Reaction of SO₃ with H₂SO₄ and Its Implication for Aerosol Particle Formation in the Gas Phase and at the Air-Water Interface

Rui Wang a, Yang Cheng a, Yue Hu a,‡, Shasha Chen a, Xiaokai Guo a, Fengmin Song a, Hao Li b,*, Tianlei Zhang **

a Shaanxi Key Laboratory of Catalysis, School of Chemical & Environment Science, Shaanxi University of Technology, Hanzhong, Shaanxi 723001, P. R. China
b State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China
c Department of Applied Chemistry, Yuncheng University, Yuncheng, Shanxi 044000, China

Abstract

The reactions between SO₃ and atmospheric acids are indispensable in improving the formation of aerosol particle. However, relative to those of SO₃ with organic acids, the reaction of SO₃ with inorganic acids has not received much attention. Here, we explore the atmospheric reaction between SO₃ and H₂SO₄, a typical inorganic acid, in the gas phase and at the air-water interface by using quantum chemical (QC) calculations and Born-Oppenheimer molecular dynamics simulations. We also report the effect of H₂S₂O₇, the product of the reaction between SO₃ and H₂SO₄, new particle formation (NPF) in various environments by using the Atmospheric Cluster Dynamics Code kinetic model and the QC calculation. The present findings show that the gas phase reactions of SO₃ + H₂SO₄ without and with water molecule are both low energy barrier processes. With the involvement of interfacial water molecules, H₂O-induced the formation of S₂O⁵⁻•••H₂O⁻ ion pair, HSO₄⁻ mediated the formation of HSO₄⁻•••H₂O⁻ ion pair and the deprotonation of H₂S₂O₇ were observed and proceeded on the picosecond time-scale. The present findings suggest the potential contribution of SO₃-H₂SO₄ reaction to NPF and aerosol particle growth as the facts that i) H₂S₂O₇ can directly participate in H₂SO₄-NH₃-based cluster formation and can facilitate the fastest possible rate of NPF from H₂SO₄-NH₃-based clusters by about a factor of 6.92 orders of magnitude at 278.15 K; and ii) the formed interfacial S₂O⁵⁻ can attract candidate species from the gas phase to the water surface, and thus, accelerate particle growth.

* Corresponding authors. Tel: +86-0916-2641083, Fax: +86-0916-2641083.
E-mail: ztianlei88@163.com (T. L Zhang) ; haol@recess.ac.cn (H. Li)
‡ Yang Cheng and Yue Hu contributed equally to this work.
1. Introduction

Sulfur trioxide (SO$_3$) is a major air pollutant (Zhuang and Pavlish, 2012; Chen and Bhattacharya, 2013; Cao et al., 2010; Kikuchi, 2001; Mitsui et al., 2011) and can be considered as the most important oxidation product of SO$_2$ (Starik et al., 2004). As an active atmospheric species, SO$_3$ can lead to the formations of acid rain and atmospheric aerosol (Sipilä et al., 2010; Mackenzie et al., 2015; England et al., 2000; Li et al., 2016; Renard et al., 2004) and thus plays a well-documented role in regional climate and human health (Zhang et al., 2012; Pöschl, 2005; Zhang et al., 2015; Pöschl and Shiraiwa, 2015; Haywood and Boucher, 2000; Lohmann and Feichter, 2005).

In the atmosphere, the hydrolysis of SO$_3$ to product H$_2$SO$_4$ (SA) is the most major loss route of SO$_3$ (Morokuma and Muguruma, 1994; Akhmatskaya et al., 1997; Larson et al., 2000; Hazra and Sinha, 2011; Long et al., 2013a; Torrent-Sucarrat et al., 2012; Ma et al., 2020). As a complement to the loss of SO$_3$, ammonolysis reaction of SO$_3$ in polluted areas of NH$_3$ can form H$_2$NSO$_3$H, which not only can be competitive with the formation of SA from the hydrolysis reaction of SO$_3$, but also can enhance the formation rates of sulfuric acid (SA)-dimethylamine (NH(CH$_3$)$_2$, DMA) clusters by about 2 times. Similarity, the reactions of SO$_3$ with CH$_3$OH and organic acids (such as HCOOH) were reported (Li et al., 2019; Hazra and Sinha, 2011; Long et al., 2013a; Torrent-Sucarrat et al., 2012; Huff et al., 2017; Smith et al., 2017; Li et al., 2018a), and both processes can provide a mechanism for incorporating organic matter into aerosol particles. However, the reaction mechanism between SO$_3$ and inorganic species are still unclear.

As a typical inorganic acid, SA can act as an important role in the new particle formation (Weber et al., 1995; Weber et al., 1996; Weber et al., 2001; Sihto et al., 2006; Riipinen et al., 2007; Sipilä et al., 2010; Zhang et al., 2012) and acid rain (Calvert et al., 1985; Finlayson-Pitts and Pitts Jr, 1986; Wayne, 2000). The source of gas-phase SA is mainly produced by the gas-phase hydrolysis reaction of SO$_3$. For the direct reaction between SO$_3$ and H$_2$O, it takes place hardly in the atmosphere due to high energy barrier (Chen and Plummer, 1985; Hofmann and Schleyer, 1994; Morokuma and Muguruma, 1994; Steudel, 1995). However the addition of a second water molecule (Morokuma and Muguruma, 1994; Larson et al., 2000; Loerting and Liedl, 2000), the hydroperoxyl radical (Gonzalez et al., 2010), formic acid (Hazra and Sinha, 2011; Long et al., 2012), nitric acid (Torrent-Sucarrat et al., 2012), nitric acid (Long et al., 2013a), oxalic acid (Lv et al., 2019) and
ammonia (Bandyopadhyay et al., 2017) have been reported to catalyze the formation of SA from the hydrolysis reaction of SO$_3$ as they can promote atmospheric proton transfer reactions. Similarly, as SA can give out protons more readily than H$_2$O, which in turn is more conducive to the proton transfer, thus we predict that the addition reaction involving the proton transfer between SO$_3$ and SA is much easier under atmospheric conditions than between SO$_3$ and H$_2$O. However, this gas-phase reaction has not been investigated as far as we know. Meanwhile, in many gas phase reactions, single water molecule can play a catalyst role by increasing the stability of pre-reactive complexes and reducing the activation energy of transition states (Kanno et al., 2006; Stone and Rowley, 2005; Chen et al., 2014; Viegas and Varandas, 2012, 2016). For example, single water molecule in the H$_2$O$^-$HO$^+ +$ SO$_3$ reaction can catalyze the formation of HSO$_5$ (Gonzalez et al., 2010). Thus, it is equally important to study the SO$_3$ + SA reaction without and with H$_2$O. In addition to the gas phase reactions, many new atmospheric processes and new reaction pathways have been observed at the air-water interface (Zhong et al., 2017; Kumar et al., 2017; Kumar et al., 2018; Zhu et al., 2016; Li et al., 2016; Zhu et al., 2017). Such as, the organic acids reacting with SO$_3$ can form the ion pair of carboxylic sulfuric anhydride and hydronium at the air-water interface (Zhong et al., 2019). This mechanism is different from the gas phase reaction in which the organic acid either serves as a catalyst for the hydrolysis of SO$_3$ or acts as a reactant reacting with SO$_3$ directly. So, water droplets may play important roles in atmospheric behaviors between SO$_3$ and SA. Thus, it is also important to study the interfacial mechanism between SO$_3$ and SA, and to compare its difference with the corresponding gas-phase reaction.

