Synergistic Reaction of SO$_2$ with NO$_2$ in Presence of H$_2$O and NH$_3$: A Potential Source of Sulfate Aerosol

Zehua Wang $^1$, Chenxi Zhang $^2$, Guochun Lv $^1$, Xiaomin Sun $^1$, Ning Wang $^1$ and Zhiqiang Li $^3$,*

$^1$ Environment Research Institute, Shandong University, Jinan 250100, China
$^2$ College of Biological and Environmental Engineering, Binzhou University, Binzhou 256600, China
$^3$ Center for Optics Research and Engineering (CORE), Shandong University, Qingdao 266237, China

* Correspondence: sxmwch@sdu.edu.cn (X.S.); lzq@sdu.edu.cn (Z.L.)

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Abstract: Effect of H$_2$O and NH$_3$ on the synergistic oxidation reaction of SO$_2$ and NO$_2$ is investigated by theoretical calculation using the molecule system SO$_2$-2NO$_2$-nH$_2$O ($n=0, 1, 2, 3$) and SO$_2$-2NO$_2$-nH$_2$O-mNH$_3$ ($n=0, 1, 2; m=1, 2$). Calculated results show that SO$_2$ is oxidized to SO$_3$ by N$_2$O$_4$ intermediate. The additional H$_2$O in the systems can reduce the energy barrier of oxidation step. The increasing number of H$_2$O molecules in the systems enhances the effect and promotes the production of HONO. When the proportion of H$_2$O to NH$_3$ is 1:1, with NH$_3$ included in the system, the energy barrier is lower than two pure H$_2$O molecules in the oxidation step. The present study indicates that the H$_2$O and NH$_3$ have thermodynamic effects on promoting the oxidation reaction of SO$_2$ and NO$_2$, and NH$_3$ has a more significant role in stabilizing product complexes. In these hydrolysis reactions, nethermost barrier energy (0.29 kcal/mol) can be found in the system SO$_2$-2NO$_2$-H$_2$O. It is obvious that the production of HONO is energetically favorable. A new reaction mechanism about SO$_2$ oxidation in the atmosphere is proposed, which can provide guidance for the further study of aerosol surface reactions.

Keywords: sulfuric acid; sulfur dioxide; nitrogen dioxide; synergistic oxidation; hydrolysis reaction

1. Introduction

Sulfur dioxide (SO$_2$), a major air pollutant, is released into the atmosphere via the combustion of sulfur containing fuels and industrial production [1–3], volcanic eruptions, and decomposition of sulfides in nature. SO$_2$ can be oxidized to form sulfuric acid (H$_2$SO$_4$) through the homogeneous or heterogeneous processes [4–6], which include gas-phase oxidation by hydroxyl radical (OH$^\cdot$) and in-cloud oxidation by dissolved ozone (O$_3$) and hydrogen peroxide (H$_2$O$_2$) [7–9]. It has been proved that sulfuric acid is the main contributor to the new particle formation, resulting in serious environmental issues such as haze and acid rain [10–12]. Thus, it is significant to investigate the SO$_2$ oxidation mechanism in the atmosphere.

In hazy weather, researchers have found that a considerable amount of PM$_{2.5}$ can be formed in the atmosphere, and sulfate is the significant component of the fine particulate matter [13–18]. Previous studies have indicated that, as the haze weather gets worse, the concentration of O$_3$ decreases, while the concentrations of NO$_2$ and sulfate increase [19]. However, widespread formation pathways (gas-phase oxidation and in-cloud oxidation) of sulfate cannot account for the phenomena of high content of sulfate. Some researchers have investigated that the oxidation reaction of SO$_2$ by NO$_2$ is proposed as a missing key pathway to form sulfate in a special condition [19–24]. Wang et al. have
considered that NO$_2$ could effectively react with SO$_2$ in the presence of H$_2$O and NH$_3$ during the severe haze period [25]:

\[
\text{SO}_2(g) + 2\text{NO}_2(g) + 2\text{H}_2\text{O}(aq) \rightarrow 2\text{H}^+(aq) + \text{SO}_4^{2-}(aq) + 2\text{HONO}(g) \tag{1}
\]

\[
2\text{NH}_3(g) + \text{SO}_2(g) + 2\text{NO}_2(g) + 2\text{H}_2\text{O}(aq) \rightarrow 2\text{NH}_4^+(aq) + \text{SO}_4^{2-}(aq) + 2\text{HONO}(g) \tag{2}
\]

From Reaction (1) and (2), it can be seen that the final products primarily include SO$_4^{2-}$ and HONO.

