Understanding the catalytic role of oxalic acid in the SO$_3$ hydration to form H$_2$SO$_4$ in the atmosphere

Guochun Lv[1], Xiaomin Sun[1,*], Chenxi Zhang[2], Mei Li[3,4*]

[1]Environment Research Institute, Shandong University, Jinan 250100, China

5   [2]College of Biological and Environmental Engineering, Binzhou University, Binzhou 256600, China

[3]Institute of Mass Spectrometer and Atmospheric Environment, Jinan University, Guangzhou 510632, China

[4]Guangdong Provincial Engineering Research Center for on-line source apportionment system of air pollution, Guangzhou

510632, China

10   *Corresponding authors: Xiaomin Sun (sxmwch@sdu.edu.cn); Mei Li (limei2007@163.com)

Abstract: The hydration of SO$_3$ plays an important role in atmospheric sulfuric acid formation. Some atmospheric species can involve 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$_3$

15   hydration reaction catalyzed by oxalic acid (cTt, tTt, tCt and cCt conformers) is about or below 1 kcal mol^{-1}, which is lower than the energy barrier of 5.73 kcal mol^{-1} for water-catalyzed SO$_3$ hydration. By comparing the rate of SO$_3$ hydration reaction catalyzed by oxalic acid and water, it can be found that the oxalic acid-catalyzed SO$_3$ hydration can compete with water-catalyzed SO$_3$ hydration in the upper troposphere. This leads us to conclude that the involvement of oxalic acid in SO$_3$ hydration to form H$_2$SO$_4$ is significant in the atmosphere.

20

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$_2$O), as the most traditional HAT reactions, can be widely found in the atmosphere (Alvarez-Idaboy

et al., 2001;Cameron et al., 2002;Steckler et al., 1997;Atkinson et al., 2006). 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) also are the important HAT reaction in the atmosphere. These atmospheric HAT reactions have a main feature that two-point

5   hydrogen bond can occur and can facilitate hydrogen atom transfer (Kumar et al., 2016). The presence of water, acid and other catalysts, as the hydrogen donors and acceptors, contributes 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 of atmospheric scientists.

The hydration of SO_3 to form sulfuric acid is a typical addition reaction involving the hydrogen atom transfer. In the

10   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 firstly is formed, and the complex then rearrange to form 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, due to high energy barrier, this hydration reaction involving a single water molecule cannot takes place in the atmosphere (Hofmann and Schleyer, 1994;Morokuma and Muguruma, 1994;Steudel, 1995). The inclusion

15   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 reduce 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 atmosphere molecules can behave as a catalyst to promote the hydration of SO_3. To the best of our

20   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 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 accumulating 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.,

5   2017;Zhang, 2010). Theoretical studies about the effect of oxalic acid on atmospheric particle nucleation and growth have shown that it can form 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. 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. Thus, it

10   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. As is known, 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

15   were calculated using the kinetics analysis, and compared with that for 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 in the second water as a catalyst to form sulfuric acid.

2. Computational details

Gaussian 09 suit of software (Frisch et al., 2010) were used in this work to perform all electronic structure calculations.

20   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. For M06-2X method, the ultrafine integration grid was chosen to enhance calculation accuracy at reasonable additional cost. The frequency calculations were carried out with the same level after geometric optimization to verify the local minimum points and transition states through the criterion that no

Atmospheric
Chemistry
and Physics
Discussions

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 also can 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 connected with the corresponding reactants and products. A high level ab initio method,

5   CCSD(T) method (Purvis and Bartlett, 1982;Pople et al., 1987), with the 6-311++G(3df,3pd) basis set was used to refine the

single-point energies of these optimized species. To obtain the conformational population of oxalic acid in different

temperature more accurately, the quantum chemistry composite method, Gaussian 4 (G4) theory (Curtiss et al., 2007), also

was performed for oxalic acid conformers.

For the kinetics analysis, the electronic energies based on the CCSD(T)/6-311++G(3df,3pd) level of theory, while the

10   partition functions 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 analysis was executed in the KiSThelP program (Canneaux et al., 2014). The

kinetics analysis is summarized as follows.

