Point-by-point response to the reviewers' comments

Editor

Dear Editor,

Thank you for allowing us to revise our manuscript. We also thank the reviewers for their helpful comments. We largely agree with the constructive advice of the reviewers, and have carefully revised our initial manuscript. In the following, the detailed response to comments of reviewers is listed. All changes in revised manuscript have been marked with green color. The marked-up manuscript version is also appended to the response file.

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.

Yours sincerely,

Guochun Lv
On behalf of all co-authors

Author Responses to Anonymous Referee #1 (RC1)

Using quantum chemical calculations combined with high level ab initio method; the authors studied the catalytic ability of the most common dicarboxylic acid in the atmosphere - oxalic acid - for the hydration reaction of SO3. Further, taking the real atmosphere into consideration, they found that oxalic acid-catalyzed hydration reaction can compete with the water-catalyzed reaction in the upper troposphere, which has certain significance for the formation of H_2SO_4 in the atmosphere. The work is performed with care and I believe it can be published after the following concerns are fully addressed.

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 described below.

Major comments:

1. In previous paper (Hazra et al, J. Am. Chem. Soc. 2011, 133, 17444), hydrolysis of SO3 catalyzed by formic acid in the gas phase has been studied and the result shows a near barrierless mechanism for sulfuric acid formation. Moreover, we note that formic acid is considered to be the most abundant carboxylic acid, ubiquitous in the atmosphere (Millet et al. Atmos. Chem. Phys., 2015, 15, 6283; Bannan et al. J. Geophys. Res. - Atmos, 2017, 122, 488). Thus, to make this story more interesting, I think the authors should highlight the specific characteristic of oxalic acid compared with formic acid, and add more discussion about the advantages of oxalic acid acting as a catalyst.

Reply: Thank you for your advice. Oxalic acid, as the prevalent dicarboxylic acid, really has some specific characteristic compared with formic acid. The studies have shown that dicarboxylic acid can enhance nucleation in two directions compared with momocarboxylic acid. Thus, in the oxalic acid-catalyzed SO_3 hydration reaction, the post-reactive complex (PC) still has a free carboxylic group. The PC has the potential to continue to catalyze SO_3 hydration by the free carboxylic group. In addition, the result of the manuscript shows that the PC is stable with respect to the isolate oxalic acid conformers and H_2SO_4. Thus, the PC also has the potential to promote nucleation.

We also added more discussion about the advantages of oxalic acid acting as a catalyst. In this revised manuscript, we compared the catalytic effect of oxalic acid with the nitric acid, sulfuric acid, formic acid, ammonia.

The added contents are shown in revised manuscript with the marked green color. We also put these contents below:

In Introduction section, page 3, line 9 - 11: Opposite to monocarboxylic acids, dicarboxylic acids such as oxalic acid has been proved to enhance nucleation in two directions because of its two acid moieties (Xu and Zhang, 2012).

Page 9, the last paragraph: In addition, compared to formic acid (Millet et al., 2015;Bannan et al., 2017), the SO_3 hydration reaction catalyzed by oxalic acid display some specific characteristics. Both acids can obviously decrease the energy barrier of the hydration reaction. But because oxalic acid is a dicarboxylic acid, only one in the carboxylic groups participates in the hydration reaction, and the other is free. This characteristic indicates that post-reactive complexes (PC_{tTt} and PC_{tCt}) can serve as a catalyst to continue to promote the SO_3 hydration. For these post-reactive complexes (PC_{cTt}, PC_{tTt}, PC_{tCt} and PC_{cCt}), the above result has shown that these complexes are stable compared to the isolate H_2SO_4 and oxalic acid conformers. The free carboxylic group in these complexes can also provide the interaction site when these complexes interact with other species. The free carboxylic group of these stable post-reactive complexes indicates that these complexes have the potential to participate in nucleation.

Page 10 - 11, line 21 - 23 (page 10) and line 1 - 7 (page 11): 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_{cTt1}/k_{w1}: 1.53×10^3; k_{tTt1}/k_{w1}: 5.50×10^4; k_{tCt1}/k_{w1}: 9.70×10^4; k_{cCt1}/k_{w1}: 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 an 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 (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 and sulfuric acid, and similar to formic acid, but weaker than ammonia.

2. For method and basis set of the single point energy, the CCSD(T) method with the 6-311++G(3df,3pd) is not a good match, I think it is available using at least cc-pVTZ level. If the author prefer the 6-311++G(3df,3pd) basis set when using CCSD(T) to perform the single point energy, please give the corresponding reasons.

Reply: Thank you for your comment and advice. We have recalculated the single point energy at CCSD(T)/cc-pV(T+d)Z level. As the influence of single point energy is overall, the potential energy profile and the rate constant are changed after using the new theoretic level (CCSD(T)/cc-pV(T+d)Z). For potential energy, we do not mark the changed data in the manuscript because all data are changed. Although the changed data are not marked in the revised manuscript, old and new figures are put below for showing the change:

The old Figure 1:

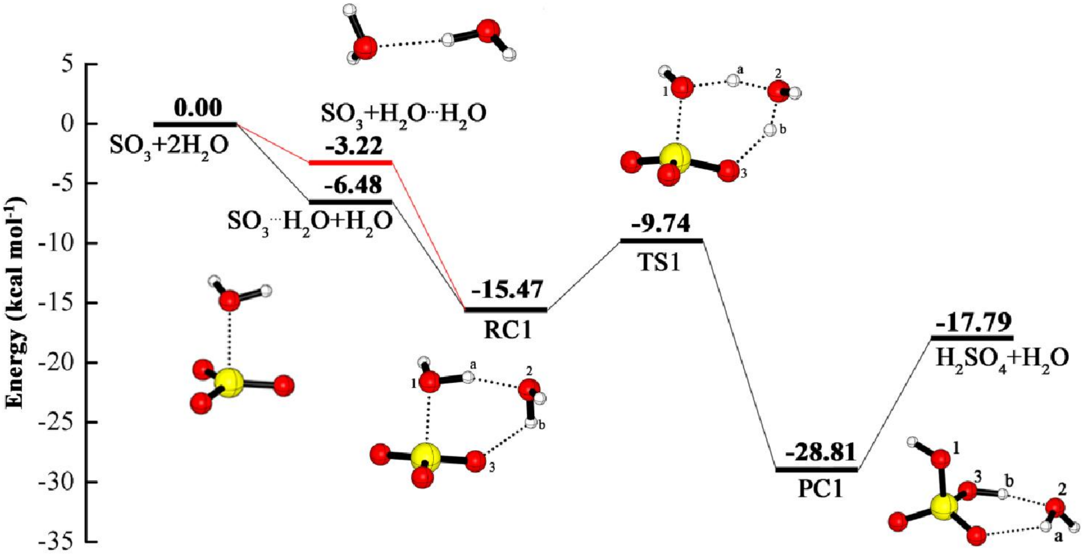


Figure 1. Calculated potential energy profile for the hydration of SO_3 with the second water as a catalyst at the CCSD(T)/6-311++G(3df,3pd)//M06-2X/6-311++G(3df,3pd) level.

The new Figure 1:

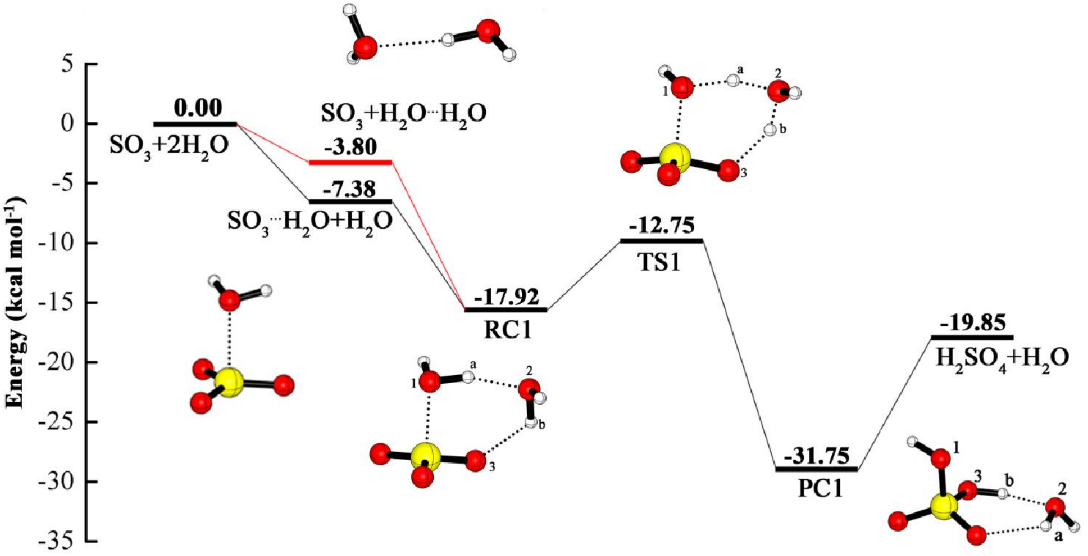
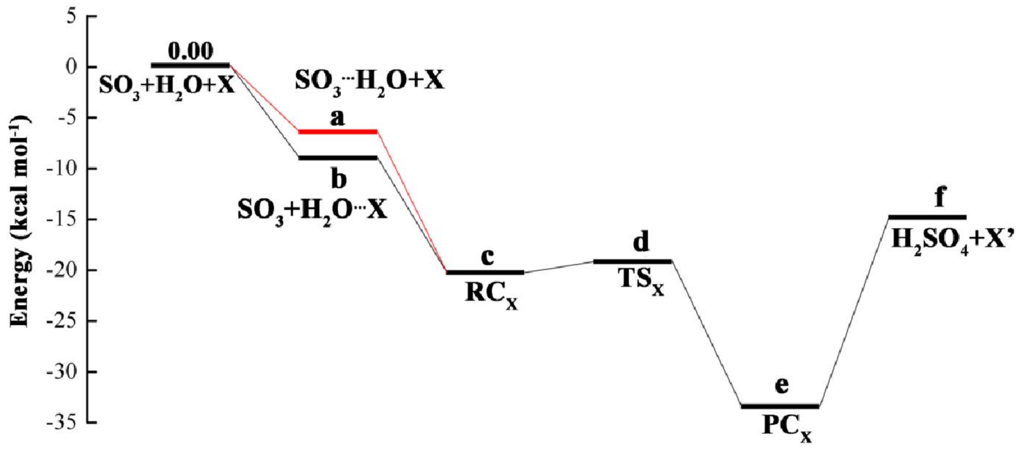


Figure 1. Calculated potential energy profile for the hydration of SO_3 with the second water as a catalyst at the CCSD(T)/cc-pV(T+d)Z//M06-2X/6-311++G(3df,3pd) level.

