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Comment on Dovrou et al

Becky Alexander (Referee)

Referee comment on "Towards a chemical mechanism of the oxidation of aqueous sulfur dioxide via isoprene hydroxyl hydroperoxides (ISOPOOH)" by Eleni Dovrou et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-176-RC1, 2021

Dovrou et al use a laboratory study to determine the mechanism, rate constants, and products of aqueous-phase reactions between ISOPOOH and SO2,aq over a pH range of 3-6, which is typical of cloud water pH. They find that under relatively high cloud water pH conditions (pH = 5.5) that the rate constant for the reaction of one of the two ISOPOOH isomers and SO2,aq is similar to that for the reaction of H2O2 and SO2,aq, the latter of which is thought to be the dominant SO2 oxidant in the atmosphere. They identify the products of the reaction of SO2,aq with the two ISOPOOH isomers, and from that propose reaction mechanisms. They utilize a global model to determine the importance of this reaction for sulfate formation globally, and also where it's most important regionally.

In general, I find this paper very well written and is an important and useful advance in our understanding the products of this reaction and its implications for the atmosphere. The information provided will be useful for implementation in chemical models, as they have shown (sort of, see below). I have two significant issues, and then some more minor ones detailed below.

Significant issue #1: SO2 dissolves in cloud water to form SO2H2O, bisulfite (HSO3-) and sulfite (SO32-). The authors refer to SO2,aq throughout the text, but never refer to specific species in the aqueous phase. The relative importance of each species is pH dependent, and since they are evaluating the pH dependence of the reactions, this seems important. The mechanisms proposed all involve reactions with bisulfite, with sulfite not mentioned, even for the higher pH values where sulfite concentration will be significant. They also show that the sulfate product yield is lower at the higher pH values, and I wonder if this has to do with less of the dissolved SO2 being present as bisulfite, and more present as sulfite. Does the reaction of ISOPOOH not occur with sulfite? This should be discussed.

Significant issue #2: I'm confused by the modeling. Section 2.3 describes the model simulation (though I would not consider the description of the model simulations to be complete). The model results are not discussed until the conclusion, in the very last paragraph of the paper. This is not an appropriate place to present results for the first time. The conclusion section refers to Dovrou et al. (2019), suggesting that no new model simulations were performed for this paper. If no new model simulations were performed, then the existence of section 2.3 is misleading. If indeed no new model simulations were performed, then I don't see the point of discussing model results if the results of the laboratory experiments were not included in the model for the present study. If the model was run with the new information gleaned from the presented laboratory studies, then model results (with figures) should be shown in the results section. In sum, I have no idea what to make of the model results discussed in the last paragraph of the paper or if the model includes the new information learned from the laboratory studies.

Minor issues:

Line 91: Should this be referencing Dovrou et al. (2019a) (not b)?

Section 2.3: Model needs a doi. You included a reference that describes the isoprene chemistry, but you also need to provide a reference that describes the sulfur chemistry in the model. You need to state which met fields were used (MERRA2? GEOS-FP?). What cloud pH calculation is being used? This seems relevant and should be referenced. Provide a reference for how bromine chemistry impacts SO2 oxidation (Chen et al, 2017), or delete this line as I'm not sure how it's directly relevant to this work.

Reaction R3 has CH3OOH as a reactant, while in R3a and R3b its CH3COOH (there's an extra C in 3a and 3b).