

We thank the reviewer for your helpful comments. We largely agree with your constructive advice, and have carefully revised our manuscript. In the following, the detailed response to your comments is listed. All changes in revised manuscript have been marked with green color. In the responses below, responses are marked in purple color. And the corresponding content in revised manuscript still is shown in green in these responses.

Author Responses to Anonymous Referee #3 (RC2)

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.

Reply: We appreciate the reviewer for your comments and advice. We have revised the manuscript on the basis of your comments and advice. The detail replies are itemized below.

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 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.

Reply: The expression "the oxalic acid-catalyzed SO₃ hydration can compete with water-catalyzed SO₃ hydration" is really inappropriate. We have changed the expression to "the oxalic acid-catalyzed SO₃ hydration can play an important role in promoting the SO₃ hydration". In the oxalic acid or water catalyzed SO₃ hydration reaction, two factors (rate constant and concentration) affect the reaction rate. As shown in Equation 11 and Equation 12 in the manuscript, the comparison of the rate for oxalic acid

and water catalyzed SO₃ hydration is equal to the product of rate constant ratio ($k_{\text{OA}}/k_{\text{water}}$) and concentration ratio ($[\text{OA}]/[\text{water}]$). Although the concentration of water is great larger than that of oxalic acid, on certain conditions, the higher catalytic effect of oxalic acid for SO₃ hydration (higher rate constant) can compensate for the highly concentration difference between water vapor and oxalic acid. According to the analysis about the two factors, it has shown that the oxalic acid-catalyzed reaction just is 2 orders of magnitude slower than water-catalyzed reaction at 10 km altitude, and at 12 km altitude, the water-catalyzed hydration reaction is approximately 10 times faster than the oxalic acid-catalyzed SO₃ hydration. These results indicate that the oxalic acid-catalyzed SO₃ hydration can play an important role in promoting the SO₃ hydration in the upper troposphere. However, the expression "the oxalic acid-catalyzed SO₃ hydration can compete with water-catalyzed SO₃ hydration", especially using the word "compete", is inappropriate. We have changed it in the revised manuscript, which also is put below:

Abstract, Page 1, line 16 - 18: Compared with the rates of SO₃ hydration reaction catalyzed by oxalic acid and water, it can be found that, in the upper troposphere, the oxalic acid-catalyzed SO₃ hydration can play an important role in promoting the SO₃ hydration.

Conclusion, Page 13, line 2 - 3: Based on the two factors, our calculation shows that, in the upper troposphere, the oxalic acid can play an important role in SO₃ hydration to form H₂SO₄.

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!

Reply: Thank you for your comments. Using the sentence, we want to express that the HAT process in the atmosphere can occur in some addition, decomposition, isomerization, and abstraction reactions. We know that these reactions are parallel. We express our thought unclearly, and we thank you for pointing out this. We have corrected the sentence in the revised manuscript. The new sentence is also shown below:

Page 2, line 1 - 4: The hydrogen atom transfer process can also be found in some addition (Steudel, 1995; Williams et al., 1983; Courmier et al., 2005; Zhang and Zhang, 2002), decomposition (Rayez et al., 2002; Kumar and Francisco, 2015; Gutbrod et al., 1996), isomerization (Zheng and Truhlar, 2010; Atkinson, 2007), and abstraction reactions (Ji et al., 2013; Ji et al., 2017).

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.

Reply: Thank you for your comments. We have added some contents to compare binding energies of water dimers, $\text{SO}_3 \cdots \text{H}_2\text{O}$ complex and RC1 in our manuscript with that in the previous paper, and have deleted the content about the binding energies of PC1. For the binding energies, it always is used in the quantum chemical calculations to describe the reaction pathway.

The added contents are as follows:

Page 7, line 9 - 13: Moreover, the binding energy of water dimer is consistent with its experimental value of $3.15 \pm 0.03 \text{ kcal mol}^{-1}$ (Rocher-Casterline et al., 2011), and with theoretical results of 2.90 (Torrent-Sucarrat et al., 2012), 2.97 (Long et al., 2013), 3.14 (Hazra and Sinha, 2011) and 3.30 kcal mol^{-1} (Klopper et al., 2000). In $\text{SO}_3 \cdots \text{H}_2\text{O}$ complex, the binding energy of 7.38 kcal mol^{-1} in our paper agrees with that from theoretical estimates in the literature: 7.60 (Torrent-Sucarrat et al., 2012), 7.42 (Long et al., 2013), 7.25 (Hazra and Sinha, 2011) and 7.77 kcal mol^{-1} (Long et al., 2012).

