

We thank the reviewer for the positive feedback and the appreciation of our work.

Below, we address the general and specific comments and suggestions point by point. The review comments are repeated here in black, our replies are given in blue.

I would recommend the elaboration and restructuring of the work before final publication. Generally, I would stress the importance of oxidative and environmental drivers of OCS production from DMS oxidation throughout the work as well as the role of chloride and photolysis within DMS oxidation.

This is largely addressed by changes made in response to the specific comments below. We also add the following sentence in the conclusions:

Based on some of our observations, future experiments to fully establish and quantify this mechanism should probably include HPMTF photolysis and the role of chlorine radicals as a potentially relevant oxidant under certain atmospheric conditions.

I would also recommend remaking the figures with updated legends to help the reader better understand which time traces are which.

We rework all figures to improve quality and readability.

Specific Comments

Line 112: A clarification of why photolysis is not a driving reaction would be greatly appreciated. 254 nm light is a higher energy light. Do you assume insignificant due to OH concentration or low light flux?

We add the following in Section 2.2 that should clarify this:

While the high O₃ absorption cross section of $1.1 \times 10^{-17} \text{ cm}^2$ at 254 nm allows for substantial photolysis and OH production, other trace gases present in the experiments have much smaller absorption cross sections at 254 nm (DMS $\sim 2 \times 10^{-20} \text{ cm}^2$; OCS $< 1 \times 10^{-20} \text{ cm}^2$; SO₂ $\sim 1 \times 10^{-19} \text{ cm}^2$, not photolyzing; DMSO $< 1 \times 10^{-21}$; HPMTF has no structure where strong absorption is expected as peroxides and aldehydes absorb little in that spectral range, i.e. on the order of 10^{-20} cm^2), and we do not expect the low intensity radiation of the lamps to photolyze any of these in a relevant amount.

Table 2: TPA or Thioperformic acid is not referenced before this point. Would recommend adding the full name of the species before adding the abbreviation.

In the revised manuscript, the full name is included in the text describing the instrument.

Line 140: Ye et al and Jernigan et al found other DMS related products within their PTR-MS. Were any additional sulfur species found using the PTR implemented in this chamber experiment. Even uncalibrated signal could help understand when potential intermediates react to the perturbations within the chamber.

We add traces for uncalibrated signals in the PTR-MS data that potentially corresponded to relevant species (DMSO, DMSO₂, CH₃SCHO, CH₃SCH₂OOH) in the supplementary Figures (S1 – S4) and add the following statement in Section 2.3:

DMS was monitored by a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS, Ionicon, Jordan et al., 2009), which unfortunately was not calibrated in our experiment for any other sulfur gases that were observed by PTR-MS in the DMS oxidation experiments by Jernigan et al. (2022) and Ye et al. (2022). Raw signals at m/z ratios where DMSO, DMSO₂, CH₃SCHO and CH₃SCH₂OOH would be expected to show up are shown in Supplementary Figures S1 – S4, but as these signals are uncalibrated and may partly or even entirely be caused by interferences from different organic compounds, they are not considered in the results and discussion below.

Line 168: If the signal from HPMTF is significant then the isotopic pattern of the sulfur from HPMTF should dominate over the potential pattern of N₂O₅. This could provide an experimental constraint on the identity of the 235 m/z species.

In Section 2.3, we add a detailed discussion of this effort, which, however, did not help on with the exclusion of any significant contribution of N₂O₅:

We also tried to explore the isotopologue signatures for the HPMTF and the N₂O₅ clusters. The exercise was done for measurement day II. The 237 and 235 m/z peaks (the HPMTF ³⁴S and ³²S clusters, respectively) show a similar temporal evolution. However, the average ratio found for the areas was very noisy and about 4-fold the expected 4.2%, indicating that the 237 m/z peak is blended by some isobaric unknown ion. Therefore, this method could not be used to ensure the absence or low significance of N₂O₅. For the 236 m/z peak (the blended ³³S-HPMTF (0.8%) and ¹⁵NNO₅ (0.4%) cluster) no significant peak was detected at all, which due to the generally low signal to noise ratios also cannot rule out some contribution by N₂O₅. This applies to days III and IV as well since S/N is very similar.

