

Response to the comments of Reviewer 2

Thanks to reviewer 2 for his or her valuable comments, we have made significant improvements on the manuscript.

Comments:

1. Abstract. P.14670 Poorly written, in terms of the flow of the study and experiments conducted.
 - a.) For example the opening sentence . . . “ to advance the photooxidation of dimethyl sulfide (DMS) in the gas phase”. The study is not advancing the photooxidation per se, and needs to be written more clearly. It is the photooxidation reaction mechanism that is being extended and improved. The abstract only introduces the DMS and DMS in the presence of isoprene chamber experiments, whereas the experimental section begins with developing a DMSO submodel, using experiments on DMSO/NO_x.
 - b.) P.14670 line 17. This sentence contradicts what is presented in figure 4. The figure does not show increasing yields of MSA and H₂SO₄ with increased isoprene concentration. The model simulation shows the opposite trend for MSA, and the scale for the H₂SO₄ makes it difficult to judge the differences. The experimental data for MSA concentrations look very similar for the Iso-DMS-2 and Iso-DMS-3 charts, and should not stated to be increasing. This is difficult for the reader to qualify with no indication of the error bars associated with these low MSA and H₂SO₄ concentration determination.

Response:

- a) The abstract has been rewritten. It now reads as follows.

“To improve the model prediction for the formation of sulfuric acid and methanesulfonic acid (MSA), heterogeneous reactions of gaseous dimethyl sulfide (DMS) oxidation products (e.g., dimethyl sulfoxide (DMSO)) in aerosol have been included in the DMS kinetic model with the recently reported reactions and their rate constants. To determine the rate constants of aerosol-phase heterogeneous reactions of both DMSO and its major gaseous products, such as dimethyl sulfone (DMSO₂) and methanesulfinic acid (MSIA), DMSO was photooxidized in the presence of NO_x using a 2m³ Teflon film chamber. The rate constants tested in the DMSO kinetic mechanisms were then incorporated into the DMS photooxidation mechanism. The model simulation using newly

constructed DMS oxidation mechanisms was compared to chamber data obtained from the photooxidation of DMS in the presence of NO_x . The model predicted concentrations of MSA increase by 200%~400% and those of sulfuric acid, by 50% to 200% within 120-minute simulation due to heterogeneous chemistry. This was well substantiated with experimental data. To study the effect of coexisting volatile organic compounds, the photooxidation of DMS in the presence of isoprene and NO_x has been simulated using the newly constructed DMS kinetic model integrated with the Master Chemical Mechanism (MCM) for isoprene oxidation, and compared to chamber data. With the high concentrations of DMS (250 ppb) and isoprene (560~2248 ppb) in the chamber experiments, both the model simulation and experimental data showed an increase in the yields of MSA and H_2SO_4 as the isoprene concentration increased.”

- b) The decay of DMS due to photooxidation in Figure 4 was not corrected for wall loss and chamber dilution, while the MSA production was collected for both the wall loss and chamber dilution. The MSA yields in Table 3 were estimated using the DMS consumption corrected for both the wall loss and chamber dilution.

Caption for Figure 4: “The time profiles of isoprene, DMS, MSA and sulfuric acid for the photooxidation of DMS and NO_x in the presence of 560 ppb (Exp iso-DMS-1), 1360 ppb (Exp iso-DMS-2), and 2248 ppb (Exp iso-DMS-3) of isoprene. “E” denotes the experimentally observed concentrations of chemical species and “S” for those simulated using the kinetic model. The decay of DMS and isoprene were not corrected for wall loss and chamber dilution while the production of MSA and sulfuric acid was collected for both the wall loss and chamber dilution.”

2. P.14670 line 25. The IPCC reference used is rather old and dated. How does this fit with the more recent reports? If DMS aerosol remains a major uncertainty, a more up to date reference should be included, using the 1995 report as identifying the issue.

Response:

In the recent IPCC report, DMS is not included as a major uncertainty although it has not been fully understood. We have deleted the original sentence.

3. P.14671 line 25-27. This sentence refers to “the existing model”, but does not state or reference what this existing model is.

Response:

We have added a reference in the revised manuscript.

“No expression of aerosol-phase reactions in the DMS mechanism is another reason why important DMS oxidation products such as MSA and H₂SO₄ have been underpredicted using the existing gas phase kinetic model (Yin et al., 1990a).”

4. P.14672 line 6. MSIA is used here, but not defined until later in the text.

Response:

The full name of the acronym of MSIA (Methanesulfinic acid) has been included.

5. P.14672 line 21. “The resulting DMSO mechanisms” would read better as “ The resulting DMSO reactions”

Response:

This has been changed.

6. P.14762 line 23. This last sentence is very poorly constructed, and the MCM requires better referencing.

Response:

We have rewritten the sentence and provided a better reference for the MCM.