The old Figure 3:



When X = cTt,

a = -6.48 b = -9.05 c = -20.29 d = -18.92 e = -33.40 f = -14.86 (X'=cCt)

When X = tTt,

a = -6.48 b = -8.76 c = -21.58 d = -21.14 e = -35.33 f = -17.27 (X'=tCt)

When X = tCt,

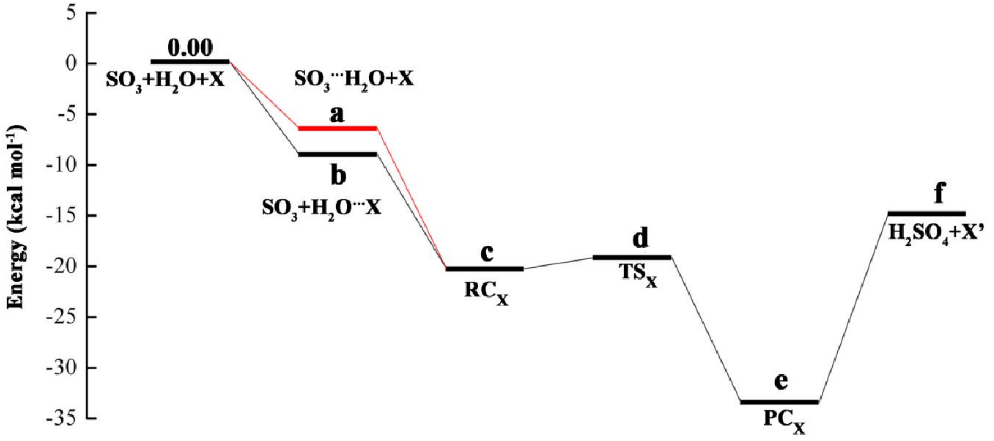
a = -6.48 b = -8.93 c = -22.04 d = -21.76 e = -36.05 f = -18.32 (X'=tTt)

When X = cCt,

a = -6.48 b = -9.92 c = -22.53 d = -22.27 e = -37.60 f = -20.73 (X'=cTt)

Figure 3. Calculated potential energy profile for the hydration of SO_3 with oxalic acid conformers (cTt, tTt, tCt and cCt) as catalysts at the CCSD(T)/6-311++G(3df,3pd) //M06-2X/6-311++G(3df,3pd) level.

The new Figure 3:



When X = cTt,

a = -7.38 b = -10.25 c = -21.20 d = -20.01 e = -34.52 f = -16.74 (X'=cCt)

When X = tTt,

a = -7.38 b = -9.92 c = -22.51 d = -22.27 e = -36.56 f = -19.22 (X'=tCt)

When X = tCt,

a = -7.38 b = -10.09 c = -23.01 d = -22.96 e = -37.45 f = -20.47 (X'=tTt)

When X = cCt,

a = -7.38 b = -11.10 c = -23.48 d = -23.49 e = -39.10 f = -22.95 (X'=cTt)

Figure 3. Calculated potential energy profile for the hydration of SO_3 with oxalic acid conformers (cTt, tTt, tCt and cCt) as catalysts at the CCSD(T)/cc-pV(T+d)Z //M06-2X/6-311++G(3df,3pd) level.

For the kinetics analysis, to make the rate constant more meaningful, we adjusted the entrance for rate constant calculation from SO_3 + $H_2O\cdots H_2O$ (or $SO_3\cdots H_2O$ + H_2O) and SO_3 + $H_2O\cdots$OA (or $SO_3\cdots$OA + H_2O) to SO_3 + H_2O + H_2O and SO_3 + H_2O + OA. And the adjustment will not affect the result of the rate comparison. The adjustment caused the great changes for Table 1, which lists the rate constant. Using the new level of theory to calculate the single point energy, it can be found from the old and new Table 5 that the relative rate decreases from 6.78 to around 0.1 at 12 km altitude. It still indicates that the oxalic acid can play a significant role in enhancing SO_3 hydration to H_2SO_4. The correspond content in revised manuscript also are described as follows:

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.

We also put the changed tables as follows:

The old Table 1:

Table 1. Rate constants (in cm^3 $molecule^{-1}$ 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}	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_{cTt1}	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_{cTt2}	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_{tTt1}	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_{tTt2}	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_{tCt1}	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_{tCt1}	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_{cCt1}	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_{cCt1}	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 cm^6 $molecule^{-2}$ s^{-1}) of SO_3 hydration reaction catalyzed by water and by oxalic acid at different altitudes.

altitude	0	0	2	4	6	8	10	12

(km)								
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_{cTt1} (k_{cTt2})	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_{tTt1} (k_{tTt2})	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_{tCt1} (k_{tCt2})	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_{cCt1} (k_{cCt2})	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_{cTt1}/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_{cTt2}/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_{tTt1}/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_{tTt2}/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_{tCt1}/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_{tCt2}/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_{cCt1}/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_{cCt2}/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 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_{cTt1}/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_{tTt1}/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_{tCt1}/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_{cCt1}/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 SO_3 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]$\nu_{SO3\cdots H2O+OA}/\nu_{SO3\cdots H2O+H2O}$	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

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

The new Table 5:

Table 5. Relative rate of SO_3 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]ν_{OA1}/ν_{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}

[a]The rate ν_{OA1} represents the sum of reaction rate for Reaction X1 (X=cTt, tTt, tCt, cCt). The rate (ν_{cTt1}/ν_{w1}, ν_{tTt1}/ν_{w1}, ν_{tCt1}/ν_{w1}, ν_{cCt1}/ν_{w1}) are shown in Table S10.

3. In Section 3.1: it is better to compare the results with previous studies to enrich the text.

Reply: Thank you for your advice. We have added the discussion about the comparison of the results with literatures. The added contents are shown in the revised manuscript (Page 7, line 8 - 14), which also are put below:

Page 7, line 9 - 13: Moreover, the binding energy of water dimer is consistent with its experimental value of 3.15 ± 0.03 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 $SO_3\cdots H_2O$ 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 $SO_3+H_2O\cdots H_2O$, which is in accord with 13.60 (Torrent-Sucarrat et al., 2012) and 13.76 kcal mol^{-1} (Long et al., 2013).

Minor comments:

1. Page1, line 12(Abstract), "can involve in" should be "can be involved in".

Reply: Thank you for pointing out our mistake. We have corrected this error. The corrected content can be seen from Abstract (Page 1, line 13), which also is shown as follows:

Some atmospheric species can be involved in and facilitate the reaction.

2. Page1, line 16 (Abstract), "the rate of SO3 hydration" should be "the rates of SO3 hydration".

Reply: We have corrected this error in the revised manuscript (Page 1, line 16). The new content is listed below:

Compared with the rates of SO_3 hydration reaction catalyzed by oxalic acid and water, it can be found that, in the upper troposphere, the oxalic acid-catalyzed SO_3 hydration can play an important role in promoting the SO_3 hydration.

3. Page 2, line 5: is it better to change the second "can" to "thus"?

Reply: We have corrected this error in the revised manuscript (Page 2, line 5). The new content is listed below:

These atmospheric HAT reactions display a main feature that two-point hydrogen bond can occur and thus facilitate hydrogen atom transfer

4. Page 2, line 11: "firstly is" should be "is firstly".

Reply: We have corrected this error in the revised manuscript (Page 2, line 11). The new content is listed below:

For the reaction $SO_3+H_2O \rightarrow H_2SO_4$, the pre-reactive $SO_3 \cdots H_2O$ complex is firstly formed, and the complex is then rearranged to produce H_2SO_4, which was proposed by Castleman et al (Holland and Castleman, 1978;Hofmann-Sievert and Castleman, 1984).

5. Page 2, line 11: "rearrange" should be "rearranges".

Reply: We have corrected this error in the revised manuscript (Page 2, line 11). The new content is listed below:

For the reaction $SO_3+H_2O \rightarrow H_2SO_4$, the pre-reactive $SO_3 \cdots H_2O$ complex is firstly formed, and the complex is then rearranged to produce H_2SO_4, which was proposed by Castleman et al (Holland and

Castleman, 1978;Hofmann-Sievert and Castleman, 1984).

6. Page 2, line 14:"takes" should be "take".

Reply: We have corrected this error in the revised manuscript (Page 2, line 13). The new content is listed below:

But the subsequent research found that this hydration reaction involving a single water molecule cannot take place in the atmosphere due to high energy barrier.

7. Page 2, line 17: "reduce" should be "reduces"

Reply: We have corrected this error in the revised manuscript (Page 2, line 17). The new content is listed below:

The promoting effect can be mainly attributed to the formation of the two-point hydrogen bond, which reduces the ring strain...

8. Page 3, line 15: "for" should be "of".

Reply: We have corrected this error in the revised manuscript (Page 3, line 17). The new content is listed below:

The rate constants of oxalic acid-catalyzed SO_3 hydration were calculated using the kinetics analysis, and compared with that of water-catalyzed hydration reaction.

9. Page 3, line 17: "... the hydration of SO3 in the second water ..." should be "... the hydration of SO3 with the second water ...".

Reply: We have corrected this error in the revised manuscript (Page 3, line 19). The new content is listed below:

...we evaluated the importance of the hydration process involving the oxalic acid relative to the hydration of SO_3 with the second water as a catalyst to form sulfuric acid

10. Page 3, line 20: "reactant, complex, transition state" should be "reactants, complexes, transition states".

Reply: We have corrected this error in the revised manuscript (Page 3, line 22). The new content is listed below:

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.

11. Page 4, lines 9-10: "..., the electronic energies based on the ..., while the partition functions obtained from ..." should be "..., the electronic energies were based on the ..., while the partition functions were obtained from ...".

Reply: We have corrected this error in the revised manuscript (Page 4, line 11 - 12). The new content is listed below:

In the kinetics analysis, the electronic energies were based on the CCSD(T)/cc-pV(T+d)Z level of theory, while the partition functions were obtained from the M06-2X/6-311++G(3df,3pd) level of theory.

12. Page 4, line 14: "..., it can conclude that the ..." should be "..., it can be concluded that the ...".

Reply: We have corrected this error in the revised manuscript (Page 4, line 16). The new content is listed below:

Base on the discussion in this paper, it can be concluded that the SO_3 hydration reactions begin with the formation of pre-reactive complex...

13. Page 5: "The corresponding rate constants are that" should be "The corresponding reaction rates are that".

Reply: We have corrected this error in the revised manuscript (Page 5, line 7). The new content is listed below:

The corresponding rates are that: ...

14. Page 6, line 10: "react" should be "reacts".

Reply: We have corrected this error in the revised manuscript (Page 7, line 2). The new content is listed below:

One is that water dimer reacts with SO_3 to obtain pre-reactive complex, then this complex is rearranged to form $H_2SO_4\cdots H_2O$ complex (channel 1); the other begins with the reaction of $SO_3\cdots H_2O$ complex with water, the following rearrangement is the same as the channel 1 (channel 2).

15. Page 6, line 11: "rearrange" should be "rearranges" and "begin" should be "begins".

Reply: We have corrected this error in the revised manuscript (Page 7, line 3). The new content is listed below:

One is that water dimer reacts with SO_3 to obtain pre-reactive complex, then this complex is rearranged to form $H_2SO_4\cdots H_2O$ complex (channel 1); the other begins with the reaction of $SO_3\cdots H_2O$ complex with water, the following rearrangement is the same as the channel 1 (channel 2).

16. Page 7, line 10: "Table S2-S5" should be "Tables S2-S5".

Reply: We have corrected this error in the revised manuscript (Page 8, line 4). The new content is listed below:

Energies, enthalpies and free energies of all relevant species for oxalic acid catalyzed hydration of SO_3 are summarized in Supplement (Tables S2 - S5).

17. Page 10, line 23: is it better to change "real" to "potential".

Reply: We have corrected this error in the revised manuscript (Page 12, line 15). The new content is listed below:

The main conclusion of this work is that oxalic acid, the most abundant dicarboxylic acid in the atmosphere, has the remarkable ability to catalyze SO_3 hydration to H_2SO_4, and has the potential impact on the H_2SO_4 formation in the atmosphere.

