A novel formation mechanism of sulfamic acid~~NH_2SO_3H~~ and its enhancing effect on methanesulfonic acid-methylamine aerosol particle formation in agriculture-developed and coastal industrial areas

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Abstract

Sulfamic acid (SFA) significantly impacts atmospheric pollution and poses potential risks to human health. Although traditional source of SFA and its role on sulfuric acid-dimethylamine new particle formation (NPF) has received increasing attention, the formation mechanism of SFA from $HNSO_2$ hydrolysis with ~~CH_3SO_3H~~ methanesulfonic acid (MSA)and its enhancing effect on MSA-methylamine (MA) NPF~~methanesulfonic acid-methylamine APF~~ has not been studied, which will limit the understanding for the source and loss of SFA in agriculture-developed and coastal industrial areas. Here, the gaseous and interfacial formation of SFA from $HNSO_2$ hydrolysis with MSA ~~CH_3SO_3H~~ was investigated using quantum chemical calculations and BOMD simulations. Furthermore, the role of SFA in MSA-MA~~CH_3SO_3H-CH_3NH_2~~ system was assessed using the ACDC kinetic model. Our simulation results indicate that the gaseous SFA formation from the hydrolysis of $HNSO_2$ with MSA~~CH_3SO_3H~~ can be competitive with that catalyzed by H_2O within an altitude of 5-15 km. At the air-water interface, two types of reactions, the ions forming mechanism and the proton exchange mechanism to form SFA^- ~~NH_2SO_3~~$\cdots H_3O^+$ ion pair were observed on the timescale of picosecond. Considering the overall environment of sulfuric acid emission reduction, the present findings suggest that SFA may play a significant role in NPF and the growth of aerosol particle as *i*) SFA can directly participate in the formation of MSA-MA~~CH_3SO_3H-CH_3NH_2~~ -based cluster and enhance the rate of NPF from these clusters by approximately 10^3 times at 278.15 K; and *ii*) the SFA^- ~~NH_2SO_3~~ species at the air-water interface can attract gaseous molecules to the aqueous surface, and thus promote particle growth.

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1 Introduction

As a well-studied nitrogen derivative of sulfuric acid (Rennebaum et al., 2024), sulfamic acid (SFA)(~~NH_2SO_3H~~) was not only recognized as a potent aerosol and cloud nucleating agent (Xue et al., 2024; Zhang et al., 2023; Pszona et al., 2015; Li et al., 2018), but also can harm human health through atmospheric deposition into water bodies (Van Stempvoort et al., 2019). In agriculture-developed and industrial areas with high ammonia (NH_3) concentrations, such as the Yangtze River Delta in China (Yu et al., 2020), Indo-Gangetic Plains (Kuttippurath et al., 2020), Pakistan, Bangladesh (Warner et al., 2016), and the southern Italy (Tang et al., 2021), the atmospheric concentration of SFA estimated by theoretical method of CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6-311++G(3*df*,3*pd*) (Li et al., 2018) was expected to reach up to10^8 molecules·cm^{-3}~~the atmospheric concentration of NH_2SO_3H was expected to reach up to10^8 molecules·cm^{-3}~~, and thus lead to it becoming a significant air pollutant. So, the sources of SFA in the atmosphere has been focused by several groups~~So, the sources of NH_2SO_3H in the atmosphere have been well investigated~~ (Lovejoy and Hanson, 1996; Pszona et al., 2015; Li et al., 2018; Larson and Tao, 2001; Manonmani et al., 2020; Zhang et al., 2022). The traditional source of SFA~~NH_2SO_3H~~ was mainly taken from the ammonolysis of SO_3 (Lovejoy and Hanson, 1996; Larson and Tao, 2001; Li et al., 2018). Experimentally, the rate coefficient for the ammonolysis of SO_3 was detected to be 2.0×10^{-11} cm^3·$molecules^{-1}$·s^{-1} at 295 K (Lovejoy and Hanson, 1996), which was close to the value for the hydrolysis of SO_3 assisted by water molecule (10^{-11}-10^{-10} cm^3 $molecule^{-1}$ s^{-1}) (Kim et al., 1998; Hirota et al., 1996; Shi et al., 1994; Kolb et al., 1994; Long et al., 2013; Long et al., 2023; Ding et al., 2023; Cheng et al., 2023; Wang et al., 2024)~~(Kim et al., 1998; Hirota et al., 1996; Shi et al., 1994)~~. Theoretically, the ammonolysis of SO_3 to produce SFA~~NH_2SO_3H~~ can be catalyzed by NH_3. In arid and heavily polluted regions with high NH_3 concentrations, the effective rate coefficient for the ammonolysis of SO_3 can be sufficiently rapid, making it competitive with the conventional loss pathway of SO_3 with water (Li et al., 2018).

In addition to the ammonolysis of SO_3, new sources of SFA~~NH_2SO_3H~~ formation have received increasing attention (Zhang et al., 2022; Manonmani et al., 2020, Li et al., 2018, Xue et al., 2024). The existence of $HNSO_2$ was proposed in the reaction between SO_3 and NH_3, and was regarded as the most stable for nine different isomers of $HNSO_2$, HONSO, HOSNO, HOS(O)N, $HSNO_2$,

HSONO, HON(O)S, HOOSN, and HOONS (Deng et al., 2016). Owing to its similarity with SO_3 and the potential role of SO_3 in the atmosphere, the hydrolysis of $HNSO_2$ to produce SFA~~NH_2SO_3H~~ formation has been focused by several groups (Zhang et al., 2022; Manonmani et al., 2020). As the direct hydrolysis of $HNSO_2$ with a high energy barrier takes place hardly in the gas phase (Zhang et al., 2022; Manonmani et al., 2020), the addition of a second water molecule (Manonmani et al., 2020), formic acid and sulfuric acid (H_2SO_4, SA) (Zhang et al., 2022) have been proved to promote the product of SFA~~NH_2SO_3H~~ through the hydrolysis of $HNSO_2$. It was noted that, with the global reduction in the concentration of H_2SO_4 resulting from SO_2 emission restrictions, the contribution of methanesulfonic acid (MSA) to aerosol nucleation has received the widespread attention of scientists. As a major inorganic acidic air pollutant (Chen et al., 2020), the concentration of MSA in the atmosphere was noted to be notably high across various regions, spanning from coastal to continental, with levels found to be between 10% and 250% of those measured for SA (Shen et al., 2019; Dawson et al., 2012; Bork et al., 2014; Shen et al., 2020; Berresheim et al., 2002; Hu et al., 2023). However, to the best of our knowledge, the gaseous hydrolysis of $HNSO_2$ with MSA has not yet been investigated, which will confine the understanding for the source of SFA in regions with significant pollution and high levels of MSA. ~~However, to the best of our knowledge, the gaseous hydrolysis of $HNSO_2$ with CH_3SO_3H has not yet been investigated. It was noted that, with the global reduction in the concentration of H_2SO_4 resulting from SO_2 emission restrictions, the contribution of CH_3SO_3H to aerosol nucleation has received the widespread attention of scientists. As a major inorganic acidic air pollutant (Chen et al., 2020), the concentration of CH_3SO_3H in the atmosphere was noted to be notably high across various regions, spanning from coastal to continental, with levels found to be between 10% and 250% of those measured for SA (Shen et al., 2019; Dawson et al., 2012; Bork et al., 2014; Shen et al., 2020; Berresheim et al., 2002; Hu et al., 2023).~~ Thus, understanding the hydrolysis of $HNSO_2$ with MSA~~CH_3SO_3H~~ in the gas phase was necessary for exploring its impact on aerosols and human health.

$$HNSO_2 + H_2O + \text{MSA}\text{~~}CH_3SO_3H\text{~~} \rightarrow \text{SFA}\text{~~}NH_2SO_3H\text{~~} + \text{MSA}\text{~~}CH_3SO_3H\text{~~} \quad (1)$$

As a supplement to gas-phase reactions, interfacial reactions at the air-water interface not only can accelerate the rates of atmospheric reactions but also may introduce new mechanisms (Freeling et al., 2020; Zhong et al., 2019). For instance, the Criegee intermediates reacting with MSA~~CH_3SO_3H~~ at the air-water interface can form the ion pair of $CH_3C(H)(OOH)(SO_3CH_3)$

anhydride and H_3O^+ (Ma et al., 2020), which differs from the corresponding gaseous reaction where the MSA~~CH_3SO_3H~~ molecule acts solely as a reactant reacting with Criegee intermediates directly. As far as we know, $HNSO_2$ exhibit a significant interfacial preference, as the fact that the total duration time of $HNSO_2$ at the interface approximately accounts for 49.1% of the 150 ns simulation time (Fig. S1). However, the hydrolysis of $HNSO_2$ with MSA ~~CH_3SO_3H~~ has not been studied at the air-water interface, which will limit our understanding of how the hydrolysis of $HNSO_2$ with MSA differs in the gas phase and air-water interfaces.~~which will confine the understanding for the source of NH_2SO_3H in regions with significant pollution and high levels of CH_3SO_3H.~~

From a structural point of view, two functional groups of $-NH_2$ and $-SO_3H$ in the SFA~~NH_2SO_3H~~ molecule can act as both hydrogen donors and acceptors to interact with atmospheric species. Previous studies have demonstrated that SFA has a potential role in new particle formation (NPF), as it not only clusters efficiently with itself and SA (Lovejoy and Hanson, 1996), but also can promote the nucleation rate of NPF initiated from SA-DMA by a factor of two in dry and severely contaminated areas with NH_3 (Li et al., 2018). Due to the concentration of SA in the atmosphere has decreased significantly with the scenario of SO_2 emission control measures, MSA-driven NPF has attracted growing attention (Dawson et al., 2012; Nishino et al., 2014; Chen and Finlayson-Pitts, 2017; Chen et al., 2020; Shen et al., 2020). Initially, the binary nucleation of MSA with inorganic ammonia and organic amines in the atmosphere has been reported, where MA exhibits the strongest enhancing capability~~Initially, the binary nucleation of MSA with inorganic ammonia and organic amines in the atmosphere has been reported, where MA exhibits the strongest enhancing capability~~ (Chen et al., 2016; Chen and Finlayson-Pitts, 2017; Shen et al., 2019; Hu et al., 2023). Subsequently, some reported results suggested that the triadic MSA-MA-driven NPF can exhibit greater nucleation rates competed to the binary of MSA-driven (Zhang et al., 2022: Hu et al., 2023). For example, both formic acid (Zhang et al., 2022) and trifluoroacetic acid (Hu et al., 2023) exhibit an excellent catalytic influence on MSA-MA-driven NPF. However, the SFA involved in MSA-MA-driven NPF has not been investigated, which is worth important to investigate whether SFA can exhibit a similar enhancing effect in MSA-MA as observed in SA-DMA.