“To study the influence of atmospheric VOCs on DMS oxidation, the newly updated DMS photooxidation mechanisms were coupled with the isoprene photooxidation kinetic model included in the Master Chemical Mechanism (MCM) v3.2 (Jenkin et al., 1997; Saunders et al., 2003), which is available *via* the website at <http://mcm.leeds.ac.uk/MCM>. The resulting model simulated for the chamber data.”

7. P.14673 Experimental procedures. a) Line 7 Experiments were not “operated” rather “conducted”. b) No indication here of chamber characterization experiments. The results section p.14677 talks about “dark chamber experiments”, but how these are conducted is not provided.

Response:

a) This has been changed.

b) To determine the wall loss of the compounds (e.g., ozone, H₂O₂, DMS, DMSO, or DMSO₂) of the interest, the compound was injected into the chamber without light sources and then continuously monitored its concentration.

8. P.14783 sections 2.12, 2.2. The overview of the sample analysis procedure is adequate, however there is scant information provided on any calibration work, the errors associated with the various measurements, the limits of detection or indeed how QA/QC is conducted. For example, p.14674 refers to DMSO and DMSO₂ analysis following a reference of Takeuchi et al. (2010). The GC operation conditions are given and figure S1 gives retention time and mass fragmentation spectra. This should be supported by reference to the quality of fit of the MS, and how similar or different they are to the work of Takeuchi et al. (2010).

Response:

Although operation conditions of our GC/MS are not exactly the same as the one used by Takeuchi et al., the same technique in analyzing DMSO and DMSO₂ was used in this study with them. The concentrations of DMSO and DMSO₂ were determined using the GC/MS calibration curve with authentic standards. To make it clear, we have added the following sentences in the revised manuscript.

“Figure S1 in the supporting information summarizes the retention time and the mass spectra of DMSO, DMSO₂ and *d*₆-DMSO for the GC/MS analysis. The concentrations of DMSO and DMSO₂ were determined by the calibration curve produced using authentic standards (DMSO and DMSO₂) and internal standard (*d*₆-DMSO). The associated error with the measured concentrations of DMSO and DMSO₂ is ±20%.”

As stated in the manuscript, the detailed analytical procedures of isoprene SOA products have been described in the previous study. We feel it is not necessary to describe the detail analytical procedures. We changed the sentence in the revised manuscript as follows:

“The description of detailed analytical procedures for the quantification of products can be found in the previous study (Im et al., 2011). The errors associated with GC/MS analyses for isoprene products are ±30%.”

9. a) P.14674 line 21. Needs to state which major isoprene photooxidation products were analyzed. b) Line 23. Bornyl Acetate does not require capitalization.

Response:

- a) The sentence has been modified by adding the names of products. This reads now:

“In addition to the monitoring of ozone, NO_x, and DMS, major isoprene photooxidation products [methacrolein (P1), methyl vinyl ketone (P2), glyoxal (P3), and methylglyoxal (P4)] were sampled every 30 min (10 minutes sampling) for 2.5 hours (5 samples in total) with a flow rate of 1.0

L min⁻¹ using an impinger that contained 12 mL of acetonitrile with bornyl acetate (internal standard).”

b) Changed from “Bornyl Acetate” to bornyl acetate.

10. P.14674 line 23-24. This sentence indicates chamber background air is analyzed prior to each experiment, to check for any contamination. a) Is this only for the DMS isoprene experiments? This seems out of place. b) If this is general operating practice for the chamber it needs to be described early in the experimental procedures, and followed through with what is considered to be a “clean” chamber. For example is flushing after each experiment conducted until the levels of any of the species analyzed fall to a minimum level and if so what are those levels.

Response:

a) We have moved the following sentences to the experimental section.

“Prior to each photoirradiation experiment, the chamber background air was analyzed to determine the carryover from the previous experiments (e.g., DMSO and DMSO₂).”

b) We have added the following description to the experimental section

“After flushing the chamber with the clean air, the background aerosol concentration was below 0.2 μg m⁻³ and the concentrations of both DMSO and DMSO₂ in the background air were below 2% of the initial sulfur concentrations (Table 1, 2 and 3) of each chamber experiment.”

11. P.14675 line 9. The Morpho kinetic solver needs referencing.

Response:

The reference for the Morpho kinetic solver has been included.

12. P.14675 line 11. a) Tables S1-S3 contain the “recent literature” references and this should be stated in the text here. b) And again correct referencing for the MCM is needed.

Response:

a) Words “(see Table S1~3 for the references)” has been added to the end of the following sentence.

“Table S1~3 (in supplementary material) summarize the kinetic mechanisms related to DMS oxidation along with their reaction rate constants, which were collected from the recent literature.”

b) The reference for the MCM has been included.

13. P.14676. This section is poorly described, with no indication of how the rate values given in R1-R9 have been determined. The non-standard notation used should be explained.

Response: Please see the response to question #2 of reviewer 1.

