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Comment

***Interactive comment on* “Chamber simulation of photooxidation of dimethyl sulfide and isoprene in the presence of NO_x” by T. Chen and M. Jang**

Anonymous Referee #2

Received and published: 28 August 2012

This paper describes experimental atmospheric chamber together with modeling studies on dimethyl sulfoxide(DMSO), dimethyl sulfide(DMS), isoprene and NO_x, aiming to give an improved representation of the photooxidation mechanisms for the gas phase reactions and also through the inclusion of heterogeneous reactions of the gaseous DMS products, leading to the formation of sulfuric and methanesulfonic acid.

Overall the work presents a series of well-conducted experiments combined with an extensive model development and investigation, and should be published eventually, however there are places where details are lacking and improvements are needed. The English language construct awkward in places, and in a number of places there are omissions of references.

There are some contradictions between the text and figures presented in discussing the

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results. This is confusing and somewhat misleading, therefore significant clarification is needed. Some of the general statements need further elaboration and are detailed below.

I can recommend publication only after revisions addressing the reviewers' (#1 and #2) comments.

Specific comments

1. Abstract

P.14670 Poorly written, in terms of the flow of the study and experiments conducted. 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.

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 looks 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.

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.

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

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4. P.14672 line 6. MSIA is used here, but not defined until later in the text.
5. P.14672 line 21. ‘The resulting DMSO mechanisms’ would read better as ‘The resulting DMSO reactions’
6. P.14762 line 23. This last sentence is very poorly constructed, and the MCM requires better referencing.
7. P.14673 Experimental procedures. Line 7 Experiments were not ‘operated’ rather ‘conducted’. 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.
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).
9. P.14674 line 21. Needs to state which major isoprene photooxidation products were analyzed. Line 23. Bornyl Acetate does not require capitalization.
10. P.14674 line 23-24. This sentence indicates chamber background air is analyzed prior to each experiment, to check for any contamination. Is this only for the DMS-isoprene experiments? This seems out of place. 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.

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11. P.14675 line 9. The Morpho kinetic solver needs referencing.
12. P.14675 line 11. Tables S1-S3 contain the ‘recent literature’ references and this should be stated in the text here. And again correct referencing for the MCM is needed.
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.
14. P.14677. 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. Figure 4 legend distinguishes between wall loss and chamber dilution, however the chamber dilution is not discussed in the text. Does this mean that all other experimental figures have been corrected for both wall loss and chamber dilution?..if so this should be stated.
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?
16. P.14678-79 line 25. Again which ‘existing models’ are referred to?
17. P.14680 line 20. Coexisting should be replaced by presence.
18. P.14680 discussion needs elaborating. The NO₂ simulation deviates significantly from the experimental data beyond 60 mins, but is much better represented in the other series of experiments. 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.
19. P.14682 line 12. Would read better as “The heterogeneous chemistry on SOA for isoprene is not included..’

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.

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

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 14669, 2012.

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