On the basis of the discussion in this paper, it can conclude that the hydration reactions begin with the formation of

15   pre-reactive complex, and then undergo a transition state to form post-reactive complex. This process can be characterized

by the following equation:

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} pre - reactive\ complex \xrightarrow{k_{uni}} post - reactive\ complex \qquad (1)$$
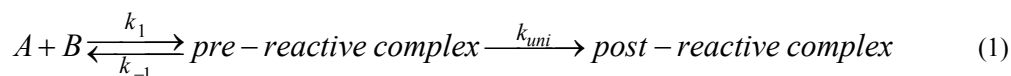
Assuming that the pre-reactive complex is in equilibrium with the reactants and the steady state approximation is

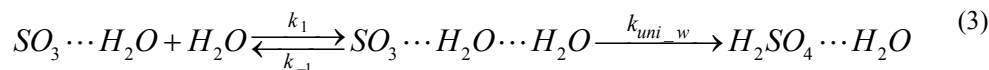applied to pre-reactive complex, the reaction rate can be formulated as

20
$$v = \frac{k_1}{k_{-1}} k_{uni} [A][B] = K_{eq} k_{uni} [A][B] \qquad (2)$$

where K_{eq} is the equilibrium constant of the first step and k_{uni} is the rate constant for unimolecular reaction of pre-reactive
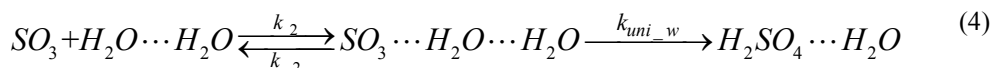
complex to post-reactive complex.

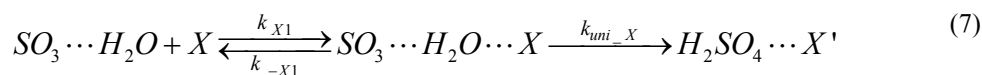For water-catalyzed hydration process, its two channels can be written as:

Recation 1 :

$$SO_3 \cdots H_2O + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SO_3 \cdots H_2O \cdots H_2O \xrightarrow{k_{uni\_w}} H_2SO_4 \cdots H_2O \quad (3)$$

Reaction 2 :

$$SO_3 + H_2O \cdots H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} SO_3 \cdots H_2O \cdots H_2O \xrightarrow{k_{uni\_w}} H_2SO_4 \cdots H_2O \quad (4)$$

The corresponding rate constants are that:

$$v_{SO_3\cdots H_2O+H_2O} = \frac{k_1}{k_{-1}} k_{uni\_w}[SO_3 \cdots H_2O][H_2O] = K_{eq1}k_{uni\_w}[SO_3 \cdots H_2O][H_2O]$$
$$= k_{w1}[SO_3 \cdots H_2O][H_2O] \quad (5)$$
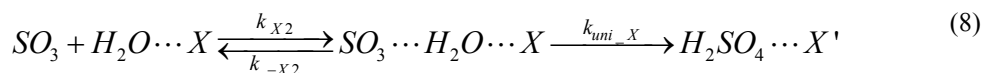
$$v_{SO_3+H_2O\cdots H_2O} = \frac{k_{w2}}{k_{-w2}} k_{uni\_w}[SO_3][H_2O \cdots H_2O] = K_{eq2}k_{uni\_w}[SO_3][H_2O \cdots H_2O]$$
$$= k_{w2}[SO_3][H_2O \cdots H_2O] \quad (6)$$

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. The two channels can be shown as following:

Reaction $X1$:

$$SO_3 \cdots H_2O + X \underset{k_{-X1}}{\overset{k_{X1}}{\rightleftharpoons}} SO_3 \cdots H_2O \cdots X \xrightarrow{k_{uni\_X}} H_2SO_4 \cdots X' \quad (7)$$

Reaction $X2$:

$$SO_3 + H_2O \cdots X \underset{k_{-X2}}{\overset{k_{X2}}{\rightleftharpoons}} SO_3 \cdots H_2O \cdots X \xrightarrow{k_{uni\_X}} H_2SO_4 \cdots X' \quad (8)$$

