Response to Reviewers for Manuscript egusphere-2023-1912
"Chamber studies of OH + dimethyl sulfoxide and dimethyl disulfide: insights into the dimethyl sulfide oxidation mechanism"

We thank the reviewers for their insightful comments and engagement with our work. We have copied the reviewer comments below and addressed each one. Our responses are given in red italics and any text quoted from the manuscript is given in blue.

Reviewer 1:

This is a nice manuscript detailing a series of experiments meant to probe the molecular pathways contributing to aerosol formation from DMDS and DMSO. The authors present a detailed discussion of the results, their relation to previous published results and the implications of the agreements or lack thereof. I support the publication of this manuscript but think that the author could do a little bit to add some context to ambient conditions in the discussion section to place their results in perspective. Very well written and clear. Timely results in this resurgence of marine sulfur interest.

Thank you for these positive comments.

One thing that is apparent throughout this manuscript and in previous studies of sulfur oxidation is the role of water in the product yields and distributions, particularly aerosol. This study, performed in dry conditions (< 5% relative humidity), while expertly done, seems to have limited application to the true atmospheric environment where these oxidation schemes are likely to occur in regions where aqueous aerosols are present, e.g., MBL, higher wind speeds that drive DMS emissions & sea spray. It would be good if the authors would try to put their results in context with respect to how we can think about the result in the marine environment. Where may these results apply relative to other chamber experiments that utilized conditions > 5% relative humidity.

Thanks for this comment. The choice of dry conditions was made to focus on gas-phase oxidation processes, minimize experimental artifacts, and facilitate comparison of experimental results with prior experiments, most of which were also conducted under dry conditions (Barnes et al., 1989, 1994; Sørensen et al., 1996; Urbanski et al., 1998; Arsene et al., 2002; Kukui et al., 2003; Librando et al., 2004; Berndt et al., 2020) or relatively low RH conditions (Berndt et al., 2023). Sulfuric acid, a prominent product in these experiments, takes up water at very low humidities so we chose to operate the chamber dry to focus on gas-phase processes. The use of higher relativity humidity in chambers also poses additional challenges, for example by affecting wall loss rates of semivolatile species (Loza et al., 2010) or by leading to the formation of a thin liquid water film that can influence the uptake of products on the walls (Wollesen de Jonge et al., 2021). The choice of low RH is now explicitly discussed on line 137:

This allows this work to focus on gas-phase oxidation processes, and facilitates comparison with prior studies, most of which have also been carried out under dry, room-temperature conditions.

We agree that similar experiments under higher RH conditions, particularly considering the known role of aqueous chemistry in DMS oxidation (Hoffmann et al., 2016), would be valuable and have updated the concluding sentence to recommend this as an area for future study in the conclusions:

Line 512: While this work highlights necessary changes to DMS oxidation mechanisms, additional laboratory and computational studies that focus on key intermediates and that further explore the influence of environmental parameters (e.g., RH and T) are needed to develop a mechanism that can fully explain the observed aerosol formation from the oxidation of DMS under the full range of atmospheric conditions.

Does temperature play a role in the product distributions as it does with DMS oxidation, OH addition versus abstraction? Similar to the ambient water question how may this impact the application of these result to an explicit chemical mechanism in ambient conditions? Perhaps additional discussion on the impact of experimental conditions, e.g. temperature.

The reviewer is correct to point out that temperature may play an important role in the chemistry of DMSO and DMDS oxidation. For example, based on the Master Chemical Mechanism, the decomposition rates of key intermediates CH_3SO_2 and CH_3SO_3 to form SO_2 and SO_3 respectively slow dramatically as the temperature decreases, likely affecting product distributions (Saunders et al., 2003). Regarding the T-dependence of the abstraction vs addition pathways, this could be important for DMDS oxidation (the abstraction pathway for DMSO appears to be unimportant), but to our knowledge this has not been examined previously beyond a measurement of the total OH + DMDS temperature dependence (Wine et al., 1981).

Since the present study sought to primarily explore the impact of changing NO_X regime on DMSO and DMDS chemistry, we ran experiments at only one temperature. This enables comparisons with other similar studies, most of which have been run at or near room-temperature.

We've now noted this in the new sentence on line 137 (see above) and encouraged further exploration of this chemistry at different temperatures in the conclusion (line 512, see above).

Page 10, line ~235: Does experiment order matter here? Is there residual NOx in the chamber that could be impacting product distributions such as those seen on replicate runs. Also how does the NOX in the replicate HONO runs compare? Could NOx dependencies explain the changes between the replicate (red) HONO runs?