18. Page 11, line 3: is it better to change "The energy barrier of hydration reaction of SO3 is about or below 1 kcal mol-1" to "Other conformers can catalyze the hydration reaction and the corresponding energy barrier is a little higher or less than 1 kcal mol-1".

Reply: Thank you for your advice. We have changed this sentence in the revised manuscript (Page 12, line 20). We also put is below:

Other conformers can catalyze the hydration reaction and the corresponding energy barrier is a little higher or less than 1 kcal mol^{-1}.

19. Page 11, line 4: add "that" after "signify".

Reply: We have corrected this error in the revised manuscript and changed the word "signify" to "demonstrate" (Page 12, line 21). The new content is listed below:

The results demonstrate that oxalic acid has the higher catalytic ability than water for SO_3 hydration to form H_2SO_4.

20. Page 11, line 5: add "from the view of barrier" after "H2SO4".

Reply: Thank you for your advice. We combined the sentence with the previous sentence into a new sentence, and mentioned the two factors (rate constant and concentration). Because the rate constant contains the meaning from the view of barrier, we did not add the content. The new sentence is shown as follows:

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 SO_3 hydration to form H_2SO_4.

21. Page 22, the caption of Figure 4. Please add the unit of hydrogen bond length.

Reply: Thank you for your advice. We have added the unit in the caption of Figure 4. The new content is listed below:

Figure 4. Optimized M06-2X/6-311++G(3df,3pd) structures of reactant complexes, pre-reactive complexes, transition states and post-reactive complexes for the oxalic acid-catalyzed SO_3 hydration reaction (distance unit: angstrom).

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 SO_3 hydration can compete with water-catalyzed SO_3 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 SO_3, 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 SO_3 hydration is much great smaller than that of the oxalic acid-catalyzed SO_3 hydration. If so, maybe "the oxalic acid-catalyzed SO_3 hydration can compete with water-catalyzed SO_3 hydration" is not correct, except that the authors can prove it.

Reply: The expression "the oxalic acid-catalyzed SO_3 hydration can compete with water-catalyzed SO_3 hydration" is really inappropriate. We have changed the expression to "the oxalic acid-catalyzed SO_3 hydration can play an important role in promoting the SO_3 hydration". In the oxalic acid or water catalyzed SO_3 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 SO_3 hydration is equal to the product of rate constant ratio (k_{OA}/k_{water}) and concentration ratio ([OA]/[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 SO_3 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 SO_3 hydration. These results indicate that the oxalic acid-catalyzed SO_3 hydration can play an important role in promoting the SO_3 hydration in the upper troposphere. However, the expression "the oxalic acid-catalyzed SO_3 hydration can compete with water-catalyzed SO_3 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 SO_3 hydration reaction catalyzed by oxalic acid and water, it can be found that, in the upper troposphere, the oxalic acid-catalyzed SO_3 hydration can play an important role in promoting the SO_3 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 SO_3 hydration to form H_2SO_4.

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, $SO_3\cdots H_2O$ 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 ± 0.03 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 $SO_3 \cdots H_2O$ 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 $SO_3 + H_2O \cdots H_2O$, 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 SO_3", "Oxalic acid-catalyzed hydration reaction of SO_3" 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 SO_3, 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 SO_3.

For oxalic acid-catalyzed hydration reaction of SO_3, 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 SO_3 hydration reaction by making a bridge when the hydrogen atom transfers from H_2O to SO_3.

5. The authors pointed out that oxalic acid as one of the hydrogen donors and/or acceptors could catalyze the hydration reaction of SO_3, through the formation of twopoint hydrogen bond. Is it possible that all the hydration reaction of SO_3 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 SO_3.

Reply: Thank you for your comments and advice. All species, which can form the two-point hydrogen bond with SO_3 and H_2O, have the potential to catalyze SO_3 hydration reaction. However, the enhancement effect of these species on SO_3 hydration reaction in the atmosphere needs to evaluate. Although some species can catalyze SO_3 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 SO_3 hydration.

We accept your advice. We summarized the relationship with these species and the enhancement of the hydration reaction of SO_3 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 SO_3 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 SO_3, it has the potential to promote the SO_3 hydration reaction. However, the real atmospheric importance about the species-catalyzed SO_3 hydration reaction needs to be evaluated. That is, compared to water catalyzed SO_3 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} cm^{3} 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 SO_3 hydration reaction can be formulated as (M represents H_2O or oxalic acid conformers in this manuscript):

channel 1:

$$SO_3 + H_2O \rightleftharpoons SO_3 \cdots H_2O \qquad (1a)$$

$$SO_3 \cdots H_2O + M \rightleftharpoons SO_3 \cdots M \cdots H_2O \rightarrow H_2SO_4 \cdots M \qquad (1b)$$

channel 2 :

$$M + H_2O \rightleftharpoons M \cdots H_2O \qquad (2a)$$

$$SO_3 + M \cdots H_2O \rightleftharpoons SO_3 \cdots M \cdots H_2O \rightarrow H_2SO_4 \cdots M \qquad (2b)$$

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 $\nu = k[SO_3 \cdots H_2O][M]$. And the relative rate between oxalic acid and water catalyzed SO_3 hydration is $\nu_{OA}/\nu_{water} = k_{OA}[SO_3 \cdots H_2O][OA]/k_{water}[SO_3 \cdots H_2O][H2O] = k_{OA}[OA]/k_{water}[H2O]$. The concentration of $SO_3 \cdots H_2O$ 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:

$$\begin{gathered} A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C \\ C + D \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} pre-reactive\ complex \xrightarrow{k_{uni}} post-reactive\ complex \end{gathered} \tag{1}$$

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:

$$\begin{gathered} Recation\ 1: \\ SO_3 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SO_3 \cdots H_2O \\ SO_3 \cdots H_2O + H_2O \underset{k_{-2}^{w1}}{\overset{k_2^{w1}}{\rightleftarrows}} SO_3 \cdots H_2O \cdots H_2O \xrightarrow{k_{uni\_w}} H_2SO_4 \cdots H_2O \end{gathered} \tag{3}$$

$$\begin{gathered} Reaction\ 2: \\ H_2O + H_2O \underset{k_{-1}^{w2}}{\overset{k_1^{w2}}{\rightleftarrows}} H_2O \cdots H_2O \\ SO_3 + H_2O \cdots H_2O \underset{k_{-2}^{w2}}{\overset{k_2^{w2}}{\rightleftarrows}} SO_3 \cdots H_2O \cdots H_2O \xrightarrow{k_{uni\_w}} H_2SO_4 \cdots H_2O \end{gathered} \tag{4}$$

The corresponding rates are that:

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

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

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

$Reaction\ X1:$

$$SO_3 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SO_3 \cdots H_2O \qquad (7)$$

$$SO_3 \cdots H_2O + X \underset{k_{-2}^{X1}}{\overset{k_2^{X1}}{\rightleftarrows}} SO_3 \cdots H_2O \cdots X \xrightarrow{k_{uni\_X}} H_2SO_4 \cdots X'$$

$Reaction\ X2:$

$$H_2O + X \underset{k_{-1}^{X2}}{\overset{k_1^{X2}}{\rightleftarrows}} H_2O \cdots X \qquad (8)$$

$$SO_3 + H_2O \cdots X \underset{k_{-2}^{X2}}{\overset{k_2^{X2}}{\rightleftarrows}} SO_3 \cdots H_2O \cdots X \xrightarrow{k_{uni\_X}} H_2SO_4 \cdots X'$$

Page 6, line 5 - 13:

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

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

To assess the importance of oxalic acid in SO_3 hydration to H_2SO_4 in the atmosphere, the relative rate can be used as:

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

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

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 ν_{X1}/ν_{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 cm^3 molecule^{-1} 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}	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_{cTt1}	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_{cTt2}	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_{tTt1}	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_{tTt2}	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_{tCt1}	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_{tCt1}	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_{cCt1}	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_{cCt1}	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 cm^6 molecule^{-2} s^{-1}) of SO_3 hydration reaction catalyzed by water and by oxalic acid at different altitudes.

altitude	0	0	2	4	6	8	10	12

(km)								
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_{cTt1} (k_{cTt2})	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_{tTt1} (k_{tTt2})	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_{tCt1} (k_{tCt2})	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_{cCt1} (k_{cCt2})	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_{cTt1}/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_{cTt2}/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_{tTt1}/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_{tTt2}/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_{tCt1}/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_{tCt2}/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_{cCt1}/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_{cCt2}/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 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_{cTt1}/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_{tTt1}/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_{tCt1}/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_{cCt1}/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 SO_3 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
$^{a}\nu_{SO3\cdots H2O+OA}/\nu_{SO3\cdots H2O+H2O}$	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

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

The new Table 5:

Table 5. Relative rate of SO_3 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
$^{a}\nu_{OA1}/\nu_{w1}$	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}

^{a}The rate ν_{OA1} represents the sum of reaction rate for Reaction X1 (X=cTt, tTt, tCt, cCt). The rate (ν_{cTt1}/ν_{w1}, ν_{tTt1}/ν_{w1}, ν_{tCt1}/ν_{w1}, ν_{cCt1}/ν_{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 4.21×10^{-31} cm^{6} $molecule^{-2}$ s^{-1} (298.15 K at 0 km altitude) to 3.92×10^{-27} cm^{6} $molecule^{-2}$ 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_{cTt1}: from 6.45×10^{-28} to 3.35×10^{-22}; k_{tTt1}: from 2.32×10^{-26} to 4.97×10^{-20}; k_{tCt1}: from 4.08×10^{-26} to 1.35×10^{-19}; k_{cCt1}: from 1.39×10^{-25} to 6.61×10^{-19} cm^6 molecule^{-2} 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_{cTt1}/k_{w1}: 1.53×10^3; k_{tTt1}/k_{w1}: 5.50×10^4; k_{tCt1}/k_{w1}: 9.70×10^4; k_{cCt1}/k_{w1}: 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 $SO_3+H_2O \rightarrow H_2SO_4$, the pre-reactive $SO_3 \cdots H_2O$ 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 $SO_3 + H_2O \rightarrow H_2SO_4$, the pre-reactive $SO_3 \cdots H_2O$ 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 SO_3 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 SO_3, 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 SO_3, 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 SO_3 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 SO_3 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 SO_3 to obtain pre-reactive complex, then this complex rearrange to form $H_2SO_4\cdots H_2O$ complex (channel 1); the other begin with the reaction of $SO_3\cdots H_2O$ 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 $H_2SO_4\cdots H_2O$ complex (channel 1); the other begins with the reaction of $SO_3\cdots H_2O$ 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 tCt$\cdots H_2O$ + SO_3 entry and $SO_3\cdots H_2O$ + tCt entry, the same pre-reactive complex (RC_{tCt}) can be formed with the binding energy of 13.11 kcal mol^{-1}, 15.56 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 kcal mol^{-1} into post-reactive complex (PC_{tCt}), which is 14.01 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 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 kcal mol^{-1} relative to tCt$\cdots H_2O$ + SO_3, 15.63 kcal mol^{-1} with respect to $SO_3\cdots H_2O$ + tCt, respectively. The RC_{tCt} proceeds via the transition state (TS_{tCt}) (with energy barrier of 0.05 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 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 SO_3 hydration to form H_2SO_4" is modified to "The results demonstrate that oxalic acid has the stronger catalytic ability than water for SO_3 hydration to form H_2SO_4".