Herein, this work studied the catalytic effect of SFA on $HNSO_2$ hydrolysis and MSA-MA nucleation particle formation. Specifically, quantum chemical calculations were used firstly to

assess the atmospheric processes of the gaseous hydrolysis of $HNSO_2$ with MSA~~CH_3SO_3H~~. Then, the gaseous and interfacial mechanisms differences of the $HNSO_2$ hydrolysis with MSA were investigated applying the Born-Oppenheimer Molecular Dynamic (BOMD) simulation method. Finally, the atmospheric implications and mechanism of SFA in the MSA-MA-dominated NPF process have been evaluated through density functional theory and the Atmospheric Clusters Dynamic Code (ACDC) (McGrath et al., 2012; Hu et al., 2023; Zhao et al., 2020; Zhang et al., 2024; Tsona Tchinda et al., 2022; Liu et al., 2020) models to evaluate the potential effect of SFA on nucleation and NPF. This work will not only deepen our understanding of the source of SFA, but also reveal significant implications for new particle formation and aerosol particle growth in MSA polluted areas.

2 Methodology

2.1 Quantum Chemical Calculations

The gaseous hydrolysis of $HNSO_2$ with MSA~~CH_3SO_3H~~ was comprehensively studied through quantum chemistry simulations. Optimization of all the species were carried out by using the method of M06-2X with 6-311++G(2*df*,2*pd*) basis set (Zhao and Truhlar, 2008; Elm et al., 2012; Bork et al., 2014). Vibrational frequencies were subsequently computed at the M06-2X/6-311++G(2*df*,2*pd*) ~~same~~ level to ensure the reality of all stationary point's frequencies and the presence of only one imaginary frequency in transition states. It is noted that the calculated bond distances and bond angles at the M06-2X/6-311++G(2*df*,2*pd*) level (Fig. S2) agree well with the available values (Fig. S2) from the experiment and three different theoretical levels of M06-2X/6-311++G(3*df*,2*pd*), M062X/6-311++G(3*df*,3*pd*) and M06-2X/aug-cc-pVTZ levels. Also, at the M06-2X/6-311++G(2*df*,2*pd*) level, internal reaction coordinate (IRC) analyses were conducted to verify the connection from the transition states to the corresponding products (or reactants). All calculations regarding for geometries and frequency were conducted with the aid of the Gaussian 09 (Frisch, 2009) program. Furthermore, single point energies were performed at the CCSD(T)-F12/cc-pVDZ-F12 (Kendall et al., 1992; Adler et al., 2007) level utilizing the ORCA (Neese, 2012) program, based on the optimized geometries mentioned above. The CCSD(T)/aug-cc-pVDZ method was chosen to calculate the relative energies as the fact that, compared with unsigned error (Table S1) calculated at the CCSD(T)/CBS//M06-2X/6-311++G(2*df*,2*pd*) level, unsigned errors calculated at

CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6-311++G(2*df*,2*pd*) was 0.71 kcal·mol^{-1}.

2.2 Rate coefficients calculations

The rate coefficients for the hydrolysis of $HNSO_2$ with MSA~~CH_3SO_3H~~ were calculated through a two-step process. Initially, the high-pressure-limit (HPL) rate coefficients were computed applying VRC-VTST methods within the Polyrate package (Chuang et al., 1999). It's worth noting that the electronic structure method for VRC-TST calculations is based on Gaussian 09 program using the M06-2X/6-311++G(2*df*,2*pd*). Meanwhile, two pivot points were selected (Bao et al., 2016; Long et al., 2021; Georgievskii and Klippenstein, 2003; Meana-Pañeda et al., 2024) to produce a single-faceted dividing surface for the $HNSO_2$ hydrolysis (shown in Part S1 in the Supplement). Subsequently, on the basis of the HPL rate coefficients, the rate coefficients for the hydrolysis of $HNSO_2$ with MSA~~CH_3SO_3H~~ were calculated within the temperature range of 212.6-320.0 K and pressures applying the Master Equation Solver for Multi-Energy Well Reactions (MESMER) program (Glowacki et al., 2012). The rate coefficients for the barrierless steps transitioning between reactants and pre-reactive complexes were assessed applying the Inverse Laplace Transform (ILT) method within MESMER calculations, while the step transitioning between pre-reactive complexes and post-reactive complexes via transition states were evaluated using the RRKM theory (Mai et al., 2018) in combination with the asymmetric Eckart model. The details of the rate coefficient for the hydrolysis of $HNSO_2$ without and with X (X = H_2O and MSA~~CH_3SO_3H~~) were given in Part 1, Table 1 and Table S4.

2.3 BOMD Simulations

BOMD simulations were conducted applying DFT implemented in CP2K program (Vandevondele et al., 2005; Hutter et al., 2014). The exchange and correlation interactions were addressed using the Becke-Lee-Yang-Parr (BLYP) functional (Becke, 1988; Lee et al., 1988), while Grimme's dispersion was applied to address weak dispersion interaction (Grimme et al., 2010). The Goedecker-Teter-Hutter (GTH) conservation pseudopotential (Goedecker et al., 1996; Hartwigsen et al., 1998) combine with Gaussian DZVP basis set (Vandevondele and Hutter, 2007) and an auxiliary plane wave basis set were used to represent core and valence electrons. Energy cutoffs (Zhong et al., 2017; Zhong et al., 2018; Zhong et al., 2019) of 280 Ry for the plane wave basis set and 40 Ry for the Gaussian basis set were applied. The gaseous reactions were simulated in the NVT ensemble at 300 K, with 15 × 15 × 15 Å^3 supercells and the

time step of 1 fs. To simulate the water microdroplet, the system containing 191 water molecules (Zhong et al., 2017) was utilized in 35 × 35 × 35 Å^3 supercells. This setup included $HNSO_2$ and MSA~~CH_3SO_3H~~ along with the water drop. Prior to the interfacial simulation, a 10 ps relaxation period in the BOMD simulation was used to equilibrate the water microdroplet system with 191 molecules.

2.4 ACDC kinetics simulation

The ACDC model (McGrath et al., 2012; Hu et al., 2023; Zhao et al., 2020; Zhang et al., 2024; Tsona Tchinda et al., 2022; Liu et al., 2020) was utilized to simulate the $(MSA)_x(MA)_y(SFA)_z$ ($0 \le y \le x + z \le 3$) cluster formation rates and explore the potential mechanisms, where the most stable structure of $(SFA)_x(MSA)_y(MA)_z$ ($0 \leqslant z \leqslant x + y \leqslant 3$) clusters were searched with ABCluster software (Zhang and Dolg, 2015) (The details in Part S1 of the Supplement).~~The ACDC model was utilized to simulate the $(MSA)_x(MA)_y(SFA)_z$ ($0 \le y \le x + z \le 3$) cluster formation rates and explore the potential mechanisms.~~ This simulation encompasses a variety of temperatures and monomer concentrations to capture the dynamics under different environmental conditions. Thermodynamic parameters, obtained from quantum chemical calculations executed at the M06-2X/6-311++G(2*df*,2*pd*) level, were used as inputs for the ACDC model. Notably, many benchmark studies (Zhao et al., 2020; Zhang et al., 2024; Tsona Tchinda et al., 2022; Liu et al., 2020) show that the M06-2X functional has good performance compared to other common functionals for gaining the Gibbs free energies. For all the M06-2X calculations with the 6-311++G(2*df*,2*pd*) basis set was used, as it is a good compromise between accuracy and efficiency and does not yield significant errors in the thermal contribution to the free energy compared to much larger basis sets such as 6-311++G(3*df*,3*pd*), with the differences of relative ΔG less than 1.75 kcal·mol^{-1} (Table S7).The temporal progression of cluster concentrations was determined by numerically integrating the birth-death equation, leveraging MATLAB's ode15s solver for enhanced accuracy.

$$\frac{dc_i}{dt} = \frac{1}{2}\sum_{j<i}\beta_{j,(i-j)}c_j c_{(i-j)} + \sum_j \gamma_{(i+j)\to i}c_{i+j} - \sum_j \beta_{i,j}c_i c_j - \frac{1}{2}\sum_{j<i}\gamma_{i\to j}c_i + Q_i - S_i \qquad (2)$$

Here, c_i represents the concentration of a specific cluster, labelled as i; the term $\beta_{i,j}$ was used to denote the collision coefficient, which was a measure of the frequency at which clusters i and j collide with each other in a given environment or system; the coefficient $\gamma_{(i+j)\to i}$ was defined

as the evaporation rate constant that describes the process of a larger cluster, consisting of combined elements *i* and *j*, breaking down into the individual smaller clusters *i* and *j*; and Q_i encompasses all other source terms contributing to the formation of cluster *i*. S_i signifies alternative sink terms for cluster *i* that may remove it from the system. Considering the formation Gibbs free energy (Table S8) and evaporation rates (Table S9) of all clusters, the clusters containing pure MSA and MA molecules as well as the clusters containing a SFA molecule are mostly more stable and therefore are allowed to form larger clusters and contribute to particle formation rates. In this case, clusters $(MSA)_4 \cdot (MA)_3$, $(MSA)_4 \cdot (MA)_4$ and $SFA \cdot (MSA)_3 \cdot (MA)_3$ are set as the boundary clusters.