This is a good question as NO_X carryover can be a source of error in chamber experiments. Low NO_X experiments were run first in each series of experiments to reduce the influence of any NO_X carryover. As mentioned in the methods section (line 143), background [NO] has previously been estimated to be around 10 ppt in the presence of H_2O_2 and UV light. The statement

Line 143: For lower-NO experiments (defined as experiments with no added source of NO_X; est. background NO ≈ 10 ppt in the presence of H_2O_2 and UV light (Ye et al., 2022))...

Line 146: Lower-NO experiments were run first in each series of experiments to reduce the influence of possible residual NO_X.

The replicate experiments 2 and 4 are not influenced by residual NO_X since the total NO_X added via the addition of HONO would far exceed any potential carryover. As can be seen in Figure S4, starting $HONO/NO_X$ were quite similar between these two experiments, but HONO continued to diffuse into the chamber at a slightly greater rate on Experiment 4. The overall NO_X conditions are similar but not identical.

The most likely explanation for the difference between replicates is uncertainty in the DMSO concentration. The main text has been changed slightly (see below), and evidence of this is now demonstrated by a new figure below, which appears in the supporting information:

Line 243: ...this likely explains the majority of the x-offset in the duplicate experiments (red traces) (see also Fig. S12).
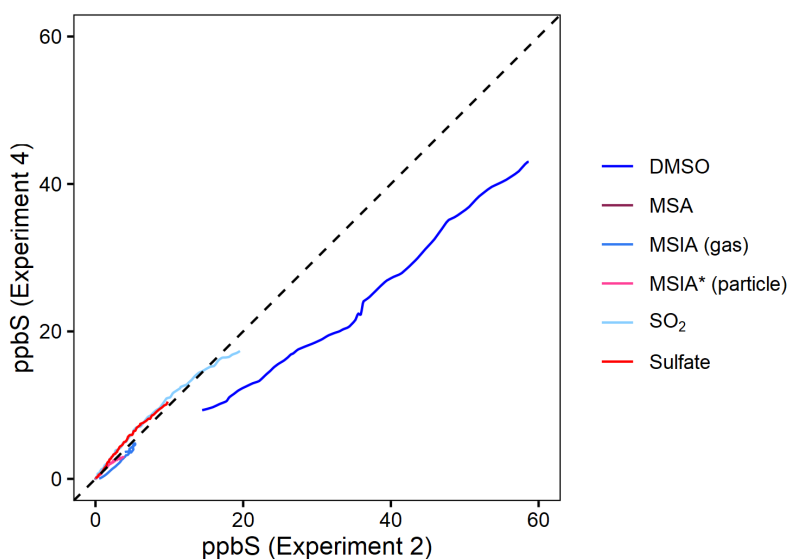

Figure S12: Comparison of replicate DMSO + HONO experiments. The timeseries of each species from Experiment 2 (DMSO + HONO) is plotted against its complement from Experiment 4 (DMSO + HONO replicate). All species fall near the 1:1 line, with the exception of DMSO. This suggests that the majority of the discrepancies between these two experiments as presented in Figure 3 are due to the discrepancy in the measured DMSO concentration.

Page 10, line 252: Maybe give the range of NOx concentrations used and how it compares to this study. Lower (high) NOX here versus previous studies?

We agree that this statement should be clarified. The following text has been updated/added:

Line 264: The strong increase in SO_2 formation with increased NO_X has not been reported in previous studies, possibly due to the range of NO_X concentrations used. While some studies (Barnes et al., 1989; Sørensen et al., 1996) were run with ppm levels of NO_X, exceptions include Librando et al. (2004), whose lower-NO_X case was < 20 ppb, which may not be sufficiently low to see evidence of this chemistry, and Arsene et al. (2002), who used synthetic air to obtain low-NO conditions and saw a minor shift in SO_2 yield.

Page 14, line 344: It seems a bit selective to label MSIA differently between the DMSO and DMDS experiments. If you cannot tell the difference between MSIA and other two sulfur containing peaks you must make that blanket statement for all MSIA determined from the AMS spectra. AMS MSIA in all experiments should therefore be labeled as MSIA*.