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 as following:

$$v_{SO_3\cdots H_2O+X} = \frac{k_{X1}}{k_{-X1}} k_{uni\_X}[SO_3 \cdots H_2O][X] = K_{eq\_X1}k_{uni\_X}[SO_3 \cdots H_2O][X]$$
$$= k_{X1}[SO_3 \cdots H_2O][X] \quad (9)$$

$$v_{SO_3+H_2O\cdots X} = \frac{k_{X2}}{k_{-X2}} k_{uni\_X}[SO_3][H_2O\cdots X] = K_{eq2\_X2} k_{uni\_X}[SO_3][H_2O\cdots X] \qquad (10)$$
$$= k_{X2}[SO_3][H_2O\cdots X]$$

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

$$\frac{v_{SO_3\cdots H_2O+X}}{v_{SO_3\cdots H_2O+H_2O}} = \frac{k_{X1}[SO_3\cdots H_2O][X]}{k_{w1}[SO_3\cdots H_2O][H_2O]} = \frac{k_{X1}[X]}{k_{w1}[H2O]} \qquad (11)$$

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

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 talked about many times, we still include it in our paper so as to compare this reaction with the following SO_3 hydration reaction catalyzed by oxalic acid at the same theoretical level, that is, at CCSD(T)/6-311++G(3df,3pd)//M06-2X/6-311++G(3df,3pd) level. For the reaction SO_3+2H_2O, the existence of two pathways has become a consensus. 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). The potential energy profile and geometric structures can be found from Fig. 1. Other results calculated about the reaction are put into Supplement (Table S1).

For the two channel, it is clear that the binding energy of water dimer is 3.22 kcal mol^{-1}, and that of $SO_3\cdots H_2O$ complex is 6.48 kcal·mol^{-1}. As shown in the Fig. 1, the two pathways share the same pre-reactive complex (RC1) and the following processes. The RC1 has the binding energy of 15.47 kcal mol^{-1} relative to SO_3+2H_2O, and consist of 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 the rate-limiting step with the barrier energy of 5.73 kcal mol^{-1} with respect to the RC1. 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.

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 of all relevant species for

oxalic acid catalyzed hydration of SO$_3$ are summarized in Supplement (Table 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 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 (see Fig. 4). The hydration reactions catalyzed by the remaining four conformers have the

same feature (Fig. 3), which is that the pre-reactive complex formed from SO$_3$···H$_2$O complex with oxalic acid (OA) or

OA···H$_2$O complex with water can evolve into product complex (H$_2$SO$_4$···OA complex) via transition state of hydrogen

atom transfer. For the reaction catalyzed by cTt conformer, the binding energy of cTt···H$_2$O complex is 9.05 kcal mol^{-1}.

Compared to the cTt···H$_2$O complex with SO$_3$, the binding energy of pre-reactive complex is 11.24 kcal mol^{-1}, while that is

13.81 kcal mol^{-1} relative to SO$_3$···H$_2$O 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 1.37 kcal mol^{-1} with respect to RC$_{cTt}$. The

post-reactive complex (PC$_{cTt}$) lies below the RC$_{cTt}$ by 13.11 kcal mol^{-1}. It should be noted that the cTt conformer from RC$_{cTt}$

has transform to the cCt conformer in PC$_{cTt}$. The binding energy of PC$_{cTt}$ is 18.54 kcal mol^{-1} compared to H$_2$SO$_4$ and cCt

conformer.

For hydration reaction involving the tTt conformer, the tTt···H$_2$O complex is stabilized by 8.76 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 12.82 kcal mol^{-1}, whereas RC_{tTt} has the binding energy of 15.10 kcal mol^{-1} when it come from the $SO_3\cdots H_2O$ + tTt channel. The TS_{tTt} lies above the RC_{tTt} by 0.44 kcal mol^{-1}, and proceed with the formation of PC_{tTt}, which is 13.75 kcal mol^{-1} more stable than RC_{tTt}. The formed PC_{tTt} needs to overcome 18.06 kcal mol^{-1} to disaggregate into H_2SO_4 and tCt conformer.

For tCt conformer, the binding energy of tCt$\cdots H_2O$ complex is 8.93 kcal mol^{-1}. 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}.