In the presence of water, the process of NO$_2$ dimerization is likely to occur in polluted atmospheric conditions [26,27]. Some studies have demonstrated that N$_2$O$_4$, the dimer of NO$_2$, serves as the oxidant to oxidize SO$_2$ on the aerosol surface [28–30]. For NO$_2$ dimer, three isomers, symmetric sys-O$_2$N-NO$_2$, and asymmetric t-ONONO$_2$, c-ONONO$_2$, can be found. The sys-O$_2$N-NO$_2$ is very stable due to its symmetry, while asymmetric ONO-NO$_2$ can be rapidly converted to NO$^+$ and NO$_3^-$ in the presence of water [31–34]. The ion pairs (NO$^+$NO$_3^-$) can also oxidize many organic and inorganic compounds [35]. Although these studies have shown that SO$_2$ can react with NO$_2$ to produce H$_2$SO$_4$, the reaction mechanism is not completely understood.

In this paper, we researched the gas-phase reaction of SO$_2$ with NO$_2$ using the density functional theory (DFT) method. The different number of water molecules is added to the reaction so as to investigate the role of water molecules in the oxidation reaction. In addition, the effect of NH$_3$ in the oxidation reaction also is considered.

2. Results and Discussion

2.1. The Reaction of SO$_2$-2NO$_2$-nH$_2$O (n = 0, 1, 2, 3)

2.1.1. The Reaction of SO$_2$-2NO$_2$

In the absence of H$_2$O, the equilibrium structures and potential energy are shown in Figure 1, Tables 1 and 2 present the corresponding energy data and the numerical value of charge distribution of NO$^+$NO$_3^-$ and NO$^+$NO$_2^-$. The relative energies, enthalpies and Gibbs free energies in all relevant species for the system SO$_2$-2NO$_2$ are summarized in Table S1. Two main pathways are found due to the formation of two NO$_2$ dimers, t-ONONO$_2$ and c-ONONO$_2$. The pre-reactive complexes (RC1 and RC2) are produced by a collision of SO$_2$. The IM1 (a binding of $-23.27$ kcal/mol) is formed via transient state (TS1) with the energy barrier and reaction energy of $45.48$ kcal/mol and $-11.49$ kcal/mol, respectively. The IM2 is produced by TS2 with the energy barrier and reaction energy of $52.45$ kcal/mol and $-5.77$ kcal/mol, respectively. These two processes are similar in that an O atom from NO$^+$NO$_3^-$ fragments transforms into SO$_2$ to lead to the formation of SO$_3$. As shown in Table S1, the reaction SO$_2$-2NO$_2$$\rightarrow$IM1 is exothermic and spontaneous ($\Delta H$ of $-24.50$ kcal/mol and $\Delta G$ of $-0.29$ kcal/mol at 298.15K). Due to the absence of H$_2$O molecule, the hydrolysis process cannot be carried out, and HONO cannot be generated, finally.
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**Table 1.** Energy barriers and reaction energies for the integrated reactions 2NO₂-SO₂-mH₂O-nNH₃ (m = 0, 1, 2; n = 0, 1, 2) (unit: kcal/mol).

| Reaction Systems | Oxidation Reaction | Hydrolysis Reaction |
|------------------|--------------------|---------------------|
|                  | Energy Barrier     | Reaction Energy     | Energy Barrier | Reaction Energy |
| SO₂-2NO₂         | 45.48 kcal/mol     | −11.49 kcal/mol     | 0.29 kcal/mol  | −3.27 kcal/mol  |
| SO₂-2NO₂-H₂O     | 41.80 kcal/mol     | −13.16 kcal/mol     | 0.29 kcal/mol  | −3.27 kcal/mol  |
| SO₂-2NO₂-2H₂O    | 40.14 kcal/mol     | −14.75 kcal/mol     | 3.06 kcal/mol  | −1.85 kcal/mol  |
| SO₂-2NO₂-3H₂O    | 41.47 kcal/mol     | −15.87 kcal/mol     | −1.59 kcal/mol | −4.15 kcal/mol  |
| SO₂-2NO₂-NH₃     | 38.77 kcal/mol     | −21.34 kcal/mol     | 1.87 kcal/mol  | −6.56 kcal/mol  |
| SO₂-2NO₂-H₂O-NH₃ | 40.60 kcal/mol     | −20.10 kcal/mol     | −1.59 kcal/mol | −6.56 kcal/mol  |
| SO₂-2NO₂-2H₂O-NH₃| 38.92 kcal/mol     | −17.85 kcal/mol     | 4.15 kcal/mol  | −13.45 kcal/mol |
| SO₂-2NO₂-H₂O-2NH₃| 40.30 kcal/mol     | −18.60 kcal/mol     | 3.94 kcal/mol  | −13.06 kcal/mol |
| SO₂-2NO₂-2H₂O-2NH₃| 39.21 kcal/mol    | −18.61 kcal/mol     | 6.26 kcal/mol  | −13.06 kcal/mol |