Page 7, line 15 - 16: The RC1 has the binding energy of 14.12 kcal mol^{-1} relative to $\text{SO}_3 + \text{H}_2\text{O} \cdots \text{H}_2\text{O}$, which is in accord with 13.60 (Torrent-Sucarrat et al., 2012) and 13.76 kcal mol^{-1} (Long et al., 2013).

For PC1, we have deleted the content about binding energies (old page 6, line 20, and old page 7 1 - 2). The deleted contents are list with strikethrough as follows:

~~The post-reactive complex (PC1) which is the complex of sulfuric acid with water is 13.34 kcal mol^{-1} below the RC1. In addition, the binding energy of PC1 is 11.02 kcal mol^{-1} compared to isolated sulfuric and water.~~

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.

Reply: We have added the description about the catalyzed process. For water-catalyzed hydration reaction of SO₃, the added content can be found in Page 7, line 4 - 6, which also is shown as follows:

In the hydration process, the additional water molecule serves as a catalyst that can promote the reaction by making a bridge in the hydrogen atom transfer from water to SO₃.

For oxalic acid-catalyzed hydration reaction of SO₃, we have written the new content to describe the catalyzed process (Page 8, line 10 - 11), which also is put below:

In this process, oxalic acid serves as a catalyst to promote SO₃ hydration reaction by making a bridge when the hydrogen atom transfers from H₂O to SO₃.

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 twopoint 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.

Reply: Thank you for your comments and advice. All species, which can form the two-point hydrogen bond with SO₃ and H₂O, have the potential to catalyze SO₃ hydration reaction. However, the enhancement effect of these species on SO₃ hydration reaction in the atmosphere needs to evaluate. Although some species can catalyze SO₃ hydration, the catalytic effect of the species is not enough to compensate for the very high difference in the concentration of water vapor and the species. For these species, it is of minor importance in the atmosphere for enhancing SO₃ hydration.

We accept your advice. We summarized the relationship with these species and the enhancement of the hydration reaction of SO₃ in the revised manuscript. The corresponding contents also are shown as follows:

Page 12, line 6 - 12: It has been shown that some species including nitric acid, sulfuric acid, formic acid, ammonia, hydroperoxy radical and oxalic acid in our study can catalyze the SO₃ hydration reaction. By forming two-point hydrogen bond, these species can make a bridge to promote the hydration reaction. It may be concluded that, as long as the species can form two-point hydrogen bond with water molecule and SO₃, it has the potential to promote the SO₃ hydration reaction. However, the real atmospheric importance about the species-catalyzed SO₃ hydration reaction needs to be evaluated. That is, compared to water catalyzed SO₃ hydration reaction, the species must have the sufficient catalytic effect, leading to the increase of rate constants, so as to compensate for the highly concentration difference between water vapor and the species.

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. 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.

Reply: For the rate constant, we will firstly explain the reason for the result and then describe how to adjust it. When a catalyst occurs, the process of SO₃ hydration reaction can be formulated as (M represents H₂O or oxalic acid conformers in this manuscript):

channel 1:



channel 2 :

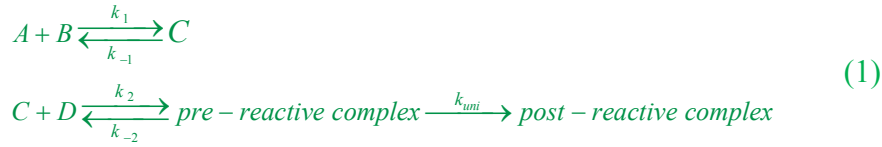


In the initial manuscript, rate calculation started from (1b) and (2b), and (1a) and (1b) are not considered. The reason is that the rate from (1b) can be described as $v = k[SO_3 \cdots H_2O][M]$. And the relative rate between oxalic acid and water catalyzed SO₃ hydration is $v_{OA}/v_{water} = k_{OA}[SO_3 \cdots H_2O][OA]/k_{water}[SO_3 \cdots H_2O][H_2O] = k_{OA}[OA]/k_{water}[H_2O]$. The concentration of SO₃⋯H₂O complex can be eliminated.