Previous experimental studies (Otto and Steudel, 2001; Abedi and Farrokhpour, 2013) found that disulfuric acid (H$_2$SO$_7$, DSA) is the product of the reaction between SO$_3$ and SA. From the perspective of structure, DSA possesses two HO functional groups. Both HO groups can act as hydrogen donors and acceptors to interact with atmospheric particle precursors. It has been shown that the products of SO$_3$ with some important atmospheric species have been identified in promoting NPF process. For example, the products of NH$_3$SO$_3$H, HOOCOSO$_3$H, CH$_3$OSO$_3$H and HOOCOSO$_3$H from the reactions of SO$_3$ with NH$_3$ (Li et al., 2018a), H$_2$C$_2$O$_4$ (Yang et al., 2021), CH$_3$OH (Liu et al., 2019) and HOOCCHO (Rong et al., 2020) all have a catalytic effect on the formation of new particles in aerosols. However, whether DSA produced by the reaction between SO$_3$ and SA contributes to aerosol formation or not is still unclear. Thus, another main question that
we intend to address here is the role of DSA in atmospheric SA-NH$_3$ (A) nucleation, which have been recognized as dominant precursors in highly polluted areas, especially in some megacities in Asia.

In this work, using quantum chemical calculations and Master Equation, we first studied the gas-phase reaction between SO$_3$ and SA to product DSA with H$_2$O acting as a catalyst. Then, we use the Born-Oppenheimer Molecular Dynamic (BOMD) simulations to evaluate the reaction mechanism of SO$_3$ with SA at the air-water interface. Finally, we used Atmospheric Clusters Dynamic Code (ACDC) and quantum chemical calculations to investigate atmospheric implications of SO$_3$-SA reaction to the atmospheric particle formation. Particular attention of this work is focused on the study of i) the mechanism difference of the SO$_3$ + SA reaction in the gas phase and at the air-water interface; ii) the fate of DSA in atmospheric NPF and its influence at various environmental conditions.

2. Computational Details

2.1 Quantum Chemical Calculation. For the gas-phase reaction of SO$_3$ + SA without and with water molecule, the optimized geometries and vibrational frequencies of reactants, pre-reactive complexes, transition states (TSs), post-reactive complexes and products were calculated using M06-2X method (Frisch et al., 1990) with 6-311++G(2df,2pd) basis set by Gaussian 09 packages (Frisch, 2009). At the same level, the connectivity between the TSs and the suitable pre- and post-reactant complexes was performed by intrinsic reaction coordinate (IRC) calculations. Then, single point energy calculations were calculated at the CCSD(T)-F12/cc-pVDZ-F12 level by using ORCA (Bork et al., 2014; Myllys et al., 2016; Elm and Kristensen, 2017).

A multistep global minimum sampling technique was used to search for the global minima of the (DSA)$_x$(SA)$_y$(A)$_z$ ($z \leq x + y \leq 3$) molecular clusters. In the first step, the initial structure of 1000 clusters were autogenerated by the ABCluster program (Zhang and Dolg, 2015, 2016) with the CHARMM force field (MacKerell et al., 1998). Then, these structures were optimized firstly by the semiempirical PM6 method in Mopac 2016 (Stewart, 2016). Next, up to 100 isomers were reoptimized at the M06-2X/6-31+G(d,p) level. Finally, 10 lowest-lying structures were optimized by the M06-2X/6-311++G(2df,2pd) level to determine the global minimum. The optimized structures and the formation Gibbs free energy of the stable clusters were summarized in Fig. S9.
and Table S8 of the SI Appendix, respectively.

2.2 Rate constant calculations. Using the Rice-Ramsperger-Kassel-Marcus based Master Equation (ME/RRKM) model (Miller and Klippenstein, 2006), the kinetics for the \( \text{SO}_3 + \text{SA} \) reaction without and with water molecule were calculated by adopting a Master Equation Solver for Multi Energy-well Reactions (MESMER) code (Glowacki et al., 2012). In the MESMER calculation, the rate coefficients for the bimolecular barrierless association step (from reactants to pre-reactive complexes) were evaluated by the Inverse Laplace Transform (ILT) method (Horváth et al., 2020), meanwhile the unimolecular step was performed by the RRKM theory combined with the asymmetric Eckart model. The ILT method and RRKM theory can be represented in Eq (1) and Eq (2), respectively.

\[
k^s(\beta) = \frac{1}{Q(\beta)} \int_0^\infty k(E)\rho(E)\exp(-\beta E)dE
\]

(1)

\[
k(E) = \frac{W(E-E_0)}{\hbar \rho(E)}
\]

(2)

Where \( \hbar \) is denoted as Planck’s constant; \( \rho(E) \) is denoted as the active density of state of the reactant at energy level \( E \); \( E_0 \) is denoted as the reaction threshold energy and \( W(E-E_0) \) is denoted as the sum of the rovibrational states of the transition state (TS) geometry (excluding the degree of freedom related to passing the transition state). The input parameters for electronic geometries, vibrational frequencies, and rotational constants were calculated at the M06-2X/6-311++G(2df,2pd) level and single-point energy calculations were refined at the CCSD(T)-F12/cc-pVDZ-F12 level for the modeling.

2.3 Born-Oppenheimer Molecular Dynamic (BOMD) Simulation. The CP2K code (Hutter et al., 2014) was used in the BOMD simulations. The Becke-Lee-Yang-Parr (BLYP) functional (Becke, 1988; Lee et al., 1988) was chosen to treat with the exchange and correlation interactions, and the Grimme’s dispersion was carried out to account for the weak dispersion interaction (Grimme et al., 2010). The Goedecker-Teter-Hutter (GTH) conservation pseudopotential (Goedecker et al., 1996; Hartwigsen et al., 1998) with the Gaussian DZVP basis set (VandeVondele and Hutter, 2007) and the auxiliary plane wave basis set was applied to correct the system valence electrons and the core electrons, respectively. For the plane wave basis set and Gaussian basis set, the energy cut off (Zhong et al., 2017; Zhong et al., 2018;
Zhong et al., 2019) were set to 280 and 40 Ry, respectively. For each simulation in the gas phase, a $15 \times 15 \times 15 \, \text{Å}^3$ supercell with periodic boundary condition was adopted with a time step of 0.5 fs. The air-water interfacial system included 191 water molecules, SO$_3$ and SA in the BOMD simulation. To avoid periodic interactions between adjacent water droplets, the size of the simulation box (Kumar et al., 2017; Kumar et al., 2018; Ma et al., 2020) was set as $35 \times 35 \times 35 \, \text{Å}^3$ with a time step of 1.0 fs. For all the simulations in the gas phase and at the air-water interface, the Nose-Hoover thermostat (Zhong et al., 2017; Zhong et al., 2018; Zhong et al., 2019; Kumar et al., 2017; Kumar et al., 2018; Ma et al., 2020) was selected the NVT ensemble to control the temperature around 300 K.