Understanding the catalytic role of oxalic acid in the SO_3 hydration to form H_2SO_4 in the atmosphere

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Abstract: The hydration of SO_3 plays an important role in atmospheric sulfuric acid formation. Some atmospheric species can be involved in and facilitate the reaction. In this work, using quantum chemical calculations, we show that oxalic acid, the most common dicarboxylic acid in the atmosphere, can effectively catalyze the hydration of SO_3. 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}, which is lower than the energy barrier of 5.17 kcal mol^{-1} for water-catalyzed SO_3 hydration. Compared with the rates of SO_3 hydration reaction catalyzed by oxalic acid and water, it can be found that, in the upper troposphere, the oxalic acid-catalyzed SO_3 hydration can play an important role in promoting the SO_3 hydration. It leads us to conclude that the involvement of oxalic acid in SO_3 hydration to form H_2SO_4 is significant in the atmosphere.

1. Introduction

In the atmosphere, hydrogen atom transfer (HAT) reactions play a significant role in many processes. The radical reaction (R-H+OH→R+H_2O), as the most traditional HAT reaction, can be widely found in the atmosphere (Alvarez-Idaboy et al., 2001;Cameron et al., 2002;Steckler et al., 1997;Atkinson et al., 2006). 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). These atmospheric HAT reactions display a main feature that two-point hydrogen bond can occur and thus facilitates hydrogen atom transfer (Kumar et al., 2016). Water molecules, acids and other catalysts, acting as hydrogen donors and acceptors, can contribute to the formation of two-point hydrogen bond (Vöhringer-Martinez et al., 2007;da Silva, 2010;Gonzalez et al., 2010;Bandyopadhyay et al., 2017). Thus, the effect of catalysts on promoting atmospheric HAT reactions has attracted more attention from atmospheric scientists.

The hydration of SO_3 to form sulfuric acid is a typical addition reaction involving the hydrogen atom transfer. In the atmosphere, this hydration reaction is regarded as the main source of gas-phase sulfuric acid. For the reaction $SO_3 + H_2O \rightarrow H_2SO_4$, the pre-reactive $SO_3 \cdots H_2O$ complex is formed firstly, and the complex is then rearranged to produce H_2SO_4, which was proposed by Castleman et al (Holland and Castleman, 1978;Hofmann-Sievert and Castleman, 1984). But the subsequent research found that this hydration reaction involving a single water molecule cannot take place in the atmosphere due to its high energy barrier (Hofmann and Schleyer, 1994;Morokuma and Muguruma, 1994;Steudel, 1995). The inclusion of a second water molecule in the above reaction has been proven to significantly reduce the hydration energy barrier (Morokuma and Muguruma, 1994;Loerting and Liedl, 2000;Larson et al., 2000). The promoting effect can be mainly attributed to the formation of the two-point hydrogen bond, which reduces the ring strain occurring in the pre-reactive complex, and facilitates the rearrangement of the pre-reactive complex via double hydrogen atom transfer. It has also been shown that some other atmospheric molecules can serve as a catalyst to promote the hydration of SO_3. To the best of our knowledge, hydroperoxy radical (Gonzalez et al., 2010), formic acid (Hazra and Sinha, 2011;Long et al., 2012), sulfuric acid (Torrent-Sucarrat et al., 2012), nitric acid (Long et al., 2013) and ammonia (Bandyopadhyay et al., 2017) have been reported to replace the second water molecule to catalyze the hydration reaction of SO_3.

Oxalic acid (OA), the most prevalent dicarboxylic acid in the atmosphere (Ho et al., 2015;Kawamura and Ikushima, 1993), is the water-soluble organic acid, so it has high concentration in aerosols (Kawamura et al., 2013;van Pinxteren et al., 2014;Deshmukh et al., 2016;Wang et al., 2016). In addition to its accumulation in aerosols, oxalic acid, as an organic acid in the gas phase, has been found to enhance the new particle formation (NPF) (Xu et al., 2010;Weber et al., 2012;Xu and Zhang, 2012;Weber et al., 2014;Peng et al., 2015;Miao et al., 2015;Zhao et al., 2016;Chen et al., 2017;Xu et al., 2017;Arquero et al., 2017;Zhang, 2010). Theoretical studies about the effect of oxalic acid on atmospheric particle nucleation and growth have shown that it can generate stable complexes with water (Weber et al., 2012), sulfuric acid (Xu et al., 2010;Xu and Zhang, 2012;Miao et al., 2015;Zhao et al., 2016), ammonia (Weber et al., 2014;Peng et al., 2015) and amines (Chen et al., 2017;Xu et al., 2017;Arquero et al., 2017) via intermolecular hydrogen bond. 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. Opposite to monocarboxylic acids, dicarboxylic acids such as oxalic acid has been proved to enhance nucleation in two directions because of its two acid moieties (Xu and Zhang, 2012). Thus, it can be believed that oxalic acid is good candidate for catalyzing the hydrogen atom transfer reaction in the atmosphere.

In this paper, we reported the hydration reaction of SO_3 in the presence of oxalic acid, aiming to study the catalytic effect and importance of oxalic acid in the hydration of SO_3. It is known that oxalic acid can exist in several conformational forms (Buemi, 2009), which can be identified through the nomenclature used by Niemen et al (Nieminen et al., 1992). Thus, five stable conformers of oxalic acid were considered in this work. The rate constants of oxalic acid-catalyzed SO_3 hydration were calculated using the kinetics analysis, and compared with that of water-catalyzed hydration reaction. Finally, combining concentrations of reactants with the rate constants, we evaluated the importance of the hydration process involving the oxalic acid relative to the hydration of SO_3 with the second water as a catalyst to form sulfuric acid.

2. Computational details

Gaussian 09 suite of software (Frisch et al., 2010) was used in this work to perform all electronic structure calculations. 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. For M06-2X method, the ultrafine integration grid was chosen to enhance calculation accuracy at reasonable additional cost. The frequency calculations were carried out at the same level after geometric optimization to verify the local minimum points and transition states through the criterion that there are no imaginary frequencies for the local minimum point and one imaginary frequency for transition states. According to frequency calculations, the zero point energies (ZPE) and thermal corrections can also be obtained. The intrinsic reaction coordinate (IRC) calculation (Fukui, 1981;Hratchian and Schlegel, 2004;Hratchian and Schlegel, 2005) was performed to ensure that the transition states are connected with the corresponding reactants and products. A high level ab initio method, CCSD(T) method (Purvis and Bartlett, 1982;Pople et al., 1987), with the cc-pV(T+d)Z basis set was used to refine the single-point energies of these optimized species. To obtain more accurate conformational population of oxalic acid in different temperature, the quantum chemistry composite method, Gaussian 4 (G4) theory (Curtiss et al., 2007), also was performed for oxalic acid conformers.

In the kinetics analysis, the electronic energies were based on the CCSD(T)/cc-pV(T+d)Z level of theory, while the partition functions were obtained from the M06-2X/6-311++G(3df,3pd) level of theory. The rate constants for the rearrangement process of SO_3 hydration reaction was estimated using conventional transition-state theory (TST) (Truhlar et al., 1996) with Wigner tunneling correction. All kinetics analyses were executed in the KiSThelP program (Canneaux et al., 2014). The kinetics analyses are summarized as follows.

Base on the discussion in this paper, it can be concluded that SO_3 hydration reactions begin with the formation of pre-reactive complex, and then pass by a transition state to form a post-reactive complex. This process can be characterized by the following equation:

$$\begin{gathered} A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C \\ C + D \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} pre-reactive\ complex \xrightarrow{k_{uni}} post-reactive\ complex \end{gathered} \tag{1}$$

Assuming that the complexes are in equilibrium with their reactants and that the steady state approximation is applied to the pre-reactive complex, the reaction rate can be formulated as

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

where K_{eq1} , K_{eq2} are the equilibrium constants and k_{uni} is the rate constant for a unimolecular reaction from the pre-reactive complex to post-reactive complex.

In the water-catalyzed hydration process, two channels can be written as:

$$Recation\ 1:$$

$$SO_3 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_3 \cdots H_2O \qquad (3)$$

$$SO_3 \cdots H_2O + H_2O \underset{k_{-2}^{w1}}{\overset{k_2^{w1}}{\rightleftharpoons}} SO_3 \cdots H_2O \cdots H_2O \xrightarrow{k_{uni\_w}} H_2SO_4 \cdots H_2O$$

$$Reaction\ 2:$$

$$H_2O + H_2O \underset{k_{-1}^{w2}}{\overset{k_1^{w2}}{\rightleftharpoons}} H_2O \cdots H_2O \qquad (4)$$

$$SO_3 + H_2O \cdots H_2O \underset{k_{-2}^{w2}}{\overset{k_2^{w2}}{\rightleftharpoons}} SO_3 \cdots H_2O \cdots H_2O \xrightarrow{k_{uni\_w}} H_2SO_4 \cdots H_2O$$

The corresponding rates are:

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

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

For oxalic acid-catalyzed hydration reaction of SO_3, there are two reaction channels and the same features as in the water-assisted hydration process. The two channels can be shown as follows:

$$Reaction\ X1:$$

$$SO_3 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_3 \cdots H_2O \qquad (7)$$

$$SO_3 \cdots H_2O + X \underset{k_{-2}^{X1}}{\overset{k_2^{X1}}{\rightleftharpoons}} SO_3 \cdots H_2O \cdots X \xrightarrow{k_{uni\_X}} H_2SO_4 \cdots X'$$

$Reaction\ X2:$

$$H_2O + X \underset{k_{-1}^{X2}}{\overset{k_1^{X2}}{\rightleftarrows}} H_2O \cdots X \tag{8}$$

$$SO_3 + H_2O \cdots X \underset{k_{-2}^{X2}}{\overset{k_2^{X2}}{\rightleftarrows}} SO_3 \cdots H_2O \cdots X \xrightarrow{k_{uni\_X}} H_2SO_4 \cdots X'$$

Here, the symbol X in these two equations represents the different conformers of oxalic acid (namely, cTt, tTt, tCt and cCt conformer).

The corresponding rate of SO_3 hydration involving in oxalic acid can be obtained from the following equations:

$$v_{X1} = \frac{k_1}{k_{-1}}\frac{k_2^{X1}}{k_{-2}^{X1}} k_{uni\_X}[SO_3][H_2O][X] = K_{eq1}K_{eq2}^{X1}k_{uni\_X}[SO_3][H_2O][X] = k_{X1}[SO_3][H_2O][X] \tag{9}$$

$$v_{X2} = \frac{k_1^{X2}}{k_{-1}^{X2}}\frac{k_2^{X2}}{k_{-2}^{X2}} k_{uni\_X}[SO_3][H_2O][X] = K_{eq1}^{X2}K_{eq2}^{X2}k_{uni\_X}[SO_3][H_2O][X] = k_{X2}[SO_3][H_2O][X] \tag{10}$$

To assess the importance of oxalic acid in SO_3 hydration to H_2SO_4 in the atmosphere, the relative rate can be used as

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

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

It can be easily inferred from these equations that rate constants are the 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 the same. On account of these reasons, we will only compare the relative rate ν_{X1}/ν_{w1} in this paper.

