

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-176

Anonymous Referee #2

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-RC2>, 2021

General comments

This manuscript describes laboratory experiments that aim to investigate the mechanism by which isoprene hydroxyl hydroperoxide (ISOPOOH) oxidizes sulfur dioxide dissolved in cloud droplets. Specifically, the work uses ion chromatography to track the production of sulfate and NMR to identify and quantify the organic products of the reaction. The main findings are that the sulfur dioxide oxidation mechanism for ISOPOOH is different than hydrogen peroxide with two distinct pathways: 1) a high yielding fragmentation pathway that produces methyl vinyl ketone (MVK) and formaldehyde and 2) a low yielding non-fragmentation pathway that yields isoprene-derived diols (ISOPDH). Global simulations indicate that ISOPOOH oxidation of sulfur dioxide is likely not a major source of MVK, but could be a regional driver of sulfate product. The work is well-designed, carefully performed, and clearly analyzed. Because knowledge of the oxidative pathways for sulfur dioxide (and its interaction with the isoprene oxidation mechanism) is critical to the development of accurate models for aqueous atmospheric particles, this work will be of interest to readers of *Atmospheric Chemistry and Physics*. Below are some suggestions and questions for the authors to consider in their preparation of a revised version of the manuscript.

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 HSO₃⁻.

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.

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?

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."

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

Technical comments

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

Line 108: Since the experiments use HSO_3^- as the reactant (and don't actually add gaseous SO_2 to an aqueous solution), it would be more clear if HSO_3^- 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.

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