**Figure 1.** Potential energy profile for the reaction of SO₂-2NO₂. The yellow spheres are S atoms, the red spheres are O atom, and the blue spheres are N atom, respectively. (Unit: Energies in kcal/mol; bond lengths in angstroms). The black and red lines are the different pathways. The black line represents the reaction of t-ONONO₂-SO₂, and the red line is the reaction of c-ONONO₂-SO₂.

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SO₂⁻(g) + 2NO⁻(g) + 2H⁺(aq) → 2SO₄²⁻(aq) (1) ... to the absence of H₂O molecule, the hydrolysis process cannot be carried out, and HONO cannot be generated, finally.

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The relative energies, enthalpies and Gibbs free energies in all relevant species for the SO$_2$-2NO$_2$ reaction cannot produce HONO. The result indicates that H$_2$O molecule reacts as the solvent to reduce activation energy and stable structures and also is a critical reactant in the formation of HONO.

Table 2. The charge distribution for the NO$^+$NO$_3^-$ and NO$^+$NO$_2^-$ in reactant complexes (RC) and intermediates (IM).

| Reactant Complexes | NO$^+$ | NO$_3^-$ | Intermediate | NO$^+$ | NO$_2^-$ |
|--------------------|--------|----------|--------------|--------|----------|
| SO$_2$-2NO$_2$     | 0.330  | -0.328   | IM1          | 0.502  | -0.201   |
|                    | 0.405  | -0.394   | IM2          | 0.501  | -0.217   |
| SO$_2$-2NO$_2$-H$_2$O | 0.472  | -0.437   | IM1-1W       | 0.712  | -0.250   |
|                    | 0.506  | -0.472   | IM2-1W       | 0.688  | -0.280   |
| SO$_2$-2NO$_2$-2H$_2$O | 0.644  | -0.605   | IM1-2W       | 0.772  | -0.290   |
|                    | 0.592  | -0.532   | IM2-2W       | 0.726  | -0.259   |
| SO$_2$-2NO$_2$-3H$_2$O | 0.730  | -0.695   | IM1-3W       | 0.767  | -0.309   |
|                    | 0.705  | -0.724   | IM2-3W       | 0.621  | -0.282   |
| SO$_2$-2NO$_2$-NH$_3$ | 0.448  | -0.442   | IM1-1A       | 0.241  | -0.222   |
|                    | 0.458  | -0.635   | IM2-1A       | 0.643  | -0.228   |
| SO$_2$-2NO$_2$-H$_2$O-NH$_3$ | 0.599  | -0.569   | IM1-1W-1A    | 0.640  | -0.261   |
|                    | 0.508  | -0.672   | IM2-1W-1A    | 0.596  | -0.279   |
| SO$_2$-2NO$_2$-2H$_2$O-NH$_3$ | 0.675  | -0.673   | IM1-2W-1A    | 0.773  | -0.296   |
|                    | 0.722  | -0.625   | IM2-2W-1A    | 0.717  | -0.241   |
| SO$_2$-2NO$_2$-H$_2$O-2NH$_3$ | 0.440  | -0.696   | IM1-1W-2A    | 0.549  | -0.297   |
|                    | 0.449  | -0.691   | IM2-1W-2A    | 0.488  | -0.283   |

2.1.2. The Reaction of SO$_2$-2NO$_2$-H$_2$O

Figure 2 explores the equilibrium structures and potential energy of SO$_2$-2NO$_2$-H$_2$O. The corresponding energy data and the numerical value of charge distribution are put in Tables 1 and 2. In these two pathways, the complexes (t-ONONO$_2$H$_2$O and c-ONONO$_2$H$_2$O) are firstly produced via the interaction between an N$_2$O$_4$ molecule and a water molecule. Through a collision with SO$_2$, the two complexes can transform into the pre-reactive complex (RC1-1W and RC2-1W).