For cCt conformer, the binding energy of cCt$\cdots H_2O$ complex is 9.92 kcal mol^{-1}. Beginning with cCt$\cdots H_2O$ + SO_3 channel and $SO_3\cdots H_2O$ + cCt channel, the hydration reaction undergo the same RC_{cCt} complex, which is more stable than the two reactants (by 12.61 kcal mol^{-1}, 16.05 kcal mol^{-1}, respectively), and a transition state (TS_{cCt}) with the energy barrier of 0.26 kcal mol^{-1}, to form the $H_2SO_4\cdots cTt$ complex (PC_{cCt}), which lies below RC_{cCt} complex by 15.07 kcal mol^{-1} and below H_2SO_4 + cTt by 16.87 kcal mol^{-1}.

In the light of the analysis above, it is obvious that energy barrier of the hydration reaction catalyzed by oxalic acid is about or below 1 kcal mol^{-1}. 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 nearly 6 kcal mol^{-1}. Another thing we want to mention is that one oxalic acid conformer involving in SO_3 hydration transfer to another conformer type after the completion of hydration reaction (cTt → cCt, tTt → tCt, tCt → tTt, cCt → cTt).

3.3. Atmospheric implications

For evaluating 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

Atmospheric
Chemistry
and Physics
Discussions

reaction with that of water-catalyzed hydration at different altitudes in the troposphere. The corresponding temperature, pressure, density of air and water vapor content at an 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, we can confirm that the ratio of rate constant and relative concentrations, are both 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 constants for the Reaction cTt1 at 298.15 K and altitude of 0 km (5.87 × 10^{-8} cm^3 molecule^{-1} s^{-1}) is about 10^4 times than, whereas the Reaction tTt1, tCt1 and cCt1 (k_{tTt1}: 1.99 × 10^{-6}, k_{tCt1}: 3.10 × 10^{-6}, k_{cCt1}: 1.02 × 10^{-5} cm^3 molecule^{-1} s^{-1}) are 6 orders of magnitude greater than, that for the Reaction 1 (1.52×10^{-12} cm^3 molecule^{-1} s^{-1}). From the comparison of rate constants between the reaction of the $H_2O\cdots X$ complex with SO_3 (Reaction X2) and the reaction of water dimer with SO_3 (Reaction 2), it is also clear that the rate constant of Reaction X2 is higher than Reaction 2 (at 298.15 K and altitude of 0 km, k_{cTt2}/k_{w2}: ~10^2, k_{tTt2}/k_{w2}: ~10^4, k_{tCt2}/k_{w2}: ~10^4, k_{cCt2}/k_{w2}: ~10^4). All corresponding rate constant ratios at various altitudes are described in Table 2. It can be seen from Table 2 that rate constant ratios increase with the temperature decreasing (that is, with altitude increasing).

Another factor in the rate comparison, as shown in Eq. (11) and Eq. (12), is the reactant concentration. For Eq. (11), the concentration considered is about oxalic acid conformers and water vapor, while the concentration in Eq. (12) is about oxalic acid-water complex and water-water complex. For simplicity, we will only talk about the rate comparison between the Reaction X1 and the Reaction 1 in the following part.

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). The calculation method about the conformational population is shown in Supplement (Text S1). The most stable conformer, cTc conformer, accounts for more than 95 % of oxalic acid in the altitude range 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 assisting the SO_3 hydration do not excess 5 % of oxalic acid. In some studies (Martinelango et al., 2007;Bao et al., 2012), observed concentration 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 molecule cm^{-3}) for total oxalic acid at 298.15 K and altitude of 0 km, which are measured by Bao et al (2012). Combining

5   mole fractions for conformers (cTt, tTt, tCt and cCt) and the total concentration of oxalic acid 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, the ratio of the total reaction rate for $SO_3 \cdots H_2O$ complex with oxalic acid conformers (cTt, tTt,

10   tCt and cCt) to the rate for $SO_3 \cdots H_2O$ complex with H_2O are described. At altitude of 0 km, the rate ratio for these two reactions is in the range of 10^{-4}-10^{-5} at two temperatures (298.15 K and 288.15 K), which indicates that the oxalic acid-catalyzed SO_3 hydration cannot compete with the water-catalyzed hydration at 0 km with different temperatures. However, as the altitude increase, the oxalic acid has an increasing impact on the SO_3 hydration because of obvious increase of the ratio. When the altitude increases to 6 km, the water-catalyzed hydration reaction is approximately 55 times faster than