3. Results and discussion

3.1. Water-catalyzed hydration reaction of SO_3

Although the hydration of SO_3 involving two water molecules has been discussed many times, we still include it in our paper so as to compare it with the following SO_3 hydration reactions catalyzed by oxalic acid at the same theoretical level, that is, at CCSD(T)/cc-pV(T+d)Z//M06-2X/6-311++G(3df,3pd) level. For the reaction SO_3+2H_2O, the existence of two pathways has become a consensus. One is that water dimer reacts with SO_3 to obtain the pre-reactive complex, then this complex is rearranged to form $H_2SO_4\cdots H_2O$ complex (channel 1); the other begins with the reaction of $SO_3\cdots H_2O$ complex with water, the following reaction process is the same as the channel 1 (channel 2). 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 SO_3. The potential energy profile and geometric structures can be found in Fig. 1. Other results about the reaction are put into Supplement (Table S1).

From the two channels, it is clear that the binding energy of water dimer is 3.80 kcal mol^{-1}, and that of $SO_3\cdots H_2O$ complex is 7.38 kcal·mol^{-1}. Moreover, the binding energy of water dimer is consistent with its experimental value of 3.15 ± 0.03 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 $SO_3\cdots H_2O$ 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). As shown in the Fig. 1, the two pathways involve the formation of the same pre-reactive complex (RC1) and the same subsequent processes. The RC1 has the binding energy of 14.12 kcal mol^{-1} relative to $SO_3+H_2O\cdots H_2O$, which is in accord with 13.60 (Torrent-Sucarrat et al., 2012) and 13.76 kcal mol^{-1} (Long et al., 2013). The RC1 consists of a six-membered ring structure, in which two hydrogen bonds (or called two-point hydrogen bond) between H_a and O_2, H_b and O_3, can be found. The formation of sulfuric acid from the RC1 needs to go through the rearrangement process with a transition state, which is a rate-limiting step with the barrier energy of 5.17 kcal mol^{-1} with respect to the RC1.

3.2. Oxalic acid-catalyzed hydration reaction of SO_3

Oxalic acid conformers, as shown in Fig. 2, are named according to the configurations of H-O-C-C and O=C-C=O dihedral angle: the low-case letters refer to cis (c) or trans (t) configuration of H-O-C-C; the upper-case letters relate to cis (C) or tans (T) configuration of O=C-C=O. The nomenclature about conformers of oxalic acid is proposed by Nieminen et al(Nieminen et al., 1992).

The calculated potential energy profile for oxalic acid-catalyzed hydration reaction of SO_3 is depicted in Fig. 3, and the corresponding geometry structures are shown in Fig. 4. Energies, enthalpies and free energies in all relevant species for oxalic acid catalyzed hydration of SO_3 are summarized in Supplement (Tables S2 - S5). From the two figures, it is obvious that the cTc conformer cannot act as a catalyst in the hydration reaction because the hydrogen atom transfer cannot occur. 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 (see Fig. 4). The hydration reactions catalyzed by the remaining four conformers exhibit the same feature (Fig. 3), that is the pre-reactive complex formed from $SO_3\cdots H_2O$ complex with oxalic acid (OA) or $OA\cdots H_2O$ complex with water can evolve into product complex ($H_2SO_4\cdots OA$ complex) via transition state of hydrogen atom transfer. In this process, oxalic acid serves as a catalyst to promote SO_3 hydration reaction by making a bridge when the hydrogen atom transfers from H_2O to SO_3. In the reaction catalyzed by cTt conformer, the binding energy of $cTt\cdots H_2O$ complex is 10.25 kcal mol^{-1}. The binding energy of pre-reactive complex is 10.95 kcal mol^{-1} compared to the $cTt\cdots H_2O$ complex with SO_3, while that is 13.82 kcal mol^{-1} relative to $SO_3\cdots H_2O$ complex with cTt. The transformation from RC_{cTt} to PC_{cTt} corresponds to hydrogen atom transfer process, and has a transition state (TS_{cTt}) with the energy barrier of 1.19 kcal mol^{-1} with respect to RC_{cTt}. The post-reactive complex (PC_{cTt}) lies below the RC_{cTt} by 13.32 kcal mol^{-1}. It should be noted that the cTt conformer from RC_{cTt} has transformed to the cCt conformer in PC_{cTt}. The binding energy of PC_{cTt} is 17.78 kcal mol^{-1} compared to H_2SO_4 and cCt conformer.

In hydration reaction involving the tTt conformer, the $tTt\cdots H_2O$ complex is stabilized by 9.92 kcal mol^{-1}, relative to tTt + H_2O. Starting with the $tTt\cdots H_2O + SO_3$ channel, the pre-reactive complex (RC_{tTt}) can be formed with binding energy of 12.59 kcal mol^{-1}, whereas the binding energy of RC_{tTt} is 15.13 kcal mol^{-1} when it comes from the $SO_3\cdots H_2O$ + tTt channel. The TS_{tTt} lies above the RC_{tTt} by 0.24 kcal mol^{-1}. And the reaction proceeds with the formation of PC_{tTt}, which is more stable than RC_{tTt} (14.05 kcal mol^{-1}). The formed PC_{tTt} needs to obtain the energy of 17.34 kcal mol^{-1} to disaggregate into H_2SO_4 and tCt conformer.

For tCt conformer, the binding energy of tCt···H_2O complex is 10.09 kcal mol^{-1}. In the two channels, the same pre-reactive complex (RC_{tCt}) can be formed with the binding energy of 12.92 kcal mol^{-1} relative to tCt···H_2O + SO_3, 15.63 kcal mol^{-1} with respect to SO_3···H_2O + tCt, respectively. The RC_{tCt} proceeds via the transition state (TS_{tCt}) (with energy barrier of 0.05 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 kcal mol^{-1} of energy.

For cCt conformer, the binding energy of cCt···H_2O complex is 11.10 kcal mol^{-1}. Beginning with cCt···H_2O + SO_3 channel and SO_3···H_2O + cCt channel, the hydration reaction undergo the same RC_{cCt} complex, which is more stable than the two reactants (by 12.38 kcal mol^{-1}, 16.10 kcal mol^{-1}, respectively), and a transition state (TS_{cCt}), and then produces the H_2SO_4···cTt complex (PC_{cCt}), which lies below RC_{cCt} complex by 15.62 kcal mol^{-1} and below H_2SO_4 + cTt by 16.15 kcal mol^{-1}. The pre-reactive complex (RC_{cCt}) is nearly iso-energetic with the transition state (TS_{cCt}).

In the light of the analysis above, it is obvious that energy barrier of the hydration reaction catalyzed by oxalic acid is around 1.00 kcal mol^{-1} for cTt conformer, and approximates 0.00 kcal mol^{-1} for another three conformers. The result shows that the oxalic acid is more effective than water in catalyzing the SO_3 hydration because the hydration reaction catalyzed by water has energy barrier of 5.17 kcal mol^{-1}. Another point worth mentioning is that one oxalic acid conformer involving in SO_3 hydration transfers to another conformer type after the completion of hydration reaction (cTt → cCt, tTt → tCt, tCt → tTt, cCt → cTt).

In addition, compared to formic acid (Millet et al., 2015;Bannan et al., 2017), the SO_3 hydration reaction catalyzed by oxalic acid display some specific characteristics. Both acids can obviously decrease the energy barrier of the hydration reaction. But because oxalic acid is a dicarboxylic acid, only one in the carboxylic groups participates in the hydration reaction, and the other is free. This characteristic indicates that post-reactive complexes (PC_{tTt} and PC_{tCt}) can serve as a catalyst to continue to promote the SO_3 hydration. For these post-reactive complexes (PC_{cTt}, PC_{tTt}, PC_{tCt} and PC_{cCt}), the above result has shown that these complexes are stable compared to the isolate H_2SO_4 and oxalic acid conformers. The free carboxylic group in these complexes can also provide the interaction site when these complexes interact with other species.

The free carboxylic group of these stable post-reactive complexes indicates that these complexes have the potential to participate in nucleation.

3.3. Atmospheric implications

To evaluate the importance of oxalic acid in enhancing H_2SO_4 formation in atmosphere, we calculated the rate constants of SO_3 hydration catalyzed by oxalic acid and water, and compared the rate of oxalic acid-catalyzed hydration reaction with that of water-catalyzed hydration at different altitudes in the troposphere. The temperature, pressure, density of air and water vapor content at the corresponding altitude are taken from U.S. Standard Atmosphere, 1976 (NASA and NOAA), and are put into the Table S6.

According to these calculation methods described in computational details section, it can be confirmed that both the ratio of rate constants and relative concentrations are important elements to estimate the effect of oxalic acid-catalyzed SO_3 hydration. Thus, the rate constants for hydration reaction of SO_3 catalyzed by oxalic acid and water at different altitudes are firstly analyzed and summarized in Table 1. The corresponding K_{eq} and k_{uni} are included in Supplement (Table S7).

As shown in Table 1, the rate constant in Reaction 1 changes from 4.21×10^{-31} cm^6 $molecule^{-2}$ s^{-1} (298.15 K at 0 km altitude) to 3.92×10^{-27} cm^6 $molecule^{-2}$ s^{-1} (216.15 K at 12 km altitude). For the Reaction X1, the transformation of rate constants within the range of altitudes can also be found (k_{cTt1}: from 6.45×10^{-28} to 3.35×10^{-22}; k_{tTt1}: from 2.32×10^{-26} to 4.97×10^{-20}; k_{tCt1}: from 4.08×10^{-26} to 1.35×10^{-19}; k_{cCt1}: from 1.39×10^{-25} to 6.61×10^{-19} cm^6 $molecule^{-2}$ s^{-1}). All corresponding rate constant ratios at various altitudes are described in Table 2. 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. It can be seen from Table 2 that rate constant ratios increase with the temperature decreasing (that is, with altitude increasing).

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_{cTt1}/k_{w1}: 1.53×10^3; k_{tTt1}/k_{w1}: 5.50×10^4; k_{tCt1}/k_{w1}: 9.70×10^4; k_{cCt1}/k_{w1}: 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 an 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 reaction 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 and sulfuric acid, and similar to formic acid, but weaker than ammonia.

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). The calculation method for the conformational population is shown in Supplement (Text S2). The most stable conformer, cTc conformer, accounts for more than 95 % of oxalic acid at different altitudes ranging from 0 km to 12 km. But this conformer cannot participate in catalyzing the hydration reaction of SO_3. In other words, the conformers involving in catalyzing the SO_3 hydration do not exceed 5 % of oxalic acid. In some studies (Martinelango et al., 2007;Bao et al., 2012), observed concentrations of oxalic acid in gas phase range from approximately 10 ng m^{-3} to close 1 μg m^{-3}. To obtain actual concentrations of oxalic acid conformers, we assumed a 302 ng m^{-3} (2.02×10^9 molecules cm^{-3}) for total oxalic acid at 298.15 K and an altitude of 0 km, which are measured by Bao et al (2012). Combining mole fractions for conformers (cTt, tTt, tCt and cCt) and the total concentration of oxalic acid and considering the temperature and pressure effect using idea gas equation (see Table S9), the concentration of oxalic acid conformers involving in the hydration reaction at various altitudes can be calculated, which is tabulated in Table 4. The water vapor concentration also is included in Table 4.

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 within 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 in different temperatures. However, as the altitude increase, the oxalic acid has an increasing impact on the SO_3 hydration because of an obvious increase in the ratio. 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 rates shows that, in the upper troposphere, the oxalic acid can play a significant role in enhancing SO_3 hydration to H_2SO_4.

