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Comment on acp-2021-784

Anonymous Referee #1

Referee comment on "Pyruvic acid, an efficient catalyst in SO₃ hydrolysis and effective clustering agent in sulfuric-acid-based new particle formation" by Narcisse Tsona Tchinda et al., Atmos. Chem. Phys. Discuss.,
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Tsona and co-workers report their results of a theoretical investigations aiming the study the role of pyruvic acid (PA) in the atmospheric formation of sulfuric acid along with the formation of clusters between pyruvic acid, sulfuric acid and ammonia, as precursors of aerosols, an issue which is interesting for atmospheric purposes. This article has two parts. The first one dealing with the role of pyruvic acid as catalyst in the hydrolysis of SO₃, and the second one focused on the thermodynamic and the formation paths of the clusters. In my opinion, the issue has potential for publication in Atmospheric Chemistry and Physics. However, I have several points to address the authors.

Regarding the role of pyruvic acid as catalyst in the hydrolysis of SO₃.

- As a general point, the authors take as zero of energies the energy of the separate species, namely SO₃ + H₂O + PA (or SO₃ + 2H₂O). Although numerically this correct, in my opinion this may led to confusion, as one would infer three particle collisions along the processes.
- In Figure 1 the authors report their results on the gas phase water hydrolysis of SO₃, and the relative energies are collected in the supplementary information. Although the authors mention previous works regarding this issue, no comparison has been done with results from the literature
- Regarding the reaction mechanism, there are two ways in which the hydrolysis can take place. The first one, involve the reaction of SO₃···H₂O with PA and the second one the reaction of PA···H₂O + SO₃. Along the text the authors suggest that preferably proceeds by reaction of PA···H₂O + SO₃. From Figure 2, it seems that the authors consider only the reaction of SO₃···H₂O with the most stable PA (PA^{tc}) whereas the reaction of the naked SO₃ takes place with the PA^{tl} and PA^{ct} complexes. In my opinion the authors miss some preliminary steps in the reaction mechanisms, which may have effect on the kinetics. a) The SO₃···H₂O can react with both, PA^{tl} and PA^{ct} so that

these processes should be considered. b) The $\text{PA}^{\text{H}}\cdots\text{H}_2\text{O}$ and $\text{PA}^{\text{C}}\cdots\text{H}_2\text{O}$ complexes are held together by two hydrogen bonds, one between the acidic hydrogen of PA and the oxygen atom of water, and the other between the carbonyl oxygen of PA with one hydrogen atom of H_2O . In both cases the complexes form a ring structure which should be broken to form the RC^{H} and RC^{C} complexes. This requires the existence of a transition state that should be taken into account. Moreover, for instance, the pre-reactive complexes $\text{PA}\cdots\text{H}_2\text{O}\cdots\text{SO}_3$ (namely RC's) arising from $\text{PA}\cdots\text{H}_2\text{O} + \text{SO}_3$ could also decompose, without energy barrier, into $\text{PA} + \text{SO}_3\cdots\text{H}_2\text{O}$ which should be considered.

- It is not clear how the authors have considered all these reactions weighted according to the concentration of the different reactants (naked or forming complexes with water). The authors do not report values of the kinetic/equilibrium constants (for instance for the reaction of the reactant complexes) at different temperatures to support the discussion in the paragraph 215. This information is necessary and the values of the bimolecular rate constants should be detailed. By the same way, the discussion in paragraph 240 should be supported by the specific values of concentrations and relative humidity.

Regarding the cluster formation:

- My main point here is why the authors do not have included any water molecule in the formation of clusters. It is well known that sulfuric acid is fully hydrated at ground level in the atmosphere (see references in line 490 and ff among others) so that water should play a role in the formation of these clusters. This issue must be discussed.
- Another point is how the authors have chosen the structures to calculate the clusters. Have they performed a previous scan or a dynamic calculation to select them?