Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC1
https://doi.org/10.5194/acp-2022-566-RC1, 2022
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Comment on acp-2022-566

Anonymous Referee #1

Referee comment on "Product distribution, kinetics, and aerosol formation from the OH oxidation of dimethyl sulfide under different RO_2 regimes" by Qing Ye et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-566-RC1, 2022

Summary:

This manuscript describes a system of environmental chamber experiments to examine the kinetics and product distribution both in the gas and aerosol phase of DMS oxidation under a variety of oxidative and environmental conditions. The work progresses the field by providing a stronger constraint on a gas-phase production and loss pathway of a recently discovered sulfur oxidation product, hydroperoxymethyl thioformate (HPMTF). The authors present an isomerization rate constant that fits within existing literature values as well as a constrained OH loss rate with a method for calculation validated by the co-observation of the OH loss rate of a previously calculated sulfur species, methyl thioformate. The work adds to the field through a reexamination of the MSA to sulfate yield within their chamber experiments under differing relative humidity and NO concentrations. They propose that future work focus on better constraining the oxidation mechanism leading to the formation of MSA and sulfate. The manuscript reads well and the results are robust. The manuscript should be published after the following comments have been addressed.

General comments:

The manuscript focuses on the gas-phase oxidation pathways of DMS with a focus on HPMTF. The chamber was run under a variety of different oxidative environments that drastically change the RO2 lifetime with the inclusion of NO. I recommend adding a minor discussion and reminder of the reactions that could occur in the chamber under the various oxidative conditions that may be amplified compared to those occurring in typical marine boundary layer conditions. In particular, including the H2O2 + OH reaction and its ability to form HO2 a reactant with methylthiomethyl peroxy radical (MTMP) as a competing reaction with isomerization. A review will help the reader understand the experiments and how the oxidative conditions were set up.

There is a discussion on the role of MSA formation and its relationship to sulfate. The focus is on the gas-phase mechanisms that yield MSA and H2SO4. I recommend the authors comment on the role of the heterogeneous and aqueous processing of the sulfur compounds and their tie to MSA and sulfate formation. In particular, the ability for water soluble species (i.e. HPMTF, MSIA, DMSO, DMSO2) to condense onto available aerosol surface and contribute to sulfate or MSA formation. The authors utilize a variety of seed particles without any reference in the main text or SI to their impact on the fate of the sulfur molecules. Is there future work in preparation or was there no observable effect on the seed composition?

I recommend citing additional literature on the previous work looking at the MSA and sulfate yields when higher concentrations of NOx are present (Chen et al 2012, www.atmos-chem-phys.net/12/10257/2012/, Patroescu et al 1999, https://doi.org/10.1016/S1352-2310(98)00120-4). I would recommend making connections between these previous chamber reports and this current work to see if connections and chemical pathways can be made.

Lastly, a major advancement is the tighter constraint on the HPMTF + OH rate constant. I would recommend moving the S5 figure showing this result to the main text.

Technical comments:

Line 56: I recommend a further discussion of the importance of RO2 reactions with other RO2 species present in the chamber. A comment is made about insignificance in the atmosphere, but this reaction pathway could be significant in the chamber. In addition, methyl thioformate (MTF) is thought to form through the reaction of MTMP with HO2, O2, OH or other RO2 species. The only channel explained later is through the OH oxidation of the product of MTMP with HO2 (CH3SCH2OOH). Could you please elaborate on the other potential chamber specific reactions here and why they were not addressed?

Line 58: “believed to rapidly form SO2, sulfate, and methanesulfonic acid (MSA)” is slightly misleading. I would provide more clarification on this point. Most climate models have the H-abstraction lead to only SO2 while the OH addition leads to MSA and some SO2. I would specify that the rapid formation of MSA from this channel is only prominent under high HO2 and NOx conditions atypical of the marine environment.

Line 64: Jernigan et al GRL 2022 also provided an isomerization rate constant, highlighted later but not here.

Line 106: You cite two authors that found the MSA fragment ($CH_3SO_2^+$) in the AMS is unique to MSA. Do these citations address the potential for DMSO2 to contribute to the $CH_3SO_2^+$ fragment? There is significant discussion on DMSO2, so I wounder if you can kick off a CH_3 from DMSO to make $CH_3SO_2^+$.

Line 115: How were the atomized seed particles added to the chamber? Were the particles dried before introduction to the chamber or were they added wet? I would recommend clarifying the phase state of the seed particles added to the chamber under the high RH conditions. Line 297 starts to addresses this, but additional clarification would be greatly appreciated.

Line 119: I would recommend changing "high" to long for the description of the lifetime. A long lifetime reads better than high lifetime.

Line 125: How was the H_2O_2 concentration added calculated? I assume the 30% H_2O_2 is in water and that would add water vapor to the chamber, was this dried before or is the mass of water added insignificant on the scale of the chamber?

Line 138: Only Sulfate and MSA were permitted to partition to the particle phase. Could

the exclusion of DMSO, DMSO2, HPMTF, and MSIA known to be lost via heterogeneous processes add to the disconnect between MSA and sulfate yield in the model and experiment discussed later?

Line 141: Adding the LOD for the NOx instrument would be helpful as well as adding the LOD for all the detectable species in the SI table would be greatly appreciated.