We agree that this is a better way to describe this. We have made this change throughout. In addition to adding stars, this includes:

Added to methods. Line 199: As discussed below, there is some ambiguity in the particle-phase MSIA assignment, especially for the DMDS experiments; given this uncertainty we denote this species MSIA. This assignment, and the AMS quantification methods generally, are described in greater detail in the SI.*

A sentence on ~line 366 originally introducing "MSIA" was removed.*

In the SI, the final paragraph of S.2 is modified: The discrepancy in apparent gas-aerosol partitioning for MSIA in DMSO vs DMDS data is described in the main text, and used to conclude that the MSIA fraction may consist of additional organosulfur species. Given this uncertainty, MSIA concentrations derived from AMS measurements are labeled MSIA.*

The phrase "giving additional confidence in the MSIA measurement" is removed from the final paragraph of section S.10.

S.1.3 What are the NOx and SO2 monitors used in this experiment? Considering the low NOx condition what are the detection limits of the two instruments?

The gas monitor models were mentioned in the main text but are now also described in the SI, along with additional discussion of the detection limits:

The SO_2 monitor (Teledyne T100) and NO_X monitor (Thermo Scientific Model 42i) were calibrated using analytical standard gas cylinders. The quoted detection limits for these instruments are < 0.4 ppb and 0.4 ppb (with 60 second averaging) respectively, however the limit of detection based on the standard deviation of the signals (3σ) when sampling zero air suggest that these limits are slightly below 1 ppb and slightly above 1 ppb respectively. Under low NO_X conditions (H_2O_2 + UV + VOC) after several days of flushing with clean air, the total NO levels in our chamber have previously been estimated to be around 10 ppt (Ye et al., 2022),

based on the changing yield of an organonitrate species measured with the NH₄⁺-CIMS before and after NO addition.

Reviewer 2:

This study focuses on the oxidation of DMSO and DMDS, two sulfur compounds directly emitted in the atmosphere but also formed during the oxidation of DMS. The experimental work was performed in an atmospheric simulation chamber for different levels of NOx in dry conditions. The oxidation was performed by OH radicals. One of the goals of the experiments was the investigation of the aerosol formation for different conditions. The identification of different products via NH4-CIMS was also used to validate the expected chemical mechanisms.

The manuscript is well written, and with a good structure and the figures are clear and useful. Though, I find the message for the gas-phase a little bit weak. For the DMSO oxidation the finding from this study is not in agreement with the currently used mechanisms. In the paper 3 alternative mechanisms are suggested though for neither rate coefficients are given so that it is not possible to test them. I would recommend to provide rate coefficients (even just best estimates from SAR could help) and even the most likely paths so that those could be tested on other experiments maybe helping in finding the correct mechanism.

Thanks for this suggestion. We've now included estimates of reaction rates in Table S2 in the SI, and model output from a simple box plot comparing the mechanisms (Figure S16). These are briefly discussed in the main text.

Line 299: Caption of Figure 4: Estimated rates for these reactions and box model simulation results are included in the SI.

Line 308: Estimated rates for reaction pathways shown in Figure 4, as well as box model simulations that demonstrate the effects of these pathways using the Framework for 0-Dimensional Atmospheric Modeling (Wolfe et al., 2016) can be found in the SI (Table S2 and Fig. S16).

Line 339: In box-model simulations of these pathways (see SI section S.9), we are unable to reproduce all of the experimental results presented here (especially the NOₓ dependence of SO₂ formation).

In doing this work, we also revised statements about the CH₃SO₃ pathway and the OH abstraction pathway. We have slightly changed the wording on the impact of HO₂.

Line 314: However, under higher-NO conditions where measured MSA and sulfate yields are highest, the HO₂ concentration is suppressed. Since HO₂ + CH₃SO₃ is the final reaction leading to MSA, this mechanism can sometimes underpredict MSA (Ye et al., 2022).

And we have added a citation to Shen et al. (2022), and corrected the interpretation of the computational studies:

Line 323: The OH addition channel represents a straightforward pathway to MSA (Shen et al., 2022), but is inconsistent with our observation that MSA forms in greatest yield at elevated [NO_X]. While computational studies support this OH addition step as a minor pathway, they have not investigated the possibility of reaction with O_2 to form MSA (Tian et al., 2007; González-García et al., 2007).

During the oxidation of DMSO ozone was also introduced and it was mentioned that it did not change the product distribution. Why was ozone injected? Was there any expectation that the product distribution would change?

