

Nitric acid catalyzed hydrolysis of SO₃ in the formation of sulfuric acid: A theoretical study



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ABSTRACT

The gas-phase hydrolysis of SO₃ in the presence of one water molecule, two water molecules, and nitric acid is investigated utilizing high level quantum chemical methods and transition state theory. The calculated results demonstrate that nitric acid exerts a strong catalytic role in the hydrolysis of SO₃ because the activated barrier of hydrolysis of SO₃ with the assistance of nitric acid is reduced to about 3.7 kcal/mol, which is about 20 kcal/mol lower than that of the SO₃ reaction with water relative to the respective pre-reactive complex.

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1. Introduction

Amidst the atmospheric chemistry in which sulfuric acid plays an important role, it makes main contributions to the formation of acid rain [1–3] and atmospheric sulfate aerosols [4–10], having great influences on human health, radiation balance and climate. Thus, the formation of sulfuric acid in the atmosphere is of particular interest from both experimental and theoretical points of view. In the gas-phase chemistry of atmosphere, sulfuric acid is formed via the two steps as follows. The first step is that sulfur dioxide is oxidized to sulfur trioxide by the OH and O₂ [11] or carbonyl oxides [12]. The second step is that sulfuric trioxide is hydrolyzed to yield sulfuric acid.

Of currently increasing concern is how the hydrolysis of SO₃ occurs in the gas-phase atmospheric chemistry because the direct reaction of SO₃ with H₂O does not take place in the atmosphere due to the high activated barrier [13,14]. The first suggested mechanism is that a second water molecule [14–18] is introduced into the gas-phase reaction of SO₃ with H₂O. It is noted that when a second molecule is added into the reaction of SO₃ with H₂O, the second molecule acts as catalyst that promotes the hydrogen transfer from water to SO₃. However, the rate constant of SO₃ + H₂O + H₂O reaction is reported to be about 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ from both experimental and theoretical results [19–21]. Therefore, of particular interest is whether there are other molecules that can play the same role in the reaction of SO₃ + H₂O. In the literature, the HO₂ [22], HCOOH [21,23], or H₂SO₄ [24] is substituted for a

second water molecule, which plays an important role in the atmospheric chemistry.

In this work, we consider that HNO₃ catalyzes the hydrolysis of SO₃ to result in the formation of sulfuric acid. The nitric acid is chosen mainly because the concentration is higher than that of HO₂ or H₂SO₄. The goal of the present investigation is to elucidate the reaction mechanisms of nitric acid-catalyzed hydrolysis of SO₃, evaluate the catalytic role that nitric acid plays in the formation of sulfuric acid, and determine whether this process is of great importance responsible for the formation of sulfuric acid in the atmosphere.

2. Computational methods

All the reactants, transition states, complexes, and products are optimized at the B3LYP/aug-cc-pv(T+d)z [25,26] level of theory because the theoretical method has been reliably utilized to investigate sulfur-containing molecules. The corresponding frequencies are also evaluated at the same level to ensure the optimized stationary points without imaginary frequencies and the transition state with only one imaginary frequency. In addition, if necessary, the intrinsic reaction path (IRC) is executed to examine whether the transition state is connected with the designated reactant and product. To obtain the relative energies reliably, single point energies are refined using the CCSD(T) and CCSD(T)-F12A theoretical methods at the aug-cc-pv(T+d)z, VDZ-F12 basis sets, respectively based on the B3LYP-optimized geometries. It has been shown that the CCSD(T)-F12A/VDZ-F12 theoretical method [27,28] can reach the similar accuracy of the CCSD(T)/aug-cc-pvQz level of theory. Finally, rate constants of these elementary

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processes are estimated using the conventional transition state theory with Eckart tunneling correction. All the electronic calculations are carried out on the Gaussian 09 [29] and Molpro 2009 [30], while rate constants are computed using the TheRate code [31,32].