Line 175: I*SO₂ is highly water dependent with the cluster only able to be used if the conditions are dry and the ratio of I*H₂O to I are very low. The high and changing RH in the system would make this measurement hard.

We decided to move this mention of the obvious I-CIMS technique, which we did not use, to the end of this paragraph. We also decided not to discuss the water vapor dependence because it is of no relevance to the work presented here:

The iodide cluster I*SO₂⁻ could not be detected with our setup, most probably due to the electric fields generated within the ion funnel leading to collision induced dissociation.

Line 177: CO₃⁻ can arise from O₂⁻ chemistry and ozone. The variability on the SO₂ measurement using this technique could be also due to the varying O₃ concentration. See Novak et al (<https://doi.org/10.5194/amt-13-1887-2020>) for an in dept description of the CO₃⁻ chemistry and its correlation to O₃. This interplay could change the sensitivity of SO₂ in the CIMS.

We thank the reviewer for pointing out the ion chemistry discussed in the Novak et al. Paper and potential interferences. However, we do not think that this can be the source of the CO_3^- ions observed in our study. This has been updated to the manuscript:

The possible origin of the CO_3^- ions from O_2^- chemistry in a two-step process involving CO_2 and O_3 as described by Novak et al. (2020, see R4a/b and R5a/b) also seems rather improbable due to the very low O_2^- signals involved. This is supported by the absence of any correlation of the CO_3^- and SO_5^- signals even for significant changes in O_3 as, e.g., encountered for the second ozone addition (see Fig. 2 around 8.5 h). Unfortunately, a detailed pathway for the CO_3^- formation cannot be given.

Line 181: I understand the difficulty in calibrating the sulfur intermediates and understand the use of ncts for the observation of HPMTF and TPA. Were the ncts for HPMTF, TPA, and SO_2 background subtracted? Showing the signal as a delta would help illustrate the change in signal over the course of the chamber experiment.

We agree that this point should be further detailed and have added a paragraph separately for SO_2 and HPMTF/TPA. This has also induced some restructuring of the CIMS section in order to be easier to follow by the reader:

We referenced all SO_2 data to the starting signal (ncts) once humidification and CO_2 injection were completed and signals stabilized (days III and IV). For day II due to a late measurement start of the CIMS (just before turning on UV lamps and about one hour after the DMS addition) the reference signal was derived from the very first measurement points somewhat later than for days III and IV. However, the SO_2 reference signals which corresponded to about 200 ppt agreed within about +/- 100 ppt for all days. This is well below the other main error sources. We cannot assign the origin of this background. Presented SO_2 therefore represented the increase from the start of the DMS oxidation which corresponds to the reacted DMS. Uncertainties resulting from this procedure mainly due to changing humidity and ozone are estimated to a maximum of +50 and -350 ppt of SO_2 , respectively. However, the comparison to the DOAS instrument shows a quite good agreement of better than 10 % for experiment IV when both measurements were operating (Fig. 4) giving further confidence into the applied procedures.

Calibrations for HPMTF or TPA were not carried out for this campaign, therefore just the ratios of counts for detected product ions over the sum of the I^- and $\text{I}^*\text{H}_2\text{O}^-$ signals are reported here. The change in this quantity, here termed normalized counts or ncts, is to first order proportional to concentrations of the neutral analytes (e.g. Huey, 2007). However, missing a proper way to scrub the relevant species detected by the CIMS while retaining ozone and humidity, we could not establish a proper zero background here. For the HPMTF and TPA measurements this procedure did not produce consistent starting values and we report none-background corrected values. These background values before expected presence of OH (UV light for days II and III and O_3 for day IV) were below 20% of the maximum observed signals also for day II with the late measurement start of the CIMS. Clearly, we cannot exclude preexisting HPMTF or TPA at these starting points. Therefore, in our view it is also not possible to establish a HPMTF formation from DMS and ozone alone based on the available data. Also, some background variations expected due to variations in relative

humidity, which usually dropped slowly but significantly over the experiments (up to 35% over a 8h measurement, see Supplementary Fig. 2) cannot be ruled out.

