Reply to comments of Anonymous Referee for the manuscript “Towards a Chemical Mechanism of the Oxidation of Aqueous Sulfur Dioxide via Isoprene Hydroxyl Hydroperoxides (ISOPOOH)

We would like to thank the referee for the comments, that helped the revise and improve our manuscript. The comments are mentioned below with italic followed by our responses.

Specific comments

Line 60: For the benefit of readers with less knowledge of the sulfur dioxide oxidation mechanism, please include reactions that include the accommodation and dissolution of gaseous sulfur dioxide and its conversion to HSO_3^-.

We would like to thank the referee for the recommendation. As suggested we added the following statement in the main text and the following information as a new section in the Supplement.

We add the following statement in line 47 page 2:

“$SO_{2,aq}$ reacts with water to form sulfurous acid ($SO_2 \cdot H_2O$), which dissociates to bisulfite (HSO_3^-) when pH>2. At higher pH (pH > 6), HSO_3^- subsequently dissociates to form sulfite (SO_3^{2-}) (Seinfeld and Pandis, 2016). In the cloud pH range of 3-6 the dominant form of $SO_{2,aq}$ is HSO_3^- and our study investigated pH values of 3, 4.5 and 5.5 (Fig. S1).”

We add in Supplemental information:

“**1. Sulfur dioxide**

Sulfur dioxide (SO_2) has a Henry’s law constant of H_{SO_2}=1.3 M atm^{-1} and mass accommodation coefficient of γ_{SO_2}=0.11, which does not significantly change with temperature (Worsnop et al., 1989). Thus, SO_2 can dissolve ($SO_{2,aq}$) into cloud and fog water, where it can be rapidly oxidized to form sulfate.(Lind et al., 1987; Hegg and Hobbs, 1982; Shen et al., 2012; Harris et al., 2014; Dovrou et al., 2019b) $SO_{2,aq}$ reacts with water to form bisulfite (HSO_3^-) at pH$\gtrsim$2, which dissociates to form sulfite (SO_3^{2-}) at pH$\gtrsim$6 (RS1-RS3, Fig. S1) (Seinfeld and Pandis, 2016).

$$SO_{2,g} + H_2O \rightleftharpoons SO_2 \cdot H_2O \qquad \text{(RS1)}$$

$$SO_2 \cdot H_2O \rightleftharpoons H^+ + HSO_3^- \qquad \text{(RS2)}$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \qquad \text{(RS3)”}$$

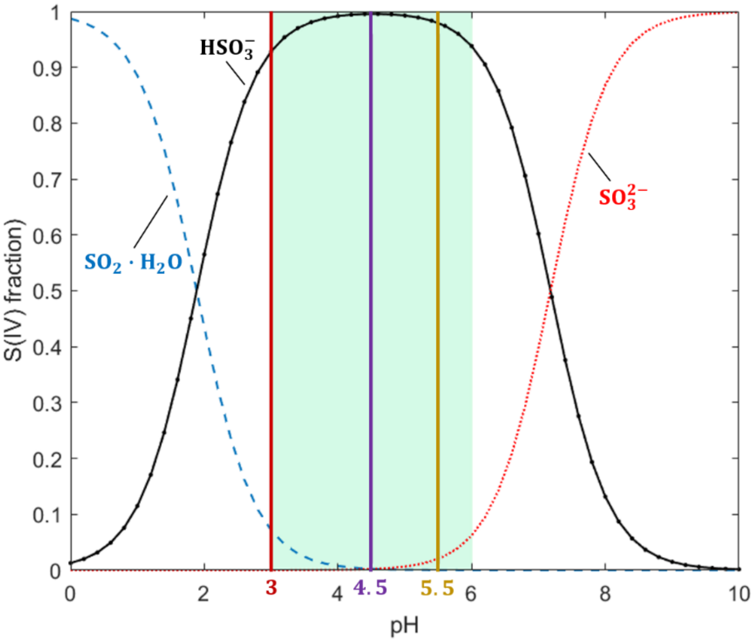

Figure S1. Mole fraction concentrations of S(IV) species vs pH. The green shaded area shows the pH range of 3-6 and the three pH values examined in the present work: pH=3 (crimson), pH=4.5 (purple) and pH=5.5 (dark yellow). The dominant form of $SO_{2,aq}$ under these conditions is bisulfite (HSO_3^-) (Seinfeld and Pandis, 2016).