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 SO_3 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 SO_3, it has the potential to promote the SO_3 hydration reaction. However, the real atmospheric importance about the species-catalyzed SO_3 hydration reaction needs to be evaluated. That is, compared to water catalyzed SO_3 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.

4. Conclusion

The main conclusion of this work is that oxalic acid, the most abundant dicarboxylic acid in the atmosphere, has the remarkable ability to catalyze SO_3 hydration to H_2SO_4, and has the potential impact on the H_2SO_4 formation in the atmosphere.

We have shown that water catalyzed hydration reaction of SO_3 has energy barrier of 5.17 kcal mol^{-1}. For oxalic acid, four conformers (cTt, tTt, tCt and cCt) can involve in the hydration reaction, whereas the most stable conformer (cTc) cannot catalyze the hydration reaction because the formed hydrogen bond structure rejects hydrogen atom transfer. Other conformers can catalyze the hydration reaction and the corresponding energy barrier is a little higher or less than 1 kcal mol^{-1}. The results demonstrate that oxalic acid has the stronger catalytic ability than water for SO_3 hydration to form H_2SO_4.

According to the kinetics analysis, the rate constant of oxalic acid-catalyzed hydration reaction is greater than that of water-catalyzed reaction by orders of magnitude, which also reflects the obvious catalytic ability of oxalic acid. In addition to the rate constant, the reactant concentration is also an important factor to assess the effect of oxalic acid on SO_3 hydration. Based on the two factors, our calculation shows that, in the upper troposphere, the oxalic acid can play an important role in SO_3 hydration to form H_2SO_4.

This work not only gives insight into the new mechanism of SO_3 hydration in the atmosphere, but also has potential importance for investigating the catalytic effect of oxalic acid on other atmosphere reaction.

Supplement

Competing interests

The authors declare that they have no conflict of interest.

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Reference

Alvarez-Idaboy, J. R., Mora-Diez, N., Boyd, R. J., and Vivier-Bunge, A.: On the Importance of Prereactive Complexes in Molecule−Radical Reactions: Hydrogen Abstraction from Aldehydes by OH, J. Am. Chem. Soc., 123, 2018-2024, doi: 10.1021/ja003372g, 2001.

Arquero, K. D., Xu, J., Gerber, R. B., and Finlayson-Pitts, B. J.: Particle formation and growth from oxalic acid, methanesulfonic acid, trimethylamine and water: a combined experimental and theoretical study, Phys. Chem. Chem. Phys., 19, 28286-28301, doi: 10.1039/C7CP04468B, 2017.

Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and Subcommittee, I.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species, Atmos. Chem. Phys., 6, 3625-4055, doi: 10.5194/acp-6-3625-2006, 2006.

Atkinson, R.: Rate constants for the atmospheric reactions of alkoxy radicals: An updated estimation method, Atmos. Environ., 41, 8468-8485, doi: 10.1016/j.atmosenv.2007.07.002, 2007.

Bandyopadhyay, B., Kumar, P., and Biswas, P.: Ammonia Catalyzed Formation of Sulfuric Acid in Troposphere: The Curious Case of a Base Promoting Acid Rain, J. Phys. Chem. A, 121, 3101-3108, doi: 10.1021/acs.jpca.7b01172, 2017.

Bannan, T. J., Murray Booth, A., Le Breton, M., Bacak, A., Muller, J. B. A., Leather, K. E., Khan, M. A. H., Lee, J. D., Dunmore, R. E., Hopkins, J. R., Fleming, Z. L., Sheps, L., Taatjes, C. A., Shallcross, D. E., and Percival, C. J.: Seasonality of Formic Acid (HCOOH) in London during the ClearfLo Campaign, Journal of Geophysical Research: Atmospheres, 122, 12,488-412,498, doi: doi:10.1002/2017JD027064, 2017.

Bao, L., Matsumoto, M., Kubota, T., Sekiguchi, K., Wang, Q., and Sakamoto, K.: Gas/particle partitioning of low-molecular-weight dicarboxylic acids at a suburban site in Saitama, Japan, Atmos. Environ., 47, 546-553, doi: 10.1016/j.atmosenv.2009.09.014, 2012.

Buemi, G.: DFT study of the hydrogen bond strength and IR spectra of formic, oxalic, glyoxylic and pyruvic acids in vacuum, acetone and water solution, J. Phys. Org. Chem., 22, 933-947, doi: 10.1002/poc.1543, 2009.

Cameron, M., Sivakumaran, V., Dillon, T. J., and Crowley, J. N.: Reaction between OH and CH3CHO Part 1. Primary product yields of CH3 (296 K), CH3CO (296 K), and H (237-296 K), Phys. Chem. Chem. Phys., 4, 3628-3638, doi: 10.1039/B202586H, 2002.

Canneaux, S., Bohr, F., and Henon, E.: KiSThelP: A program to predict thermodynamic properties and rate constants from quantum chemistry results†, J. Comput. Chem., 35, 82-93, doi: 10.1002/jcc.23470, 2014.

Chen, J., Jiang, S., Liu, Y.-R., Huang, T., Wang, C.-Y., Miao, S.-K., Wang, Z.-Q., Zhang, Y., and Huang, W.: Interaction of oxalic acid with dimethylamine and its atmospheric implications, RSC Adv., 7, 6374-6388, doi: 10.1039/C6RA27945G, 2017.

Courmier, D., Gardebien, F., Minot, C., and St-Amant, A.: A computational study of the water-catalyzed formation of NH2CH2OH, Chem. Phys. Lett., 405, 357-363, doi: 10.1016/j.cplett.2004.12.121, 2005.

Curtiss, L. A., Redfern, P. C., and Raghavachari, K.: Gaussian-4 theory, J. Chem. Phys., 126, 084108, doi: 10.1063/1.2436888, 2007.

da Silva, G.: Carboxylic Acid Catalyzed Keto-Enol Tautomerizations in the Gas Phase, Angew. Chem. Int. Ed., 49, 7523-7525, doi: 10.1002/anie.201003530, 2010.

Deshmukh, D. K., Kawamura, K., Lazaar, M., Kunwar, B., and Boreddy, S. K. R.: Dicarboxylic acids, oxoacids, benzoic acid, α-dicarbonyls, WSOC, OC, and ions in spring aerosols from Okinawa Island in the western North Pacific Rim: size distributions and formation processes, Atmos. Chem. Phys., 16, 5263-5282, doi: 10.5194/acp-16-5263-2016, 2016.

Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G. A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H. P., Izmaylov, A. F., Bloino, J., Zheng, G., Sonnenberg, J. L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J. A., Peralta, J. E., Ogliaro, F., Bearpark, M., Heyd, J. J., Brothers, E., Kudin, K. N., Staroverov, V. N., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Rega, N., Millam, J. M., Klene, M., Knox, J. E., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Martin, R. L., Morokuma, K., Zakrzewski, V. G., Voth, G. A., Salvador, P., Dannenberg, J. J., Dapprich, S., Daniels, A. D., Farkas, Foresman, J. B., Ortiz, J. V., Cioslowski, J., and Fox, D. J.: Gaussian 09, Revision B.01, Gaussian Inc. Wallingford CT, 2010.

Fukui, K.: The path of chemical reactions - the IRC approach, Acc. Chem. Res., 14, 363-368, doi: 10.1021/ar00072a001, 1981.

Gonzalez, J., Torrent-Sucarrat, M., and Anglada, J. M.: The reactions of SO3 with HO2 radical and H2O[three dots, centered]HO2 radical complex. Theoretical study on the atmospheric formation of HSO5 and H2SO4, Phys. Chem. Chem.

Phys., 12, 2116-2125, doi: 10.1039/B916659A, 2010.

Gutbrod, R., Schindler, R. N., Kraka, E., and Cremer, D.: Formation of OH radicals in the gas phase ozonolysis of alkenes: the unexpected role of carbonyl oxides, Chem. Phys. Lett., 252, 221-229, doi: 10.1016/0009-2614(96)00126-1, 1996.

Hazra, M. K., and Sinha, A.: Formic Acid Catalyzed Hydrolysis of SO3 in the Gas Phase: A Barrierless Mechanism for Sulfuric Acid Production of Potential Atmospheric Importance, J. Am. Chem. Soc., 133, 17444-17453, doi: 10.1021/ja207393v, 2011.

Ho, K. F., Huang, R. J., Kawamura, K., Tachibana, E., Lee, S. C., Ho, S. S. H., Zhu, T., and Tian, L.: Dicarboxylic acids, ketocarboxylic acids, α-dicarbonyls, fatty acids and benzoic acid in PM_{2.5} aerosol collected during CAREBeijing-2007: an effect of traffic restriction on air quality, Atmos. Chem. Phys., 15, 3111-3123, doi: 10.5194/acp-15-3111-2015, 2015.

Hofmann-Sievert, R., and Castleman, A. W.: Reaction of sulfur trioxide with water clusters and the formation of sulfuric acid, J. Phys. Chem., 88, 3329-3333, doi: 10.1021/j150659a038, 1984.

Hofmann, M., and Schleyer, P. v. R.: Acid Rain: Ab Initio Investigation of the H2O.cntdot.SO3 Complex and Its Conversion to H2SO4, J. Am. Chem. Soc., 116, 4947-4952, doi: 10.1021/ja00090a045, 1994.

Holland, P. M., and Castleman, A. W.: Gas phase complexes: considerations of the stability of clusters in the sulfur trioxide—water system, Chem. Phys. Lett., 56, 511-514, doi: 10.1016/0009-2614(78)89028-9, 1978.

Hratchian, H. P., and Schlegel, H. B.: Accurate reaction paths using a Hessian based predictor–corrector integrator, J. Chem. Phys., 120, 9918-9924, doi: 10.1063/1.1724823, 2004.

Hratchian, H. P., and Schlegel, H. B.: Using Hessian Updating To Increase the Efficiency of a Hessian Based Predictor-Corrector Reaction Path Following Method, J. Chem. Theory Comput., 1, 61-69, doi: 10.1021/ct0499783, 2005.

Ji, Y., Zhao, J., Terazono, H., Misawa, K., Levitt, N. P., Li, Y., Lin, Y., Peng, J., Wang, Y., Duan, L., Pan, B., Zhang, F., Feng, X., An, T., Marrero-Ortiz, W., Secrest, J., Zhang, A. L., Shibuya, K., Molina, M. J., and Zhang, R.: Reassessing the atmospheric oxidation mechanism of toluene, Proc. Natl. Acad. Sci. U. S. A., 114, 8169, 2017.

Ji, Y. M., Wang, H. H., Gao, Y. P., Li, G. Y., and An, T. C.: A theoretical model on the formation mechanism and kinetics of highly toxic air pollutants from halogenated formaldehydes reacted with halogen atoms, Atmos. Chem. Phys., 13, 11277-11286, doi: 10.5194/acp-13-11277-2013, 2013.

Kawamura, K., and Ikushima, K.: Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere, Environ. Sci. Technol., 27, 2227-2235, doi: 10.1021/es00047a033, 1993.

Kawamura, K., Tachibana, E., Okuzawa, K., Aggarwal, S. G., Kanaya, Y., and Wang, Z. F.: High abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in the mountaintop aerosols over the North China Plain during wheat burning season, Atmos. Chem. Phys., 13, 8285-8302, doi: 10.5194/acp-13-8285-2013, 2013.