Line 157: The fate of the sulfene and sulfur PAN are not addressed in this manuscript. Were any observations made across the experiments that could be used to constrain other sulfur oxidation channels? I wonder about the potential for MTMP + NO2 to form other PAN species. The thioacid species is not reference later in the text, nor is it shown in Figure 1. Do the authors have any ideas where this sulfur compound could be originating from? Jernigan et al 2022 found that thioacids could form from the OH oxidation of HPMTF, while Chen et al 2021 and others promote a minor channel where the CH3S* radical could yield a thioformaldehyde (CH2S) capable of oxidizing to a thioacid. I would recommend adding a minor discussion on the state of knowledge concerning these molecules.

Line 160: The concentration for HO2 was determined utilizing a model. Do you have any species or HO2 specific products within the chamber that could be used to constrain the model? The loss of H2O2 detected by Iodine CIMS or the formation of ROOH from MTMP + HO2?

Line 172: Berndt et al JPCL (2019) stated in their SI that they observed HPMTF with ammonia CIMS.

Line 175: Was only 3% of sulfur found in the aerosol phase for the Low-NO experiments consistent in both the high and low RH experiments or only the low RH? I would assume 65% RH would increase the water content on the walls and the aerosols which would promote soluble molecules to be lost heterogeneously. I would recommend specifying the RH and NOx state at each point in the main text.

Line 185: You discuss the gas-phase mechanisms to MSA, could aqueous processing of MSIA lead to the formation of MSA? MSIA + OH yields SO2 while MSIA + Oxidant in the aqueous phase yields MSA. Could this lead to a disconnect in the MSA to Sulfate yield?

Line 196: Chen et al ACP (2012) discusses the role of MSA yields under high Nox oxidation of DMS. I recommend looking at their previous work to see if there is any comparisons that could be made.

Line 207 and Table S2: The iodine CIMS should be sensitive to ROOH species (e.g. HPMTF), while I would assume the harsher ionization of the PTR would induce decomposition of the ROOH. In contrast, the PTR should be able to detect DMSO/DMSO2 while the iodine CIMS would be less sensitive. Could the differing ionization mechanism isolate the isobaric compounds?

Line 223: The calculation of the isomerization rate does not take into account RO2 + RO2 reactions. Do you have evidence that the RO2 concentration or bimolecular rate is insignificant within the chamber. In addition, MTF could form via RO2 + RO2 reactions. I recommend clarifying this point.

Line 247: Patroescu et al JPC (1996) calculates the absorption cross section for MTF with a

focus on the aldehyde photolysis. Would the use of this experimental sulfur containing value compared to that of the MCM value change the fraction of HPMTF and MTF lost by photolysis in your chamber?

Line 255: I recommend citing Vermeuel et al EST (2019) and Novak et al PNAS (2021) as they also made this argument using field measurements.

Line 256: I recommend adding a citation here as the formation of MTF could arise from multiple different channels. Does your model support that the ROOH + OH channel as the dominant channel?

Line 258: The inclusion of the MTF + OH rate constant and its strong agreement with the previous value provides a nice validation to the method calculating the OH rate constant. Is there any reason one could not use a rate comparison method using DMS + OH and/or MTF + OH to solve the HPMTF rate constant?

The rate compare method through the ln (x/x) would remove the need for sensitivity of the species as well as remove the need to use a model for oxidant concentrations. DMS and MTF OH rate constants were determined using classic flow tube experiments with pure sources of DMS/MTF. For this reason, I would put stock in their calculated value. Would this method greatly change the HPMTF + OH value?

I would recommend adding a figure that shows the fit of the HPMTF + OH and MTF + OH rate. This will help the reader see the calculation.

Line 276: What is the ozone concentration within the chamber? Could the ozone concentration and its partition to the particle lead to oxidation of condensed sulfur on the timescale of the experiment? Also, ozone can promote SO2 formation through the CH3S*

+ O3 reaction.

Line 281: Could this be an ozone adduct? [IO3 * SO3]?

Line 287: Vermeuel et al 2019 found in their SI that HPMTF has a negative humidity dependence at RH higher than 30%. This is a different instrument and voltages, but the trend in the water dependence should be comparable.

Line 291: You state that the HPMTF, DMSO and DMSO2 concentrations are not much different from the High and Low RH. Why would the wall ("surfaces") provide a larger sink for the sulfur species compared to that of the seed particles? You stated earlier the lifetime to the seeds is orders of magnitude greater. I would recommend clarifying "initial yields" and why only the first 6 hours of the experiment was considered (Figure 4).

Line 297: Jernigan et al JPCA (2022) found an increased uptake (10x) of HPMTF to deliquesced NaCl aerosols compared to that of dried NaCl. This provides good support that a major sink within your seeded high RH chamber is aerosol uptake. I would recommend comparing the lifetime of HPMTF to aerosol uptake and OH loss utilizing their value.

Line 302: I recommend citing Vermeuel et al EST (2019) as they pointed out the importance of clouds in controlling the fate, lifetime and concentration of HPMTF.

Figure 1: Do you mind labeling the major sulfur species you discuss in the main text? In particular, I would highlight DMSO, DMSO2, MSIA, MSA and HPMTF. The boxed DMS and red HPMTF mechanism is helpful, but finding MSA was not trivial. Jernigan et al GRL (2022) has an extended mechanism with thioacids, if you would like to add a route to the sulfene species you detect.

Figure 2: Any comments on the loss of sulfur at the start of the experiment in Figure 2b. Where is the sulfur going? Could the initial unconstrained drop be attributed to the coating the walls of the chamber and setting up an equilibrium with the walls?