Comment on "Chamber simulation of photooxidation of dimethyl sulfide and isoprene in the presence of NOx" by T. Chen and M. Jang

A large experimental dataset on DMS chemistry obtained in a 2 m^3 chamber is presented in this study. The approach to study DMSO chemistry in separate experiments and to study mixtures of DMS and isoprene was helpful to gain additional information on reaction mechanisms. The attempt to simulate the chamber data is highly appreciated. The newly constructed kinetic model includes detailed gas phase chemistry of DMS, DMSO, and isoprene and also considers DMS reactions that occur in small chambers with high concentrations of reactants, such as the reaction of DMS with the CH3S· radical. An important outcome of the study is that apparently heterogeneous reactions of DMS products on aerosol particles were necessary to explain concentrations of MSA and H2SO4 in the experiments.

Abstract and Introduction are not well written. More quantitative information needs to be added to the abstract and the relevance of the conducted chamber experiments for atmospheric modelling needs to be highlighted. Unfortunately, too little details are provided on the heterogeneous chemistry part of the kinetic model to assess the chosen approach.

The main concern is the treatment of heterogeneous chemistry in the kinetic model and its description in the manuscript. Experiments were carried out at about 20-30% relative humidity and the chamber aerosol most probably consisted of liquid droplets, i.e. highly concentrated solutions of H2SO4 and MSA in water. Partitioning of DMS oxidation products to the chamber aerosol is then best described as reactive uptake, i.e. mass transfer to the droplet (gas phase diffusion and mass accommodation) followed by reaction on the surface or in the bulk of the droplet. In cases where surface and/or bulk reactions are dominating the uptake, the total uptake coefficient and the reactive uptake coefficient will be identical. Thus reactions (R1)-(R9) could be greatly simplified since only one parameter (the total uptake coefficient) needs to be adjusted for each DMS product instead of several parameters (kads, kdes, kr). Data on mass accommodation and reactive uptake coefficients can be found in JPL publication 10-6 (Sander et al., 2011). In this way, also the reactive uptake of SO2 could be handled consistently.

The abstract and introduction text suggests that heterogeneous reactions were treated as surface reaction. The formulation of reactions (R7)-(R9) does not explicitly refer to surface or bulk process. In the chamber aerosol probably both surface reactions and bulk reactions occurred. It should be clarified whether reactions (R7)-(R9) were treated in the kinetic model as surface reactions (by surface area) or as bulk reactions (by mass or volume). Also partitioning of DMS oxidation products is defined as adsorption / desorption (to surface) and not as sorption / desorption, while reactions (R1)-(R6) are formulated as bulk processes (by aerosol mass). It

should be clarified whether reactions (R1)-(R6) were treated as surface partitioning (by surface area) or as bulk partitioning (by mass or volume).

The very extensive set of experiments and the rather successful simulation of the experiments with a detailed kinetic model qualify this manuscript for publication in ACP. However, before I could recommend publication the heterogeneous chemistry issues have to be properly addressed and the specific comments below need to be considered point-by-point.

Specific comments

Point 1

To better understand the impact of heterogeneous chemistry, the average percentage increase of MSA and H2SO4 concentrations in the DMS and DMSO experiments compared to a simulation with only gas phase chemistry should be provided in the abstract.

Point 2

The reference to the 1995 report of IPCC is too old and science on climate change has made great advances since then. What does the most recent IPCC report conclude about the climate relevance of DMS?

Point 3

A further important complication when comparing results from kinetic models on DMS products with ambient measurements is the propagation of uncertainties of gas-phase reaction rate constants into the computed particle phase concentrations of H2SO4 and MSA (Karl et al., 2007).

> Karl, M., Gross, A., Leck, C., Pirjola, L., Intercomparison of dimethylsulfide oxidation mechanisms for the marine boundary layer: Gaseous and particulate sulfur constituents. J. Geophys. Res., 112, D15304, doi:10.1029/2006JD007914,2007.

The reaction of DMS with halogen atoms and halogen oxides should also be mentioned. The review by Barnes et al. (2006) also provides an excellent overview of these. With respect to liquid phase reactions of DMS, the model study by Campolongo et al. (1999) should be cited.

Campolongo, F., Saltelli, A., Jensen, N. R., Wilson, J., Hjorth, J., The role of multiphase chemistry in the oxidation of dimethylsulphide (DMS). A latitude dependent analysis. J. Atmos. Chem., 32, 327-356, 1999.

A literature survey of observed isoprene concentration over oceans should be made and the observed concentration range should be added when discussing the impact of isoprene on DMS chemistry. While the co-existence of DMS and isoprene is probably relevant over the remote oceans (low NOx levels); it should be elaborated in which environments with high NOx levels it could be relevant.

Point 4

In section 2.1.1, does the chamber allow to control temperature and relative humidity in the experiments? More details on the chamber operation should be provided (temperature control, ventilation, replenishment of air, etc.)

Point 5

It is stated that the nucleation of MSA and H2SO4 produces an initial aerosol mass. The nucleation potential of MSA (binary homogenous nucleation with water molecules, ternary homogenous nucleation with H2SO4 and water) is less known and there exist only a few studies in literature. Please provide appropriate citation. Was a detailed model for nucleation of MSA and H2SO4 used?