3. Results and discussion

3.1. The reaction of SO_3 with water

The reaction of SO_3 with water or water dimer has been extensively investigated from both experimental and theoretical views of point. Thus, the reaction is discussed here to conveniently compare the catalytic role of nitric acid in the formation of sulfuric acid. The SO_3 reaction with H_2O begins with the formation of pre-reactive complex $\text{H}_2\text{O} \cdots \text{SO}_3$ prior to the transition state $[\text{SO}_3 \cdots \text{H}_2\text{O}]^+$ responsible for the formation of sulfuric acid. The binding energy of the formed $\text{SO}_3 \cdots \text{H}_2\text{O}$ complex is -7.42 kcal/mol, which is consistent with the reported values of -7.8 [21], -7.6 [24], -7.4 [33], and -7.7 kcal/mol [34], respectively at the CCSD(T)-F12A/VDZ-F12//B3LYP/aug-cc-pv(T+d)z level of theory. The energy barrier for unimolecular isomerization reaction of the $\text{H}_2\text{O} \cdots \text{SO}_3$ complex to lead to the formation of sulfuric acid is calculated to have a barrier of 23.73 kcal/mol relative to the pre-reactive complex $\text{SO}_3 \cdots \text{H}_2\text{O}$ at the CCSD(T)-F12A/VDZ-F12//B3LYP/aug-cc-pv(T+d)z level in Table 1, which is in accord with the values of 23.74 kcal/mol from our previous result [21], 23.5 kcal/mol [24], while the present calculated barrier does not agree reasonably with the earlier results about 28 to 32 kcal/mol [13,14,35,36] because the calculations are based on the low-level theoretical methods.

As for the reaction $\text{SO}_3 + \text{H}_2\text{O} + \text{H}_2\text{O}$, the reactants are possibly SO_3 and the formed $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ complex or H_2O and the formed $\text{H}_2\text{O} \cdots \text{SO}_3$ complex, which is described in Figure 1. The computed binding energy of water dimer at 0 K is -2.97 kcal/mol with re-

spect to the separate water molecule at the CCSD(T)-F12A/VDZ-F12//B3LYP/aug-cc-pv(T+d)z level of theory in Table 1, which is in good agreement with the experimental and theoretical results in the literature 3.15 ± 0.03 [37], 2.9 [24], 2.91 [28], 3.30 [38], 3.01 – 3.12 [39], 2.99 – 3.15 [40], and 2.86 kcal/mol [41], respectively. Additionally, the binding enthalpy at 298 K is calculated to be -3.45 kcal/mol, which compares well with the experimental value of -3.59 ± 0.50 [42] at 358–386 K, -3.98 ± 0.90 [43] at 573–723 K, -3.58 ± 0.72 [44] at 373–673 K, and -3.24 ± 0.95 kcal/mol [45], respectively.

The reaction of SO_3 with water dimer occurs through the pre-reactive complex C1 before the transition state TS1 and the post-reactive complex $\text{H}_2\text{O} \cdots \text{H}_2\text{SO}_4$, leading to the formation of sulfuric acid and water. In Figure 1, the binding energy of C1 is 13.76 kcal/mol lower than that of $\text{SO}_3 + \text{H}_2\text{O} \cdots \text{H}_2\text{O}$, which agrees well with the reported value of 13.6 kcal/mol [24]. The transition state TS1 is lower than that of $\text{SO}_3 + \text{H}_2\text{O} + \text{H}_2\text{O}$, $\text{SO}_3 \cdots \text{H}_2\text{O} + \text{H}_2\text{O}$, respectively by 8.24 kcal/mol, 3.69 kcal/mol, which compares reasonably with the calculated value of 8.6 kcal/mol, 3.9 kcal/mol [24]. In addition, the unimolecular rearrangement reaction of C1 to $\text{H}_2\text{O} \cdots \text{HSO}_4$ is a rate-limiting step. Thus, the activated barrier of TS1 relative to C1 is calculated to be 5.52 kcal/mol, which is qualitatively close to the most recent investigation about 5 kcal/mol [24], 6.53 kcal/mol [23], 6.6 – 6.7 kcal/mol [33], and around 6 kcal/mol [15,18]. Also, the interaction energy of the $\text{H}_2\text{O} \cdots \text{H}_2\text{SO}_4$ complex is -10.32 kcal/mol with respect to the isolated H_2O and H_2SO_4 , which is in accord with the value -10.3 kcal/mol at the CCSD(T)/CBS//B3LYP/cc-pv(T+d)Z level of theory [24].