2.4 Atmospheric Clusters Dynamic Code (ACDC) Model

The Atmospheric Cluster Dynamics Code (ACDC) (McGrath et al., 2012) was used to simulate the cluster formation rates and mechanisms of $(\text{DSA})_i(\text{SA})_j(\text{A})_z$ $(z \leq x + y \leq 3)$ clusters at different temperatures and monomer concentrations. The thermodynamic data of quantum chemical calculation at the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(2df,2pd) level of theory can be used as the input of ACDC. The birth-death equation (Eq. 3) for clusters solves the time development of cluster concentrations by numerical integration using the ode15s solver in MATLAB program (Shampine and Reichelt, 1997).

$$\frac{dc_i}{dt} = \frac{1}{2} \sum_{j \neq i} \beta_{ij} c_i c_j + \sum_j \gamma_{(i-j)\rightarrow i} c_{i-j} - \sum_j \beta_{ij} c_i c_j - \frac{1}{2} \sum_{j \neq i} \gamma_{i \rightarrow j} c_i + Q_i - S_i$$  \hspace{1cm} (3)

Where $c_i$ is the concentration of cluster $i$, $\beta_{ij}$ is the collision coefficient between clusters $i$ and $j$, $\gamma_{(i-j)\rightarrow i}$ is the evaporation coefficient of cluster $i+j$ evaporating into clusters $i$ and $j$, and $Q_i$ is all other source term of cluster $i$. (See more details of $\beta$ and $\gamma$ in SI Appendix Part 4). Besides, a constant coagulation sink coefficient $2 \times 10^{-2} \, \text{s}^{-1}$ (corresponding to the median observed in contaminated areas) was used for taking into account external losses (Yao et al., 2018; Zhang et al., 2022; Liu et al., 2021b). The details for the boundary conditions and concentration ranges of SA, A and DSA are presented in the SI Appendix Part 5.

3. Results and discussion

3.1 Reactions in the gas phase

The addition reaction involving the proton transfer between SO$_3$ and SA (Channel DSA)
proceeded through the formation of SO$_3$$^\cdot$$\cdot$$\cdot$H$_2$SO$_4$ complex followed by unimolecular transformation through transition state TSOA to form H$_2$SO$_7$ (Fig. 1(a)). The reactant complex SO$_3$$^\cdot$$\cdot$$\cdot$H$_2$SO$_4$ was a double six-membered ring complex with a relative Gibbs free energy of -1.6 kcal mol$^{-1}$. After the formation of SO$_3$$^\cdot$$\cdot$$\cdot$H$_2$SO$_4$ complex, Channel DSA overcame a Gibbs free energy barrier of 2.3 kcal mol$^{-1}$, which was lower by 4.2 kcal mol$^{-1}$ than that of H$_2$O-catalyzed hydrolysis of SO$_3$ (Fig. S1). Rate constant for the SO$_3$ + SA reaction was calculated at various temperatures (Table 1).

Within the temperature range of 280-320 K, the rate constants for the SO$_3$ + SA reaction were calculated to be $2.57 \times 10^{12}$-5.52 $\times 10^{12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, which were larger by 3.43-4.03 times than the corresponding values of H$_2$O-catalyzed hydrolysis of SO$_3$. Therefore, it can be said that the direct reaction between SO$_3$ and SA is more favorable over H$_2$O-catalyzed hydrolysis of SO$_3$ energetically and kinetically.

As the probability of simultaneous collision (Pérez-Ríos et al., 2014; Elm et al., 2013) of three molecules of SO$_3$, SA and H$_2$O is quite low under realistic conditions, the SO$_3$ + SA reaction with H$_2$O (Channel DSA_WM) can be considered as a sequential bimolecular process. In other words, Channel DSA_WM occurs via the collision between SO$_3$ (or SA) and H$_2$O to form dimer (SO$_3$$^\cdot$$\cdot$$\cdot$H$_2$O and H$_2$SO$_4$$^\cdot$$\cdot$$\cdot$H$_2$O) first, and then the dimer encounters with the third reactant SA or SO$_3$. The computed Gibbs free energies of dimer complexes SO$_3$$^\cdot$$\cdot$$\cdot$H$_2$O and H$_2$SO$_4$$^\cdot$$\cdot$$\cdot$H$_2$O were respectively 0.8 kcal mol$^{-1}$ and -1.9 kcal mol$^{-1}$, which were respectively consistent with the previous values (the range from -0.2 to 0.62 kcal mol$^{-1}$ for SO$_3$$^\cdot$$\cdot$$\cdot$H$_2$O complex (Bandyopadhyay et al., 2017; Long et al., 2012) and the range from -1.82 to -2.63 kcal mol$^{-1}$ for H$_2$SO$_4$$^\cdot$$\cdot$$\cdot$H$_2$O complex (Long et al., 2013b; Tan et al., 2018)). The Gibbs free energy of H$_2$SO$_4$$^\cdot$$\cdot$$\cdot$H$_2$O was lower by 2.7 kcal mol$^{-1}$ than that of SO$_3$$^\cdot$$\cdot$$\cdot$H$_2$O, thus leading to that the equilibrium constant of the former complex is larger by at least one order of magnitude than that of the latter one in Table S2. Additionally, the larger equilibrium constant of H$_2$SO$_4$$^\cdot$$\cdot$$\cdot$H$_2$O complex leads to its higher concentration in the atmosphere.