Klopper, W., van Duijneveldt-van de Rijdt, J. G. C. M., and van Duijneveldt, F. B.: Computational determination of equilibrium geometry and dissociation energy of the water dimer, Phys. Chem. Chem. Phys., 2, 2227-2234, doi: 10.1039/A910312K, 2000.

Kumar, M., and Francisco, J. S.: Red-Light-Induced Decomposition of an Organic Peroxy Radical: A New Source of the HO2 Radical, Angew. Chem. Int. Ed., 54, 15711-15714, doi: 10.1002/anie.201509311, 2015.

Kumar, M., Sinha, A., and Francisco, J. S.: Role of Double Hydrogen Atom Transfer Reactions in Atmospheric Chemistry, Acc. Chem. Res., 49, 877-883, doi: 10.1021/acs.accounts.6b00040, 2016.

Larson, L. J., Kuno, M., and Tao, F.-M.: Hydrolysis of sulfur trioxide to form sulfuric acid in small water clusters, J. Chem. Phys., 112, 8830-8838, doi: 10.1063/1.481532, 2000.

Loerting, T., and Liedl, K. R.: Toward elimination of discrepancies between theory and experiment: The rate constant of the atmospheric conversion of SO3 to H2SO4, Proc. Natl. Acad. Sci. U. S. A., 97, 8874-8878, doi: 10.1073/pnas.97.16.8874, 2000.

Long , B., Long, Z.-w., Wang, Y.-b., Tan, X.-f., Han, Y.-h., Long, C.-y., Qin, S.-j., and Zhang, W.-j.: Formic Acid Catalyzed Gas-Phase Reaction of H2O with SO3 and the Reverse Reaction: A Theoretical Study, ChemPhysChem, 13, 323-329, doi: 10.1002/cphc.201100558, 2012.

Long, B., Chang, C.-R., Long, Z.-W., Wang, Y.-B., Tan, X.-F., and Zhang, W.-J.: Nitric acid catalyzed hydrolysis of SO3 in the formation of sulfuric acid: A theoretical study, Chem. Phys. Lett., 581, 26-29, doi: 10.1016/j.cplett.2013.07.012, 2013.

Martinelango, P. K., Dasgupta, P. K., and Al-Horr, R. S.: Atmospheric production of oxalic acid/oxalate and nitric acid/nitrate in the Tampa Bay airshed: Parallel pathways, Atmos. Environ., 41, 4258-4269, doi: 10.1016/j.atmosenv.2006.05.085, 2007.

Miao, S.-K., Jiang, S., Chen, J., Ma, Y., Zhu, Y.-P., Wen, Y., Zhang, M.-M., and Huang, W.: Hydration of a sulfuric acid-oxalic acid complex: acid dissociation and its atmospheric implication, RSC Adv., 5, 48638-48646, doi: 10.1039/C5RA06116D, 2015.

Millet, D. B., Baasandorj, M., Farmer, D. K., Thornton, J. A., Baumann, K., Brophy, P., Chaliyakunnel, S., de Gouw, J. A., Graus, M., Hu, L., Koss, A., Lee, B. H., Lopez-Hilfiker, F. D., Neuman, J. A., Paulot, F., Peischl, J., Pollack, I. B., Ryerson, T. B., Warneke, C., Williams, B. J., and Xu, J.: A large and ubiquitous source of atmospheric formic acid, Atmos. Chem. Phys., 15, 6283-6304, doi: 10.5194/acp-15-6283-2015, 2015.

Morokuma, K., and Muguruma, C.: Ab initio Molecular Orbital Study of the Mechanism of the Gas Phase Reaction SO3 + H2O: Importance of the Second Water Molecule, J. Am. Chem. Soc., 116, 10316-10317, doi: 10.1021/ja00101a068, 1994.

NASA, and NOAA: Technical Report (1976), https://ntrs.nasa.gov/archive/nasa/casi.ntrs.nasa.gov/19770009539.pdf.

Nieminen, J., Rasanen, M., and Murto, J.: Matrix-isolation and ab initio studies of oxalic acid, J. Phys. Chem., 96, 5303-5308, doi: 10.1021/j100192a024, 1992.

Peng, X.-Q., Liu, Y.-R., Huang, T., Jiang, S., and Huang, W.: Interaction of gas phase oxalic acid with ammonia and its atmospheric implications, Phys. Chem. Chem. Phys., 17, 9552-9563, doi: 10.1039/C5CP00027K, 2015.

Pople, J. A., Head‐Gordon, M., and Raghavachari, K.: Quadratic configuration interaction. A general technique for determining electron correlation energies, J. Chem. Phys., 87, 5968-5975, doi: 10.1063/1.453520, 1987.

Purvis, G. D., and Bartlett, R. J.: A full coupled‐cluster singles and doubles model: The inclusion of disconnected triples, J. Chem. Phys., 76, 1910-1918, doi: 10.1063/1.443164, 1982.

Rayez, M.-T., Picquet-Varrault, B., Caralp, F., and Rayez, J.-C.: CH3C(O)OCH(O[radical dot])CH3 alkoxy radical derived from ethyl acetate: Novel rearrangement confirmed by computational chemistry, Phys. Chem. Chem. Phys., 4, 5789-5794, doi: 10.1039/B207511N, 2002.

Rocher-Casterline, B. E., Ch'ng, L. C., Mollner, A. K., and Reisler, H.: Communication: Determination of the bond dissociation energy (D0) of the water dimer, (H2O)2, by velocity map imaging, J. Chem. Phys., 134, 211101, doi: 10.1063/1.3598339, 2011.

Steckler, R., Thurman, G. M., Watts, J. D., and Bartlett, R. J.: Ab initio direct dynamics study of OH+HCl→Cl+H2O, J. Chem. Phys., 106, 3926-3933, doi: 10.1063/1.473981, 1997.

Steudel, R.: Sulfuric Acid from Sulfur Trioxide and Water—A Surprisingly Complex Reaction, Angew. Chem. Int. Ed. Engl., 34, 1313-1315, doi: 10.1002/anie.199513131, 1995.

Torrent-Sucarrat, M., Francisco, J. S., and Anglada, J. M.: Sulfuric Acid as Autocatalyst in the Formation of Sulfuric Acid, J. Am. Chem. Soc., 134, 20632-20644, doi: 10.1021/ja307523b, 2012.

Truhlar, D. G., Garrett, B. C., and Klippenstein, S. J.: Current Status of Transition-State Theory, J. Phys. Chem., 100, 12771-12800, doi: 10.1021/jp953748q, 1996.

Vöhringer-Martinez, E., Hansmann, B., Hernandez, H., Francisco, J. S., Troe, J., and Abel, B.: Water Catalysis of a Radical-Molecule Gas-Phase Reaction, Science, 315, 497-501, doi: 10.1126/science.1134494, 2007.

van Pinxteren, D., Neusüß, C., and Herrmann, H.: On the abundance and source contributions of dicarboxylic acids in size-resolved aerosol particles at continental sites in central Europe, Atmos. Chem. Phys., 14, 3913-3928, doi: 10.5194/acp-14-3913-2014, 2014.

Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, Proc. Natl. Acad. Sci. U. S. A., 113, 13630, 2016.

Weber, K. H., Morales, F. J., and Tao, F.-M.: Theoretical Study on the Structure and Stabilities of Molecular Clusters of Oxalic Acid with Water, J. Phys. Chem. A, 116, 11601-11617, doi: 10.1021/jp308499f, 2012.

Weber, K. H., Liu, Q., and Tao, F.-M.: Theoretical Study on Stable Small Clusters of Oxalic Acid with Ammonia and Water, J. Phys. Chem. A, 118, 1451-1468, doi: 10.1021/jp4128226, 2014.

Williams, I. H., Spangler, D., Femec, D. A., Maggiora, G. M., and Schowen, R. L.: Theoretical models for solvation and catalysis in carbonyl addition, J. Am. Chem. Soc., 105, 31-40, doi: 10.1021/ja00339a008, 1983.

Xu, J., Finlayson-Pitts, B. J., and Gerber, R. B.: Proton Transfer in Mixed Clusters of Methanesulfonic Acid, Methylamine, and Oxalic Acid: Implications for Atmospheric Particle Formation, J. Phys. Chem. A, 121, 2377-2385, doi: 10.1021/acs.jpca.7b01223, 2017.

Xu, W., and Zhang, R.: Theoretical Investigation of Interaction of Dicarboxylic Acids with Common Aerosol Nucleation Precursors, J. Phys. Chem. A, 116, 4539-4550, doi: 10.1021/jp301964u, 2012.

Xu, Y., Nadykto, A. B., Yu, F., Jiang, L., and Wang, W.: Formation and properties of hydrogen-bonded complexes of common organic oxalic acid with atmospheric nucleation precursors, J. Mol. Struct. THEOCHEM, 951, 28-33, doi: 10.1016/j.theochem.2010.04.004, 2010.

Zhang, D., and Zhang, R.: Mechanism of OH Formation from Ozonolysis of Isoprene: A Quantum-Chemical Study, J. Am. Chem. Soc., 124, 2692-2703, doi: 10.1021/ja011518l, 2002.

Zhang, R.: Getting to the Critical Nucleus of Aerosol Formation, Science, 328, 1366, 2010.

Zhao, H., Zhang, Q., and Du, L.: Hydrogen bonding in cyclic complexes of carboxylic acid-sulfuric acid and their atmospheric implications, RSC Adv., 6, 71733-71743, doi: 10.1039/C6RA16782A, 2016.

Zhao, Y., and Truhlar, D. G.: The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals, Theor. Chem. Acc., 120, 215-241, doi: 10.1007/s00214-007-0310-x, 2008.

Zheng, J., and Truhlar, D. G.: Kinetics of hydrogen-transfer isomerizations of butoxyl radicals, Phys. Chem. Chem. Phys., 12, 7782-7793, doi: 10.1039/B927504E, 2010.