Line 183: How much did the humidity drop? Could this also affect the potential for humidity wall driven reactions throughout the chamber experiment? I would reference supp. Figure 1 as it presents the change in RH over the experiment

We have quantified the drops in relative humidity observed over the experiments referring to Supplementary Fig. 2 showing the highest changes (see last lines of the previous reply). We cannot completely rule out that such gradual humidity changes may change wall uptake or desorption but do not think that this will have major effects on the conclusions taken in this work.

Line 204: Looking at Figure S1 it seems that the temperature within the chamber changes by almost 10 C over the time of the experiment and that temperature never seems to reach 25 C. I would add a comment on this and how this much change in temp could alter the observed DMS + OH and the fraction of DMS shutting down either the OH addition and abstraction channels.

In the revised manuscript, we add the following paragraph with a discussion of this temperature dependence to Section 3.1:

Effects from the observed temperature variations of ~10 °C in Experiment I (see Supplementary Figure S1c) on the DMS + OH reactions are impossible to discern due to the low precision of the observed DMS decay and lacking observations of the OH concentration and variability. Nevertheless, it should be noted that while the rate constant of the DMS + OH abstraction reaction has a moderate temperature dependence (< 5 % over temperature range of 16 – 35 °C over all four experiments, see Supplementary Figures S1 – S4), the rate constant of the DMS + OH addition reaction changes from 3.3×10^{-12} at 16 °C to 1.3×10^{-12} at 35 °C (Burkholder et al., 2019). This means that at the lower end of the temperature range in our experiments, we expect about 60 % to react through abstraction and 40 % through addition, while at the upper end, it is more like 80 % going through abstraction and 20 % through addition. As a consequence, we would expect more OCS production at higher temperatures as we get more HPMTF from getting more of the primary RO₂ and a faster isomerization rate due to the temperature.

Line 205: How was dilution determined within the chamber? Were experiments performed elsewhere or was there a dilution tracer added and monitored within the experiment?

The dilution is determined from the volume flow rate into the chamber, and the observed decrease of CO₂ that was added to the chamber early in the experiment confirms this. We make a note of this in Section 2.1 in the revised manuscript and show an additional figure to illustrate this in the supplement.

Line 213: Were any experiments done without sulfur (DMS) present while the system was oxidized utilizing the entire array of instrumentation. I am wondering if there is potential for the contribution of contaminants that could lead to prompt formation of OCS. You state that other

VOC (line 208) may have off gassed leading to higher CO, could this lead to a prompt/background OCS?

Prior to the 2020 DMS oxidation experiments described in our paper, the SAPHIR chamber had not been used for any dedicated experiments involving sulfur species. Therefore, an accumulation of significant amounts of OCS or precursors thereof on the chamber walls that would explain the formation of the observed mole fractions can be ruled out.

Line 215: I think it is important to say that the OCS yield is an experimental yield that takes into the environmental parameters. This removes the ease to quickly see this value as a way to simplify the global yield of OCS from DMS oxidation.

Indeed, we do not want to see the yields observed in our experiments to be directly applied in global models or simple budget calculations. We add the following statement at the end of Section 3.1 to make this clear already at this point:

This, as well the OCS yields given in the following Sections, are experimental results that strongly depend on the conditions in the SAPHIR chamber. We expect OCS yields from DMS oxidation in the real atmosphere to be significantly lower, as will be discussed in Section 4.

Could you also describe how the OCS yield was calculated throughout the chamber experiment? Was the OCS yield calculated from comparing the DMS loss rate to OCS production rate as is shown in the figures or was the yield calculated from the change in signal of DMS and OCS ($d[\text{OCS}]/d[\text{DMS}]$)? Adding an equation would help illustrate this cleanly.

We now include a detailed description on the yield calculation and an equation:

This was calculated by dividing the amount of OCS present at the end of the experiment by the dilution corrected total sulfur in the chamber (any sulfur was present as DMS at the beginning of the Experiment, see Supplementary Figure S5) minus the DMS still present:

$$\Phi_{\text{OCS}}(t) = \frac{[\text{OCS}](t)}{\sum_{\text{DMS additions}} [\text{DMS}]_{\text{init}} \times (1 - k_{\text{SAPHIR}})^{t-t_{\text{init}}} - [\text{DMS}](t)} \quad (1)$$

where k_{SAPHIR} is the observed chamber dilution rate and the summation is carried out for each DMS injection.