Using the method above, the calculated rate constant is not the rate constant of the whole hydration process. So, the rate constant is larger than the limit value. As we focus on the relative rate, when reaction processes (1b) and (2b) are selected as the entrance of rate calculation, we can also obtain the relative rate so as to evaluate the importance of oxalic acid. This is the reason that we select the (1b) and (2b) as the entrance of rate calculation, and that the rate constant is larger than the limit value.

But for making the rate constant more meaningful, we recalculated rate constants of the whole hydration process (for channel 1, including (1a) and (1b); for channel, including (2a) and (2b)). The method has been adjusted in the revised manuscript. The changed content also is shown below:

Page 4, line 18 - 19:

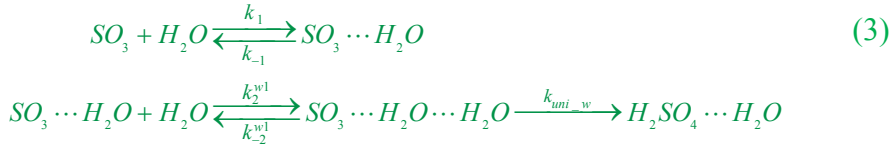


Page 5, line 1:

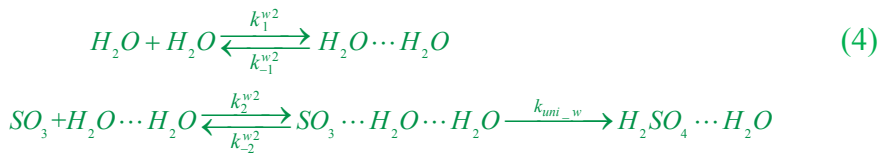
$$v = \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}} k_{uni} [A][B][D] = K_{eq1} K_{eq2} k_{uni} [A][B][D] \tag{2}$$

Page 5, line 5 - 10:

Reaction 1:



Reaction 2:



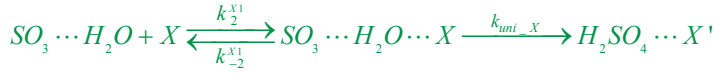
The corresponding rates are that:

$$v_{w1} = \frac{k_1}{k_{-1}} \frac{k_2^{w1}}{k_{-2}^{w1}} k_{uni-w} [SO_3][H_2O][H_2O] = K_{eq1} K_{eq2}^{w1} k_{uni-w} [SO_3][H_2O][H_2O] = k_{w1} [SO_3][H_2O][H_2O] \tag{5}$$

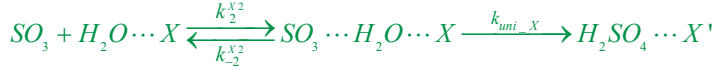
$$v_{w2} = \frac{k_1^{w2}}{k_{-1}^{w2}} \frac{k_2^{w2}}{k_{-2}^{w2}} k_{uni-w} [SO_3][H_2O][H_2O] = K_{eq1}^{w2} K_{eq2}^{w2} k_{uni-w} [SO_3][H_2O][H_2O] = k_{w2} [SO_3][H_2O][H_2O] \tag{6}$$

Page 5, line 12 - 14 and Page 6, line 1 - 2:

Reaction X1:



Reaction X2:



Page 6, line 5 - 13:

$$v_{X1} = \frac{k_1}{k_{-1}} \frac{k_2^{X1}}{k_{-2}^{X1}} k_{uni_X} [SO_3][H_2O][X] = K_{eq1} K_{eq2}^{X1} k_{uni_X} [SO_3][H_2O][X] = k_{X1} [SO_3][H_2O][X] \quad (9)$$

$$v_{X2} = \frac{k_1^{X2}}{k_{-1}^{X2}} \frac{k_2^{X2}}{k_{-2}^{X2}} k_{uni_X} [SO_3][H_2O][X] = K_{eq1}^{X2} K_{eq2}^{X2} k_{uni_X} [SO_3][H_2O][X] = k_{X2} [SO_3][H_2O][X] \quad (10)$$

To assess the importance of oxalic acid in SO₃ hydration to H₂SO₄ in the atmosphere, the relative rate can be used as:

$$\frac{v_{X1}}{v_{w1}} = \frac{k_{X1} [SO_3][H_2O][X]}{k_{w1} [SO_3][H_2O][H_2O]} = \frac{k_{X1} [X]}{k_{w1} [H_2O]} \quad (11)$$

$$\frac{v_{X2}}{v_{w2}} = \frac{k_{X2} [SO_3][H_2O][X]}{k_{w2} [SO_3][H_2O][H_2O]} = \frac{k_{X2} [X]}{k_{w2} [H_2O]} \quad (12)$$

It can easily be inferred from these equations that the rate constants are same for Reaction 1 (k_{w1}) and Reaction 2 (k_{w2}), as well as for Reaction X1 (k_{X1}) and Reaction X2 (k_{X2}) (for proof, see Supplement, Text S1). Thus, the relative rate values in Equation 11 and Equation 12 are same. Base on these reasons, we will only compare the relative rate v_{X1}/v_{w1} in this paper.