Beginning with the reactant complex RC1-1W (a binding energy of 17.78 kcal/mol), the complex IM1-1W (a binding energy 30.94 kcal/mol) can be formed via the TS1-1W with the energy barrier of 41.80 kcal/mol. In this process, an oxygen atom from NO$^+$NO$_3^-$ fragment is transferred to SO$_2$, leading to the formation of SO$_3$. The complex IM1-1W can undergo an isomerization process to form IM′-1W with the energy absorption of 0.14 kcal/mol. Because the H$_2$O molecule gets involved, the NO$^+$NO$_2^-$ fragments are divided into two parts, and the NO$^+$ fragment rotates by an angle. Once the IM′-1W is produced, the final complex SO$_3$-2HONO can be easily formed with the energy barrier of 0.29 kcal/mol and the reaction energy of 0.37 kcal/mol. From IM′-1W to SO$_3$-2HONO, the water molecule reacts with the isolated NO$^+$ fragment and NO$_2^-$ fragment to form two HONO molecules. In the other pathway, the reaction process is similar in the above step. The IM2-1W is formed from the conversion of RC2-1W via the transition state TS2-1W with the energy barrier of 47.54 kcal/mol and the reaction energy of $\sim$13.05 kcal/mol. After that, the hydrolysis process is the same as the above reaction (IM′-1W to SO$_3$-2HONO). The reactant (IM′-1W) is formed via IM2-1W releasing the energy of 0.09 kcal/mol. In the same way, the SO$_3$-2HONO is formed with the energy barrier and reaction energy of 0.30 kcal/mol and $\sim$3.27 kcal/mol, respectively.

In the absence of water, the energy barrier is higher than one H$_2$O molecule and the hydrolysis reaction cannot produce HONO. The result indicates that H$_2$O molecule reacts as the solvent to reduce activation energy and stable structures and also is a critical reactant in the formation of HONO.
2.1.3. The Reaction of SO₂-2NO₂-2H₂O

Figure 3 presents the optimized geometries of molecular species involved in the reaction of SO₂-2NO₂-2H₂O to examine the role of an additional H₂O molecule. Tables 1 and 2 show the corresponding energy data and the charge distribution. Table S3 shows the relative energies, enthalpies and Gibbs free energies in all relevant species for the SO₂-2NO₂-2H₂O. In these pathways, the pre-reactive complexes (RC1-2W and RC2-2W) are produced via the interaction between the complexes (t-ONONO₂-2H₂O and c-ONONO₂-2H₂O) and SO₂, or a collision of the complexes (t-ONONO₂-H₂O-SO₂ and c-ONONO₂-H₂O-SO₂) with H₂O.

Starting with the complex RC1-2W (−25.32 kcal/mol), the intermediate complex IM1-2W (−40.06 kcal/mol) is formed via TS1-2W with the energy barrier of 40.14 kcal/mol. The isomerized intermediate complex IM1’-2W (−40.89 kcal/mol) is formed by the H₂O(a) closing to NO⁺NO₂⁻. The H₂O(a) molecule reacts with NO⁺NO₂⁻ with an energy barrier and reaction energy of 4.36 kcal/mol and −3.94 kcal/mol, respectively. The other pathway is analogous with the above process, and the barrier (41.47 kcal/mol) is slightly higher than the reaction pathway involving in TS1-2W.

In the presence of two H₂O molecules, the H₂O(a) serves as reactant to form HONO, and the other H₂O(b) acts as a solvent molecule in this reaction pathway to reduce energy barrier and stable complex structures. Compare with the one-water reaction in the first step, the energy barrier for TS1-2W is reduced by 1.66 kcal/mol. Moreover, the energy barrier of TS2-2W is decreased by 6.07 kcal/mol for TS2-1W. It shows that the second-water molecule plays a certain role in lowering the energy barrier and stabilizing the complex structures.
As shown in Table S4, the reaction SO$_2$-2NO$_2$-3H$_2$O is still favorable thermodynamically with the number of H and lowering the energy barrier. As the number of H$_2$O increases, the releasing energy gets more and more, and the configurations of product complexes are more and more stable. The hydrolysis reaction is still favorable thermodynamically with the number of H$_2$O molecule increasing.