15   the oxalic acid-catalyzed SO_3 hydration. The oxalic acid-catalyzed reaction just is 1 order of magnitude slow than water-catalyzed reaction at altitude of 8 km. As the altitude rise to 10 km, the oxalic acid-catalyzed SO_3 hydration is competitive with water-assisted hydration. At altitude of 12 km, the oxalic acid-catalyzed hydration reaction is about 6 times faster than the water-assisted hydration.

    To sum up, the comparison of relative rate for oxalic acid and water catalyzed SO_3 hydration reaction shows that the

20   oxalic acid can play a significant role in SO_3 hydration to H_2SO_4 in the upper troposphere.

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 real 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 5.73 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. The energy barrier of hydration reaction of SO_3 is about or below 1 kcal mol^{-1}. The results signify oxalic acid has the higher catalytic

5   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 also is an important factor to assess the effect of oxalic acid on SO_3 hydration. Based on the two factors, our calculation shows that the oxalic acid-catalyzed hydration reaction can compete with the

10   water-catalyzed reaction in the upper troposphere. The results indicate that, in the upper troposphere, the oxalic acid can play an important role in SO_3 hydration to form H_2SO_4 in the atmosphere.

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.

15   **Supplement**

Competing interests

The authors declare that they have no conflict of interest.

Atmospheric
Chemistry
and Physics
Discussions

Open Access

EGU

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.

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.

Atmospheric
Chemistry
and Physics
Discussions

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 NH_2CH_2OH, 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

Atmospheric
Chemistry
and Physics
Discussions

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.

5   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.

10   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.

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.

15   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

20   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

5   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.

Morokuma, K., and Muguruma, C.: Ab initio Molecular Orbital Study of the Mechanism of the Gas Phase Reaction SO3 +

10   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

15   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.

20   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.

Steckler, R., Thurman, G. M., Watts, J. D., and Bartlett, R. J.: Ab initio direct dynamics study of OH+HCl→Cl+H2O, J.

16

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.

5   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.

10   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,

15   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.

20   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

5   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.

10   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,

15   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.

20

Atmospheric
Chemistry
and Physics
Discussions

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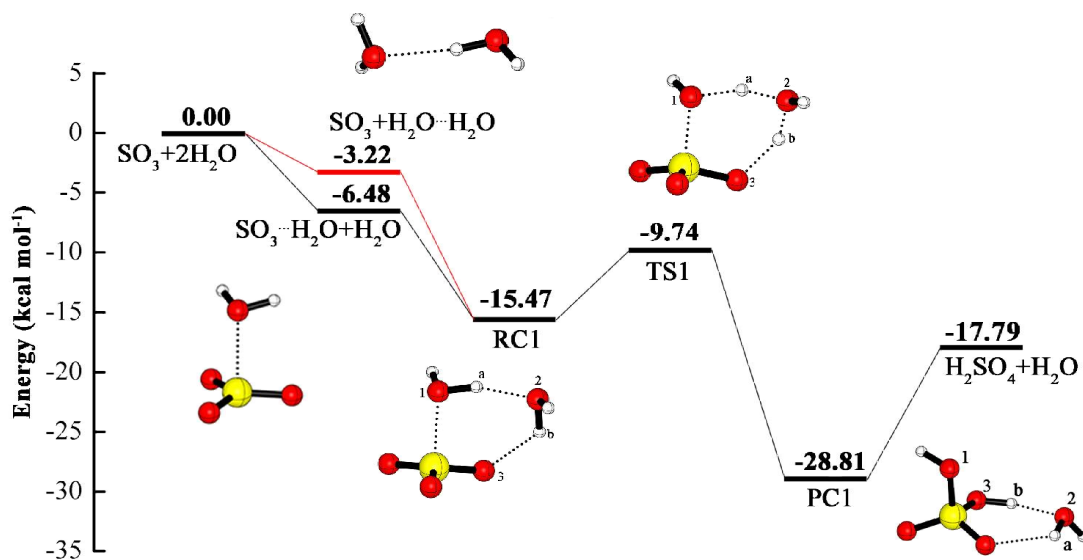
Figure 1. Calculated potential energy profile for the hydration of SO_3 with the second water as a catalyst at the CCSD(T)/6-311++G(3df,3pd)//M06-2X/6-311++G(3df,3pd) level.