In addition, we also recalculated the single point energy using the level of theory (CCSD(T)/cc-pV(T+d)Z) so as to obtain the more accurate result. By adjusting the method for the rate calculation and changing the energy calculation method, we can obtain more meaningful and accurate results. New tables about rate constants, relative rate constants and relative rate are shown in revised manuscript (Table 1, Table 2 and Table 5). We also put the old and new tables below:

The old Table 1:

Table 1. Rate constants (in cm³ molecule⁻¹ s⁻¹) of SO₃ hydration reaction catalyzed by water and by oxalic acid at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
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P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
k_{w1}	1.51×10^{-12}	2.01×10^{-12}	2.99×10^{-12}	4.62×10^{-12}	7.44×10^{-12}	1.27×10^{-11}	2.26×10^{-11}	3.13×10^{-11}
k_{w2}	3.12×10^{-12}	5.06×10^{-12}	9.95×10^{-12}	2.08×10^{-11}	4.71×10^{-11}	1.16×10^{-10}	3.15×10^{-10}	5.46×10^{-10}
k_{cT11}	5.87×10^{-8}	1.26×10^{-7}	3.67×10^{-7}	1.19×10^{-6}	4.39×10^{-6}	1.86×10^{-5}	9.33×10^{-5}	2.29×10^{-4}
k_{cT12}	1.05×10^{-9}	1.94×10^{-9}	4.60×10^{-9}	1.19×10^{-8}	3.40×10^{-8}	1.09×10^{-7}	4.02×10^{-7}	8.27×10^{-7}
k_{tT11}	1.99×10^{-6}	4.84×10^{-6}	1.69×10^{-5}	6.70×10^{-5}	3.07×10^{-4}	1.66×10^{-3}	1.10×10^{-2}	3.12×10^{-2}
k_{tT12}	5.81×10^{-8}	1.24×10^{-7}	3.60×10^{-7}	1.16×10^{-6}	4.26×10^{-6}	1.80×10^{-5}	8.96×10^{-5}	2.19×10^{-4}
k_{tC11}	3.10×10^{-6}	7.83×10^{-6}	2.88×10^{-5}	1.21×10^{-4}	5.88×10^{-4}	3.40×10^{-3}	2.42×10^{-2}	7.18×10^{-2}
k_{tC12}	7.77×10^{-8}	1.70×10^{-7}	5.13×10^{-7}	1.73×10^{-6}	6.58×10^{-6}	2.91×10^{-5}	1.53×10^{-4}	3.85×10^{-4}
k_{cC11}	1.02×10^{-5}	2.65×10^{-5}	1.02×10^{-4}	4.49×10^{-4}	2.32×10^{-3}	1.43×10^{-2}	1.09×10^{-1}	3.35×10^{-1}
k_{cC12}	5.48×10^{-8}	1.16×10^{-7}	3.37×10^{-7}	1.08×10^{-6}	3.94×10^{-6}	1.65×10^{-5}	8.21×10^{-5}	1.99×10^{-4}

The new Table 1:

Table 1. Rate constants (in $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$) of SO_3 hydration reaction catalyzed by water and by oxalic acid at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
k_{w1} (k_{w2})	4.21×10^{-31}	9.74×10^{-31}	3.19×10^{-30}	1.18×10^{-29}	4.94×10^{-29}	2.45×10^{-28}	1.46×10^{-27}	3.92×10^{-27}
k_{cT11} (k_{cT12})	6.45×10^{-28}	2.16×10^{-27}	1.18×10^{-26}	7.67×10^{-26}	6.09×10^{-25}	6.09×10^{-24}	8.00×10^{-23}	3.35×10^{-22}
k_{tT11} (k_{tT12})	2.32×10^{-26}	8.79×10^{-26}	5.81×10^{-25}	4.63×10^{-24}	4.56×10^{-23}	5.86×10^{-22}	1.02×10^{-20}	4.97×10^{-20}
k_{tC11} (k_{tC12})	4.08×10^{-26}	1.62×10^{-25}	1.13×10^{-24}	9.55×10^{-24}	1.01×10^{-22}	1.40×10^{-21}	2.64×10^{-20}	1.35×10^{-19}
k_{cC11} (k_{cC12})	1.39×10^{-25}	5.70×10^{-25}	4.17×10^{-24}	3.71×10^{-23}	4.17×10^{-22}	6.15×10^{-21}	1.24×10^{-19}	6.61×10^{-19}

