

## Reply to Comment on acp-2021-784

Anonymous Referee #1

We thank the Referee for their constructive comments. Here, we present a point-to-point response to all the comments. For clarity, the Referee's comments are reproduced in blue color text, authors' reply are in black color and modifications to the manuscript are in red color text.

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  $\text{SO}_3$ , 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  $\text{SO}_3$ .

- 1) As a general point, the authors take as zero of energies the energy of the separate species, namely  $\text{SO}_2 + \text{H}_2\text{O} + \text{PA}$  (or  $\text{SO}_3 + 2\text{H}_2\text{O}$ ). Although numerically this correct, in my opinion it may not be clear at all chemically, as one would infer three particle collisions along the processes.

Though we consider three species in the beginning of the reaction, it is obvious that only two species can collide to form a binary complex that collides thereafter with the third species to form the ternary complex, which is the pre-reactive intermediate. For example, considering the water-catalyzed reaction, it would proceed through  $\text{SO}_3 \cdots \text{H}_2\text{O} + \text{H}_2\text{O}$  and/or  $\text{H}_2\text{O} \cdots \text{H}_2\text{O} + \text{SO}_3$  interactions and form the same complex,  $\text{SO}_3 \cdots \text{H}_2\text{O} \cdots \text{H}_2\text{O}$ . This is apparent from Fig.1 where the two pathways were clearly identified to form the same complexes, according to our calculations.

The same applies to the PA-catalyzed reaction, where  $\text{PA} \cdots \text{H}_2\text{O} + \text{SO}_3$  and  $\text{PA} + \text{H}_2\text{O} \cdots \text{SO}_3$  were the main identified pathways leading to the formation of the pre-reactive intermediate,  $\text{PA} \cdots \text{SO}_3 \cdots \text{H}_2\text{O}$ .

Though this was already stated in the manuscript, we added the following text in the revised manuscript for further support:

Line 179

Indeed, due to the difficulty of termolecular interactions relative to biomolecular interaction (Buszek et al., 2012), the most likely situation is the interaction of two species to form a two-body complex followed by the interaction with the third species to form the pre-reactive intermediate.

- 2) In Figure 1 the authors report their results on the gas phase water hydrolysis of  $\text{SO}_3$ , while the relative energies are collected in the supplementary information. Although the authors mention these previous works regarding this issue, no comparison has been done with results from the literature.

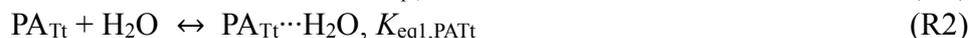
More discussion on the results of Figure 1 has been included in the revised manuscript  
Line 184:

These energies are respectively within 0.17-1.81 and 0.47-1.06 kcal mol<sup>-1</sup> similar to previously reported values for the same reaction (Hazra and Sinha, 2011; Long et al., 2013; Torrent-Sucarrat et al., 2012; Lv et al., 2019). The slight observed differences likely result from the differences in the computational approaches used in these studies.

3) Regarding the reaction mechanism, there are two ways in which the hydrolysis can take place. The first one, involve the reaction of SO<sub>3</sub>···H<sub>2</sub>O with PA and the second one the reaction of PA···H<sub>2</sub>O + SO<sub>3</sub>. Along the text the authors suggest that preferably proceeds by reaction of PA···H<sub>2</sub>O + SO<sub>3</sub>. From Figure 2, it seems that the authors consider only the reaction of SO<sub>3</sub>···H<sub>2</sub>O with the most stable PA (PA<sub>Tc</sub>) whereas the reaction of the naked SO<sub>3</sub> takes place with the PA<sub>Tl</sub> and PA<sub>Ct</sub> complexes. In my opinion the authors miss some preliminary steps in the reaction mechanisms, which may have effect on the kinetics.

a) The SO<sub>3</sub>···H<sub>2</sub>O react with both PA<sub>Tl</sub> and PA<sub>Ct</sub> so that these processes should be considered.

