consistent with S-closure in the low NO and low RH experiment?

Line 256: MTF is also formed from the reaction of CH₂SCH₂O₂ with RO₂.

Line 264: Why were the high RH experiments carried out over longer timescales and at higher initial DMS concentrations? Does the higher initial DMS concentration have any impact on tau(bi) through RO₂+RO₂ reactions?

Line 285: It would be helpful to assess the contribution of the water dependent HPMTF sensitivity on S-closure here. See Veres et al 2020 PNAS (Supplemental figure S8) for a rough idea of how much of an effect this might have.

Line 300: I think Vermeuel et al 2020 first showed the role of clouds/fog on HPMTF with field measurements.

Line 320: I agree that HPMTF delays the formation of SO₂, but it could accelerate the formation of sulfate if HPMTF multiphase chemistry is an efficient pathway to sulfate (as suggested by Novak et al).

Table 1: It appears that these experiments were run with a large number of different seed particles. There is no discussion of the effect of the seed particle on the sulfur product distribution (and the MSA-sulfate ratio).