3. Results and discussions

3.1 The hydrolysis of $HNSO_2$ with MSA~~CH_3SO_3H~~ in the gas phase

Given the low chance of three molecules of $HNSO_2$, H_2O and MSA~~CH_3SO_3H~~ colliding simultaneously under atmospheric conditions, the hydrolysis of $HNSO_2$ with MSA~~CH_3SO_3H~~ (Channel MSA) was likely a sequential bimolecular process. As the concentration of water molecule (10^{18} molecules·cm^{-3} (Anglada et al., 2013)) in the atmosphere is much higher than those of $HNSO_2$ and MSA (10^5-10^9 molecules·cm^{-3} (Shen et al., 2020)), the reaction pathway of $HNSO_2 \cdots$MSA + H_2O is hard to occur in actual atmospheric conditions. So, Channel MSA proceeds through the initial formation of dimers ($HNSO_2 \cdots H_2O$ and MSA$\cdots H_2O$) via collisions between $HNSO_2$ (or MSA) and H_2O.~~As the concentration of water molecule (10^{18} molecules·cm^{-3}) in the atmosphere is much higher than those of $HNSO_2$ and CH_3SO_3H (10^5-10^9 molecules·cm^{-3}), the reaction pathway of $HNSO_2 \cdots CH_3SO_3H + H_2O$ is hard to occur in actual atmospheric conditions. So, Channel MSA proceeds through the initial formation of dimers ($HNSO_2 \cdots H_2O$ and $CH_3SO_3H \cdots H_2O$) via collisions between $HNSO_2$ (or CH_3SO_3H) and H_2O.~~ Subsequently, the generated dimer interacts with the third reactant, either MSA~~CH_3SO_3H~~ or $HNSO_2$. As seen in Fig. 1, the calculated Gibbs free energy of MSA~~CH_3SO_3H~~$\cdots H_2O$ complex was -0.9 kcal·mol^{-1}, which was 4.5 kcal·mol^{-1} lower than that of $HNSO_2 \cdots H_2O$. Consequently, it was predicted the primary route for the hydrolysis reaction of $HNSO_2$ with MSA~~CH_3SO_3H~~ takes place via the $HNSO_2$ + MSA~~CH_3SO_3H~~$\cdots H_2O$ reaction.

Starting from the $HNSO_2$ + MSA~~CH_3SO_3H~~$\cdots H_2O$ reactants, the Channel MSA was initiated through the intermediate complex designated as IM_MSA1. From a geometric perspective,

IM_MSA1 complex exhibits a cage-like configuration by a van der Waals force (S1⋯O1, 2.00 Å) and the involvement of three hydrogen bonds of H2⋯O4 (1.53 Å), H4⋯N1 (1.60 Å) and H5⋯O3 (2.07 Å). The Gibbs free energy of IM_MSA1 complex relative to $HNSO_2$ + MSA~~CH_3SO_3H~~⋯H_2O reactants was 1.7 kcal·mol^{-1}. Subsequently, as presented in Fig. 1, Channel MSA progresses through transition state TS_MSA1 to yield complex IMF_MSA1. At TS_MSA1, the MSA~~CH_3SO_3H~~ moiety facilitates two hydrogen atom transfer, with TS_MSA1 lying only 0.8 kcal·mol^{-1} above complex IM_MSA1. Complex IMF_MSA1 exhibits a cage-like structure with a Gibbs free energy was 23.4 kcal·mol^{-1} lower than that of IM_MSA1, revealing thermodynamic favorability of $HNSO_2$ hydrolysis with MSA~~CH_3SO_3H~~. To evaluate the relative catalytic impact of MSA~~CH_3SO_3H~~ and H_2O, Fig. S4 illustrates the profiles of Gibbs free energy for the hydrolysis of $HNSO_2$ and the corresponding reaction assisted by H_2O. Compared to complex $HNSO_2$⋯$(H_2O)_2$, the Gibbs stabilization energy of IM_MSA1 increased by 5.6 kcal·mol^{-1}, potentially shortening the S1⋯O1 bond distance by 0.21 Å. Considering the Gibbs free energy barrier and rate coefficients, MSA~~CH_3SO_3H~~ demonstrates a greater catalytic role compared to H_2O in lowering the energy barrier for the hydrolysis of $HNSO_2$. In particular, MSA~~CH_3SO_3H~~ facilitates hydrogen atom to extraction from H_2O, further reducing the reaction energy barriers to 7.7 kcal·mol^{-1}. Meanwhile, the calculated rate coefficients for $HNSO_2$ hydrolysis with MSA~~CH_3SO_3H~~ was 3.08 × 10^{-11}-3.50 × 10^{-11} cm^3·molecule^{-1}·s^{-1} within 212.6-320.0 K, exceeding corresponding values for reactions involving H_2O by 2 orders of magnitude. Besides, the Gibbs free energy of IMF_MSA1 was 2.0 kcal·mol^{-1} lower than that of the product complex IMF_WM1 (SFA~~NH_2SO_3H~~ ⋯H_2O), suggesting SFA~~NH_2SO_3H~~ has a higher affinity for MSA~~CH_3SO_3H~~MSA~~CH_3SO_3H~~ compared to H_2O. Besides, MSA-assisted $HNSO_2$ hydrolysis is reduced by 4.9 kcal·mol^{-1} in energy barrier than the NH_3-assisted ammonolysis of SO_3 with its rate constant at 298 K (2.85 × 10^{-11} cm^3·molecule^{-1}·s^{-1}) close to the value of ammonolysis of SO_3 with NH_3 (4.35 × 10^{-10} cm^3·molecule^{-1}·s^{-1}) (Li et al., 2018). However, due to the absence of the concentration of $HNSO_2$, the competitiveness of these two reactions cannot be further confirmed.~~Besides, CH_3SO_3H-assisted $HNSO_2$ hydrolysis is reduced by 4.9 kcal mol^{-1} in energy barrier than the NH_3-assisted ammonolysis of SO_3 with their rate constants close each other (4.35 × 10^{-10} cm^3·molecule^{-1}·s^{-1}) (Li et al., 2018). As the absence of the concentration of $HNSO_2$, the competitiveness of these two reactions cannot be further confirmed.~~

To evaluate the comparative catalytic ability of X (X = H_2O and MSA~~CH_3SO_3H~~) in the

atmosphere, the effective rate coefficients (k') for X-assisted $HNSO_2$ hydrolysis were calculated in Table 1. Notably, k' serves as a metric for gauging the comparative catalytic ability of a series of gaseous catalysts in atmospheric reactions (Sarkar et al., 2017; Zhang et al., 2020; Zhang et al., 2019; Buszek et al., 2012; Gonzalez et al., 2011; Parandaman et al., 2018; Anglada et al., 2013). When X was present, the calculated k' was given by Eq. (3).

$$k'_X = k_X \times K_{eq}(X\cdots H_2O) \times [X] \quad (3)$$

In Eq. (3), k_X was the rate coefficient for X-assisted $HNSO_2$ hydrolysis (Table 1), while $K_{eq}(X\cdots H_2O)$ denotes the equilibrium coefficients of $X\cdots H_2O$ (Table S2). $[X]$ represents the avaiable concentrations of H_2O (Anglada et al., 2013) and MSA~~CH_3SO_3H~~ (Shen et al., 2020). As indicated in Table 1, at experimental concentrations ($[H_2O] = 5.16 \times 10^{16}$-$2.35 \times 10^{18}$ molecules·cm^{-3}) within 280.0-320.0 K (at 0 km), the computed k'_{WM} ranged from 5.99×10^{-18}-7.79×10^{-17} cm^3·molecule^{-1}·s^{-1}. This range exceeded k'_{MSA} (4.60×10^{-21}-4.81×10^{-20} cm^3·molecule^{-1}·s^{-1}) by 2-4 orders of magnitude, highlighting pronounced impact of H_2O compared to MSA~~CH_3SO_3H~~ at 0 km in enhancing the rate of $HNSO_2$ hydrolysis. However, with the significant decrease in atmospheric water molecules with increasing altitude, the calculated k'_{MSA} ranged from 1.96×10^{-19}·s^{-1}-1.30×10^{-17}·cm^3·molecule^{-1}·s^{-1}, surpassing k'_{WM} (9.85×10^{-27}-6.51×10^{-22}·cm^3·molecule^{-1}·s^{-1}) by 3-10 orders of magnitude. This illustrates that MSA~~CH_3SO_3H~~ has a significantly greater catalytic ability than H_2O in accelerating the rate of $HNSO_2$ hydrolysis within 5-15 km. So, $HNSO_2$ hydrolysis with MSA~~CH_3SO_3H~~ may represent a potential formation pathway for MSA~~CH_3SO_3H~~ across an altitude scope of 5-15 km.

3.2 Reactions at the air-water interface

The interfacial mechanism of MSA~~CH_3SO_3H~~-assisted $HNSO_2$ hydrolysis at the air-water interface has not been thoroughly investigated. Interestingly, our simulations show that $HNSO_2$ and MSA~~CH_3SO_3H~~molecules spend approximately 49.1% and 12.1% of the time, respectively, at the air-water interface during the 150 ns simulation (Fig. S1 and Fig. S6). This reveals that the presence of $HNSO_2$ and MSA~~CH_3SO_3H~~ at the air-water interface should not be disregarded. Therefore, BOMD simulations were performed to clarify the interfacial mechanism of MSA~~CH_3SO_3H~~-assisted $HNSO_2$ hydrolysis at the air-water interface. Comparable to the reactions of SO_3 at the air-water interface with acidic molecules (Cheng et al., 2023; Zhong et al., 2019a), the hydrolysis of $HNSO_2$ with MSA~~CH_3SO_3H~~ at the air-water interface may occur through three pathways: (*i*) the adsorbed

MSA$\cancel{CH_3SO_3H}$ interacts with $HNSO_2$ at the air-water interface; (*ii*) the adsorbed $HNSO_2$ interacts with MSA$\cancel{CH_3SO_3H}$ at the air-water interface; and (*iii*) the $HNSO_2$···MSA$\cancel{CH_3SO_3H}$ complex reacts at the air-water interface. Nevertheless, because of the high reactiveness of MSA$\cancel{CH_3SO_3H}$ at the air-water interface, the lifetime of MSA$\cancel{CH_3SO_3H}$ was minimal (seen in Fig. S9) on the water droplet, which was around a small number of picoseconds leading to the rapid formation of MSA$\cancel{CH_3SO_3H}^-$ ion. Meanwhile, although $HNSO_2$ remains stable at the air-water interface (seen in Fig. S8) and does not dissociate within 10 ps, the hydrated form of $HNSO_2$ illustrated in Fig. S8 was not conducive to $HNSO_2$ hydrolysis at the air-water interface. So, model (*iii*) was primarily considered for $HNSO_2$ hydrolysis with MSA$\cancel{CH_3SO_3H}$ at the air-water interface. It was worth noting that $HNSO_2$··· MSA$\cancel{CH_3SO_3H}$ complex can persist at the air-water interface for approximately 34.2% of the 150 ns simulation time (see in Fig. S7). For model (*iii*), two types of reactions were found at the air-water interface: (*a*) the $NH_2SO_3^-$ and H_3O^+ ions formation mechanism, and (*b*) the proton exchange mechanism.