Line 92: I'm puzzled by the need for the extremely long relaxation delays (45 seconds as compared to the usual 1 second for quantitative 1H NMR). I realize that there is some discussion of this problem in the SI, but I'm not quite sure I understand how the information reported establishes that the inconsistency in the integrations at different pH values is due to differences in the relaxation time for different 1H nuclei. Wouldn't this be better established by reporting the integrations (at pH = 3.0, where the inconsistencies are the greatest) for different relaxation times? I assume that the authors did this kind of a study, but I don't see it reported anywhere in the manuscript. Given what is reported in the manuscript, it seems to me that an alternative explanation for the data presented in Table S1 is simply that some species are either more volatile, less aqueous soluble, or consumed by secondary reactions at lower pHs and/or with different standards dissolved in solution.

We would like to thank the referee for the comments. Regarding the long relaxation delays, we did experimental runs varying that parameter, and 45 seconds were chosen in order to achieve optimal resolution in combination with the relatively quick experimental runs to monitor the reactions. Shorter relaxation delays were generating noise, thus unreliable spectra. All experiments were conducted under the same conditions and the only changes among same pH runs were the relaxation delay prior to setting it to 45 seconds.

The explanation provided addresses the difference between Figure S3 and Table S1 for the peak intensities. Regarding the data presented in Table S1, they are all conducted under the same conditions per pH value using two different standards. The relative ratios of the integrated peaks to the standard are similar for each standard, considering also that 0.5 mM of 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt ($(CH_3)_3Si(CH_2)_3SO_3Na$) and 0.1 mM DMSO were used. Thus, the difference in the integration values presented are due to the different concentration used in each standard. In addition, we do not have any evidence indicating interaction of the products with the standards used.

Line 124: While it might be difficult to detect a 1.2 mM (the concentration of the coproduct MVK at pH = 5.5) species with 13C NMR, the hydrated formaldehyde species could, in principle, be detected and quantified (again with long relaxation delays). In general, 13C NMR could have been useful for looking for other species that might have been overlapped in the 1H spectrum in the effort to understand why a significant amount of carbon was not quantified. Did the authors consider this approach?

We performed experiments using 13C NMR and also 2D C and H NMR and the results did not provide additional information. To be more specific, we used relaxation times of 45 seconds and longer and the hydrated formaldehyde was not able to be quantified. We also tried to use 13C NMR for additional quantification of species but, unfortunately, the spectra were not clear enough compared to the 1H NMR spectra. Thus, we chose to continue and complete the analysis using 1H NMR.

Line 128: The unidentified peak at 1.43 ppm might be more appropriately referred to as a methyl group not adjacent to a carbonyl group rather than as an "alkane."

Due to the uncertainty of the identification of the peak and the fact that an alkane typically has a 1H NMR shift of ~0.8-1.9 we chose an alkane as a possible explanation. However, we rephrased the sentence, as suggested, as:

"…at δ=1.43 ppm (Fig.1) is likely a methyl group not adjacent to a carbonyl group based on its chemical shift,…"

Line 167: I'm confused about what "2/3" refers to here. Isn't 30% of 1,2-ISOPOOH ending up as MVK?

We clarified that statement, as it is referred to the products of 1,2-ISOPOOH, 1,2-ISOPOH and MVK,:

"1,2-ISOPOH yield is only about 2/3 of the yield of MVK at all pH values…"

Technical comments

Line 83: The abbreviation IC precedes the definition of the acronym on line 88.