The old Table 2:

Table 2. Relative rate constants of oxalic acid catalyzed SO_3 hydration with respect to water catalyzed SO_3 hydration at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
k_{cT11}/k_{w1}	3.88×10^4	6.27×10^4	1.23×10^5	2.58×10^5	5.90×10^5	1.47×10^6	4.12×10^6	7.30×10^6
k_{cT12}/k_{w2}	3.36×10^2	3.83×10^2	4.63×10^2	5.70×10^2	7.22×10^2	9.41×10^2	1.28×10^3	1.52×10^3
k_{tT11}/k_{w1}	1.31×10^6	2.41×10^6	5.65×10^6	1.45×10^7	4.13×10^7	1.31×10^8	4.84×10^8	9.95×10^8
k_{tT12}/k_{w2}	1.86×10^4	2.45×10^4	3.62×10^4	5.58×10^4	9.04×10^4	1.55×10^5	2.85×10^5	4.00×10^5
k_{tC11}/k_{w1}	2.05×10^6	3.90×10^6	9.62×10^6	2.61×10^7	7.91×10^7	2.69×10^8	1.07×10^9	2.29×10^9
k_{tC12}/k_{w2}	2.49×10^4	3.37×10^4	5.16×10^4	8.26×10^4	1.40×10^5	2.51×10^5	4.88×10^5	7.06×10^5
k_{cC11}/k_{w1}	6.73×10^6	1.32×10^7	3.42×10^7	9.72×10^7	3.12×10^8	1.13×10^9	4.80×10^9	1.07×10^{10}
k_{cC12}/k_{w2}	1.76×10^4	2.30×10^4	3.39×10^4	5.19×10^4	8.37×10^4	1.43×10^5	2.61×10^5	3.65×10^5

The new Table 2:

Table 2. Relative rate constants of oxalic acid catalyzed SO₃ hydration with respect to water catalyzed SO₃ hydration at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
k_{cTt}/k_{w1}	1.53×10^3	2.21×10^3	3.70×10^3	6.52×10^3	1.23×10^4	2.49×10^4	5.49×10^4	8.54×10^4
k_{tTt}/k_{w1}	5.50×10^4	9.03×10^4	1.82×10^5	3.94×10^5	9.24×10^5	2.40×10^6	6.98×10^6	1.27×10^7
k_{cCt}/k_{w1}	9.70×10^4	1.66×10^5	3.53×10^5	8.12×10^5	2.05×10^6	5.73×10^6	1.81×10^7	3.45×10^7
k_{cCtI}/k_{w1}	3.31×10^5	5.86×10^5	1.31×10^6	3.16×10^6	8.44×10^6	2.51×10^7	8.54×10^7	1.69×10^8

The old Table 5:

Table 5. Relative rate of SO₃ hydration reaction catalyzed by oxalic acid and by water at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
${}^a v_{SO_3 \cdots H_2O+}$								
$OA/v_{SO_3 \cdots H_2O+}$	8.62×10^{-5}	3.54×10^{-4}	1.00×10^{-3}	4.08×10^{-3}	1.82×10^{-2}	9.74×10^{-2}	1.12	6.78

^aThe rate $v_{SO_3 \cdots H_2O+OA}$ represents the sum of reaction rate for SO₃⋯H₂O complex with four oxalic acid conformers (cTt, tTt, tCt, cCt). The rate ($v_{SO_3 \cdots H_2O+cTt}/v_{SO_3 \cdots H_2O+H_2O}$, $v_{SO_3 \cdots H_2O+tTt}/v_{SO_3 \cdots H_2O+H_2O}$, $v_{SO_3 \cdots H_2O+tCt}/v_{SO_3 \cdots H_2O+H_2O}$, $v_{SO_3 \cdots H_2O+cCt}/v_{SO_3 \cdots H_2O+H_2O}$) are shown in Table S10.