$NH_2SO_3^-$ and H_3O^+ ions forming mechanism. Fig. 2(a), Fig. S10 and Movie 1 illustrates the formation mechanism of $NH_2SO_3^-$ and H_3O^+ ions through the chain structure. At 4.57 ps, a chain hydrolyzed transition state was observed, accompanied by two protons transfer events. Specially, an H2 atom transferred from the OH moiety of MSA$\cancel{CH_3SO_3H}$ molecule to the terminal N atom of $HNSO_2$ molecule, resulting in the breaking of the O3-H2 bond (with the length of 1.49 Å) and forming the H2-N bond (with the length of 1.14 Å). Concurrently, an interfacial water molecule decomposes, leading to the elongation of the O1-H1 bond to over 1.00 Å, with the S1 atom of $HNSO_2$ obtaining the OH moiety of the interfacial water molecule ($d_{(S1\text{-}O1)}$ = 1.60 Å). By 4.61 ps, The N-H2 and S1-O1 bonds both shortened to 0.99 Å and 1.01 Å, revealing the formation of the SFA$\cancel{NH_2SO_3H}$ molecule. However, due to its strong acidity, the SFA$\cancel{NH_2SO_3H}$ molecule could only persist on the water droplet surface for a ps time-scale. As a result, at 7.43 ps, the proton of SFA$\cancel{NH_2SO_3H}$ transferred to another interfacial water molecule, completing the deprotonation of SFA$\cancel{NH_2SO_3H}$. The loop structure mechanism (Fig. 2(b), Fig. S11 and Movie 2) was similar with the chain structure mechanism. However, in this case, the proton of SFA$\cancel{NH_2SO_3H}$ transferred to $CH_3SO_3^-$ rather than to an interfacial water molecule.

Proton exchange mechanism. As depicted in Fig. 3, the proton exchange mechanism illustrates the deprotonation of MSA$\cancel{CH_3SO_3H}$ concurrent with $HNSO_2$ hydration at the air-water

interface. As shown in Fig. 3(a), Fig. S12 and Movie 3, MSA~~CH_3SO_3H~~-mediated hydration $HNSO_2$ with a single water molecule was observed. Initially, the $HNSO_2$···MSA~~CH_3SO_3H~~ complex quickly associates with an interfacial water molecule, and forms a loop structure complex that accelerates the rate of proton transfer. By 4.38 ps, an eight-membered loop structure complex, $HNSO_2$···H_2O···MSA~~CH_3SO_3H~~, emerges, characterized by two hydrogen bonds ($d_{(H2\text{-}N)}$ = 1.82 Å and $d_{(H1\text{-}O2)}$ = 1.92 Å) and a van der Waals forces ($d_{(S1\text{-}O1)}$ = 2.35 Å). Thereafter, at 4.77 ps, a transition state-like configuration was identified where the water molecule within the loop complex dissociated, elongating the O1-H1 bond to over 1.00 Å, and the S atom of $HNSO_2$ attaches to the OH group of the interfacial water molecule. Concurrently, the $CH_3SO_3^-$ ion receives the proton from the separated interfacial water molecule. The entire reaction for MSA~~CH_3SO_3H~~-mediated hydration $HNSO_2$ with one water molecule was completed at 4.80 ps, resulting in the formation of SFA~~NH_2SO_3H~~ and MSA~~CH_3SO_3H~~ molecules. MSA~~CH_3SO_3H~~-mediated hydration of $HNSO_2$ with two water molecules (Fig. 3(b), Fig. S13 and Movie 4) at the air-water interface was similar with mechanism identified with one water molecule. However, the inclusion of two water molecules enlarges the loop, significantly reducing the stress on the loop structures. Consistent with the prediction in Fig. 4, the loop structures preferred to include two water molecules rather than one water molecule. This observation agrees well with the reported hydration of Criegee intermediate at the air-water interface (Zhu et al., 2016; Kumar et al., 2018; Liu et al., 2021; Zhang et al., 2023a). Additionally, MSA~~CH_3SO_3H~~-mediated hydration of $HNSO_2$ with three water molecules (Fig. S14 and Movie 5) has been observed in the proton exchange mechanism. However, its probability of occurrence was smaller due to the relatively larger entropy effect. It was noteworthy that the SFA~~NH_2SO_3H~~ and MSA~~CH_3SO_3H~~ molecules formed in the proton exchange mechanism were not stable at the air-water interface, which can further interact with an interfacial water molecule to form the corresponding ions of $NH_2SO_3^-$ and $CH_3SO_3^-$.

At the air-water interface, a sum of 50 BOMD trajectories, each lasting 10 ps, were conducted to investigate $HNSO_2$ hydrolysis with MSA~~CH_3SO_3H~~. Two distinct mechanisms were observed: the formation of $NH_2SO_3^-$ and H_3O^+ ions formation (shown in blue and yellow in Fig. 4) and the proton exchange mechanism (represented by orange, purple and green in Fig. 4). In the mechanism involving the formation of $NH_2SO_3^-$ and H_3O^+ ions, approximately 22% (Fig. 2(a), Fig. 4, Fig. S10 and Movie 1) of the reactions took place via a chain structure, while the majority (~18%) (Fig. 2(b),

Fig. 4, Fig. S11 and Movie 2) proceeded through a loop structure mechanism. This discrepancy can be attributed to the uncertainty regarding the direction of proton transfer from SFA~~NH_2SO_3H~~. Since the number of water molecules near the water microdroplet far exceeded that of $CH_3SO_3^-$, protons were predominantly transferred to interface water molecules, making the loop structure mechanism weaker than the chain structure mechanism. Approximately 60% of the reactions were observed to be due to the proton exchange mechanism in BOMD simulations. Through water-mediated mechanisms, these reactions resulted in SFA~~NH_2SO_3H~~ formation. Similarly to gas-phase reactions, loop structures were observed in these reactions. Approximately 10% of the reactions formed a loop structure involving one water molecule (Fig. 3(a), Fig. 4, Fig. S12 and Movie 3), while the most common loop structure involved two water molecules (about 42%) (Fig. 3(b), Fig. 4, Fig. S13 and Movie 4). Smaller loops were found to experience more stress than loop structures with two water molecules. In cases of loop structures with three water molecules (about 8%) (Fig. 4, Fig. S14 and Movie 5), the entropy effect was deemed to be more significant than the strain effect and likely played a dominant role. The two water molecules contained in the loop structure not only acted as a reactant but also facilitated proton transfer as a bridge.

3.3 New Particle Formation from the atmospheric products

3.3.1. The influence of SFA on the stability of atmospheric MSA-MA-based clusters

Electrostatic Potential (ESP) mapping on the molecular van der Waals (vdW) surface was employed to analyze the interactions between SFA and other key nucleation precursors like MSA and MA. As shown in Fig. 5, sites with more negative ESP often attract more positive ESP sites, namely hydrogen bonds in the studied system. Specifically, the hydrogen atoms of the $-SO_3H$ and $-NH_2$ groups (site 4 and 5) in SFA, possessing more positive ESP values, have the potential to attract groups with negative ESP values, such as the oxygen atom within the $-SO_3H$ group of MSA (site 6) and the nitrogen atom of MA (site 1), thus forming hydrogen bonds as proton donors. Additionally, the sulfur atom of the $-SO_3H$ functional group (site 7) in SFA, with a negative ESP of -30.75, acts as proton acceptor, facilitating direct binding with MSA and MA molecules via the hydrogen bonds. Therefore, the introduction of SFA was believed to enhance the stability of MSA-MA clusters by promoting the formation of more hydrogen bonds and facilitating proton transfers.

3.3.2. The cluster formation rates in the SFA-MSA-MA system

Simulations were conducted to determine the cluster formation rates (J) for the MSA-MA-SFA system, varying parameters such as temperature and the concentrations of the precursors were involved. To assess the promotional impact of SFA on J under varying atmospheric conditions, the enhancement factor (R) was computed as the ratio of $J_{MSA\text{-}MA\text{-}SFA}$ to $J_{MSA\text{-}MA}$. As depicted in Fig. 6 (a), the J of MSA-MA-SFA system exhibits a negative correlation with temperature, attributed to the decrease in ΔG value and evaporation rates of clusters at lower temperatures. Conversely, a positive correlation of R with temperature was observed (Fig. 6(b)), indicating that SFA's enhancement of nucleation was more pronounced in regions with relatively higher temperatures. Furthermore, both J and R show an increase as the [SFA] increases, suggesting a positive correlation of J and R with [SFA]. In short, in regions with high [SFA], such as the Yangtze River Delta of China, Bangladesh, and the east coast of India, SFA was expected to significantly boost the J of MSA-MA based nucleation. It is noted that in Fig. 6(b), due to the competitive relationship between MSA and SFA, at low concentrations of SFA, the binding capacity of MSA with MA is stronger than that of SFA with MA, resulting in only a small amount of SFA participating in cluster formation. However, as the concentration of SFA increases, the number of $(MSA)_x \cdot (MA)_y \cdot (SFA)_z$ (where $y \leq x + z \leq 3$) ternary clusters increase, leading to the formation of more hydrogen bonds and a significant increase in R_{SFA}. Additionally, Fig. 7 illustrates the J and R of MSA-MA-SFA clusters under different [MSA] and [MA]. On one hand, larger values of [MSA] and [MA] correspond to higher J, as the increased concentration of nucleation precursors leads to a rise in the number of MSA-MA-FSA clusters. On the other hand, increasing [MSA] and [MA] result in a decrease in the R attributed to the effect of SFA on nucleation. This was because as [MSA] and [MA] increases, the prevalence of pure MSA-MA clusters rise during the clustering process, consequently reducing the impact of SFA.