2.1.4. The Reaction of SO$_2$-2NO$_2$-3H$_2$O

The consequence of three H$_2$O molecules taking part in reaction is shown in Figure 4. The corresponding energy data and the charge distribution are put in Tables 1 and 2. Table S4 summarizes the relative energies, enthalpies and Gibbs free energies in all relevant species for the SO$_2$-2NO$_2$-3H$_2$O reaction.

In the presence of two H$_2$O molecules, the H$_2$O(a) serves as reactant to form HONO, and the other H$_2$O molecules act only as a solvent without entering into the reaction. As the number of H$_2$O increases, the releasing energy gets more and more. The oxidation reaction of the other pathway is approximately similar to RC1-3W to IM1-3W. It is different from the above hydrolytic processes, and H$_2$O(c) reacts as a transporter to transmit a proton forming H$_3$O$^+$ intermediate. The relevant energy barrier and reaction energy of the process are shown in Table 1. As shown in Table S4, the reaction SO$_2$-2NO$_2$-3H$_2$O$\rightarrow$SO$_3$-2HONO-2H$_2$O-1 is exothermic and spontaneous.

In comparison to one-water molecules in the process of SO$_2$ oxidation, three H$_2$O molecules have successfully reduced the energy barrier height by 5.35 kcal/mol and 8.77 kcal/mol. In these two pathways, the two additional H$_2$O molecules act only as a solvent without entering into the reaction. It shows that the third-water molecule plays a significant role in stabilizing the complexes and lowering the energy barrier. As the number of H$_2$O increases, the releasing energy gets more and more, and the configurations of product complexes are more and more stable. The hydrolysis reaction is still favorable thermodynamically with the number of H$_2$O molecule increasing.

Figure 3. Potential energy profile for the reaction of SO$_2$-2NO$_2$-2H$_2$O. The yellow spheres are S atoms, the red spheres are O atom, the blue spheres are N atom, and the white spheres represent H atom, respectively. (Unit: Energies in kcal/mol; bond lengths in angstroms). The black and red lines are the different pathways. The black line represents the reaction of t-ONONO$_2$-2H$_2$O-SO$_2$, and the red line is the reaction of c-ONONO$_2$-2H$_2$O-SO$_2$.}

Table 1. As shown in Table S4, the reaction SO$_2$-2NO$_2$-3H$_2$O and NO$^+$NO$_2$-3H$_2$O reduces reaction energy of 19.48 kcal/mol. The reactant complex of hydrolysis IM1-3W. It is different from the above hydrolytic processes, and H$_2$O(c) reacts as a transporter to transmit a proton forming H$_3$O$^+$ intermediate. The relevant energy barrier and reaction energy of the process are shown in Table 1. As shown in Table S4, the reaction SO$_2$-2NO$_2$-3H$_2$O$\rightarrow$SO$_3$-2HONO-2H$_2$O-1 is exothermic and spontaneous.

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more, and the configurations of product complexes are more and more stable. The hydrolysis reaction is still favorable thermodynamically with the number of H2O molecule increasing.

Figure 4. Potential energy profile for the reaction of SO2-2NO2-3H2O. The yellow spheres are S atoms, the red spheres are O atom, the blue spheres are N atom, and the white spheres represent H atom, respectively. (Unit: Energies in kcal/mol; bond lengths in angstroms). The black and red lines are the different pathways. The black line represents the reaction of t-ONONO2-3H2O-SO2, and the red line is the reaction of c-ONONO2-3H2O-SO2.

2.2. The Reaction of SO2-2NO2-nH2O-mNH3 (n = 0, 1, 2; m = 1, 2)

2.2.1. The Reaction of SO2-2NO2-NH3

Figure 5 explores the equilibrium structures and potential energy of the system 2NO2-SO2-NH3. Table S5 summarizes the relative energies, enthalpies and Gibbs free energies in all relevant species. The corresponding thermodynamic data and the charge distribution are put in Tables 1 and 2. Reactant complexes (RC1-1A and RC2-1A) are formed through the collision between complexes (t-ONONO2-NH3 and c-ONONO2-NH3) and SO2, which is equivalent to replacing one H2O molecule from RC1-1W and RC2-1W with NH3. RC1-1A (−15.12 kcal/mol) is converted into IM1-1A (−35.22 kcal/mol) via the transformation of an O molecule with the energy barrier and reaction energy of 40.60 kcal/mol and −20.10 kcal/mol, respectively. The other pathway is similar to the above pathway with the energy barrier and reaction energy of 48.85 kcal/mol and −13.76 kcal/mol, respectively. The hydrolytic process cannot occur because of the absence of H2O molecule. As we can see in Table S5, the reaction SO2-2NO2-NH3 → IM1-1A is exothermic and spontaneous (ΔH = −37.16 kcal/mol and ΔG = −3.12 kcal/mol).