According to our calculations, PA<sub>Tc</sub> could interact with H<sub>2</sub>O and be converted into PA<sub>Tt</sub>, forming the PA<sub>Tt</sub>···H<sub>2</sub>O binary complex. At the same time, PA<sub>Tt</sub> interacts with H<sub>2</sub>O to form the PA<sub>Tt</sub>···H<sub>2</sub>O binary complex. Further interactions, PA<sub>Tt</sub>···H<sub>2</sub>O + SO<sub>3</sub> and PA<sub>Tt</sub> + SO<sub>3</sub>···H<sub>2</sub>O, both lead to the formation of the same PA<sub>Tt</sub>···H<sub>2</sub>O···SO<sub>3</sub> pre-reactive intermediate. Likewise, PA<sub>Ct</sub>···H<sub>2</sub>O + SO<sub>3</sub> and PA<sub>Ct</sub> + SO<sub>3</sub>···H<sub>2</sub>O interactions lead to the same PA<sub>Ct</sub>···H<sub>2</sub>O···SO<sub>3</sub> pre-reactive intermediate. Hence, the following equilibria are involved in the formation of pre-reactive intermediates:



where  $K_{\text{eq}}$  are corresponding equilibrium constants. Although in each case the pre-reactive intermediate is formed from two different interactions, we chose to include only the most energetically favorable one in **Fig. 2** for the sake of clarity. Nevertheless, the contribution of each path to the formation of the pre-reactive intermediate can be quantified by determining the relative concentrations of SO<sub>3</sub>···H<sub>2</sub>O and PA···H<sub>2</sub>O that actively participate in the formation of the pre-reactive intermediate. Application of the law of mass action to Eqs. (R1)-(R5) leads to the following expressions for PA···H<sub>2</sub>O to SO<sub>3</sub>···H<sub>2</sub>O ratio:

$$\frac{[\text{PA}_{\text{Tt}} \cdots \text{H}_2\text{O}]}{[\text{SO}_3 \cdots \text{H}_2\text{O}]} = \frac{K_{\text{eq}, \text{PATt}} [\text{PA}_{\text{Tt}}]}{K_{\text{eq}, \text{SO}_3} [\text{SO}_3]} \quad \text{and} \quad \frac{[\text{PA}_{\text{Ct}} \cdots \text{H}_2\text{O}]}{[\text{SO}_3 \cdots \text{H}_2\text{O}]} = \frac{K_{\text{eq}, \text{PACt}} [\text{PA}_{\text{Ct}}]}{K_{\text{eq}, \text{SO}_3} [\text{SO}_3]}.$$

Considering atmospheric PA and SO<sub>3</sub> concentrations of ~10<sup>10</sup> cm<sup>-3</sup> and ~10<sup>6</sup> cm<sup>-3</sup>, respectively, and taking into account the relative abundances of each PA conformer (0.95 for PA<sub>Tc</sub>, 0.04 for PA<sub>Tt</sub> and 0.01 for PA<sub>Ct</sub>), we find that regardless of the PA conformer, PA···H<sub>2</sub>O will contribute

by more than 99.99% to the formation of  $\text{PA}\cdots\text{H}_2\text{O}\cdots\text{SO}_3$  while  $\text{SO}_3\cdots\text{H}_2\text{O}$  will contribute by less than 0.01% (details are given in the Supplement). Overall, the pathway through  $\text{SO}_3\cdots\text{H}_2\text{O} + \text{PA}$  has no net effect on the kinetics of  $\text{H}_2\text{SO}_4$  formation, as it nearly does not contribute to the formation the pre-reactive intermediate. The formation of  $\text{PA}\cdots\text{H}_2\text{O}\cdots\text{SO}_3$  is essentially controlled by  $\text{PA}\cdots\text{H}_2\text{O} + \text{SO}_3$  collision, hereby supporting the sole inclusion of this pathway in **Fig. 2**.

To clarify, we added the following at Line 224:

Moreover, to evaluate the impact of each of these paths to the formation of the pre-reactive intermediate, we determined that among the two hydrates,  $\text{PA}\cdots\text{H}_2\text{O}$  will contribute by more than 99.99% while  $\text{SO}_3\cdots\text{H}_2\text{O}$  will contribute by less than 0.01% to the formation of the pre-reactive intermediate regardless of the PA conformer (details are given in the Supplement).