3.3.3. The growth paths of cluster under different atmospheric conditions

Li et al. studied the atmospheric concentration of SFA estimated by theoretical method (Li et al., 2018) was expected to reach up to10^8 molecules·cm^{-3} in high NH_3 concentrations, such as Yangtze River Delta in China (Yu et al., 2020), Indo-Gangetic Plains (Kuttippurath et al., 2020), Pakistan, Bangla desh (Warner et al., 2016), and the southern Italy (Tang et al., 2021). Considering the high-atmospheric concentrations of MSA and MA detected in coastal industrial areas (Stieger et al., 2021; Mochizuki et al., 2017;), SFA could be an important contributor to MSA-MA-driven

NPF, such as the Yangtze River Delta in China, the east coast of India, the south of Bangladesh and Italy. To further evaluate the implication of SFA for the MSA-MA nucleation in the atmosphere, the growth paths of cluster was calculated under different atmospheric conditions. In Fig. 8 (a), two main types of cluster formation routes were found: (*i*) the pure MSA-MA pathway and (*ii)* the MSA-MA-SFA pathways at 278.15 K in the studied system. In the pure MSA-MA pathway, cluster growth primarily occurs through the collisional addition of MSA or MA monomers. Conversely, in the SFA-involved pathways, SFA can directly participate in the formation of stable larger clusters subsequently, such as $(MSA)_2{\cdot}(MA)_2{\cdot}SFA$ and $(MSA)_2{\cdot}(MA)_2{\cdot}(SFA)_2$ clusters, and then subsequently grow out. The involvement of SFA in the cluster formation pathway was significantly influenced by atmospheric conditions. Firstly, as the temperature rises from 238.15 K to 278.15 K, the contribution of the SFA-involved cluster formation pathways rises from 68% to 90% (Fig. 8 (b)), implying that the pathway involving SFA becomes increasingly important at lower altitudes or in warmer conditions. Secondly, as depicted in Fig. 8(c) and Fig. S22, the contribution of SFA to the MSA-MA system is primarily influenced by [SFA] and [MSA], with negligible dependence on [MA]. To assess the role of SFA in MSA-MA nucleation in the atmosphere, the specific contribution of the MSA-MA cluster growth paths at varying [SFA] to NPF was calculated at 278.15 K, as illustrated in Fig. 8(c), under the ambient conditions typical of the corresponding regions. Generally, as [SFA] increases from 10^4 to 10^8 molecules·cm^{-3}, the contribution of the SFA-involved pathway increases gradually. Specifically, at low [SFA] (10^4 molecules·cm^{-3}), the contributions of SFA-involved clustering pathways are 77% and 41% in regions with relatively low [MSA] in non-sea regions (Berresheim et al., 2002). In regions with high [SFA] (10^6, 10^8 molecules·cm^{-3}), the contributions of the SFA-MSA-MA growth pathways are dominant in their NPF. Particularly in areas with high [MSA], such as the Pacific Rim (6.26×10^8 molecules·cm^{-3} (Saltzman et al., 1986)), the central Mediterranean Sea (2.11×10^8 molecules·cm^{-3} (Mansour et al., 2020)) and the Amundsen Sea (3.65×10^9 molecules·cm^{-3} (Jung et al., 2020)), nucleation is primarily driven by the SFA-MSA-MA pathway, contributing to approximately 88% of cluster formation. These results suggest that the influence of SFA is more pronounced in regions with relatively high [MSA]. It is important to note that the [SFA] values discussed in this work are estimated from limited observational data based on the reaction between SO_3 and NH_3 in the atmosphere. Accurate determination of atmospheric [SFA] requires extensive field observations to enable more comprehensive research.

~~Secondly, the contribution of the pathway with SFA exhibits a negative correlation with [SA] (Fig. 8 (c)), attributed to the competitive relationship between SFA and MSA. Thirdly, the contribution of the SFA-involved cluster formation pathway was positively associated with the concentration of [SFA] (Fig. 8 (d)). At [SFA]=10^4 molecules·cm^{-3}, the pathway involving SFA was not prominent, and the pure MSA-MA pathway dominates. However, as [SFA] rises from 10^4 to 10^8 molecules·cm^{-3}, the contribution of the SFA-involved pathway increased from 7% to 98% at 278.15 K. Therefore, the pathway involving SFA appears to dominate near SFA release sources in warm temperatures or at lower altitudes~~.

3.4 Interfacial implications of products on aerosol particle growth

As the discussion above, the formation of $SFA^-\cdots H_3O^+$ and $MSA^-\cdots H_3O^+$ ions pairs can occur within a few picoseconds at the air-water interface. The atmospheric affinity of MSA^-, SFA^- and H_3O^+ for gaseous precursors was further probed by evaluating the free energies of interaction. It was worth noting that compounds such as MSA, MA, HNO_3 (NA), and $(COOH)_2$ (OA) were identified as candidate species for consideration (Wang et al., 2024; Kulmala et al., 2004). As presented in Table 2, the computed binding energies demonstrate that the interactions of $SFA^-\cdots$MSA, $SFA^-\cdots$NA, $SFA^-\cdots$OA, $H_3O^+\cdots$MA, $MSA^-\cdots$MSA, $MSA^-\cdots$OA, and $MSA^-\cdots$NA were stronger than those of MSA···MA (one of the primary precursors for atmospheric aerosols), with their Gibbs free energies increased by 14.3-50.9 kcal·mol^{-1}. The findings indicate that the presence of SFA^-, MSA^-, and H_3O^+ at the interface facilitates the capture of potential gaseous species onto the surface of water microdroplet.

Furthermore, we investigated the possibility of SFA^- contributing to the enlargement of particles within the MSA-MA cluster, taking into account the geometric configuration and the free energy of formation for the $(MSA)_1\cdot(MA)_1\cdot(SFA^-)_1$ clusters aggregating. Compared with other clusters, such as $(MSA)_1\cdot(MA)_1\cdot(X)_1$ (where X = HCOOH, CH_3COOH, CHOCOOH, OA, $CH_3COCOOH$, $HOOCCH_2COOH$, $HOOC(CH)_2COOH$, $HOOC(CH_2)_2COOH$, $HOOC(CH_2)_3COOH$, $C_6H_5(COOH)$ and $C_{10}H_{16}O_3$) clusters (Zhang et al, 2022), the quantity of hydrogen bonds within the $(MSA)_1\cdot(MA)_1\cdot(SFA^-)_1$ cluster has increased, and the loop of complex was expanded. It has been demonstrated that SFA^- has the greatest capacity to stabilize MSA-MA clusters and facilitate MSA-MA nucleation in these clusters. This was attributed to its acidic nature and structural characteristics, which include a greater number of intermolecular hydrogen bond

binding sites. Therefore, relative to $(MSA)_1 \cdot (MA)_1 \cdot (X)_1$ cluster (Table 2), the Gibbs formation free energy ΔG of the $(MSA)_1 \cdot (MA)_1 \cdot (SFA^-)_1$ cluster was lower, indicating that the $NH_2SO_3^-$ ion exhibits a more potent nucleation capacity at the air-water interface compared to the *X* species in the gas phase. Consequently, our forecast was that the presence of $NH_2SO_3^-$ at the air-water interface will foster enhanced particle growth.

4. Summary and Conclusions

In this study, quantum chemical calculations, BOMD simulations and ACDC kinetic model were utilized to characterize the gaseous and interfacial hydrolysis of $HNSO_2$ with MSA~~CH_3SO_3H~~, and to examine the influence exerted by SFA~~NH_2SO_3H~~ on MSA-MA-based clusters.

In the gaseous reaction, the activation energy for the hydrolysis of $HNSO_2$ catalyzed by MSA~~CH_3SO_3H~~ was only 0.8 kcal·mol^{-1}, significantly lower by 7.7 kcal·mol^{-1} than the energy barrier of H_2O-assisted $HNSO_2$ hydrolysis. The effective rate coefficients reveal that the SFA~~NH_2SO_3H~~ formation from MSA~~CH_3SO_3H~~-catalyzed hydrolysis of $HNSO_2$ can be competitive with that catalyzed by H_2O within an altitude of 5-15 km. Moreover, kinetic simulations utilizing the ACDC have disclosed that SFA has an unexpectedly positive impact on the NPF process, markedly enhancing the assembly of MSA-MA-based cluster. Notably, the "participant" mechanism of SFA for cluster formation has been identified by tracing the growth paths of the system in agriculture-developed and coastal industrial areas, especially significant in the Yangtze River Delta of China, Bangladesh, and the east coast of India.

At the air-water interface, the $NH_2SO_3^-$ and H_3O^+ ions forming mechanism (~40%) and the proton exchange mechanism (~60%) were observed in the hydrolysis of $HNSO_2$ with MSA~~CH_3SO_3H~~, which can take place in a few picoseconds. Notably, the formed SFA~~NH_2SO_3H~~$^-$, MSA~~CH_3SO_3H~~ $^-$, and H_3O^+ ions at the air-water interface possess the ability to attract potential precursor molecules like MSA~~CH_3SO_3H~~, ~~CH_3NH_2~~MA, and HNO_3. This attraction facilitates the transition of gaseous molecules onto the surface of water microdroplet. Moreover, the assessment of the potential of *X* in the formation of the ternary MSA~~CH_3SO_3H~~A-~~CH_3NH_2~~MA-*X* cluster revealed that SFA~~NH_2SO_3H~~$^-$ exhibits the greatest propensity to stabilize MSA~~CH_3SO_3H~~-~~CH_3NH_2~~MA clusters and to foster nucleation of MSA~~CH_3SO_3H~~-~~CH_3NH_2~~-MA in the context of *X*.