Compared with the reaction pathway of SO2-2NO2 to IM1 and IM2, the result indicates that NH3 molecule can serve as catalyst and solvent to reduce the energy barrier and stable structures. The NH3 molecule cannot trigger the hydrolysis reaction to produce HONO.
Figure 5. Potential energy profile for the reaction of SO$_2$-2NO$_2$-NH$_3$. The yellow spheres are S atoms, the red spheres are O atom, the blue spheres are N atom, and the white spheres represent H atom, respectively. (Unit: Energies in kcal/mol; bond lengths in angstroms). The black and red lines are the different pathways. The black line represents the reaction of t-ONONO$_2$-NH$_3$-SO$_2$, and the red line is the reaction of c-ONONO$_2$-NH$_3$-SO$_2$.

2.2.2. The Reaction of SO$_2$-2NO$_2$-H$_2$O-NH$_3$

The relative energies, enthalpies and Gibbs free energies in all relevant species for SO$_2$-2NO$_2$-H$_2$O-NH$_3$ are summarized in Table S6. As shown in Figure 6, RC1-1W-1A and RC2-1W-1A are formed after SO$_2$ attacks the complex t/c-ONONO$_2$-H$_2$O-NH$_3$ or NH$_3$ attacks t/c-ONONO$_2$-H$_2$O-SO$_2$. The product complex IM1-W-A (~43.26 kcal/mol) is formed through TS1-W-A (13.51 kcal/mol) with the energy barrier and reaction energy of 38.92 kcal/mol and −17.85 kcal/mol, respectively. When the only water molecule gets close to the NO$^+$NO$_2^-$, the reactant complex (IM1'-W-A) of hydrolysis reaction is formed through separating the two parts, NO$^+$ and NO$_2^-$. The IM1'-W-A releases the reaction energy of 13.45 kcal/mol to form the product complex SO$_3$-HONO-NH$_4$NO$_2$-1 (~56.27 kcal/mol) via TS1'-W-A with the energy barrier of 6.44 kcal/mol. The NH$_3$ molecule and the H$_2$O molecule not only serve as catalyst and stabilizer, but also act as reactants to produce HONO and NH$_4$NO$_2$. It is different from the pathway of two H$_2$O molecules, because the NH$_3$ is more protophilia than water and the HONO is liable to provide a proton to form NH$_4$NO$_2$. The other pathway is analogous with RC1-W-A to SO$_3$-HONO-NH$_4$NO$_2$-1. The energy barrier and energy reaction are 40.30 kcal/mol and −18.60 kcal/mol in oxidation reaction and 8.55 kcal/mol and −13.06 kcal/mol in hydrolysis reaction, respectively.

Compared with the one-water reaction, the energy barrier for the SO$_2$-oxidation reaction is reduced by 2.92 kcal/mol and 7.24 kcal/mol, respectively. Compared with the two-water reaction, it shows that the NH$_3$ molecule plays a more important role in stabilizing the complexes and lowering the energy barrier. When ammonia (NH$_3$) is present in hydrolysis reaction, the product complexes form ammonium nitrite (NH$_4$NO$_2$). The most important reason is that the ability of NH$_3$ to acquire the proton is stronger than water.
2.2.3. The Reaction of SO$_2$-2NO$_2$-2H$_2$O-NH$_3$

The structure of reactant complex RC1-2W-A and RC2-2W-A is formed by replacing one H$_2$O molecule from RC1-3W and RC2-3W with NH$_3$ in Figure 7. IM1-2W-A ($\sim$51.74 kcal/mol) is formed via TS1-2W-A (6.08 kcal/mol), in which the energy barrier and energy reaction are 39.21 kcal/mol and $\sim$18.61 kcal/mol, respectively. IM1′-2W-A ($\sim$51.78 kcal/mol) is formed by the migration process of H$_2$O$_{(a)}$ molecule. The IM1′-2W-A is converted into the product complex SO$_3$-2HONO-H$_2$O-NH$_3$-1 ($\sim$48.42 kcal/mol) via the transition state TS1′-2W-A ($\sim$45.52 kcal/mol). The corresponding reaction energy and energy barrier are 3.36 kcal/mol and 6.26 kcal/mol, respectively.