Line 236: Dyke et al and others have proposed the reaction of DMS with Cl₂ can lead to the formation of CH₃SCH₂Cl (DMS-Cl). Was there any evidence in your VOC measurements (PTR) that this intermediate arose upon the addition of Cl₂? And could this intermediate and its subsequent photolysis or OH oxidation change the OCS yield? Lastly, Urbanski and Wine and Arsene et al found that the DMS + Cl could form an adduct with eventual addition of a O₂. Is there any evidence in your PTR measurements of additional OH-addition like chemistry? (i.e. increased DSMO/MSIA/DMSO₂) Shallcross et al 2006 *AtmEnv*; Copeland et al 2013 *EST*; <https://doi.org/10.1021/jp992682m> (Wine and Urbanski)

In the PTR-MS, $\text{CH}_3\text{SCH}_2\text{Cl}$ would be expected to show up at m/z 97 and 99 for the two main Cl isotopes. At neither of these m/z ratios, a strong signal or a pattern suggesting a mechanistic relation to our experiments are observed.

As stated above (in response to the comment re line 140), there are traces in the PTR-MS data that could be related to DMSO and DMSO_2 , and they are now shown in the supplementary Figures. But as even the qualitative assignment of these m/z ratios bear substantial uncertainty, we feel that the derivation of any mechanistic details from these data gets deep into the realm of speculation.

Similarly, the relative contribution of the reactions $\text{DMS} + \text{OH}$, $\text{DMS} + \text{Cl}$ and $\text{DMS} + \text{Cl}_2$ to the DMS loss in Experiment III can only be speculated upon, because there is no quantitative information on the concentration of Cl radicals. Dark experiments with $\text{DMS} + \text{Cl}_2$ are needed to confirm the published rate coefficient and products, but were unfortunately not carried out in our 2020 SAPHIR experiments.

Line 243: The temperature in the chamber is greater than 298K (S3 reads about ~305K). This elevated temperature would effect the fraction DMS oxidizing by the OH additional and abstraction as well as the isomerization rate. A comment about the variability in temperature across all experiments and if the variability in temperature would affect the product distribution would be greatly appreciated. OH-addition has a strong temperature dependence and as such would greatly change the amount of DMS shuttling down HPMTF and OCS.

Such a discussion is now included in Section 3.1 as already described in response to the comment in line 204.

Line 252: Barnes et al 1991 (<https://doi.org/10.1002/kin.550230704>) found that ClO can react with DMS at a rate constant of $(9.5 \pm 2.0) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. I think it is important to cite this finding as support for the idea that this reaction could compete.

The citation will be added here.

They also suggest that the reaction would lead to the formation of DMSO, shutting of the potential production of HPMTF and OCS. If possible a small discussion/observations of chloride chemistry would be appreciated. Iodide CIMS has the potential to observe multiple halogens (i.e. Cl_2 , ClO, ClNO₂). Do you have any observations of other halogen species (ClO, ClNO₂) that could help understand the lower observed OCS yield and the mechanisms driving the DMS oxidation? With Cl_2 , JCl and O₃ observations could you model/approximate the [ClO]?

With the setup employed we unfortunately cannot detect HCl, ClNO₂ and ClO since the appropriate cluster ions fall apart in our ion funnel and low iodide CIMS sensitivity in case of ClO.

We add two sentences describing what role of ClO in the initial DMS oxidation step we would expect:

It should be noted that the $\text{Cl} + \text{O}_3$ reaction is about ten times slower than the $\text{Cl} + \text{DMS}$ reaction and a maximum ClO concentration of $4 \times 10^7 \text{ molecules cm}^{-3}$ is estimated from

steady state calculations. Because ClO is less reactive towards DMS than Cl (ClO reacts with DMS at a rate constant of $9.5 \pm 2.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ according to Barnes et al., 1991), it is not expected to be competitive with Cl and even Cl₂ for the oxidation of DMS.