3.2. The hydrolysis of SO_3 catalyzed by HNO_3

Nitric acid as catalyst catalyzes the reaction of SO_3 with H_2O through the possible entry channels with $\text{HNO}_3 + \text{H}_2\text{O} \cdots \text{SO}_3$ or $\text{SO}_3 + \text{H}_2\text{O} \cdots \text{HNO}_3$ acting as reactants presented in Figure 2. When

Table 1

The binding, activated, and reaction enthalpies, free energies, and energies for the reactions $\text{SO}_3 + \text{H}_2\text{O}$, $\text{SO}_3 + \text{H}_2\text{O} + \text{H}_2\text{O}$, and $\text{SO}_3 + \text{H}_2\text{O} + \text{HNO}_3$ with zero-point correction (ZPE) included (in kcal/mol).

Compounds	ΔH^a (298)	ΔG^a (298)	ΔE^a	ΔH^b (298)	ΔG^b (298)	ΔE^b
$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$						
$\text{SO}_3 + \text{H}_2\text{O}$	0.00	0.00	0.00	0.00	0.00	0.00
$\text{SO}_3 \cdots \text{H}_2\text{O}^c$	-8.09	0.10	-7.64	-7.86	0.33	-7.42
$[\text{SO}_3 \cdots \text{H}_2\text{O}]^{\text{d}}$	14.40	25.44	16.05	14.67	25.70	16.31
H_2SO_4	-21.24	-10.26	-19.90	-21.71	-10.72	-20.36
$\text{SO}_3 + \text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{O}$						
$\text{SO}_3 + \text{H}_2\text{O} + \text{H}_2\text{O}$	0.00	0.00	0.00	0.00	0.00	0.00
$\text{SO}_3 + \text{H}_2\text{O} \cdots \text{H}_2\text{O}$	-3.60	2.53	-3.11	-3.45	2.68	-2.97
$\text{H}_2\text{O} + \text{H}_2\text{O} \cdots \text{SO}_3$	-8.09	0.10	-7.64	-7.86	0.33	-7.42
C1 ($\text{SO}_3 \cdots \text{H}_2\text{O} \cdots \text{H}_2\text{O}$)	-18.75	-0.38	-17.15	-18.23	0.14	-16.63
TS1 ^e	-14.44	6.74	-11.51	-14.03	7.15	-11.11
$\text{H}_2\text{O} \cdots \text{H}_2\text{SO}_4$	-32.58	-12.95	-30.61	-32.65	-13.02	-30.68
$\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$	-21.24	-10.26	-19.90	-21.71	-10.72	-20.36
$\text{SO}_3 + \text{H}_2\text{O} + \text{HNO}_3 \rightarrow \text{H}_2\text{SO}_4 + \text{HNO}_3$						
$\text{SO}_3 + \text{H}_2\text{O} + \text{HNO}_3$	0.00	0.00	0.00	0.00	0.00	0.00
$\text{HNO}_3 + \text{H}_2\text{O} \cdots \text{SO}_3$	-8.09	0.10	-7.64	-7.86	0.33	-7.42
$\text{SO}_3 + \text{H}_2\text{O} \cdots \text{HNO}_3$	-8.95	-0.36	-8.49	-8.58	0.00	-8.13
C2	-14.59	2.30	-14.44	-13.73	3.16	-13.58
TS2	-15.28	3.60	-14.66	-14.37	4.50	-13.75
C3	-19.04	0.75	-18.22	-18.00	1.80	-17.17
TS3	-16.72	6.11	-14.74	-15.45	7.38	-13.47
C3P	-29.36	-8.78	-28.25	-28.88	-8.29	-27.76
$\text{H}_2\text{SO}_4 + \text{HNO}_3$	-21.24	-10.26	-19.90	-21.71	-10.72	-20.36