For example, when the concentrations of SO$_3$ (Yao et al., 2020), H$_2$SO$_4$ (Liu et al., 2015) and H$_2$O (Anglada et al., 2013) were $10^6$, $10^6$ and $10^{17}$ molecules cm$^{-3}$, respectively, the concentrations of SO$_3$$^\cdot$$\cdot$$\cdot$H$_2$O and H$_2$SO$_4$$^\cdot$$\cdot$$\cdot$H$_2$O were $2.41 \times 10^{12}$-2.01 $\times 10^{12}$ and $5.01 \times 10^{12}$-3.01 $\times 10^{12}$ molecules cm$^{-3}$ within the temperature range of 280-320 K (see Table S3), respectively. So, we predict that Channel DSA_WM mainly takes place via the collision of H$_2$SO$_4$$^\cdot$$\cdot$$\cdot$H$_2$O with SO$_3$. In order to check this prediction, the effective rate constants for two bimolecular reactions of H$_2$SO$_4$$^\cdot$$\cdot$$\cdot$H$_2$O + SO$_3$ and...
SO\textsubscript{3}•••H\textsubscript{2}O + H\textsubscript{2}SO\textsubscript{4} were calculated, and the details were shown in SI Appendix, Part 3 and Table 203. As seen in Table 1, the SO\textsubscript{3}•••H\textsubscript{2}O + H\textsubscript{2}SO\textsubscript{4} reaction can be neglected as its effective rate constant is smaller by 16.7-48.5 times than the corresponding value of the H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O + SO\textsubscript{3} reaction. Therefore, we only consider the H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O + SO\textsubscript{3} bimolecular reaction in H\textsubscript{2}O-catalyzed SO\textsubscript{3} + SA reaction.

The H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O + SO\textsubscript{3} reaction occurred in a stepwise process as displayed in Fig. 1(b), which was similar to the favorable routes in the hydrolysis of COS, HCHO and CH\textsubscript{2}CHO catalyzed by sulfuric acid (Long et al., 2013b; Li et al., 2018b; Tan et al., 2018). When the H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O complex and SO\textsubscript{3} served as reactants, the reaction was initiated by complex IM\textsubscript{DSA,WM}' where a van der Waals interaction (S2•••O4, 2.75 Å) was found between the O4 atom of SA moiety in H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O and the S atom of SO\textsubscript{3}. After complex IM\textsubscript{DSA,WM}', the ring enlargement from IM\textsubscript{DSA,WM} to SO\textsubscript{3}•••H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O complex occurred through transition state TS\textsubscript{DSA,WM}' with a Gibbs free energy barrier of 1.2 kcal·mol\textsuperscript{-1}. Complex SO\textsubscript{3}•••H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O was 6.1 kcal·mol\textsuperscript{-1} lower in energy than IM\textsubscript{DSA,WM}'. In SO\textsubscript{3}•••H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O, SO\textsubscript{3} acted as double donors of hydrogen bond to form a cage-like hydrogen bonding network with H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O. Then, starting with SO\textsubscript{3}•••H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O complex, the H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O + SO\textsubscript{3} reaction occurred through transition state TS\textsubscript{DSA,WM} with a Gibbs free barrier energy of 0.5 kcal·mol\textsuperscript{-1} to form a quasi-planar network complex, H\textsubscript{2}S\textsubscript{2}O\textsubscript{4}•••H\textsubscript{2}O. TS\textsubscript{DSA,WM} was in the middle of a double proton transfer, where H\textsubscript{2}O played as a bridge for proton transfer, along with the simultaneous formation of the O4•••S2 bond. In order to estimate the catalytic ability of H\textsubscript{2}O in the SO\textsubscript{3} + SA reaction, the effective rate constant (\(k'\text{_{DSA,WM,L}}\)) of the H\textsubscript{2}SO\textsubscript{4}•••H\textsubscript{2}O + SO\textsubscript{3} reaction were compared with the rate constant (\(k\text{_{DSA}}\)) of the SO\textsubscript{3} + SA reaction. As seen in Table 1, under the experimental concentration (Anglada et al., 2013) ([H\textsubscript{2}O] = 5.20 \times 10^{16}-2.30 \times 10^{18} \text{ molecules·cm}^{-3}) within the temperature range of 280-320 K, the calculated \(k'\text{_{DSA,WM,L}}\) was 1.03 \times 10^{11}-4.60 \times 10^{12} \text{ cm}^{-3}·\text{molecule}^{-1}·\text{s}^{-1}, which was larger by 1.79-1.86 times than that of \(k\text{_{DSA}}\). This result shows that H\textsubscript{2}O exerts catalytic role in promoting the rate of the SO\textsubscript{3} + SA reaction.

3.2 Reactions at the Air-water interface

The mechanism for the SO\textsubscript{3} + SA reaction at the air-water interface was lacking and thus explored below. Due to the high reactivity of SO\textsubscript{3} and SA at the air-water interface, the product SA' is formed with extremely short times from both SO\textsubscript{3} (Zhong et al., 2019) and SA (Fig. S2) (on the
order of a few picoseconds) with interfacial water molecules. So, two possible models were mainly considered for SO$_3$-SA reaction on the water surface: (i) gaseous SO$_3$ colliding with SA$^-$ at the air-water interface and (ii) the DSA (the gas-phase product of SO$_3$ and SA) dissociating on water droplet. 

**Gaseous SO$_3$, Colliding with SA$^-$ at the Air-Water Interface.** At the water droplet's surface, the interaction between SO$_3$ and SA$^-$ included two main channels: (i) H$_2$O-induced formation of S$_2$O$_2^-$⋯H$_2$O$^+$ ion pair (Fig. 2, Fig. S3 and Movie S1) and (ii) SA$^-$-mediated formation of SA$^-$⋯H$_2$O$^+$ ion pair (Fig. 3, Fig. S4-S5 and Movie S2-S3). The BOMD simulations for H$_2$O-induced formation of S$_2$O$_2^-$⋯H$_2$O$^+$ ion pair was illustrated in Fig. 2, the H1 atom of SA$^-$ ion can combine with a nearby interfacial water molecule at 8.18 ps by hydrogen bond ($d_{O(3)-H1} = 1.17$ Å) interaction, thus forming hydrated hydrogen sulfate ion (SA$^-$⋯H$_2$O). Then, the H1 atom of SA$^-$ ion was moved to the O3 atom of the interfacial water molecule at 8.28 ps, revealing the formation of SO$_2^-$⋯H$_2$O$^+$ ion pair. Additionally, SO$_2^-\ (Fig. S7)$, revealing the formation of S$_2$O$_2^-$⋯H$_2$O$^+$ ion pair. Both direct (without the involvement of SA$^-$, Fig. 3(a), Fig. S4 and Movie S2) and indirect (with the involvement of SA$^-$, Fig. 3(b), Fig. S5 and Movie S3) forming mechanisms were observed in SA$^-$-mediated formation of SA$^-$⋯H$_2$O$^+$ ion pair. The direct SA$^-$-mediated formation of SA$^-$⋯H$_2$O$^+$ ion pair was a loop structure mechanism, which was consistent with gas phase hydrolysis of SO$_3$ assisted by acidic catalysts of HCOOH, HNO$_3$, H$_2$C$_2$O$_4$ and SA in the previous works (Long et al., 2012; Long et al., 2013a; Torrent-Sucarrat et al., 2012; Lv et al., 2019), and HNO$_3$-mediated Criegee hydration at the air-water interface. As for the direct formation mechanism of SA$^-$⋯H$_2$O$^+$ ion pair seen in Fig. 3(a) and movie S2, an eight-membered loop complex, SO$_3^-\cdot\cdot\cdot$H$_2$O(1)$\cdot\cdot\cdot$SA$^-$; was found at 1.46 ps with the formations of two hydrogen bonds ($d_{O(3)-O1} = 2.13$ Å; $d_{O(4)-O3} = 2.18$ Å) and a van der Waals interaction ($d_{O(3)-O1} = 2.14$ Å). Subsequently, SO$_3$ and interfacial H$_2$O(1) were close to each other. At 1.59 ps, a transition state-like loop structure was observed and proton transfer from interfacial H$_2$O(1) to another suspended H$_2$O(2) was found, where the bond lengths of S1-O1, O1-H1 and H1-O2 were 1.94 Å, 1.19 Å and 1.32 Å, respectively. At 1.70 ps, the bond lengths of S-O1 and H1-O2 were reduced to 1.73 Å and 1.01 Å, while the bond length of H1-O2 was extended to 1.61 Å, showing the formation of SA$^-$⋯H$_2$O$^+$ ion pair. During the direct formation route of SA$^-$⋯H$_2$O$^+$ ion pair, SA$^-$ played as a spectator, while interfacial water molecules acted as both a reactant and a
proton acceptor.