The new Table 5:

Table 5. Relative rate of SO₃ hydration reaction catalyzed by oxalic acid and by water at different altitudes.

altitude (km)	0	0	2	4	6	8	10	12
P (bar)	1.01325	1.01325	0.795	0.617	0.472	0.357	0.265	0.194
T (K)	298.15	288.15	275.15	262.17	249.19	236.22	223.25	216.65
${}^a v_{OA1}/v_{w1}$	3.87×10^{-6}	1.43×10^{-5}	3.47×10^{-5}	1.20×10^{-4}	4.43×10^{-4}	1.95×10^{-3}	1.80×10^{-2}	9.53×10^{-2}

^aThe rate v_{OA1} represents the sum of reaction rate for Reaction X1 (X=cTt, tTt, tCt, cCt). The rate (v_{cTt}/v_{w1} , v_{tTt}/v_{w1} , v_{tCt}/v_{w1} , v_{cCtI}/v_{w1}) are shown in Table S10.

As these data have been changed, the corresponding discussion is also different. We rewrote these corresponding contents in the revised manuscript. These new contents also are shown as follows:

Page 10, line 13 - 16: As shown in Table 1, the rate constant of the Reaction 1 changes from $4.21 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ (298.15 K at 0 km altitude) to $3.92 \times 10^{-27} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ (216.15 K at 12 km altitude). For the Reaction X1, the transformation of rate constants in the range of altitudes can also be found (k_{cTtI} : from 6.45×10^{-28} to 3.35×10^{-22} ; k_{tTtI} : from 2.32×10^{-26} to 4.97×10^{-20} ; k_{tCtI} : from 4.08

$\times 10^{-26}$ to 1.35×10^{-19} ; k_{cCtI} : from 1.39×10^{-25} to 6.61×10^{-19} $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$).

Page 10, line 17 - 19: Obviously, the rate constant in the oxalic acid-catalyzed SO_3 hydration reaction is about 10^3 - 10^8 times larger than that for water-catalyzed SO_3 hydration reaction within the range of altitudes.

Page 11, line 20 - 23: As shown in Table 5, reaction rate ratios between the SO_3 hydration reactions catalyzed oxalic acid conformers (cTt, tTt, tCt and cCt) and the SO_3 hydration reaction catalyzed by H_2O are described. At an altitude of 0 km, the rate ratio for these two reactions is in the range of 10^5 - 10^6 at two temperatures (298.15 K and 288.15 K), which indicates that the oxalic acid-catalyzed SO_3 hydration is of minor importance at 0 km with different temperatures.

Page 12, line 1 - 5: When the altitude increases to 10 km, the oxalic acid-catalyzed reaction is just 2 orders of magnitude slower than water-catalyzed reaction. At 12 km altitude, the water-catalyzed hydration reaction is approximately 10 times faster than the oxalic acid-catalyzed SO_3 hydration. To sum up, the comparison of relative rate shows that, in the upper troposphere, the oxalic acid can play a significant role in enhancing SO_3 hydration to H_2SO_4 .

7. The authors mentioned that “hydroperoxy radical, formic acid, sulfuric acid (TorrentSucarrat et al., 2012), nitric acid and ammonia have been reported to replace the second water to catalyze the hydration reaction of SO_3 .” I think the authors should compare the catalytic effect of these species with oxalic acid?

Reply: Thank you for your advice. We have compared the catalytic effect of these species with oxalic acid, and found that the oxalic acid has a good performance. That is, the catalytic effect of oxalic acid in SO_3 hydration reaction is better than nitric acid, sulfuric acid, and similar to formic acid, but weaker than ammonia. The added content are shown in revised manuscript (Page 10, line 21 - 23 and Page 11, line 1 - 7), which also is put below:

As seen from Table2, at 298.15 K, the oxalic acid-catalyzed SO_3 hydration reaction is 10^3 - 10^5 faster than the corresponding water-catalyzed reaction (k_{cTtI}/k_{wI} : 1.53×10^3 ; k_{tTtI}/k_{wI} : 5.50×10^4 ; k_{tCtI}/k_{wI} : 9.70×10^4 ; k_{cCtI}/k_{wI} : 3.31×10^5). In order to evaluate the catalytic effect of oxalic acid, we also list the rate constant ratio between other species and water catalyzed SO_3 hydration reaction. At 298