Overall, this work not only elucidates a novel mechanism underlying the hydrolysis of $HNSO_2$

with MSA~~CH_3SO_3H~~, but also highlight the potential contribution of SFA on aerosol particle growth and new particle formation.

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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.

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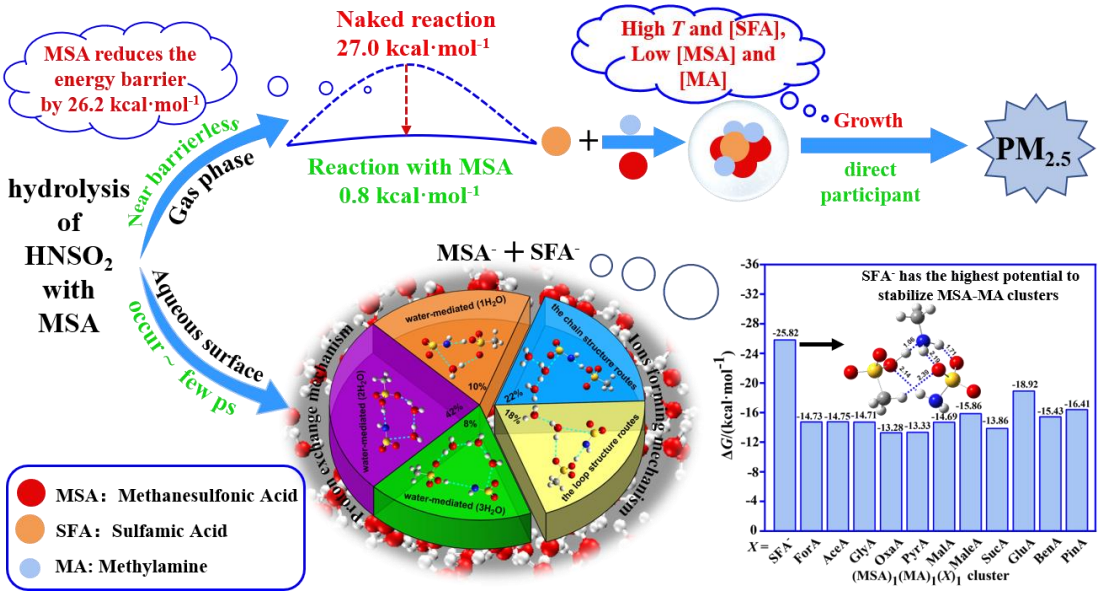


Graphical abstract

Figure Captions

Fig. 1 The potential energy profile (ΔG) for the hydrolysis reaction of $HNSO_2$ with MSA at the CCSD(T)-F12/cc-pVDZ-F12//M06-2X/6-311++G(2*df*,2*pd*) level of theory

Fig. 2 BOMD simulation trajectories and snapshots of $NH_2SO_3^-$ and H_3O^+ ions forming mechanism (chain structure (a) and loop-structure (b)) in the $HNSO_2$ hydrolysis with MSA at the air-water interface

Fig. 3 BOMD simulation trajectories and snapshots of proton exchange mechanism in MSA-mediated hydration $HNSO_2$ with one (a) and two (b) water molecules at the air-water interface

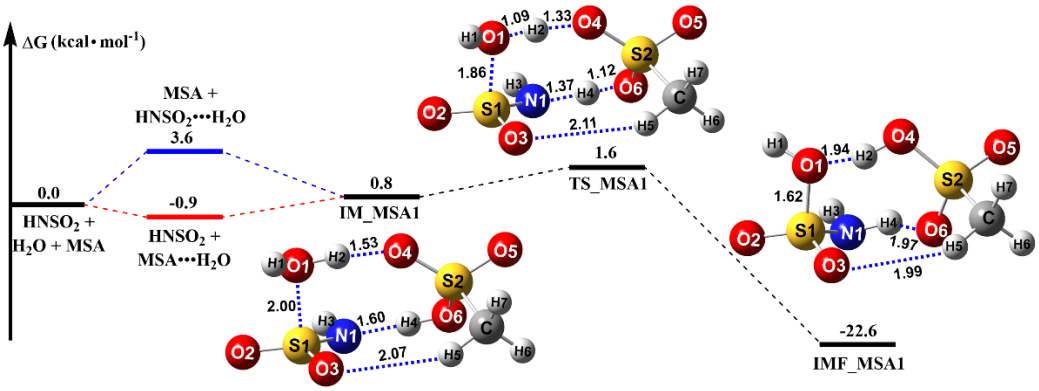
Fig. 4 Percentages of different mechanisms for the $HNSO_2$ hydrolysis with MSA at the air-water interface observed in BOMD simulations

Fig. 5 ESP-mapped molecular vdW surface of MA, SFA and MSA molecules at M06-2X/6-311++G(2*df*,2*pd*) level of theory. Surface local minima and maxima of ESP of the different functional groups in MA, SFA and MSA molecules are represented as blue and yellow spheres, respectively. The values of maximum and minimum are shown in kcal mol^{-1} in the parentheses. The green, red and blue arrows refer to the tendencies to form hydrogen bonds and proton transfer events, respectively. (green = carbon, red = oxygen, blue = nitrogen, yellow = sulfur and white = hydrogen.)

Fig. 6 The J (cm^{-3} s^{-1}) (a) and R (b) versus [SFA] with [MSA] = 10^6 molecules cm^{-3}, [MA] = 2.5 × 10^8 molecules cm^{-3} and four different temperatures (green line: 298.15 K, blue line: 278.15 K, red line: 258.15 K, black line: 238.15 K).

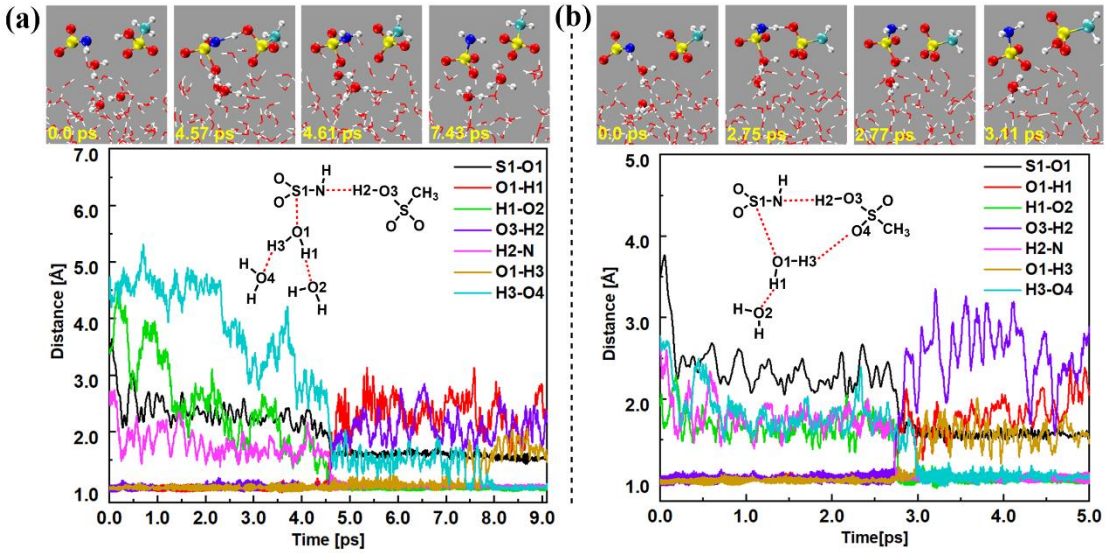
Fig. 7 The J (cm^{-3} s^{-1}) (a) and R (b) as a function of [MSA] with [SFA] = 10^8 molecules cm^{-3} and three different [MA] (black line: [MA] = 2.5 × 10^7 molecules cm^{-3}, red line: [MA] = 2.5 × 10^8 molecules cm^{-3}, blue line: [MA] = 2.5 × 10^9 molecules cm^{-3}) at 278.15 K.

Fig. 8 Main cluster formation mechanism of MSA-MA-SFA-based system at 278.15 K, [MSA] = 10^7 molecules·cm^{-3}, [MA] = 2.5 × 10^8 molecules·cm^{-3}, and [SFA] = 10^6 molecules·cm^{-3}. (a) The black arrows indicate the pure MSA-MA-based growth pathways. Blue arrows represent the pathways containing SFA. The influence of (b) temperature, (c) [SFA] and [MSA] on the relative contribution of the pure MSA-MA-based clustering pathway and the SFA participation pathway to the system flux is analyzed. Others in (b), and (c) indicate that the pathway contribution of the cluster growing out of the studied system is less than 5%


ΔG (kcal• mol-1)
MSA + HNSO2•••H2O
3.6
0.0
HNSO2 + H2O + MSA
-0.9
HNSO2 + MSA•••H2O
0.8
IM_MSA1
1.6
TS_MSA1
-22.6
IMF_MSA1

