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 ($R\text{-}H+OH \rightarrow R+H_2O$), 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:

$$\begin{aligned} &A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C \\ &C + D \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} pre-reactive\ complex \xrightarrow{k_{uni}} post-reactive\ complex \end{aligned} \qquad (1)$$

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

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

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:

$$Recation\ 1:$$

$$SO_3+H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SO_3\cdots H_2O \tag{3}$$

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

$$Reaction\ 2:$$

$$H_2O+H_2O \underset{k_{-1}^{w2}}{\overset{k_1^{w2}}{\rightleftarrows}} H_2O\cdots H_2O \tag{4}$$

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

The corresponding rates are:

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

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

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:

$$Reaction\ X1:$$

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

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

$Reaction\ X2:$

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

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

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 v_{X1}/v_{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.

Acknowledgments

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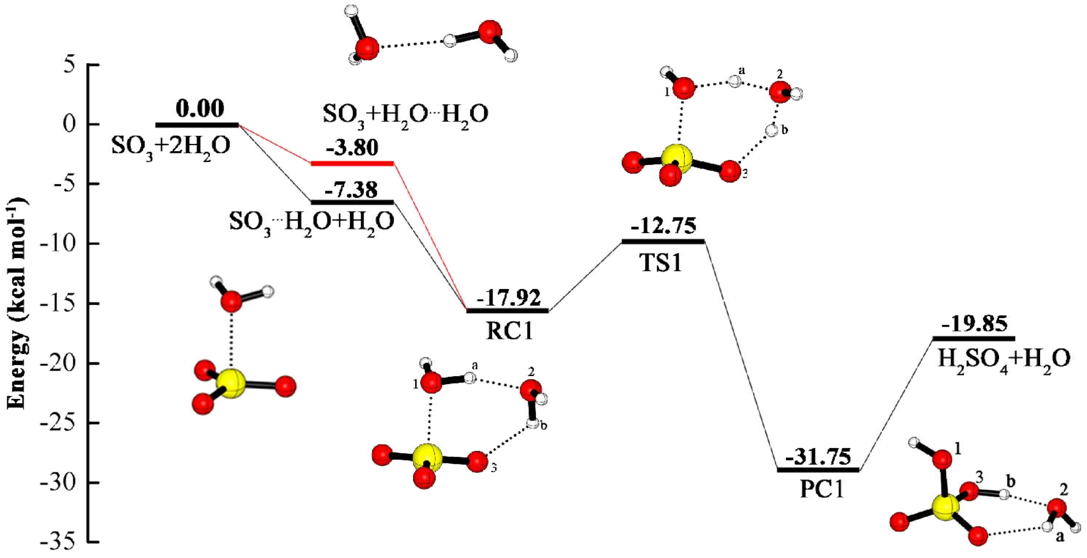
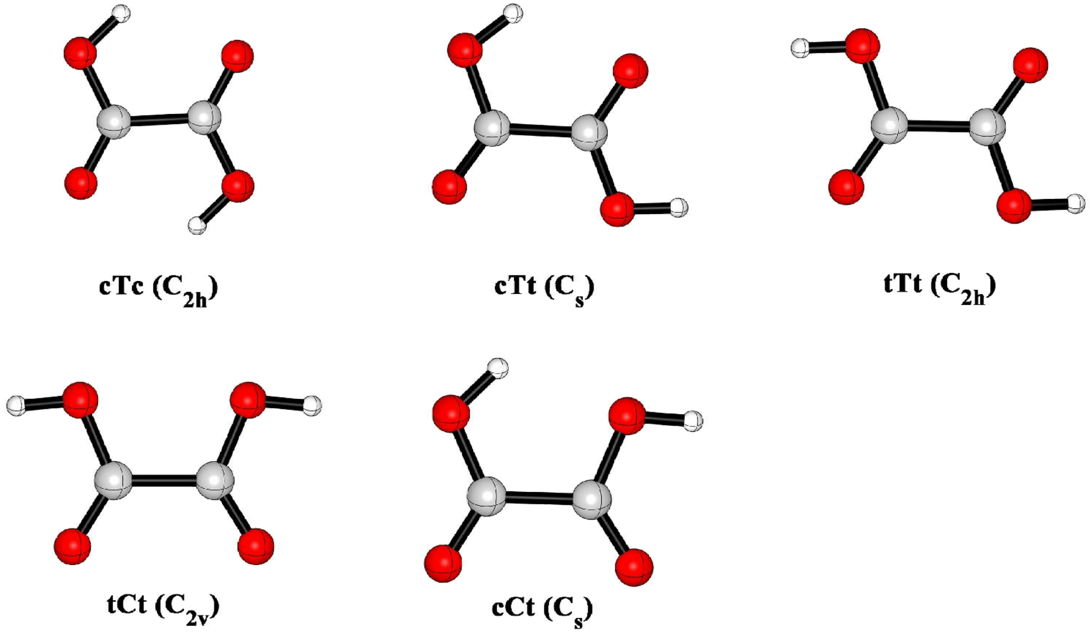


Figure 1. Calculated potential energy profile for the hydration of SO_3 with the second water as a catalyst at the CCSD(T)/cc-pV(T+d)Z//M06-2X/6-311++G(3df,3pd) level.