K, the nitric acid catalyzed rate constant is just 1.19 times larger than water catalyzed rate constant (Long et al., 2013). When sulfuric acid functions as autocatalyst, the value of rate constant ratio is around 10^2 (Torrent-Sucarrat et al., 2012). When the formic acid acts as a catalyst, its rate constant is 10^4 greater than that of water-catalyzed SO_3 hydration at 300 K (Hazra and Sinha, 2011). The rate constant for ammonia catalyzed SO_3 hydration is 7 orders of magnitude larger than that for water catalyzed rate constant at 298 K (Bandyopadhyay et al., 2017). These results indicate that the catalytic effect of oxalic acid in SO_3 hydration reaction is better than nitric acid, sulfuric acid, and similar to formic acid, but weaker than ammonia.

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

Reply: Thank you for your advice. The English language is edited by an English teacher. The revision has been marked in green color in the revised manuscript. We also put these revisions below:

Page 1, line 13: "Some atmospheric species can involve in and facilitate the reaction" is modified to "Some atmospheric species can be involved in and facilitate the reaction".

Page 1, line 15: "The energy barrier of SO_3 hydration reaction catalyzed by oxalic acid (cTt, tTt, tCt and cCt conformers) is about or below 1 kcal mol^{-1} , ..." is modified to "The energy barrier of SO_3 hydration reaction catalyzed by oxalic acid (cTt, tTt, tCt and cCt conformers) is a little higher or less than 1 kcal mol^{-1} , ...".

Page 2, line 4: "These atmospheric HAT reactions have a main feature that two-point hydrogen bond can occur ..." is modified to "These atmospheric HAT reactions display a main feature that two-point hydrogen bond can occur ...".

Page 2, line 8: "Thus, the effect of catalysts on promoting atmospheric HAT reactions has attracted more attention of atmospheric scientists" is modified to "Thus, the effect of catalysts on promoting atmospheric HAT reactions has attracted more attention from atmospheric scientists".

Page 2, line 11: "For the reaction $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$, the pre-reactive $\text{SO}_3 \cdots \text{H}_2\text{O}$ complex firstly is formed, and the complex then rearrange to form H_2SO_4 , which was proposed by Castleman et al" is modified to "For the reaction $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$, the pre-reactive $\text{SO}_3 \cdots \text{H}_2\text{O}$ complex is formed firstly, and the complex is then rearranged to produce H_2SO_4 , which was proposed by Castleman et al".

Page 2, line 19: "It has also been shown that some other atmosphere molecules can behave as a catalyst to promote the hydration of SO_3 " is modified to "It has also been shown that some other atmospheric molecules can serve as a catalyst to promote the hydration of SO_3 ".

Page 3, line 2: "In addition to accumulating in aerosols ..." is modified to "In addition to its accumulation in aerosols ...".

Page 3, line 6: "... that it can form stable complexes with water ..." is modified to "... that it can generate stable complexes with water ...".

Page 3, line 8: "The potential of oxalic acid for contributing to the NPF is mainly attributed to its capability of forming hydrogen bond with hydroxyl and/or carbonyl-type functional group" is modified to "For oxalic acid, its potential to promote the NPF is mainly attributed to its capability of forming hydrogen bond with hydroxyl and/or carbonyl-type functional group".

Page 3, line 14: "As is known, oxalic acid can exist in several conformational forms ..." is modified to "It is known that oxalic acid can exist in several conformational forms ...".

Page 3, line 22: "The geometric structures including all reactant, complex, transition state and products were optimized using M06-2X method (Zhao and Truhlar, 2008) with 6-311++G(3df,3pd) basis set" is modified to "The geometric structures, including all reactants, complexes, transition states and products, were optimized using M06-2X method (Zhao and Truhlar, 2008) with 6-311++G(3df,3pd) basis set".

Page 4, line 2 - 3: "... through the criterion that no imaginary frequencies for the local minimum point and one imaginary frequency for transition states" is modified to "... through the criterion that there are

no imaginary frequencies for the local minimum point and one imaginary frequency for transition states".

Page 4, line 8: "To obtain the conformational population of oxalic acid in different temperature more accurately ..." is modified to "To obtain more accurate conformational population of oxalic acid in different temperature ...".

Page 4, line 16 - 17: "On the basis of the discussion in this paper, it can conclude that the hydration reactions begin with the formation of pre-reactive complex, and then undergo a transition state to form post-reactive complex" is modified to "Base on the discussion in this paper, it can be concluded that SO₃ hydration reactions begin with the formation of pre-reactive complex, and then pass by a transition state to form a post-reactive complex".