Thank you for this clarifying question. Assuming that the oxidation of DMSO forms the CH_3SO_2 radical as a major product, established mechanisms include $CH_3SO_2 + O_3$ as a pathway to the CH_3SO_3 radical (a precursor to MSA and sulfate). We hypothesized that the addition of O_3 should shift the CH_3SO_2 products away from SO_2 and towards MSA and sulfate, resulting in a clear change in particle-phase product yield. Based on MCM, the first order rate constant for the reaction with 100 ppb O_3 (0.75 s^{-1} at 293 K) is faster than the competing fragmentation reaction that produces SO_2 (0.23 s^{-1} at 293 K) (the competing formation of $CH_3S(O)_2OO$ is much faster but is reversible at a similarly high rate). Despite this, no change in the product distribution was observed. This is now mentioned as a footnote in Table 1 and an additional paragraph is added on line 257.

Line 166: [d] O_3 was added to investigate the influence of $CH_3SO_2 + O_3$ chemistry on product distribution.

Line 257: In addition to using HONO to perturb the system, one lower-NO experiment (expt 3) is perturbed by the addition of O_3 to investigate the impact of the $CH_3SO_2 + O_3 \rightarrow CH_3SO_3 + O_2$ reaction (Barnes et al., 2006) (Fig. S8a). Since CH_3SO_3 is thought to be a major intermediate leading to the formation of sulfate and MSA, the addition of ozone is expected to influence the formation of particle-phase products. That no change in product distribution is observed upon the addition of O_3 suggests that the $CH_3SO_2 + O_3$ reaction is slow, or that CH_3SO_2 is not formed from the reaction under these conditions.

One sentence previously found on line ~230 briefly referencing the O_3 addition was deleted since this is now discussed in its own paragraph.

Once these two comments are considered I think the manuscript is ready for publication.

We thank the reviewer for their comments.

Additional changes:

In addition to the above responses to reviewers, we made several other minor changes to the manuscript; none of these affect the conclusions of the work.

We added additional text supporting and clarifying our statements about the relative unimportance of $RO_2 + RO_2$ reactions in the formation of MSA:

Line 329: In addition, the disproportionation reaction of $CH_3SO_2OO + RO_2$ may lead to MSA (Berndt et al., 2023), but this pathway is significant only when RO_2 concentrations are sufficiently high to outcompete other pathways. In our chamber, this reaction can occur under lower-NO conditions where a small amount of MSA is formed, but it is likely only a minor contributor to MSA production under higher-NO conditions, when the majority of MSA is formed (see modeling results in the SI).

We support this further with a new plot (Figure S17) and discussion in the SI.

We have also added a clarifying statement concerning Figure 8.

Line 445: These yields only consider rapid aerosol formation and do not include the influence of sulfate formed through SO_2 oxidation.

We also became aware of two relevant publications (Van Rooy et al., 2021a, b) that we had not cited in the original submission; in a series of minor edits we now refer to these two papers:

- We briefly discuss one additional proposed formation pathway for MSA (Line 333) and discuss a proposed mechanism for the formation of $CH_3SS(O)CH_3$ following Fig. S15 in the SI:

Line 333: Based on observations of NO_X and humidity dependence, Van Rooy et al. (2021b) suggest that CH_3SO_3 may react with NO or NO_2 to form $CH_3S(O)_2ONO$ or $CH_3S(O)_2ONO_2$ before reacting with water to form MSA and HNO_3 or HONO. We did not observe the nitrite or nitrate compound, and the subsequent hydrolysis step is unlikely under the dry conditions in our chamber.

*Text following Fig. S15: While Van Rooy et al. (2021a) lacked direct observational evidence of $CH_3SS(O)CH_3$ (product **1**), they hypothesized that this molecule might explain peaks in their AMS spectra and suggested that it may form via a condensation reaction between two CH_3SOH molecules. The gas-phase reaction of two closed-shell molecules is likely to be slow and does not explain the observed trends in $C_2H_6S_2O_2$ formation.*

- This work raises the possibility that reaction with $O(^3P)$ can contribute to the oxidation of reduced sulfur compounds. This appears to be negligible in our experiments, and we now discuss this on Line 153 and Section S.9.1 in the SI:

Line 153: Previous chamber experiments suggest that reaction with O(^{3}P) can contribute to the oxidation of reduced sulfur compounds (Van Rooy et al., 2021a), however this appears to be negligible under the lower NO$_2$ and UV flux conditions used here (see SI).

These two papers are also included in citations in lines 117, 123, 377, and in the final paragraph of section S.2 in the SI.

Citations referencing "Saltzman and Cooper, 1989" have been corrected to read "Barnes et al., 1989."

We now refer to "low-NO" and "high-NO" conditions as "lower-NO" and "higher-NO."

In the process of revising the manuscript, we have made additional minor phrasing and grammatical changes that slightly clarify the content presented.

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