14. P.14677. a) The chamber characterization section is too brief, with little discussion beyond the determination of wall loss rates, and indeed if a chamber dependent part of the kinetic model has been developed. b) Figure 4 legend distinguishes between wall loss and chamber dilution, however the chamber dilution is not discussed in the text. c) Does this mean that all other experimental figures have been corrected for both wall loss and chamber dilution?..if so this should be stated.

Response:

a) Please see the Response to question #8 of reviewer 1.

b) Please see the Response to question #7 of reviewer 1.

c) Yes. All chamber data were corrected for both wall loss and chamber dilution. To clarify this, the additional statement of whether wall loss and chamber dilution are applied has been added in the captions of the corresponding figures (Figures 1~5).

15. P.14678. line 5. The “background gas” concentrations for methane, formaldehyde and acetaldehyde are really not clear, with the experimental determination too brief. Are these background concentrations from the “clean” air generator? How are the concentrations validated?

Response:

The half of the volume of our chamber can be compressed. For cleaning chamber air, we filled the chamber with the clean air and venting the half volume of the chamber air. This procedure is repeated several times until the chamber air reaches to the desired concentration. There is a limit to remove all the particles from the chamber. We used both a dry air generator and a clean air generator. Our clean air generator does not remove the methane. The methane concentrations are almost constant at 1.8 ppm. Formaldehyde and acetaldehyde can be partially removed by the clean air generator. The GC/MS integrated with a carbonyl derivatization method is used to measure the concentration of formaldehyde and acetaldehyde. The concentrations of formaldehyde and acetaldehyde in the background air were measured for several chamber experiments and an averaged number is applied to the simulation for all the experiments. Since the concentrations of formaldehyde and acetaldehyde in the background are much smaller than those originating from the photooxidation of

isoprene and DMS in chamber studies, the formaldehyde and acetaldehyde in the background air will not significantly influence the simulation results.

16. P.14678-79 line 25. Again which “existing models” are referred to?

Response:

Reference has been added in section 3.3.2 (DMS photooxidation).

17. P.14680 line 20. Coexisting should be replaced by presence.

Response:

Done.

18. P.14680 discussion needs elaborating. a) The NO₂ simulation deviates significantly from the experimental data beyond 60 mins, but is much better represented in the other series of experiments. b) In addition the ozone simulation is in closest agreement with the experimental data in Iso-DMS-2, and changes from over prediction at lower isoprene concentration to under prediction at higher isoprene concentration.

Response:

a) Please find the response to question #14b of reviewer 1.

b) For lower isoprene concentrations (Iso-DMS-1 and Iso-DMS-2 in supporting information), the model simulations for ozone relatively accord with experimental data while the model under predicted for high isoprene concentrations (over 2 ppm). It is known that RO₂ radical chemistry in the MCM is oversimplified for the reaction with RO₂ radicals, HO₂ radicals, or NO. At the high concentration of isoprene, if the RO₂ radical reaction with either RO₂ radicals or HO₂ radicals is overestimated, the reaction of RO₂ radical with NO can be relatively suppressed. In this situation, the prediction of NO₂ as well as ozone might be under predicted.

19. P.14682 line 12. Would read better as “The heterogeneous chemistry on SOA for isoprene is not included..”

Response:

The sentence has been changed to “The heterogeneous chemistry on isoprene SOA is not included in this study and this may possibly lead to the deviation of the model’s predictions from experimental data.”

20. P.14682 section 3.4. This section needs further elaboration. The generalized statement of “lower concentrations” and potential suitability for “ambient simulation”, need to be given more explicitly. The reader has to refer to figure 5, to find the concentrations used, and here for the Iso-DMS-5 experiment, at the

lowest DMS (20 ppb) and isoprene (40 ppb) concentrations the decay of the DMS and isoprene is not provided for comparison. What is known about ambient concentrations of DMS and isoprene should also be given, so that the reader can determine how much higher than ambient the concentrations used in Iso-DMS-4 and Iso-DMS-5 are.

Response:

The section has been modified according to reviewer's comment. This reads now,

“Due to the detection limits of instruments, chamber experiments relevant to ambient concentrations of isoprene and DMS cannot be conducted in this study but simulated using the kinetic model. The simulation of the photooxidation of lower concentrations of isoprene and DMS is beneficial to evaluate the effect of both NO_x and isoprene on the yields of MSA and H₂SO₄ and to understand the role of the heterogeneous reactions of DMS oxidation product in the prediction of the production of MSA and H₂SO₄.”

21. P.14683 para from line 3. This paragraph seems to be contradictory to the experimental and simulation data provided “MSA production appeared to be increased as the initial isoprene concentration increased”(figure 4). MSA concentrations are lower in the higher isoprene concentration experiment Iso-DMS-3, than in Iso-DMS-1.

- a) So the following statement “reaction of DMS with O(³P) is enhanced, eventually causing higher yields of MSA and H₂SO₄” does not make sense.
- b) And how would the O(³P) reaction significance relate to moving towards more realistic ambient conditions?

Response:

- a) See the response to question #1c of reviewer 2.
- b) See the response to question #15 of reviewer 1.