As seen in Fig. 3(b) and Movie S3, the indirect forming process of SA⋅⋅⋅H_3O^+ ion pair contained two steps: (i) SO_3 hydration along with SA formation and (ii) SA deprotonation. Specifically, as for step (i), at 0.70 ps, a transition state like structure of SO_3 hydration was observed with SO_3, SA^- and an interfacial water molecule involved. Note that at this time the H1 atom in interfacial H_2O molecule migrated to the O2 atom of SA^- ion instead of the surrounding water molecule. At 0.96 ps, the O1-H1 bond of H_2O was broken with the length of 1.56 Å, while the S1-O1 bond was formed with the length of 1.75 Å, demonstrating the completion of hydrolysis reaction of SO_3 and the formation of SA molecule. Then, at 8.08 ps, the H2 proton transfer from SA to the O4 atom of SA^- ion to the O5 atom of the nearby water molecule was occurred, where the O3-H2 and O1-H3 bonds extended to 1.13 Å and 1.22 Å, and the length of O4-H2 and O5-H3 bonds shortened to 1.45 Å and 1.20 Å. Finally, SA deprotonation was completed at 8.23 ps with the formation of SA⋅⋅⋅H_3O^+ ion pair. During the whole indirect forming process of SA⋅⋅⋅H_3O^+ ion pair, SA^- played as protons donor and acceptor, and water molecules acted as hydration reactants and proton acceptors.

The H_2S_2O_7 Dissociating on Water Droplet. In addition to the gaseous SO_3 colliding with SA^- at the air-water interface, DSA, the product of the barrierless reaction between SO_3 and SA, can further quickly react with interfacial water molecule at the air-water interface. As seen in Fig. 4, Fig. S6 and Movie S4, DSA is highly reactive at the air-water interface and can undergo two deprotonations to form S_2O_7^{2-} ion. Specifically, the DSA can firstly form a H-bond with interfacial water molecule at 0.45 ps. After that, the H1 atom of DSA transferred to interfacial water and produced HS_2O_7^- and H_3O^+ ions. The formed HS_2O_7^- ion can survive for ~3 ps on water droplet. At 4.14 ps, the H2 atom of HS_2O_7^- ion moved to O4 atom of nearby interfacial water molecule and produced the formation of S_2O_7^{2-}⋅⋅⋅H_3O^+ ion pair, which was stable at the air-water interface over a simulated time scale of 10 ps. Note that the second deprotonation of DSA indeed needs more time than its first deprotonation as the pK_a1 (pK_a1 = -16.05) of DSA is much smaller than its pK_a2 (pK_a2 = -4.81) (Abedi and Farrokhpour, 2013). In brief, at the air-water interface, both these two routes of the formation of S_2O_7^{2-}⋅⋅⋅H_3O^+ ion pair occur on the picosecond time scale.

3.3 Atmospheric Implications

In the gas-phase, the main sink route of SO_3 is H_2O-assisted hydrolysis of SO_3 (Morokuma
and Muguruma, 1994; Akhmatskaya et al., 1997; Larson et al., 2000; Hazra and Sinha, 2011; Long et al., 2013a; Torrent-Sucarrat et al., 2012; Ma et al., 2020). To study the atmospheric importance of the SO$_3$ + SA reaction without and with H$_2$O, the rate ratio ($v_{DSA}/v_{SA}$) between the SO$_3$ + SA reaction and H$_2$O-assisted hydrolysis of SO$_3$ was compared, which was expressed in Eq. (4).

$$\frac{v_{DSA}}{v_{SA}} = \frac{k_{DSA} \times [SO_3] \times [H_2SO_4] + k_{SA,WM} \times K_{eq[H_2SO_4=H_3O]} \times [SO_3] \times [H_2SO_4] \times [H_2O]}{k_{SA,WM} \times K_{eq[SO_3+H_2O]} \times [SO_3] \times [H_2O] \times [H_2O]}$$

(4)

In Eq. (4), $K_{eq1}$ and $K_{eq2}$ were the equilibrium constant for the formation of complex H$_2$SO$_4$+$\cdot$H$_2$O and SO$_3$$\cdot$$\cdot$H$_2$O shown in Table S2, respectively; $k_{DSA}$, $k_{DSA,WM}$ and $k_{SA,WM}$ were respectively denoted the bimolecular rate coefficient for the H$_2$SO$_4$ + SO$_3$, H$_2$SO$_4$$\cdot$$\cdot$H$_2$O + SO$_3$ and SO$_3$$\cdot$$\cdot$H$_2$O + H$_2$O reactions; [H$_2$O] and [H$_2$SO$_4$] were respectively represented the concentration of H$_2$O and SA taken from references (Anglada et al., 2013; Liu et al., 2015); The value of $v_{DSA}/v_{SA}$ was listed in Table S6. As seen in Table S6, the hydrolysis reaction of SO$_3$ + (H$_2$O)$_2$ is usually the major sink route of SO$_3$, as the [H$_2$O] is much larger than that of [H$_2$SO$_4$] ($10^4$-$10^5$ molecules$\cdot$cm$^{-3}$). However, the formation of H$_2$SO$_4$ from the gas phase reaction of SO$_3$ with SA investigated in the present work could play a role in the chemistry of the Earth’s atmosphere.

