

Replies to re-review of Cala et al.

Dear Prof. Orlando,

Please accept further apologies for the time it's taken us to reply to the re-review of this paper and to address your editorial comments/suggestions.

We appreciate the referees comments that this is a publishable study but that it was too long – even after we expanded the SI. We have placed more material into the SI, including the original S2.2 describing how we put our new mechanism together. We hope that the paper is now shortened sufficiently to make it more widely readable. We have also added some very specific comments for the need for more laboratory studies on small organo-sulfur radicals that are urgently required to reduce uncertainties in mechanisms.

Comments from Anonymous Referee#2 in grey, replies in **black** and **blue**.

The manuscript is still a bit on the long side and a bit difficult to get the overview and find the key messages. In my previous review I wrote: "The comparison with the box-model of the different chemical mechanisms is very interesting and I think it could strengthen the paper if the authors based on this could come up with a list of concrete key problems to address in laboratory and field studies to help constrain models on DMS oxidation and fate of the oxidation products."

The current text about future lab and field work in the conclusion is very broad and general. As far as I can see, the authors have not added such as concrete list? I still think it would strengthen the paper if they could add such recommendations based on their model results.

Thanks for re-reading this and for your helpful comments. We agree about adding a more concrete list and have added such statements into the conclusions and abstract.

"Our results suggest that as a priority laboratory studies are performed that address 1) the uptake of HPMTF onto aerosol surfaces and the products of this reaction. 2) The kinetics and products of the following reactions:  $\text{CH}_3\text{SO}_3$  decomposition;  $\text{CH}_3\text{S} + \text{O}_2$ ;  $\text{CH}_3\text{SOO}$  decomposition;  $\text{CH}_3\text{SO} + \text{O}_3$ ."

Line 135-136: It should be stated that the authors chose the higher value for DMS emission in Glasow and Crutzen 2004.

Corrected.

Page 16 line 371 – 372 The authors refer to S1.3.1 in the supporting material – I cannot find such a table.

Sorry, this is a typo and refers to S1.4.1. We have corrected this.

Also the temperature sensitivity between 270 and 290 K is attributed to difference in the rate constant of DMS oxidation through the OH-addition channel. Did the authors test this statement by running the models with the same rate constant for this reaction?

I do not understand the authors reply – which rate constants are compared at 298 K and 1 atm? The authors should address the question in the manuscript text also.

Reply from the authors:

That's a great question, we didn't do that but as we use a consistent inorganic chemistry and we checked that things like OH are very similar between the model runs we felt we could safely assess this by just comparing the rate constants at 298 K and 1 atm. These are inconsistent across mechanisms hence we attribute this as the initiator of the divergence.

We apologise for the poor and confusing reply. The text here refers to the divergence shown in Figure 3 between the different UKCA DMS schemes; the ST (StratTrop) family (ST and ST~CS2) and the CS2 family (CS2, CS2-UPD-DMS, CS2-HPMTF). We infer (from inspection of the reaction fluxes and mechanism) that the cause of the difference in temperature dependence of the MSA profile in

Figure 3b (the gradient of  $d[\text{MSA}]/dT$ ) is the difference in kinetics used for the DMS+OH addition channel. The expressions are given in Table 2 for the CS2 family of schemes and in S1.4.1 for the ST family of schemes and are visualised in Figure R1 to clearly have different gradients.

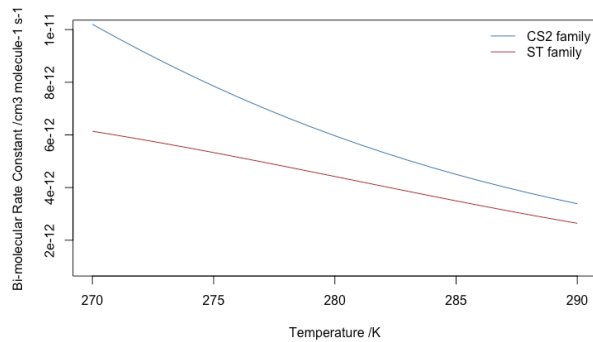


Figure R1: A comparison of  $k$  DMS+OH addition channel as a function of temperature in the CS2 schemes and ST schemes shown in Figure 3.

We have modified the text to make the point clearer that we are inferring it's the difference in the two expressions for the rate constants for the DMS+OH addition channel that drive the difference between MSA-Temperature gradients seen in the CS2 and ST families.

“We attribute this to differences in the rate constant of DMS oxidation through the OH-addition channel (see **Table 2** and **S1.4.1**) used in the UKCA ST schemes and the UKCA CS2 schemes. The expression used in the ST family of schemes (the provenance of which is Pham et al. (1995), see S1.4.1) has a much shallower gradient with temperature than the expression used in the CS2 family of schemes (which is based on the latest IUPAC recommendation).”