On account of the similarity to the above pathway, we will not describe the details about the other pathway. The energy barrier and reaction energy are shown in the Table 1. As shown in Table S7, the reaction SO$_2$-2NO$_2$-2H$_2$O-NH$_3$ $\rightarrow$ SO$_3$-2HONO-H$_2$O-NH$_3$-2 is exothermic and spontaneous.

In presence of one NH$_3$ molecule, the NH$_3$ molecule and two H$_2$O molecules serve as solvent to reduce energy barrier and stable structures, and the one H$_2$O molecule and the NH$_3$ molecule serve as reactant to produce HONO and NH$_4$NO$_2$. 

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Figure 6. Potential energy profile for the reaction of SO$_2$-2NO$_2$-H$_2$O-NH$_3$. The yellow spheres are S atoms, the red spheres are O atom, the blue spheres are N atom, and the white spheres represent H atom, respectively. (Unit: Energies in kcal/mol; bond lengths in angstroms). The black and red lines are the different pathways. The black line represents the reaction of t-ONONO$_2$-H$_2$O-NH$_3$-SO$_2$, and the red line is the reaction of c-ONONO$_2$-H$_2$O-NH$_3$-SO$_2$. 

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2.2.4. The Reaction of \( \text{SO}_2-2\text{NH}_3\)

Figure 8 explores the equilibrium structures and potential energy of \( \text{SO}_2-2\text{NO}_2-\text{H}_2\text{O}-2\text{NH}_3 \). Table S8 summarizes the relative energies, enthalpies and Gibbs free energies in all relevant species. Similar to the previous reactions, the reactant complexes (RC1-W-2A and RC2-W-2A) are formed through combining \( \text{NH}_3-\text{NH}_3 \) and \( t/c-\text{ONONO}_2-\text{H}_2\text{O}-\text{SO}_2 \) or \( \text{SO}_2 \) and \( t/c-\text{ONONO}_2-\text{H}_2\text{O}-(\text{NH}_3)_2 \), which equally replaces two \( \text{H}_2\text{O} \) molecules from RC1-3W or RC2-3W with two \( \text{NH}_3 \) molecules. Starting with the reactant complex RC1-W-2A, the reaction occurs through the transition state TS1-W-2A forming the product complex IM1-W-2A. The process requires an energy barrier of 38.85 kcal/mol and reaction energy of −18.80 kcal/mol, respectively. The IM1'-W-2A, with a binding energy of 51.69 kcal/mol, can serve as the reactant complex in the next step. The \( \text{SO}_3\text{-HONO-H}_4\text{NO}_2-\text{NH}_3-1 \) (−71.15 kcal/mol) is resulted from IM1'-W-2A by the only \( \text{H}_2\text{O} \) molecule reacting between the NO\(^-\) and NO\(_2^-\), along with energy barrier and energy reaction of 9.04 kcal/mol and −19.46 kcal/mol, respectively. As shown in Figure 8, the other pathway is similar to the reaction of RC1-W-2A to \( \text{SO}_3\text{-HONO-H}_4\text{NO}_2-\text{NH}_3-1 \). There are energy barrier and reaction energy of 40.26 kcal/mol and −19.51 kcal/mol in oxidation reaction, respectively. In the hydrolysis process, the energy barrier and reaction energy are 12.68 kcal/mol and −16.28 kcal/mol, respectively. Table S8 indicates that both reaction pathways \( \text{SO}_2-2\text{NO}_2-\text{H}_2\text{O}-2\text{NH}_3 \rightarrow \text{SO}_3\text{-HONO-H}_4\text{NO}_2-1 \) and \( \text{SO}_3\text{-HONO-H}_4\text{NO}_2-2 \) are exothermic and spontaneous.

In presence of two \( \text{NH}_3 \) molecules, two \( \text{NH}_3 \) molecules and the only \( \text{H}_2\text{O} \) molecule serve as catalyst and stabilizer, and the one \( \text{NH}_3 \) molecule and \( \text{H}_2\text{O} \) molecule serve as reactant to produce \( \text{NH}_4\text{NO}_2 \).