Page 5, line 2: "... k_{uni} is the rate constant for unimolecular reaction of pre-reactive complex to post-reactive complex" is modified to "... k_{uni} is the rate constant for a unimolecular reaction from the pre-reactive complex to post-reactive complex".

Page 5, line 10 - 11: "For oxalic acid-catalyzed hydration reaction of SO₃, it also has two reaction channels and has the similar features as the water-assisted hydration process" is modified to "For oxalic acid-catalyzed hydration reaction of SO₃, there are two reaction channels and the same features as in the water-assisted hydration process".

Page 6, line 16 - 17: "Although the hydration of SO₃ involving two water molecules has been talked about many times, we still include it in our paper so as to compare this reaction with ..." is modified to "Although the hydration of SO₃ involving two water molecules has been discussed many times, we still include it in our paper so as to compare it with ...".

Page 7, line 2 - 4: "The one is that water dimer react with SO₃ to obtain pre-reactive complex, then this complex rearrange to form H₂SO₄···H₂O complex (channel 1); the other begin with the reaction of SO₃···H₂O complex with water, the following rearrangement is the same as the channel 1 (channel 2)"

is modified to "One is that water dimer reacts with SO_3 to obtain the pre-reactive complex, then this complex is rearranged to form $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$ complex (channel 1); the other begins with the reaction of $\text{SO}_3 \cdots \text{H}_2\text{O}$ complex with water, the following reaction process is the same as the channel 1 (channel 2)".

Page 8, line 6: "The failure of this transfer is due to that the hydrogen and oxygen atom involving in two-point hydrogen bond do not come from the same carboxyl group" is modified to "The transfer failure is attributed to the fact that the hydrogen and oxygen atom involving in two-point hydrogen bond do not come from the same carboxyl group".

Page 9, line 1 - 5: "In the two channels starting from the $\text{tCt} \cdots \text{H}_2\text{O} + \text{SO}_3$ entry and $\text{SO}_3 \cdots \text{H}_2\text{O} + \text{tCt}$ entry, the same pre-reactive complex (RC_{tCt}) can be formed with the binding energy of $13.11 \text{ kcal mol}^{-1}$, $15.56 \text{ kcal mol}^{-1}$, respectively, with respect to the two reactants. The RC_{tCt} proceeds via the transition state (TS_{tCt}) lying above RC_{tCt} by $0.28 \text{ kcal mol}^{-1}$ into post-reactive complex (PC_{tCt}), which is $14.01 \text{ kcal mol}^{-1}$ more stable than the RC_{tCt} complex. The PC_{tCt} complex also can be formed from the H_2SO_4 and tTt conformer with the energy release of $17.73 \text{ kcal mol}^{-1}$ " is modified to "In the two channels, the same pre-reactive complex (RC_{tCt}) can be formed with the binding energy of $12.92 \text{ kcal mol}^{-1}$ relative to $\text{tCt} \cdots \text{H}_2\text{O} + \text{SO}_3$, $15.63 \text{ kcal mol}^{-1}$ with respect to $\text{SO}_3 \cdots \text{H}_2\text{O} + \text{tCt}$, respectively. The RC_{tCt} proceeds via the transition state (TS_{tCt}) (with energy barrier of $0.05 \text{ kcal mol}^{-1}$) into post-reactive complex (PC_{tCt}). The PC_{tCt} complex can also be generated from the H_2SO_4 and tTt conformer releasing $16.98 \text{ kcal mol}^{-1}$ of energy".

Page 9, line 14: "Another thing we want to mention is that ..." is modified to "Another point worth mentioning is that ...".

Page 11, line 8: "Based on the calculated Gibbs free energy at G4 level (see Table S8), and assuming a Boltzmann distribution, the mole fractions for oxalic acid conformers can be obtained (Table 3)" is modified to "Based on the calculated Gibbs free energy at G4 level (see Table S8) and an assumption of Boltzmann distribution, mole fractions for oxalic acid conformers can be obtained (Table 3)".

Page 12, line 21: "The results signify oxalic acid has the higher catalytic ability than water for SO₃ hydration to form H₂SO₄" is modified to "The results demonstrate that oxalic acid has the stronger catalytic ability than water for SO₃ hydration to form H₂SO₄".