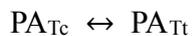
b) The  $\text{PA}^{\text{tl}}\cdots\text{H}_2\text{O}$  and  $\text{PA}^{\text{ct}}\cdots\text{H}_2\text{O}$  complexes are held together by two hydrogen bonds, one between the acidic hydrogen of PA and the oxygen atom of water, and the other between with the carbonyl oxygen of PA with one hydrogen atom of  $\text{H}_2\text{O}$ . In both cases the complexes form a ring structure which should be broken to form the  $\text{RC}^{\text{tl}}$  and  $\text{RC}^{\text{ct}}$  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 obvious that the approaches of  $\text{SO}_3$  and PA towards  $\text{PA}\cdots\text{H}_2\text{O}$  and  $\text{SO}_3\cdots\text{H}_2\text{O}$ , respectively, lead to rearrangements prior to the formation of the pre-reactive intermediate,  $\text{PA}\cdots\text{H}_2\text{O}\cdots\text{SO}_3$ . However, these rearrangements are not believed to lead to the formation of other particular minima prior to  $\text{PA}\cdots\text{H}_2\text{O}\cdots\text{SO}_3$  formation. DePalma et al. demonstrated that minima formed from such rearrangements would be separated by transition states commonly larger than  $RT$  (DePalma et al., 2014). Furthermore, following the energy paths in  $\text{SO}_3 + \text{PA}\cdots\text{H}_2\text{O}$  and  $\text{PA} + \text{SO}_3\cdots\text{H}_2\text{O}$  optimizations from our calculations indicates that the formation of  $\text{PA}\cdots\text{H}_2\text{O}\cdots\text{SO}_3$  was downhill, being  $\sim 13$  to  $15 \text{ kcal mol}^{-1}$  exothermic, with no remarkable barrier. For such low-lying complex formation, the decomposition of the pre-reactive intermediate to  $\text{PA} + \text{SO}_3\cdots\text{H}_2\text{O}$  or  $\text{SO}_3 + \text{PA}\cdots\text{H}_2\text{O}$  would be highly prevented, relative to its conversion to  $\text{PA}\cdots\text{H}_2\text{SO}_4$  by overcoming energy barriers around  $0 \text{ kcal mol}^{-1}$  or below. Hence, the kinetics of  $\text{PA}\cdots\text{H}_2\text{O}\cdots\text{SO}_3$  formation either from  $\text{SO}_3 + \text{PA}\cdots\text{H}_2\text{O}$  or  $\text{PA} + \text{SO}_3\cdots\text{H}_2\text{O}$  would likely not be affected by other intermediate steps, if not very weakly, while its decomposition is mainly towards  $\text{PA}\cdots\text{H}_2\text{SO}_4$  formation, its most likely fate. All fundamental steps controlling  $\text{PA}\cdots\text{H}_2\text{O}\cdots\text{SO}_3$  sources and sinks are depicted by reaction (R2) in the main manuscript, assuming pseudo steady-state approximation, and they are accounted for in the overall kinetics through their equilibrium constants and the rate constant of unimolecular decomposition of  $\text{PA}\cdots\text{H}_2\text{O}\cdots\text{SO}_3$ , executed by the KiSThEP program.

4) It is not clear how the authors have considered all these reactions weighted according 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.

Considering that different PA conformers would coexist in the atmosphere, we determined their equilibrium distribution at 298 K in order to take into account the effective role of PA in the kinetics. Using the Gibbs free energy changes of the equilibria below



and applying the law of mass action, we determined the relative abundances of PA conformers at 298 K and their values are given in the **Table R1** below, along with their formation Gibbs free energies relative to the energy of  $\text{PA}_{\text{Tc}}$ .

**Table R1** Gibbs free energies ( $\Delta G$ ) values of PA conformers, calculated at the M06-2X/6-311++G(3df,3pd) level of theory relative to  $\text{PA}_{\text{Tc}}$  energy, and their corresponding relative abundance. Energies are calculated at 298 K and 1 atm, and units are kcal mol<sup>-1</sup>.

Conformer	$\text{PA}_{\text{Tc}}$	$\text{PA}_{\text{Tt}}$	$\text{PA}_{\text{Ct}}$	$\text{PA}_{\text{Cc}}$
$\Delta G$	0	1.81	3.13	9.18
Relative abundance	0.95	0.04	0.01	0.00

Following the expression for the reaction rate given by **Eq. (1)** in the main manuscript, the numerical values of equilibrium constants and rates constants were calculated by the following equations.

The rate constant of the unimolecular decomposition of the pre-reactive intermediate was calculated as:

$$K_{\text{uni}} = \Gamma \times \frac{k_{\text{B}}T}{hc^0} \times \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (1)$$

where  $\Delta G^\ddagger$  is the Gibbs free energy barrier separating the pre-reactive intermediate and the products,  $h$  is the Planck's constant,  $R$  is the molar gas constant,  $c^0$  is the standard gas-phase concentration, and  $\Gamma$  is the Wigner tunneling correction.