Compared with the three-water reaction, the proportion of \( \text{H}_2\text{O} \) and \( \text{NH}_3 \) molecules is 2:1 and 1:2. The result indicates that the energy barrier is slighting different from the three-water molecule in the \( \text{SO}_3 \)-oxidation reaction. In the hydrolytic reaction, the energy barrier is higher than the three-water molecule, and these processes release more reaction energy. Moreover, the binding energy of product
complexes is lower than that of the SO$_3$-2HONO-2H$_2$O. This result shows that the NH$_3$ molecule plays a significant role in stabilizing complexes.

Figure 8. Potential energy profile for the reaction of SO$_2$-2NO$_2$-H$_2$O-2NH$_3$. The yellow spheres are S atoms, the red spheres are O atom, the blue spheres are N atom, and the white spheres represent H atom, respectively. (Unit: Energies in kcal/mol; bond lengths in angstroms). The black and red lines are the different pathways. The black line represents the reaction of t-ONONO$_2$-H$_2$O-2NH$_3$-SO$_2$, and the red line is the reaction of c-ONONO$_2$-H$_2$O-2NH$_3$-SO$_2$.

3. Materials and Methods

All quantum chemistry calculations are performed by Gaussian 09 programs (vB.01, Gaussian, Inc, Wallingford, CT, USA) [36]. The structures of the reactant (RC), product (PC), intermediate (IM), and transition states (TS) are optimized using M06-2X density functional method with the 6-311++G (d, p) basis set [37]. This is relatively accurate and time-efficient when used to study the reaction mechanism and has been employed successfully in our previous studies [38,39]. The vibrational frequencies have been obtained to verify that the reactant complexes, intermediates, and product complexes have all positive frequencies and that the transition state (TS) geometries have only one imaginary frequency at the same level. According to the calculation of vibrational frequencies, zero-point energy (ZPE) and thermal correction are also obtained at the same level to decide their characteristics and thermodynamic properties. All the enthalpies (H) and Gibbs free energies (G) are calculated with thermal correction at 298.15 K. Moreover, the intrinsic reaction coordinate (IRC) calculation is used to verify whether each transition state is connected with the corresponding intermediates [40]. The single-point energies of all stationary points are refined using the more precise basis set for M06-2X/6-311++G (3df, 3pd) [41]. The ultrafine integration grid is applied to improving the accuracy during the whole gas-phase calculation. We also calculated electrostatic potential (ESP) to analyze charge distribution for NO$^+$NO$_3^-$ and NO$^+$NO$_2^-$ fragments of RC and IM with the same basis [42,43]. The geometries are visualized using the CYL view software package (v1.0b, Université de Sherbrooke, Montreal, QC, Canada) [44].

4. Conclusions

In this paper, the reaction mechanism of SO$_2$ with NO$_2$ to form SO$_3$ in the presence of H$_2$O and NH$_3$ is investigated. Table S9 represents that Cartesian coordinates for all relative Optimized
geometries (reactants, transient states and products) at M06-2X/6-311++G(d,p), x coordinate, y coordinate and z coordinate. The effects of different amounts of H₂O and NH₃ have been studied in detail. The results indicate that HONO cannot be formed in the absence of H₂O molecules. In the oxidation step of the system SO₂-2NO₂-nH₂O (n = 0, 1, 2, 3), H₂O plays a catalytic role to produce SO₃, which reduces the energy barrier. In the hydrolytic step, the energy barrier of two H₂O molecules is larger than that of one or three H₂O molecules. But it is still thermodynamically favorable. When NH₃ is involved in the reaction, the energy barrier is lower than SO₂-2NO₂ in the oxidation step. For SO₂-2NO₂-2H₂O, when the ratio of NH₃ to H₂O is 1:1, the energy barrier changes more greatly than SO₂-2NO₂-2H₂O. For SO₂-2NO₂-3H₂O, when the ratio of NH₃ to H₂O is 1:2 and 2:1, the change of the energy barrier is not obvious. Compared to pure water reactions, the role of NH₃ in stabilizing product complexes and acquiring protons is more effective than H₂O. This research provides a new insight into reaction pathways of sulfuric acid formation, and can also contribute to the further study of aerosol surface reactions.

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Abbreviations

| Abbreviation | Description                          |
|--------------|--------------------------------------|
| PM           | Particulate Matter                   |
| DFT          | Density Functional Theory            |
| RC           | Reactant complex                     |
| IM           | Intermediate                         |
| PC           | Product                              |
| TS           | Transient state                      |
| IRC          | Intrinsic reaction coordinate        |
| ESP          | Electrostatic potential              |

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