Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-490-RC2, 2018
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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Understanding the catalytic role of oxalic acid in the SO_3 hydration to form H_2SO_4 in the atmosphere" *by* Guochun Lv et al.

Anonymous Referee #3

Received and published: 14 November 2018

This paper presents quantum chemical calculations for the catalytic role of oxalic acid in the SO3 hydration to form H2SO4. This topic is appropriate for the ACP journal, and the results of this study are somewhat interesting. However, this work is incomplete and the results are poorly presented. Thus, significant revision is needed before this paper can be considered for publication in ACP.

From my perspective, the authors should strive to address the following points:

1. The authors tried to state "the oxalic acid-catalyzed SO3 hydration can compete with water-catalyzed SO3 hydration". To be frank, I cannot assess whether this is correct from the current results. The presence of oxalic acid exactly enhances the rate

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constants for the hydration of SO3, but I know that the concentration of water is much great larger than that of oxalic acid in the atmosphere. So I have reason to believe that the half-life of water-catalyzed SO3 hydration is much great smaller than that of the oxalic acid-catalyzed SO3 hydration. If so, maybe "the oxalic acid-catalyzed SO3 hydration can compete with water-catalyzed SO3 hydration" is not correct, except that the authors can prove it.

2. I remain unconvinced about whether the authors clearly know what the addition, decomposition, isomerization, and abstraction reactions are. p2: "Some addition, decomposition, isomerization, and abstraction reactions also are the important HAT reaction in the atmosphere." These reactions are parallel, rather than a containment relationship!

3. The authors gave the binding energies of water dimers, RC1, PC1, etc, but didn't discuss them. I think they are not any function in this paper? So either the author add some discussion about the binding energies or delete the binding energies. Furthermore, the authors also define what is the binding energies.

4. In the paper, the authors named the title of each section as "Water-catalyzed hydration reaction of SO3", "Oxalic acid-catalyzed hydration reaction of SO3" and so on. However, I cannot find any results about "catalyzed" in these sections.

5. The authors pointed out that oxalic acid as one of the hydrogen donors and/or acceptors could catalyze the hydration reaction of SO3, through the formation of two-point hydrogen bond. Is it possible that all the hydration reaction of SO3 could be enhanced in the presence of any species with the formation the two-point hydrogen bond? So, the authors should summary the relationship with these species and the enhancement of the hydration reaction of SO3.

6. I also cannot assess the key ingredient: whether the details of the kinetic calculations are correct. As we know, limit value of atmospheric gas phase rate constant should not be not more than 10-9 cm3 molecule-1 s-1, especially for the reaction with barrier.

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However, the calculated rate constants in this work are only 10-5, 10-6, and 10-10 cm3 molecule-1 s-1 for some reactions. So, I think the authors should check their methods and results.

7. The authors mentioned that “hydroperoxy radical, formic acid, sulfuric acid (Torrent-Sucarrat et al., 2012), nitric acid and ammonia have been reported to replace the second water to catalyze the hydration reaction of SO3 .” I think the authors should compare the catalytic effect of these species with oxalic acid?

8. The paper is required to be revised by native English speakers.

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