For two species  $A$  and  $B$  interacting to form a third species  $C$  ( $A + B \leftrightarrow C$ ), the equilibrium constant is calculated as:

$$K_{\text{eq}} = \exp\left(-\frac{\Delta G}{RT}\right) \quad (2)$$

where  $\Delta G$  is the change in standard Gibbs free energy.

The values of equilibrium constants for  $\text{SO}_3$  and PA hydration, rate constants of unimolecular decomposition of the pre-reactive intermediates and rate constants of  $\text{H}_2\text{O}/\text{PA}$ -catalyzed  $\text{SO}_3$  hydrolysis, calculated at 298 K are shown in **Tables S2** and **S3** in the Supplement.

The sentence at Line 123 was modified as given below to highlight the numerical values of equilibrium constants and reaction rate constants:

The determination of equilibrium constants and unimolecular rate constants was executed using the KiSThelP program, and their numerical values are given in **Tables S2** and **S3** in the Supplement.

5) Regarding the cluster formation:

- a) 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.

Despite the well-known clustering ability of water to sulfuric acid, several theoretical and experimental studies have shown that water would rather evaporate back from the cluster, owing to its high evaporation rate, more especially as the number of sulfuric acid molecules in the cluster increases and when there are base molecules present.

For clarifications, we have added the following in the revised manuscript.

Line 126:

Although sulfuric acid as a monomer is known to cluster effectively with water at relevant atmospheric conditions, several studies have demonstrated that the binding strength of water significantly decreases as sulfuric acid is clustered to other sulfuric acid and base molecules (Temelso et al., 2012a; Temelso et al., 2012b; Henschel et al., 2014; Tsona et al., 2015). Moreover, clusters dynamics simulations have shown that despite its clustering to sulfuric acid and sulfuric acid-based clusters, water rapidly evaporates from the cluster owing to its high evaporation rate, more especially when base molecules are present in the cluster. As a result, most atmospheric sulfuric acid-based clusters are detected in their dry state, exclusively (Almeida et al., 2013; Olenius et al., 2013). It follows that though water would play a certain role in the cluster thermodynamics, its net effect on particle formation rate is negligible. Hence, water was not included in the studied clusters.

- b) 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?

To select the cluster structures, several initial configurations were generated manually by arranging the participating molecules in different directions and pre-optimizing them. By stepwise addition of monomers to a cluster, larger clusters were built. Depending on the cluster size, 10-30 initial configurations of each cluster were pre-optimized at the M062X/6-31+G(d) level of theory and the best structures with energies within 3 kcal mol<sup>-1</sup> similar to the lowest energy configuration were re-optimized at the M062X/6-31++G(d,p) level of theory. Although the 6-31++G(d,p) basis set is somewhat smaller than the 6-311++G(3df,3pd) basis set used in the thermodynamics and reaction kinetics part, a benchmark study has shown that the use of the 6-31++G(d,p) basis set instead of 6-311++G(3df,3pd) in modeling sulfuric acid-based clusters only introduces low errors in the Gibbs free energy, yet significantly reducing the computation cost (Elm and Mikkelsen, 2014). Hence, we chose the M062X/6-31++G(d,p) method for optimizing the modeled clusters.

The following was added in the revised manuscript for clarifications:

Line 135:

A number of initial configurations of SA-NH<sub>3</sub> clusters were taken from previously published results (Ortega et al., 2012) and re-optimized with the M06-2X/6-31++G(d,p), while those containing PA were built by stepwise addition of monomers to the relevant cluster. On this basis, several starting configurations were generated manually by arranging the participating

molecules/clusters in different directions. Depending on the cluster size, 10-30 initial configurations of each cluster were pre-optimized at the M062X/6-31+G(d) level of theory and all identified structures within 3 kcal mol<sup>-1</sup> of the lowest energy structure were thereafter re-optimized with the M06-2X/6-31++G(d,p) method and the vibrational frequency analysis were subsequently performed at the same level of theory. It has been shown that the reduction from 6-311++G(3df,3pd) to 6-31++G(d,p) basis set for sulfuric acid-based cluster formation induces very little errors in the thermal contribution to the Gibbs free energy, with no further substantial effect on the single point energy, yet sufficiently reducing the computation cost (Elm and Mikkelsen, 2014). The electronic energies of M06-2X/6-31++G(d,p) optimized structures were further corrected with the DLPNO-CCSD(T)/aug-cc-pVTZ method.

## References

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