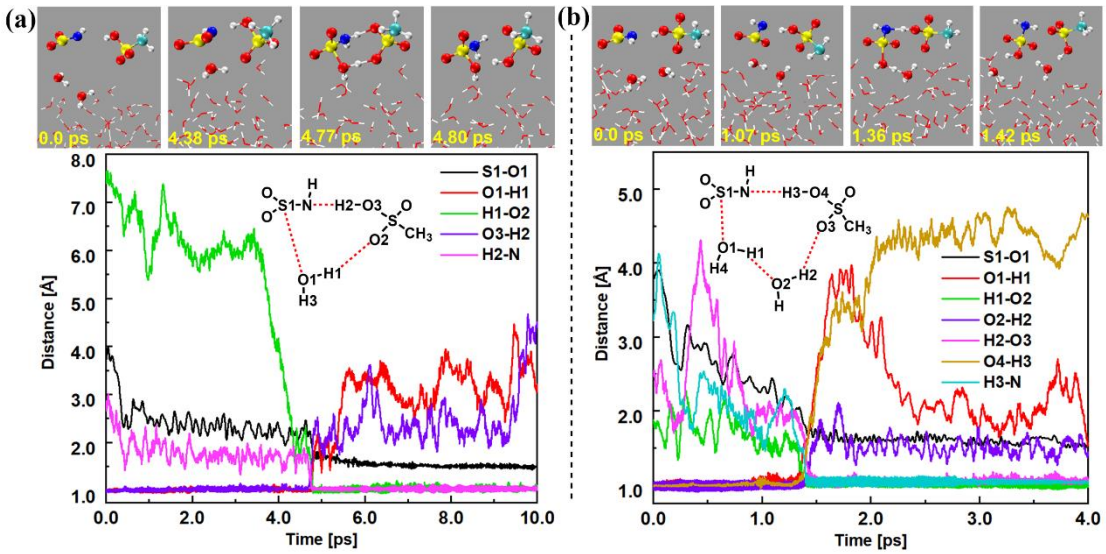
794

795 **Fig. 1**


(a)
0.0 ps
4.57 ps
4.61 ps
7.43 ps
Distance [Å]
Time [ps]
S1-O1
O1-H1
H1-O2
O3-H2
H2-N
O1-H3
H3-O4
(b)
0.0 ps
2.75 ps
2.77 ps
3.11 ps
Distance [Å]
Time[ps]
S1-O1
O1-H1
H1-O2
O3-H2
H2-N
O1-H3
H3-O4

796

797 **Fig. 2**



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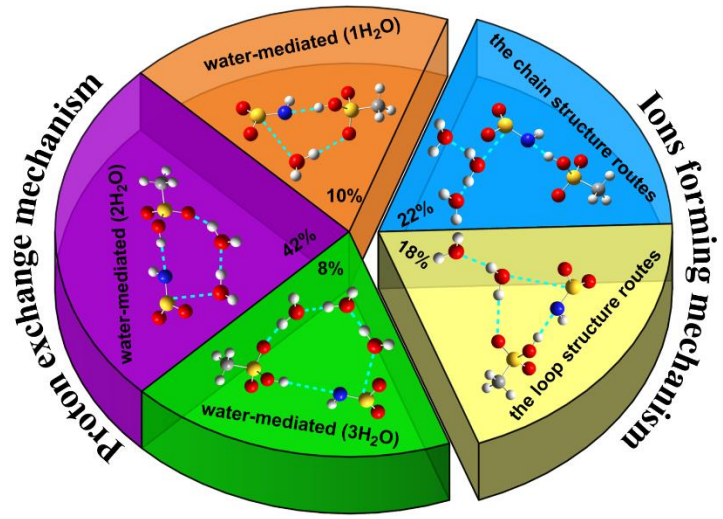
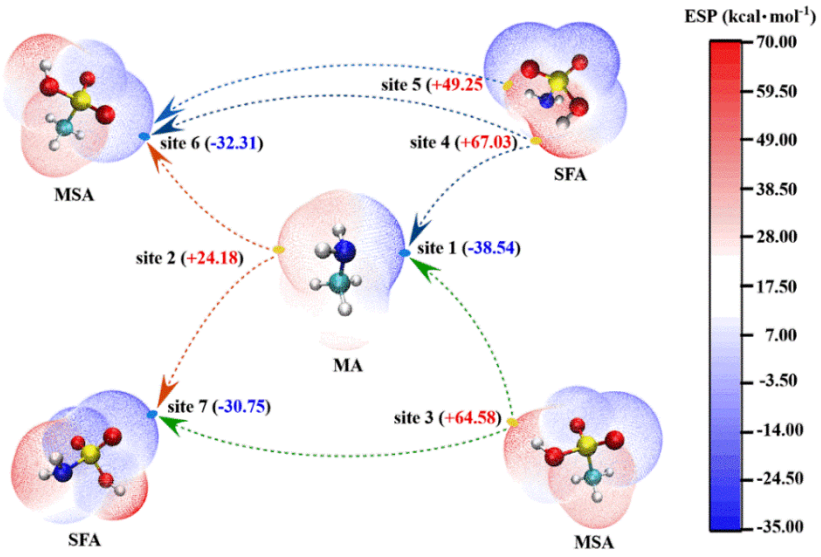
799

800 **Fig. 3**


Proton exchange mechanism
Ions forming mechanism
water-mediated (1H2O)
10%
water-mediated (2H2O)
42%
water-mediated (3H2O)
8%
the chain structure routes
22%
the loop structure routes
18%

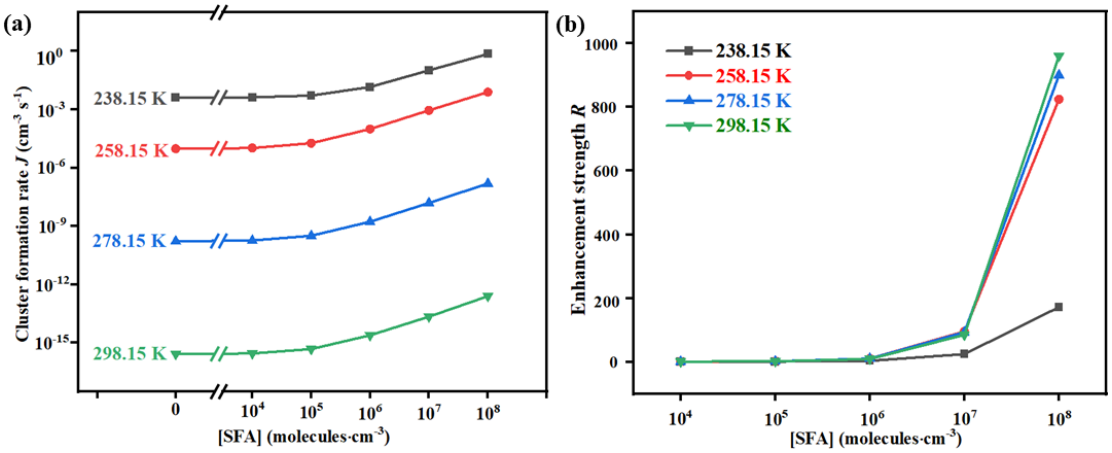
801

802 **Fig. 4**

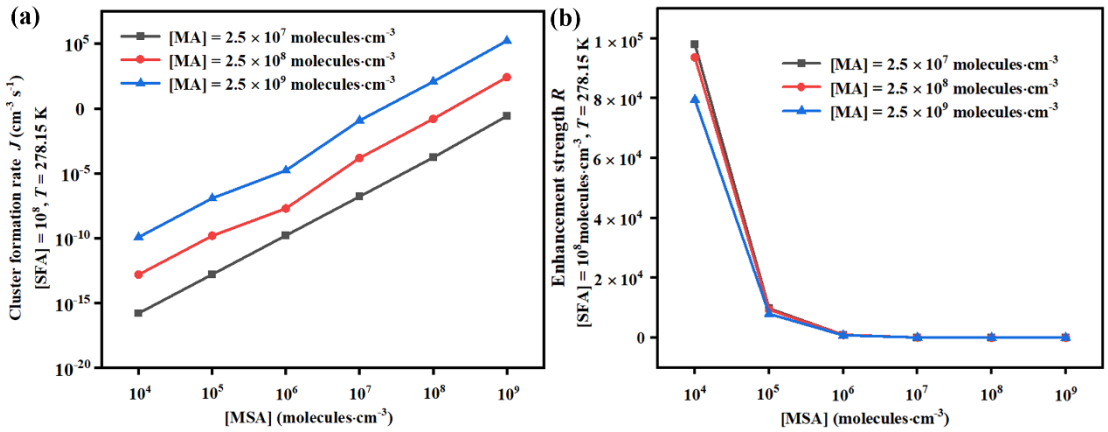

ESP (kcal·mol^{-1})
70.00
59.50
49.00
38.50
28.00
17.50
7.00
-3.50
-14.00
-24.50
-35.00
site 5 (+49.25)
site 6 (-32.31)
site 4 (+67.03)
MSA
SFA
site 2 (+24.18)
site 1 (-38.54)
MA
site 7 (-30.75)
site 3 (+64.58)
SFA
MSA

803

804 **Fig. 5**


(a)
Cluster formation rate J (cm-3 s-1)
10^0
10^-3
10^-6
10^-9
10^-12
10^-15
238.15 K
258.15 K
278.15 K
298.15 K
0
10^4
10^5
10^6
10^7
10^8
[SFA] (molecules·cm-3)
(b)
Enhancement strength R
1000
800
600
400
200
0
238.15 K
258.15 K
278.15 K
298.15 K
10^4
10^5
10^6
10^7
10^8
[SFA] (molecules·cm-3)

805
806 **Fig. 6**


(a)
[MA] = 2.5 × 10^7 molecules·cm^-3
[MA] = 2.5 × 10^8 molecules·cm^-3
[MA] = 2.5 × 10^9 molecules·cm^-3
Cluster formation rate J (cm^-3 s^-1)
[SFA] = 10^8, T = 278.15 K
[MSA] (molecules·cm^-3)
(b)
Enhancement strength R
[SFA] = 10^8 molecules·cm^-3, T = 278.15 K
[MSA] (molecules·cm^-3)