Through the configuration (shown in Fig. S9) and stability analysis (shown in Fig. S10 and Table S8-S11), DSA was found to promote intermolecular interactions between SA and A to stabilize the corresponding clusters. To figure out how DSA affects the kinetic clustering process, the potential influence of DSA to the SA-A-based particle formation was estimated by calculating the enhancement factor $R$ in Eq (5).

$$R = \frac{J_{SA-A,DSA}}{J_{SA-A}} = \frac{J([SA] = x, [A] = y, [DSA] = z)}{J([SA] = x, [A] = y, [DSA] = 0)}$$

(5)

where $J_{SA-A,DSA}$ and $J_{SA-A}$ are represented the formation rate of SA-A-DSA and SA-A nucleating system, respectively. $x$, $y$ and $z$ are the atmospheric concentration of SA, A and DSA. As the values of $R$ shown in Table S12-S16, DSA was better enhancer for NPF of SA-A based system, because $R$ were all greater than or equal to 1.0 at four different temperatures of 218.15 K, 238.15 K, 258.15 K, 278.15 K and 298.15 K as well as the nucleation precursor concentration range ([SA] = $10^5$-$10^6$ molecules$\cdot$cm$^{-3}$; [A] = $10^7$-$10^{11}$ molecules$\cdot$cm$^{-3}$ and the calculated DSA concentrations are [DSA] = $10^3$-$10^7$ molecules$\cdot$cm$^{-3}$ in Table S7).

Generally, $J$ and $R$ has been affected by the temperature and the concentrations of nucleating
precursors (Liu et al., 2021a). The $J$ of SA-A-DSA-based system in Fig. S11 is negatively dependent on temperature, and it sharply rise with the increase of [DSA] at the normal temperature (298.15 K) and the atmospheric pollution boundary layer (278.15 K). However, Fig. 5(a) showed that $R$ rises with the increase of temperature, and the rise trend of $R$ is relatively more obvious at 298.15 K and 278.15 K which can be up to 7.19 and 3.82 orders of magnitude at higher [DSA], respectively. This behavior may be because that although both the $J_{SA, A, DSA}$ and $J_{SA, A}$ decrease with the temperature increase, the reduction scale of $J_{SA, A}$ is much greater than that of $J_{SA, A, DSA}$ when the temperature is increased from 218.15 K to 298.15 K. Notedly, the values of $J$ at 298.15 K are lower by at least two orders of magnitude than that at 278.15 K at higher [DSA]. So, in the following studies, attention is mainly focused on the atmospheric pollution boundary layer (278.15 K). As illustrated in Fig. 5(b), a remarkable rise of $R$ with the increase of [A] has been discovered when [A] was larger than $10^9$ molecules/cm$^3$ at 278.15 K. The significantly negative correlation of $R$ with [SA] in all ranges of [A] (Fig. 5(b)) has been established due to a competitive relationship between SA and DSA. When [DSA] and [A] were the highest and [SA] was the lowest, the effect of $R$ was the strongest, and $R$ can reach 6.92 orders of magnitude. This conclusions about the change of $R$ with concentrations of precursors could also be applied for the other four temperatures shown in Fig. S11. Hence, it can be forecasted that the participation of DSA in SA-A-based NPF can likely enhance the number concentration of atmospheric particulates significantly in the polluted atmospheric boundary layer (278.15 K) areas with relatively high [DSA] and [A].

Two main cluster formation pathways, the pure SA-A-based cluster (a) and DSA-containing cluster (b), can be observed at 278.15 K (Fig. 6(A)). As seen, the DSA molecule exhibited an ability to directly participate in cluster formation under median concentration precursors of SA and DSA, and high [A], indicating that DSA can be a “participant” in promoting cluster formation. Interestingly, at different temperature, the DSA molecule showed different effect mechanism and contribution in SA-A system. As seen in Fig. 6(B), the cluster growth pathways were dominated by pure SA-A-based cluster formation under the conditions of 218.15 K, 238.15 K and 258.15 K, whereas the DSA-containing cluster formation was dominant at 278.15 K. By the way, the cluster growth pathways were completely dominated by the DSA-containing cluster at 298.15 K, and its contribution for growth flux out of the system reached to 100% (Fig. S13). Meanwhile, the relative contribution of the pure SA-A-based cluster pathway and the DSA-containing cluster pathway to

https://doi.org/10.5194/egusphere-2023-2009
Preprint. Discussion started: 13 October 2023
© Author(s) 2023. CC BY 4.0 License.
the growth flux out of the system may also depend on the precursors concentration. Specifically, when the temperature was fixed at 278.15 K, the contribution of DSA-containing pathway was positively correlated with [DSA] in Fig. 6(C). Of particular note, at low DSA concentration ([DSA] = 10^4 molecule cm^{-3}), DSA do not substantially contribute to the cluster growth and the pathway just involved the pure SA-A-based clusters. While at the median concentration of DSA ([DSA] = 10^5 molecule cm^{-3}), the contribution of DSA-containing clusters for growth flux out of the system can up to 84%. When [DSA] raised to 10^3 molecule cm^{-3}, the DSA-containing clusters growth mainly dominates cluster formation in the system, and its contribution for growth flux out of the system increased to 95%. Besides, the contribution of DSA-containing pathway was negatively correlated with [SA] because of the competition relationship between DSA and SA shown in Fig. 6(D). These results suggested that DSA has the ability to act as a potential contributor to SA-A-based NPF in the atmosphere, and the DSA participation pathway can be dominant in heavy sulfur oxide polluted atmospheric boundary layer and in season of late autumn and early winter.

At the air-water interface, important implication of the BOMD simulations is that the reaction between SO_3 and SA at the air-water interface can be accomplished within a few picoseconds, among which the interfacial water molecules play a significant role in promoting the formation of S_2O_7^{2-}\cdots H_2O^+ and SA\cdots H_2O^+ ion pairs. Furthermore, the adsorption capacity of the S_2O_7^{2-}, H_2O^+ and SA’ to gaseous precursors in the atmosphere was further investigated. Herein, the species of SA, NH_3, and HNO_3 have been regarded as the candidate species. (Kulmala et al., 2004; Kirkby et al., 2011). Our calculated results in Table 2 show that the interactions of S_2O_7^{2-}\cdots H_2SO_4, S_2O_7^{2-}\cdots HNO_3, S_2O_7^{2-}\cdots (COOH)_2, H_2O^+\cdots NH_3, H_2O^+\cdots H_2SO_4, SA\cdots H_2SO_4, SA\cdots (COOH)_2, and SA\cdots HNO_3 are stronger than those of H_2SO_4\cdots NH_3 (major precursor of atmospheric aerosols). These results reveal that interfacial S_2O_7^{2-}, SA’ and H_2O^+ can attract candidate species from the gas phase to the water surface, and thus in turn accelerates the growth of particle. Moreover, we evaluated the enhancing potential of S_2O_7^{2-} on SA-A cluster by considering geometrical structure and the formation free energies of the (SA)\_1(A)\_1(S_2O_7^{2-})\_1 clusters. As compared with (SA)\_1(A)\_1(X)\_1 (X = HOOCH\_2COOH, HOCCOOSO\_3H, CH\_3O\_3SO\_3H, HOOCCH\_2CH(NH\_2)COOH and HOCH\_2COOH) clusters (Zhong et al., 2019; Zhang et al., 2018; Rong et al., 2020; Gao et al., 2023; Liu et al., 2021a; Zhang et al., 2017), the number of hydrogen bonds in (SA)\_1(A)\_1(S_2O_7^{2-})\_1 cluster presented in Fig. S8 increased and the ring of the complex was enlarged. It was demonstrated that S_2O_7^{2-} has the
highest potential to stabilize SA-A clusters and promote SA-A nucleation in these clusters due to its acidity and structural factors such as more intermolecular hydrogen bond binding sites.