cTc (C_{2h})

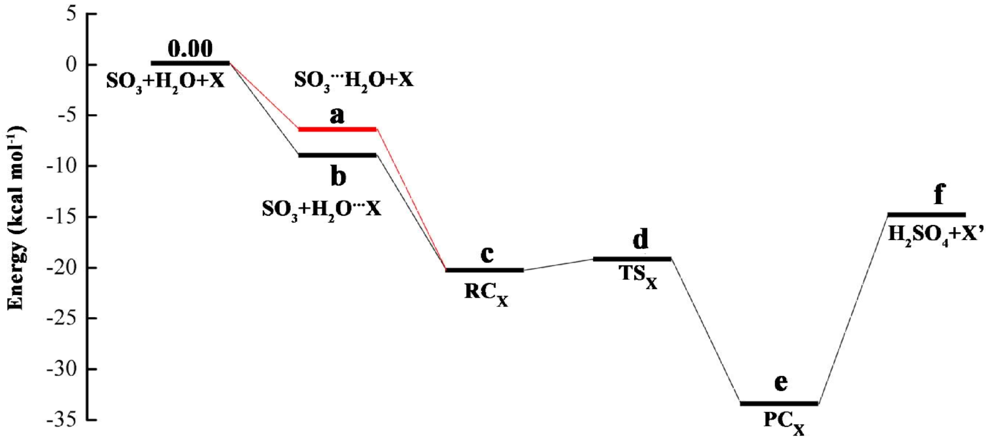
cTt (C_s)

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.

5

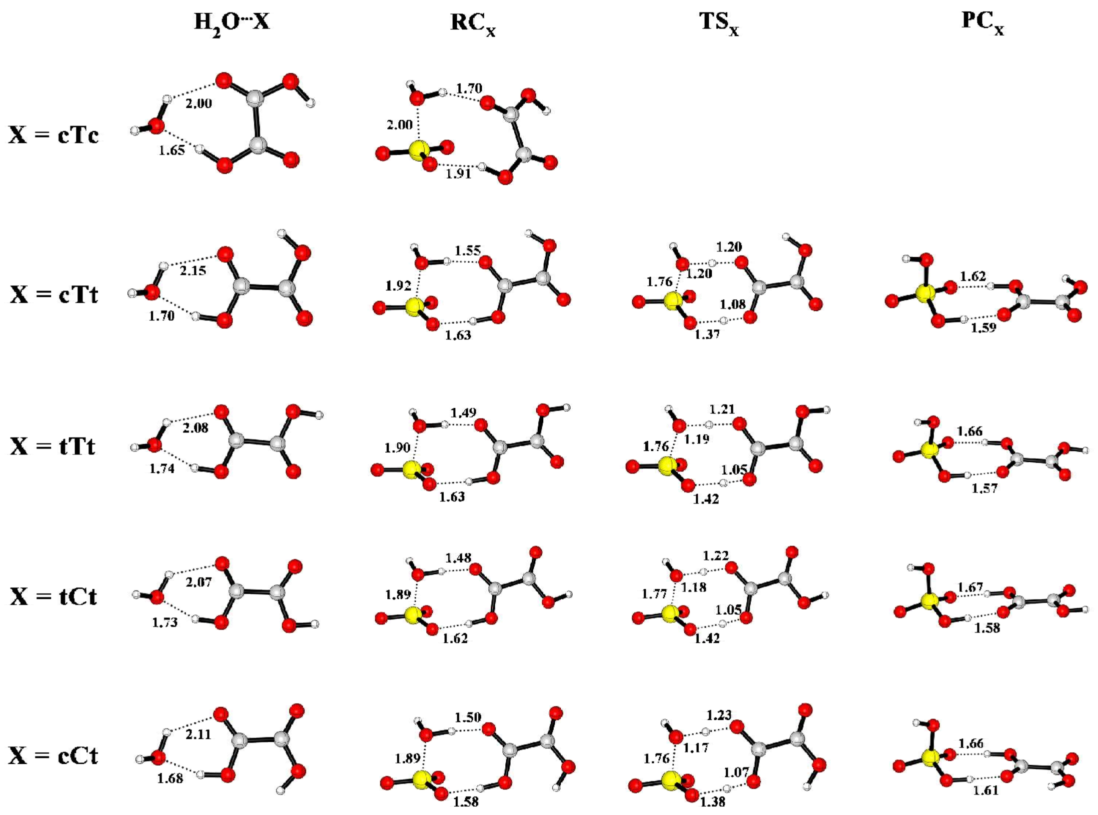


Figure 4. Optimized M06-2X/6-311++G(3df,3pd) structures of reactant complexes, pre-reactive complexes, transition states and post-reactive complexes for the oxalic acid-catalyzed SO_3 hydration reaction (distance unit: angstrom).

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
$^{a}\nu_{OA1}/\nu_{w1}$	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 ($\nu_{cTt1}/\nu_{w1,}$ $\nu_{tTt1}/\nu_{w1,}$ $\nu_{tCt1}/\nu_{w1,}$ ν_{cCt1}/ν_{w1}) are shown in Table S10.