Point 6

The concept of adsorption / desorption is used for partitioning of DMS products to aerosol particles. The partitioning coefficient Kp is defined according to Kamens et al. (1999). However, the concept of partitioning by Kamens et al. refers to absorption (expressed as forward process) and desorption (expressed as backward process) into (an organic) bulk phase. Later "Aerosol" is defined as the mass of MSA and H2SO4, which indicates that the kinetic model handled uptake as bulk phase partitioning. The definition of partitioning as adsorption / desorption process makes only sense for partitioning to surfaces of e.g. soot particles or mineral dust particles, but not for liquid droplets. If it was intended to use only surface partitioning (physical adsorption and desorption), Kamens et al. (1999) is not the proper citation. Was the uptake of MSA and H2SO4 also treated as (reversible) partitioning to the aerosol?

Point 7

The rate coefficients kad and kdes were probably very specific to the chamber aerosol and the conditions in the chamber. How were the rate values estimated?

Point 8

Are reactions (R7)-(R9) considered to be surface reactions or volume reactions? Oxidant (OH, O3 or other gas) is missing on the educt side of the reactions; consequently the reactions would also be gas-phase loss term of oxidants.

Point 9

Section 3.2.3: according to the kinetic model, which reaction of the DMS scheme was most relevant in terms of ozone production?

Note the discrepancies for the thermal decomposition of CH3SO3 in literature. A brief discussion of the published rate constant values should be added. Thermal decomposition of CH3SO3 opens an additional pathway for producing H2SO4 via SO3 + H2O. According to the kinetic model, how much more H2SO4 was produced compared to the SO2+OH reaction?

Point 10

Section 3.3.2: The increased formation of MSA (assuming particulate phase MSA) may be caused by the greater aerosol mass when SOA from isoprene oxidation is present. Was the mass concentration of isoprene-related SOA added to the concentration of "Aerosol" (i.e. [Aerosol]) in the kinetic model? It should at least be tested with the model if increased MSA concentration can be explained by partitioning of MSA (produced by the gas phase chemistry) to an increased aerosol mass.

Point 11

The contribution of the chamber experiments to the understanding of DMS gas phase chemistry in the atmosphere has not been pointed out in the conclusion. It is not clear whether the good match of the measurements of H2SO4 and MSA could also be achieved by adjustment of gas phase reaction rate constants, not considering heterogeneous reactions.

Point 12

The reaction of DMS with O(3P) is probably not relevant in the atmosphere. If this is the main reaction that catalyzes the formation of MSA and H2SO4, how relevant is the effect of VOCs on DMS chemistry in the atmosphere?

Point 13

The potential formation of organosulfates from isoprene SOA should be discussed (e.g. Surratt et al., 2007a; b). If organosulfates would form by reaction of isoprene oxidation products in the sulfate aerosol, a higher fraction of MSA and H2SO4 would partition to the aerosol. As in point

7, the apparently higher yields of MSA and H2SO4 would be due to increased partitioning to the aerosol and not due to accelerated DMS photo-oxidation.

Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, Environ. Sci. Technol., 41, 517–527, 2007a.

Surratt, J. D., Lewandowski, M., Offenberg, J. H., Jaoui, M., Kleindienst, T. E., Edney, E. O., and Seinfeld, J. H.: Effect of acidity on secondary organic aerosol formation from isoprene, Environ. Sci. Technol., 41, 5363–5369, 2007b.

Point 14

Did the kinetic model consider any cross-reactions between the isoprene and DMS chemistry mechanisms? Recently, stabilized Criegee Intermediates such as CH2OO· were found to oxidize SO2 rapidly (Jiang et al., 2010).

Jiang, L., Xu, Y., and Ding, A.: Reaction of Stabilized Criegee Intermediates from Ozonolysis of Limonene with Sulfur Dioxide: Ab Initio and DFT Study J. Phys. Chem., A 114, 12452-12461, 2010.

Comments on text and tables

P.14670, abstract and P.14671, line 8

Replace "predictability" by "predictive capability".

P.14671, line 25

Replace "missing aerosol-phase reactions" by "missing heterogeneous reactions".

P.14672, line 11

The statement "However, kinetic studies of the impact of coexisting VOCs and DMS chemistry are inadequate" needs to be explained better and a reference should be added.

P.14671, P. 14674

Full names of compounds should be given at first appearance in the text: DMSO, H2SO4, DMSO2.

P.14676, line 5

Define "Aerosol" by using an equation of the form: [Aerosol] = [MSA] +[H2SO4] + …

Where squared brackets denote concentration.

P.14672, line 15

Replace "surface of aerosol" by "surface of aerosol particles".

P.14672, line 22

A table listing the DMS related reactions for which adjustments were done based on the experimental observations (described in section 3.2.3) should be added to the manuscript.

P.14674, line 7

Replace "Acetonitrile" by "acetonitrile".

P.14678, line 21

Replace "DMS model" by "DMS chemistry scheme".

P. 14681, line 11

A mathematical equation expressing the integrated reaction rate should be provided here, together with appropriate reference.

P.14681, line 28

The sentence "The MSA and H2SO4 produced…" is not clear. Please rephrase.

P. 14688, table 1 and P. 14689, table 2

Provide standard deviations of temperature and relative humidity.

P.14692, figure 2

Add in figure capture whether MSA and H2SO4 is gas-phase, particulate phase, or total concentration. The same should be done in figure captures of figures 3-5.

Supplement, table S1

The rate constant for reaction 1 (1.50E+07) is wrong, certainly a typo. The rate constant of CH3S(O)CH3 + O3P is 8.8E-12 at 298 K, according to JPL publication 10-6 (Sander et al., 2011).