Subsequently, comparing to (SA)$_3$(A)$_3$(X)$_1$ clusters (Table 2), the Gibbs formation free energy $\Delta G$ of (SA)$_3$(A)$_2$(S$_2$O$_3^{2-}$)$_1$ cluster is lower. Therefore, we predict that S$_2$O$_3^{2-}$ at the air-water interface has important implication to the aerosol NPF in highly industrial polluted regions with high concentrations of SO$_3$.

**4. Summary and Conclusions**

In this work, we employed QC calculations, BOMD simulations and ACDC kinetic model to characterize the SO$_3$-H$_2$SO$_4$ interaction in the gas phase and at the air-water interface and to study the effect of H$_2$S$_2$O$_7$ on H$_2$SO$_4$-NH$_3$-based clusters. Results revealed that the energy barrier of the gas phase SO$_3$ + H$_2$SO$_4$ reaction without and with H$_2$O is less than 2.3 kcal·mol$^{-1}$. Rate constants indicated that though the SO$_3$ + H$_2$SO$_4$ reaction cannot compete with H$_2$O-assisted hydrolysis of SO$_3$ within the temperature range of 280-320 K, its rate constant was close to the upper limits for bimolecular reactions and H$_2$O exerts obvious catalytic role in promoting the reaction rate. Moreover, ACDC kinetic simulations showed that DSA has unexpected facilitate effects on the NPF process and can enhance the rate of NPF from SA-A by about 6.92 orders of magnitude in polluted atmospheric boundary layer. Of particular note, DSA can directly participate in the SA-A-based cluster formation pathway with its contribution up to 93% in regions with atmospheric pollution boundary layer of high concentrations of SO$_3$, especially in late autumn and early winter.

At the air-water interface, H$_2$O-induced the formation of S$_2$O$_3^{2-}$⋯H$_2$O$^+$ ion pair, SA$^-$ mediated the formation of SA$^-$⋯H$_2$O$^+$ ion pair and the deprotonation of H$_2$S$_2$O$_7$ were observed, both of which can occur within a few picoseconds. The formed interfacial S$_2$O$_3^{2-}$; SA$^-$ and H$_2$O$^+$ can attract candidate species (such as H$_2$SO$_4$, NH$_3$, and HNO$_3$) for particle formation from the gas phase to the water surface, and thus accelerates the growth of particle. Moreover, potential of $X$ ($X = $ S$_2$O$_3^{2-}$; HOOCCCH$_2$COOH, HOOC(OOSO$_2$)CH$_3$, HOOCCH$_2$CH(NH$_2$)COOH and HOCH$_2$COOH) in ternary SA-A-$X$ cluster formation indicated that S$_2$O$_3^{2-}$ has the highest potential to stabilize SA-A clusters and promote SA-A nucleation among $X$.

The present work will expand our understanding of new pathway for the loss of SO$_3$ in acidic polluted areas. Moreover, this work will also help to reveal some missing sources of metropolis
industrial regions NPF and to understand the atmospheric organic-sulfur cycle more comprehensively.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No: 22203052; 22073059; 22006158); the Natural Science Foundation of Shaanxi Province (NO: 2022JM-060); the Key Cultivation Project of Shaanxi University of Technology (No: SLG2101); The Special Scientific Research Project of Hanzhong City-Shaanxi University of Technology Co-construction State Key Laboratory (SXJ-2106); The authors thank Prof. Qingzhu Zhang and Fei Xu from Shandong University for their sincere assistance in calculating the air-water interface reaction.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Reference


Table 1 The rate constant (cm$^3$molecule$^{-1}$s$^{-1}$) for the SO$_3$ + H$_2$SO$_4$ reaction and the effective rate constant (cm$^3$·molecule$^{-1}$·s$^{-1}$) for the SO$_3$ + H$_2$SO$_4$ reaction with H$_2$O (100% RH) within the temperature range of 280-320 K.

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>280 K</th>
<th>290 K</th>
<th>298 K</th>
<th>300 K</th>
<th>310 K</th>
<th>320 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{DSA}$</td>
<td>$5.52 \times 10^{-12}$</td>
<td>$4.60 \times 10^{-12}$</td>
<td>$3.95 \times 10^{-12}$</td>
<td>$3.80 \times 10^{-12}$</td>
<td>$3.13 \times 10^{-12}$</td>
<td>$2.57 \times 10^{-12}$</td>
</tr>
<tr>
<td>$k'_{DSA, WM,o}$</td>
<td>$2.12 \times 10^{-13}$</td>
<td>$2.68 \times 10^{-13}$</td>
<td>$2.88 \times 10^{-13}$</td>
<td>$2.89 \times 10^{-13}$</td>
<td>$2.89 \times 10^{-13}$</td>
<td>$2.75 \times 10^{-13}$</td>
</tr>
<tr>
<td>$k'_{DSA, WM,s}$</td>
<td>$1.03 \times 10^{-13}$</td>
<td>$8.55 \times 10^{-13}$</td>
<td>$7.42 \times 10^{-13}$</td>
<td>$7.11 \times 10^{-13}$</td>
<td>$5.79 \times 10^{-13}$</td>
<td>$4.60 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

$k_{DSA}$ is the rate constant for the SO$_3$ + H$_2$SO$_4$ reaction; $k'_{DSA, WM,o}$ and $k'_{DSA, WM,s}$ are respectively the effective rate constants for H$_2$O-assisted SO$_3$ + H$_2$SO$_4$ reaction occurring through one-step and stepwise routes.
Table 2 Gibbs free energy ($\Delta G$, kcal·mol$^{-1}$) for the formation of S$_2$O$_7^{2-}$⋯$\cdot$H$_2$SO$_4$, S$_2$O$_7^{2-}$⋯$\cdot$HNO$_3$, S$_2$O$_7^{2-}$⋯$\cdot$(COOH)$_2$, H$_2$O⋯$\cdot$NH$_3$, H$_2$O⋯$\cdot$H$_2$SO$_4$, HSO$_4^{\cdot}$⋯$\cdot$H$_2$SO$_4$, HSO$_4^{\cdot}$⋯$\cdot$(COOH)$_2$, HSO$_4^{\cdot}$⋯$\cdot$HNO$_3$, H$_2$O⋯$\cdot$H$_2$SO$_4$, H$_2$SO$_4^{\cdot}$⋯$\cdot$NH$_3$, HOCCCH$_2$COOH⋯$\cdot$H$_2$SO$_4$⋯$\cdot$NH$_3$, HOCCCH$_2$CH(NH$_2$)COOH⋯$\cdot$H$_2$SO$_4$⋯$\cdot$NH$_3$ and HOOCCH$_2$COOH⋯$\cdot$H$_2$SO$_4$⋯$\cdot$NH$_3$ at 298 K