5
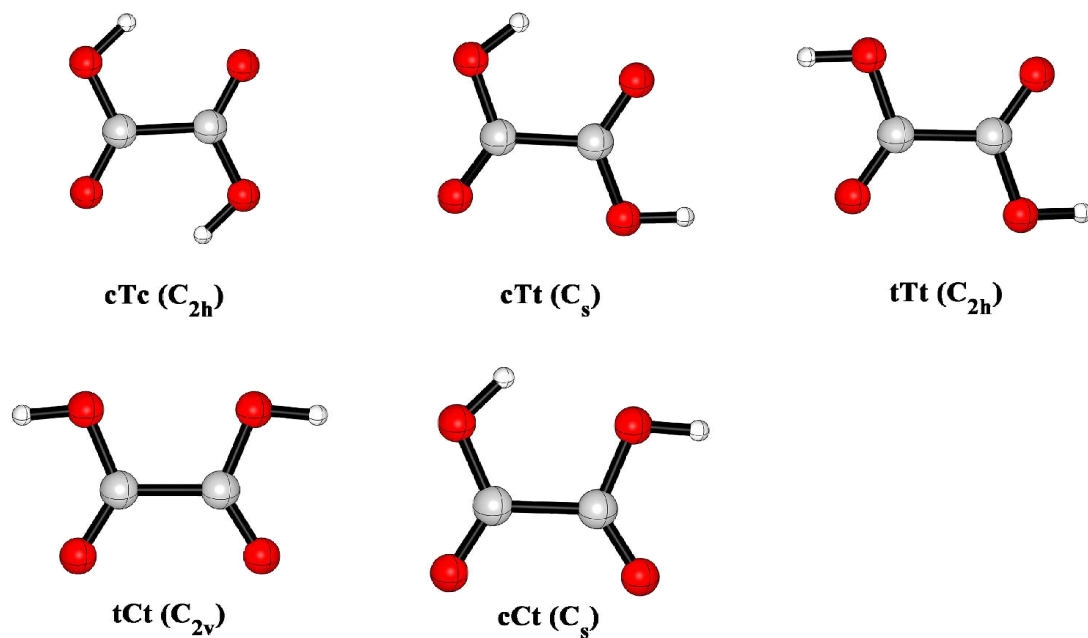
Figure 2. Structures of oxalic acid conformers optimized at the M06-2X/6-311++G(3df,3pd) level.
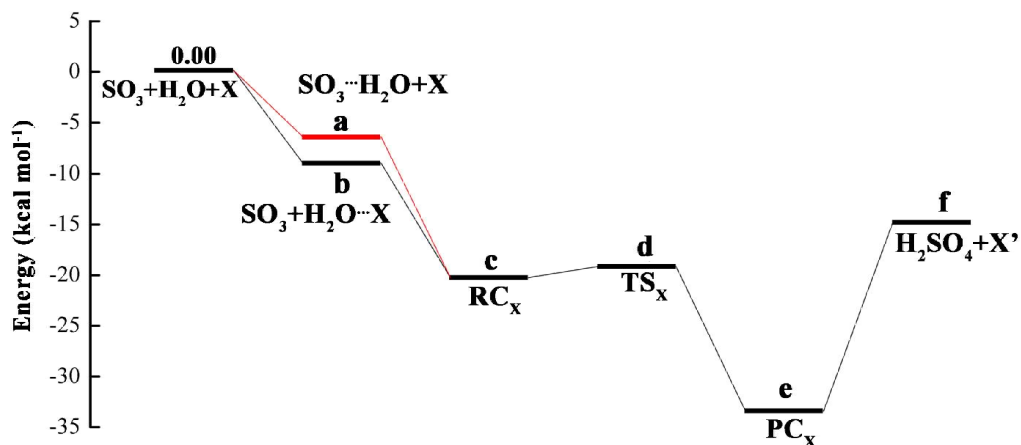
When X = cTt,

   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.