We would like to thank the referee. We added this information on line 82:

“The concentrations of the ion chromatography (IC) and nuclear magnetic resonance (NMR) spectrometry experiments…”

Line 108: Since the experiments use HSO3- as the reactant (and don’t add actually add gaseous SO2 to an aqueous solution), it would be more clear if HSO3- is specifically identified as the reactant in the discussion of the experiments. This would be made more clear if the full mechanism were given in the introduction as suggested in my comment above.

We added a clarifying statement, as mentioned above, in line 47 page 2 and we mention that the dominant form of $SO_{2,aq}$, in the experiments conducted in this work, was bisulfite.

Figure 3: It would help make the figures more “stand alone” if they also included the yield information given in Table 2.

We appreciate this comment, it is a very good suggestion. We add a new figure in the main text (Fig. 4) where the mechanism of 1,2-ISOPOOH+ $SO_{2,aq}$ at pH=5.5 is presented with the yields.

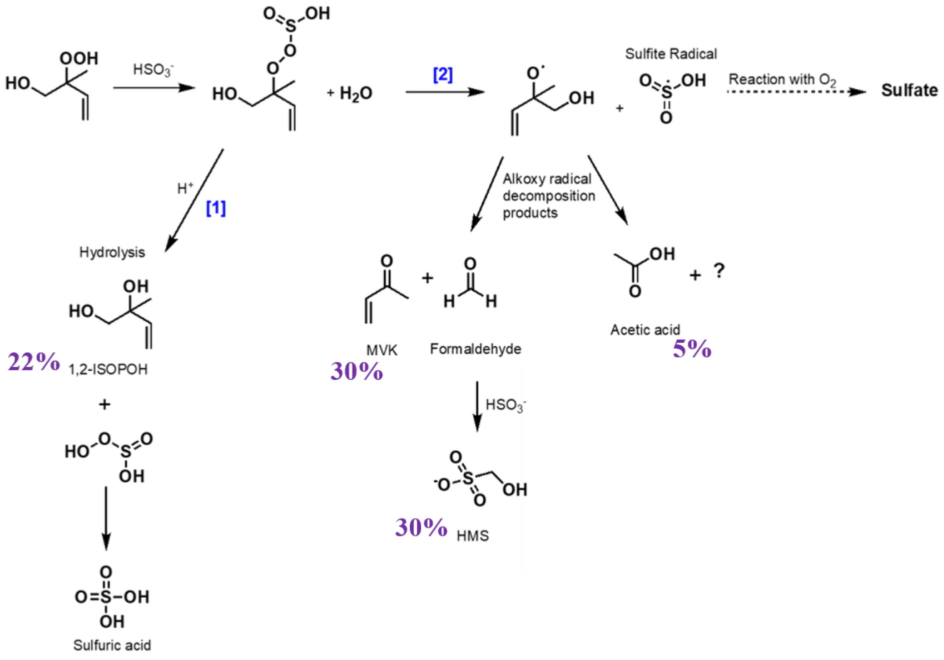

Figure 4. Proposed chemical mechanisms of the oxidation of $SO_{2,aq}$ by 1,2-ISOPOOH with carbon yields of identified products at pH=5.5 (Table 2) presented in purple. There are two competing mechanisms: after ISOPOOH reacts with $SO_{2,aq}$, displacing water, a hydrolysis reaction is taking place [1] or an O-O bond breakage [2]. In mechanism [1], the product hydrolysis results in the same intermediate that the reaction of $SO_{2,aq}$ with H2O2 is forming and either a formation of a diol or an epoxide is being generated (Figure S2). In mechanism [2], an alkoxy radical and sulfite radical are formed

leading to the production of MVK, MACR, HCHO and other products. The sum of the products' carbon yields is 57% and the remaining 43% is attributed to hydrated formaldehyde, repartition of MVK to the gas-phase and possible formation of CO or other small molecules that have repartitioned to the gas-phase, as discussed in Section 3.2.2.

References

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