Line 275: Could the drop in HPMTF also be associated with increased NO and thus less HPMTF (e.g. RO₂ + NO dominates/increases over isomerization). S3 shows a significant step change in NO_x with a subsequent sustained concentration of O₃ leading one to question the start of NO_x cycling. Could NO chemistry start upon the opening of the roof?

Similar levels of NO and NO₂ were also present in Experiment III and much of the DMS has already been removed by the time the roof is opened. Therefore, we would not expect HPMTF production to dominate the HPMTF trace here, and the drop of HPMTF is more consistent with a faster/additional removal process such as photolysis triggered by opening the roof. We add the following sentence in the revised version:

As much of the DMS has already been removed by this time, this drop would be difficult to explain by a sudden change in the HPMTF production rate (e.g., from competing binary reactions) and is more likely caused by a faster/additional removal process such as daylight photolysis. This is, however, only speculative, ...

Line 276: Could an approximate photolysis term for HPMTF be calculated using the decay in HPMTF? Using the assumption that HPMTF + OH is 1-2E-11 from Jernigan et al and Ye et al, could an approximate photolysis rate be determined from the missing HPMTF loss? This may be an oversimplification of the observations, but an approximate value could be compared to the values used in Khan et al to determine the weight of HPMTF photolysis and its potential roll in OCS formation.

We do not think that this is possible. HPMTF photolysis would only set in after the roof is opened, and the shape of the observed trace suggests a faster HPMTF decay compared to the earlier experiments already before the roof is opened.

Line 289: The clarifications done here are greatly appreciated in showing the complexity of OCS from DMS oxidation and the use of mechanism over a yield. I would still recommend the use of “experimental” or “chamber” as a clarifier for the observed OCS yields.

We appreciate this recommendation and will do so.

All Figures: If the OCS yield is calculated by relating the rates of DMS loss and OCS production, then I would recommend adding the yield as a function of time in the experiment. This could help show if the value is constant or variable depending on the various perturbations. I can also see that DMS and OCS may not be tightly correlated given the need to transition through intermediates, so this time dependent yield could be misleading. Any comments on this would be appreciated.

Rates are approximated by fitting slopes of the DMS and OCS traces over different time windows, and the time resolution of the OCS rates is too low to adequately reflect changes or events at certain points in the experiments. Therefore, as explained above, the yields were

determined only for total OCS produced by the end of the experiment, and this information is now included in Section 3.1.

Figure 1: Do any species respond to the second addition of ozone? Upon first glance nothing in the SI or figure responds to the increased O₃ and subsequent OH formation?

A small increase in RO₂ and HO₂ is observed (Figure S1a), and the first order DMS removal rate increases from about 8 to about 12 (Figure 1d), although with a large uncertainty due to the gap in DMS data just prior to the O₃ addition. We would not expect more dramatic or sharper changes because i) there is likely to be an excess in oxidant already and ii) the chamber response will take time because OH is only produced in the vicinity of the UV lamps.

Figure 3: There seems to be an abrupt and unexplained drop in Cl₂ at hour ~4.6 after DMS injection. Could you please explain what occurred at this hour and if that abrupt drop and loss of chloride could be used to understand a transition between Cl and OH dominated oxidation?

The drop in Cl₂ is entirely expected as it coincides with the stop of the Cl₂ addition. This information is given in Table 1 and in line 125, but we will repeat it in Section 3.3 and add a bar showing the addition period in the figure.

Technical comments

Line 165: Define TPA

We add the full name in the revised manuscript.

Figures: I have trouble reading the axis titles, especially the multiplier (i.e. 10⁻⁵). Could you please increase the font or resolution of the figures.

We will rework all figures to improve quality and readability.

Figure 1: Which measurement for HCOH was used here. The table states two instruments were used. Please add for this and all future figures if the concentrations are dilution corrected.

The HCHO measurement shown is from the CRD instrument, and we will add this information to all relevant figure legends.

All measured concentrations are given ‘as observed’, i.e. without applying any correction. For observed species, any dilution effects are included by definition. Only for calculated parameters such as OCS yields and the total amount of sulfur shown in Figure S6, the dilution effect is actually calculated.

Figure 4: I recommend adding labels for the three modeled lines in 4c. I see that the description is in the description, but a label will help guide the eye and discern colors.

Such labels are added in the revised version.