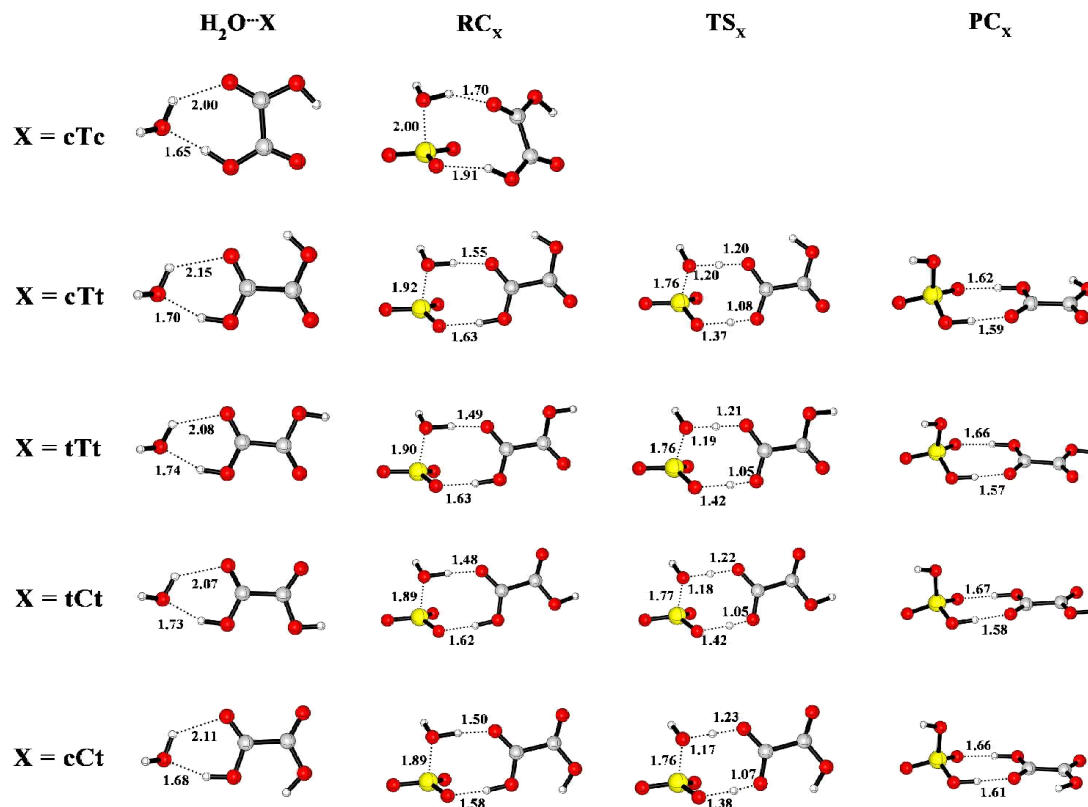**Figure 4.** Optimized M06-2X/6-311++G(3df,3pd) structures of reactant complexes, pre-reactive complexes, transition states and post-reactive complexes for the oxalic acid-catalyzed SO_3 hydration reaction.

Atmospheric
Chemistry
and Physics
Discussions

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}

Atmospheric
Chemistry
and Physics
Discussions

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

Atmospheric
Chemistry
and Physics
Discussions

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 %

Atmospheric
Chemistry
and Physics
Discussions

Table 4. Concentrations (in molecule 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]$v_{SO3\cdots H2O+OA}/v_{SO3\cdots H2O+H2O}$	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 $v_{SO3\cdots H2O+OA}$ represents the sum of reaction rate for $SO_3\cdots H_2O$ complex with four oxalic acid conformers (cTt, tTt, tCt, cCt). The rate ($v_{SO3\cdots H2O+cTt}/v_{SO3\cdots H2O+H2O}$, $v_{SO3\cdots H2O+tTt}/v_{SO3\cdots H2O+H2O}$, $v_{SO3\cdots H2O+tCt}/v_{SO3\cdots H2O+H2O}$, $v_{SO3\cdots H2O+cCt}/v_{SO3\cdots H2O+H2O}$) are shown in Table S10.