807

808 **Fig. 7**

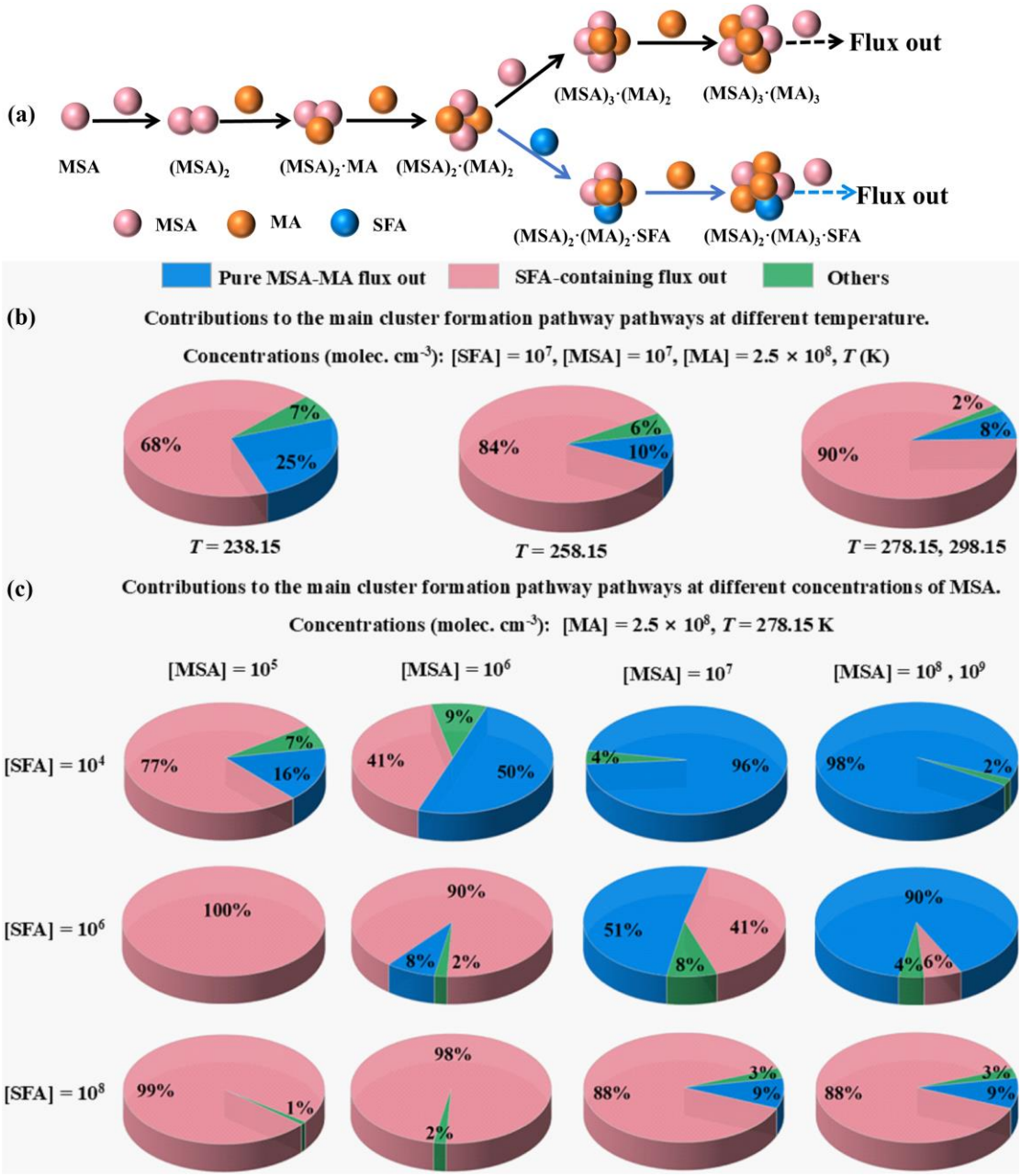

(a)
MSA
(MSA)2
(MSA)2·MA
(MSA)2·(MA)2
(MSA)3·(MA)2
(MSA)3·(MA)3
Flux out
(MSA)2·(MA)2·SFA
(MSA)2·(MA)3·SFA
Flux out
MSA
MA
SFA
Pure MSA-MA flux out
SFA-containing flux out
Others
(b)
Contributions to the main cluster formation pathway pathways at different temperature.
Concentrations (molec. cm-3): [SFA] = 10^7, [MSA] = 10^7, [MA] = 2.5 × 10^8, T (K)
68%
7%
25%
T = 238.15
84%
6%
10%
T = 258.15
90%
2%
8%
T = 278.15, 298.15
(c)
Contributions to the main cluster formation pathway pathways at different concentrations of MSA.
Concentrations (molec. cm-3): [MA] = 2.5 × 10^8, T = 278.15 K
[MSA] = 10^5
[MSA] = 10^6
[MSA] = 10^7
[MSA] = 10^8 , 10^9
[SFA] = 10^4
77%
7%
16%
41%
9%
50%
4%
96%
98%
2%
[SFA] = 10^6
100%
90%
8%
2%
51%
41%
8%
90%
4%
6%
[SFA] = 10^8
99%
1%
98%
2%
88%
3%
9%
88%
3%
9%

Fig. 8

Table 1 Rate coefficients (k, $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) and effective rate constants (k', $cm^3 \cdot molecule^{-1} \cdot s^{-1}$) for the hydrolysis of $HNSO_2$ with H_2O and MSA calculated by master equation within the temperature range of 213-320 K and altitude range of 0-15 km

Altitude		0 km						5 km	10 km	15 km
T/K		280	290	298	300	310	320	259.3	229.7	212.6
k_{WM}		7.64×10^{-13}	6.45×10^{-13}	5.63×10^{-13}	5.44×10^{-13}	4.59×10^{-13}	3.88×10^{-13}	1.09×10^{-12}	1.72×10^{-12}	2.22×10^{-12}
k_{MSA}		3.08×10^{-11}	2.96×10^{-11}	2.85×10^{-11}	2.82×10^{-11}	2.67×10^{-11}	2.52×10^{-11}	3.32×10^{-11}	3.49×10^{-11}	3.50×10^{-11}
	20%RH	5.99×10^{-18}	7.96×10^{-18}	9.64×10^{-18}	1.03×10^{-17}	1.29×10^{-17}	1.36×10^{-17}			
	40%RH	1.19×10^{-17}	1.58×10^{-17}	1.99×10^{-17}	2.07×10^{-17}	2.60×10^{-17}	3.12×10^{-17}			
k'_{WM}	60%RH	1.79×10^{-17}	2.38×10^{-17}	2.98×10^{-17}	3.11×10^{-17}	3.90×10^{-17}	4.68×10^{-17}	9.85×10^{-27}	1.71×10^{-22}	6.51×10^{-22}
	80%RH	2.39×10^{-17}	3.17×10^{-17}	3.97×10^{-17}	4.14×10^{-17}	5.21×10^{-17}	6.24×10^{-17}			
	100%RH	2.97×10^{-17}	3.96×10^{-17}	4.97×10^{-17}	5.18×10^{-17}	6.50×10^{-17}	7.79×10^{-17}			
k'_{MSA}	[MSA]=10^8	4.81×10^{-19}	2.50×10^{-19}	1.57×10^{-19}	1.40×10^{-19}	7.90×10^{-20}	4.60×10^{-20}	1.96×10^{-20}	2.37×10^{-19}	1.30×10^{-18}
k'_{MSA}/k'_{WM}		1.62×10^{-4}	6.42×10^{-5}	3.16×10^{-5}	2.69×10^{-5}	1.22×10^{-5}	5.90×10^{-5}	3.01×10^{1}	1.38×10^{3}	1.32×10^{8}

k_{WM} and k_{MSA} are respectively the rate constant for the hydrolysis of $HNSO_2$ with H_2O and MSA; k'_{WM} and k'_{MSA} are respectively the effective rate constant for the hydrolysis of $HNSO_2$ with H_2O and MSA.

Table 2. Gibbs free energy (ΔG) for the formation of $SFA^-\cdots MSA$, $SFA^-\cdots NA$, $SFA^-\cdots OA$, $H_3O^+\cdots MA$, $MSA^-\cdots MSA$, $MSA^-\cdots OA$, and $MSA^-\cdots NA$, $MSA\cdots MA$, $(MSA)_1\cdot(MA)_1\cdot(X)_1$ at 298 K

	$SFA^-\cdots MSA$	$SFA^-\cdots HNO_3$	$SFA^-\cdots OA$	$MSA^-\cdots MSA$	$MSA^-\cdots NA$
ΔG	-23.8	-21.5	-25.2	-23.9	-22.6
	$MSA^-\cdots$ OA	$MSA\cdots H_3O^+$	$MA\cdots H_3O^+$	$MSA\cdots MA$	
ΔG	-25.8	-35.8	-57.9	-7.0 (-7.2)[b]	
	HCOOH …MSA…MA	CH_3COOH …MSA…MA	CHOCOOH …MSA…MA	OA …MSA…MA	
ΔG	-14.7 (-15.8)[a]	-14.8 (-14.3)[a]	-14.7 (-15.6)[a]	-13.3 (-12.7)[a]	
	$CH_3COCOOH$ …MSA…MA	$HOOCCH_2COOH$ …MSA…MA	$HOOC(CH)_2COOH$ …MSA…MA	$HOOC(CH_2)_2COOH$ …MSA…MA	
ΔG	-13.3 (-13.0)[a]	-14.7 (-16.7)[a]	-15.9 (-15.3)[a]	-13.9 (-14.3)[a]	
	$HOOC(CH_2)_3COOH$ …MSA…MA	$C_6H_5(COOH)$ …MSA…MA	$C_{10}H_{16}O_3$ …MSA…MA	SFA^- …MSA…MA	
ΔG	-18.9 (-17.9)[a]	-15.4 (-15.3)[a]	-16.4 (-15.3)[a]	-25.8	

[a] The value was taken from reference (Zhang, R., Shen, J., Xie, H. B., Chen, J., and Elm, J.: The role of organic acids in new particle formation from methanesulfonic acid and methylamine, Atmos. Chem. Phys., 22, 2639-2650, 10.5194/acp-22-2639-2022, 2022b.)

[b] The value was taken from reference (Zhong, J., Li, H., Kumar, M., Liu, J., Liu, L., Zhang, X., Zeng, X. C., and Francisco, J. S.: Mechanistic Insight into the Reaction of Organic Acids with SO_3 at the Air–Water Interface, Angew. Chem. Int. Ed., 131, 8439-8443, 2019.)