<table>
<thead>
<tr>
<th></th>
<th>S$_2$O$_7^{2-}$⋯$\cdot$H$_2$SO$_4$</th>
<th>S$_2$O$_7^{2-}$⋯$\cdot$HNO$_3$</th>
<th>S$_2$O$_7^{2-}$⋯$\cdot$(COOH)$_2$</th>
<th>H$_2$O⋯$\cdot$NH$_3$</th>
<th>H$_2$SO$_4^{\cdot}$⋯$\cdot$NH$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G$</td>
<td>-46.3 (-49.2)$^a$</td>
<td>-30.6 (-49.2)$^a$</td>
<td>-39.9 (-49.2)$^a$</td>
<td>-51.7</td>
<td>-8.9</td>
</tr>
<tr>
<td></td>
<td>H$_2$O⋯$\cdot$H$_2$SO$_4$</td>
<td>HSO$_4^{\cdot}$⋯$\cdot$H$_2$SO$_4$</td>
<td>HSO$_4^{\cdot}$⋯$\cdot$(COOH)$_2$</td>
<td>HSO$_4^{\cdot}$⋯$\cdot$HNO$_3$</td>
<td>S$_2$O$_7^{2-}$⋯$\cdot$H$_2$SO$_4$</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>-27.5 (-27.0)$^a$</td>
<td>-41.6 (-27.0)$^a$</td>
<td>-33.6 (-27.0)$^a$</td>
<td>-27.8</td>
<td>-40.1</td>
</tr>
<tr>
<td></td>
<td>HOCCCH$_2$COOH</td>
<td>HOCCOSO$_3$H</td>
<td>CH$_3$OSO$_2$H</td>
<td>HOCCCH$_2$CH(NH$_2$)COOH</td>
<td>HOCH$_2$COOH</td>
</tr>
<tr>
<td></td>
<td>...$\cdot$H$_2$SO$_4$⋯$\cdot$NH$_3$</td>
<td>...$\cdot$H$_2$SO$_4$⋯$\cdot$NH$_3$</td>
<td>...$\cdot$H$_2$SO$_4$⋯$\cdot$NH$_3$</td>
<td>...$\cdot$H$_2$SO$_4$⋯$\cdot$NH$_3$</td>
<td>...$\cdot$H$_2$SO$_4$⋯$\cdot$NH$_3$</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>-13.1 (-13.6)$^b$</td>
<td>-20.4 (-22.5)$^f$</td>
<td>-18.8 (-20.7)$^f$</td>
<td>-13.2 (-14.0)$^f$</td>
<td>-12.8 (-13.5)$^f$</td>
</tr>
</tbody>
</table>

Energies are given in kcal·mol$^{-1}$, and calculated at the M06-2X/6-311++G(2d,2p) theoretical level. References are as follows: [a] Zhong et al., 2019.; [b] Zhang et al., 2018.; [c] Rong et al., 2020.; [d] Gao et al., 2023.; [e] Liu et al., 2021a; [f] Zhang et al., 2017.
H$_2$SO$_4$ can enhance the rate of NPF from H$_2$SO$_4$·NH$_3$ by about 6.92 orders of magnitude.

Graphic abstract
Figure Caption

**Fig. 1** Schematic potential energy surface for the $\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_7$ reaction; Distances is in angstrom at the M06-2X/6-311++G(2df,2pd) level, while the energy values correspond to the calculations at the CCSD(T)-F12/cc-pVDZ-F12/M06-2X/6-311++G(2df,2pd) level. The TS in the $\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{S}_2\text{O}_7$ reaction without and with H$_2$O is denoted by “TS$_{\text{DSA}}$” and “TS$_{\text{DSA, WM}}$”, respectively. The mark of a specific hydrogen bond complex depends on molecular formula and the connection sequence of each moiety.

**Fig. 2** Top panel: Snapshot structures taken from the BOMD simulations, which illustrate H$_2$O-induced the formation of S$_2$O$_7^{2-}$···H$_3$O$^+$ ion pair from the reaction of SO$_3$ with HSO$_4^-$ at the air-water interface. Lower panel: time evolution of key bond distances (S-O1, O2-H1, and O3-H1) involved in the induced mechanism.

**Fig. 3** Top panel: Snapshot structures taken from the BOMD simulations, which illustrate the hydration reaction mechanism of SO$_3$ mediated by HSO$_4^-$ at the air-water interface. Lower panel: time evolution of key bond distances (S-O1, O1-H2, O5-H2, O2-H1, O3-H4 and O4-H3) involved in the hydration mechanism.

**Fig. 4** Top panel: Snapshot structures taken from the BOMD simulations, which illustrate the deprotonation of H$_2$S$_2$O$_7$ at the air water interface. Lower panel: time evolution of key bond distances (O1-H1, O1-H2, O3-H2 and H2-O4) involved in the hydration mechanism.

**Fig. 5** The logarithms of the enhancement strength of DSA (lg$R$) as a function of [DSA] from $10^1$ to $10^3$ molecules cm$^{-3}$ under different temperatures (218.15, 238.15, 258.15, 278.15 and 298.15 K) where [SA] = $10^7$ molecules cm$^{-3}$ and [A] = $10^9$ molecules cm$^{-3}$ (a); The logarithms of the enhancement strength of DSA (lg$R$) as a function of [A] from $10^7$ to $10^{11}$ molecules cm$^{-3}$ at $T$ = 278.15 K and [DSA] = $10^3$ molecules cm$^{-3}$ under different [SA] = $10^6$-$10^8$ molecules cm$^{-3}$ (b).

**Fig. 6** The main pathways of clusters growing out of the research system under the conditions where $T$ = 278.15 K, [SA] = $10^7$ molecules cm$^{-3}$, [A] = $10^{11}$ molecules cm$^{-3}$, and [DSA] = $10^3$ molecules cm$^{-3}$ (A). The pure SA-A-based cluster pathway (a) and the DSA-containing pathway (b). The black and blue fluxes represent the pathways of the SA-A-based cluster and the SA-A-DSA-based cluster, respectively. The effects of temperature (B), [DSA] (C), and [SA] (D) on the relative contribution of the pure SA-A-based cluster pathway and the DSA-containing pathway to the flux out of the system. Others in (B), (C), and (D) indicate that the pathway contribution of the cluster growing out of the studied system is less than 5%.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 5
Fig. 6