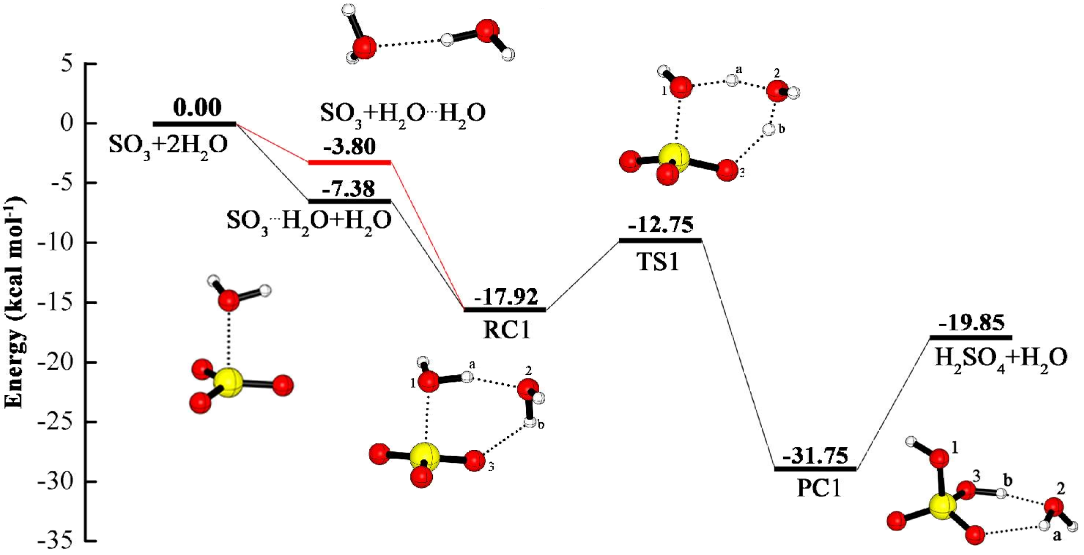
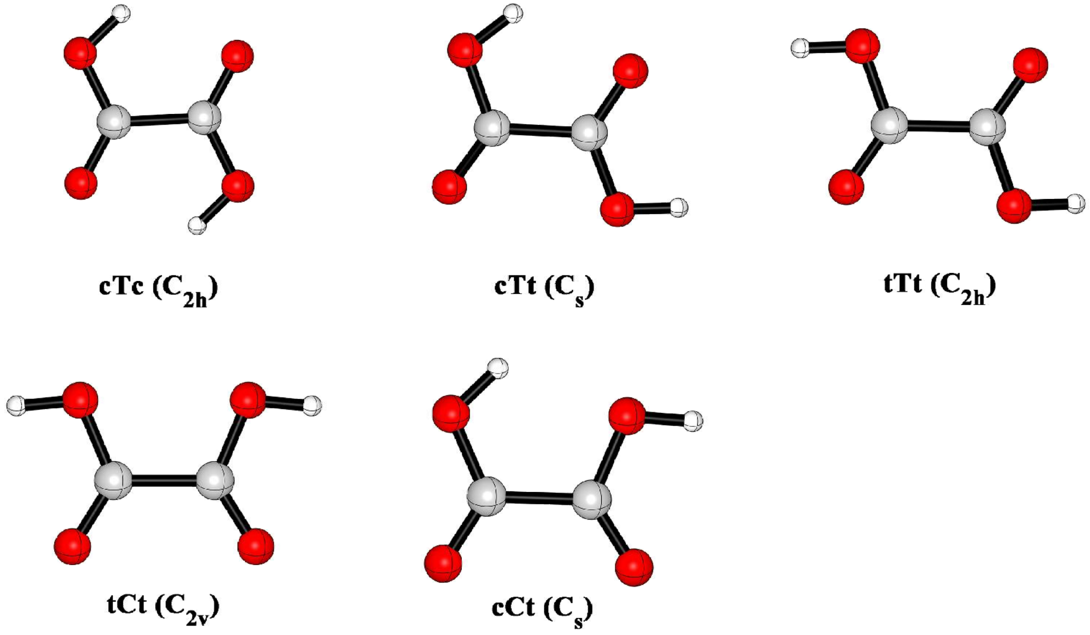
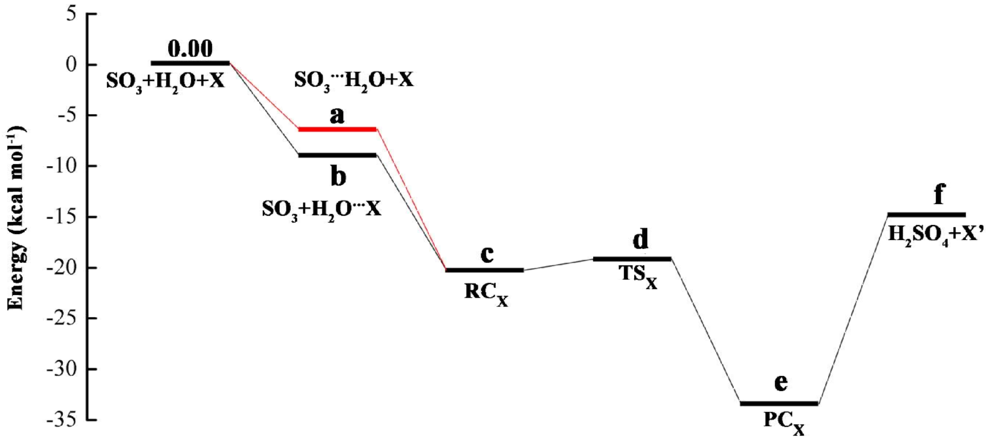


Figure 1. Calculated potential energy profile for the hydration of SO_3 with the second water as a catalyst at the CCSD(T)/cc-pV(T+d)Z//M06-2X/6-311++G(3df,3pd) level.


cTc (C_{2h}) cTt (C_s) tTt (C_{2h})

tCt (C_{2v}) cCt (C_s)

Figure 2. Structures of oxalic acid conformers optimized at the M06-2X/6-311++G(3df,3pd) level.



When X = cTt,

a = -7.38 b = -10.25 c = -21.20 d = -20.01 e = -34.52 f = -16.74 (X’=cCt)

When X = tTt,

a = -7.38 b = -9.92 c = -22.51 d = -22.27 e = -36.56 f = -19.22 (X’=tCt)

When X = tCt,

a = -7.38 b = -10.09 c = -23.01 d = -22.96 e = -37.45 f = -20.47 (X’=tTt)

When X = cCt,

a = -7.38 b = -11.10 c = -23.48 d = -23.49 e = -39.10 f = -22.95 (X’=cTt)

Figure 3. Calculated potential energy profile for the hydration of SO_3 with oxalic acid conformers (cTt, tTt, tCt and cCt) as catalysts at the CCSD(T)/cc-pV(T+d)Z//M06-2X/6-311++G(3df,3pd) level.

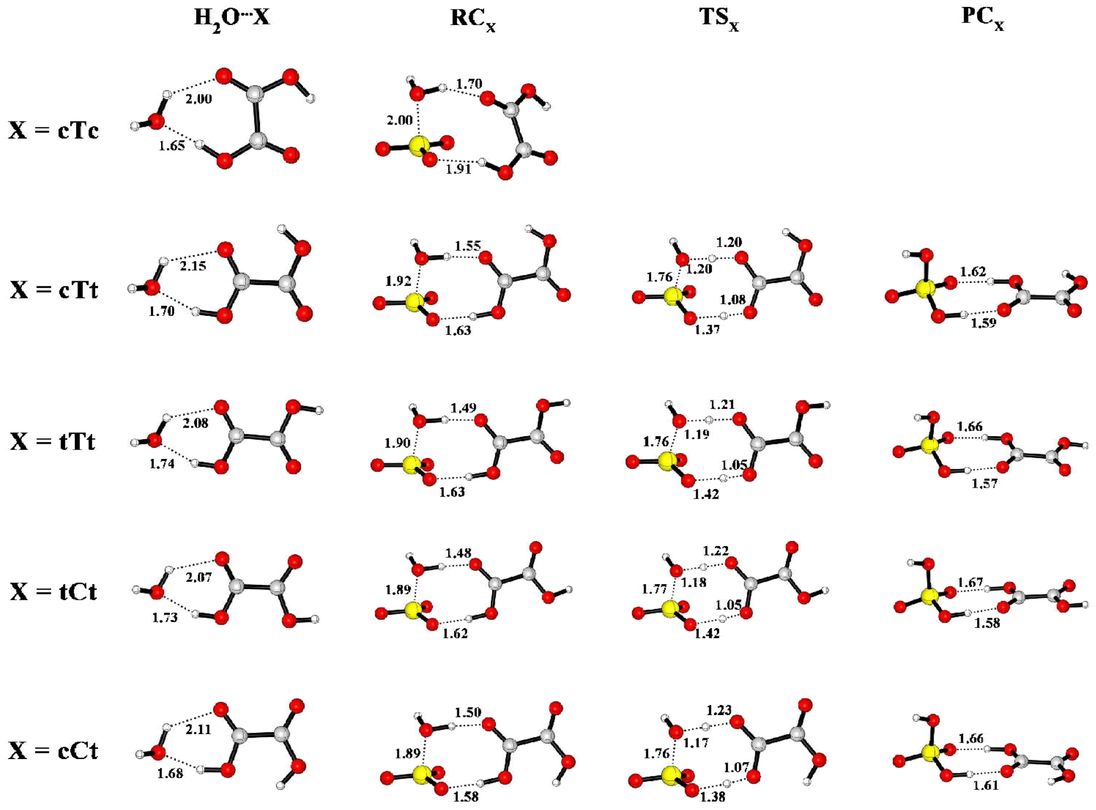


Figure 4. Optimized M06-2X/6-311++G(3df,3pd) structures of reactant complexes, pre-reactive complexes, transition states and post-reactive complexes for the oxalic acid-catalyzed SO_3 hydration reaction (distance unit: angstrom).

Table 1. Rate constants (in cm^6 molecule^{-2} 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_{cTt1} (k_{cTt2})	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_{tTt1} (k_{tTt2})	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_{tCt1} (k_{tCt2})	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_{cCt1} (k_{cCt2})	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}

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_{cTt1}/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_{tTt1}/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_{tCt1}/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_{cCt1}/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}

Table 3. Conformational population for oxalic acid conformers 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
cTc	96.51 %	97.06 %	97.69 %	98.22 %	98.66 %	99.01 %	99.30 %	99.42 %
cTt	2.27 %	1.98 %	1.62 %	1.30 %	1.02 %	0.78 %	0.57 %	0.48 %
tTt	0.71 %	0.56 %	0.41 %	0.29 %	0.20 %	0.13 %	0.08 %	0.06 %
tCt	0.48 %	0.38 %	0.26 %	0.18 %	0.11 %	0.07 %	0.04 %	0.03 %
cCt	0.03 %	0.02 %	0.02 %	0.01 %	0.01 %	0.01 %	0.01 %	0.01 %

Table 4. Concentrations (in molecules cm^{-3}) of oxalic acid conformers involving in SO_3 hydration and 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
cTt	4.59×10^{7}	4.13×10^{7}	2.78×10^{7}	1.82×10^{7}	1.15×10^{7}	6.98×10^{6}	4.05×10^{6}	2.58×10^{6}
tTt	1.42×10^{7}	1.18×10^{7}	7.08×10^{6}	4.08×10^{7}	2.25×10^{6}	1.17×10^{6}	5.74×10^{5}	3.33×10^{5}
tCt	9.72×10^{6}	7.84×10^{6}	4.53×10^{6}	2.50×10^{6}	1.31×10^{6}	6.51×10^{5}	3.01×10^{5}	1.69×10^{5}
cCt	6.35×10^{5}	4.82×10^{5}	2.56×10^{5}	1.29×10^{5}	6.13×10^{4}	2.72×10^{4}	1.11×10^{4}	5.80×10^{3}
H_2O	[a]5.18×10^{17}	1.92×10^{17}	9.57×10^{16}	3.47×10^{16}	1.22×10^{16}	3.80×10^{15}	5.97×10^{14}	1.18×10^{14}

[a] The water vapor concentration at 0 km and 298.15 K are obtained from (Torrent-Sucarrat et al., 2012). Other water vapor concentrations are taken from U.S. Standard Atmosphere, 1976.

Table 5. Relative rate of SO_3 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]ν_{OA1}/ν_{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}

[a] The rate ν_{OA1} represents the sum of reaction rate for Reaction X1 (X=cTt, tTt, tCt, cCt). The rate ($\nu_{cTt1}/\nu_{w1,}$ $\nu_{tTt1}/\nu_{w1,}$ $\nu_{tCt1}/\nu_{w1,}$ ν_{cCt1}/ν_{w1}) are shown in Table S10.