^a ΔH , ΔG , ΔE are computed at the CCSD(T)//B3LYP/aug-cc-pv(T+d)z level of theory.

^b ΔE is calculated at the CCSD(T)-F12A/VDZ-F12//B3LYP/aug-cc-pv(T+d)z level of theory.

^c For $\text{SO}_3 \cdots \text{H}_2\text{O}$ the ΔE values in the literature are -7.8 (see Ref. [21]), -7.6 (see Ref. [24]), -7.4 (see Ref. [33]), and -7.7 kcal/mol (see Ref. [34]), respectively.

^d The activated barrier of $[\text{SO}_3 \cdots \text{H}_2\text{O}]^+$ relative to the pre-reactive complex $\text{SO}_3 \cdots \text{H}_2\text{O}$ are reported to be 23.74 (see Ref. [21]), 23.5 (see Ref. [24]), about 28 to 32 kcal/mol (see Ref. [13,14,35,36]), respectively.

^e The activated barrier of TS1 relative to C1 is reported in the literature about 5 kcal/mol (see Ref. [24]), 6.53 kcal/mol (see Ref. [23]), 6.6 – 6.7 kcal/mol (see Ref. [33]), and around 6 kcal/mol (see Ref. [15,18]).

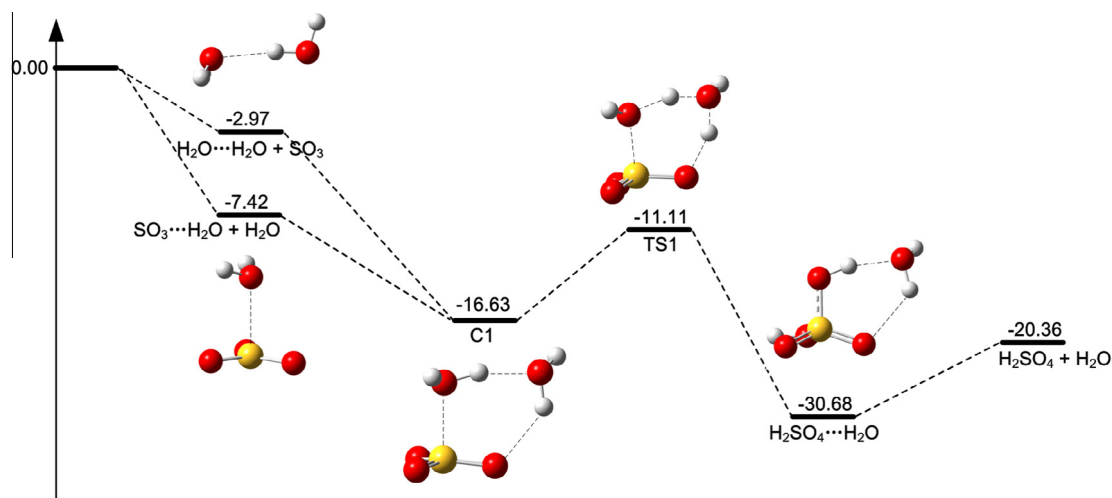


Figure 1. Schematic potential energy surface for the hydrolysis of SO_3 catalyzed by H_2O (in kcal/mol).

HNO_3 and the formed $\text{H}_2\text{O} \cdots \text{SO}_3$ complex is regarded as reactants, the reaction starts with the formation of pre-complex C3, proceeds to the transition state TS3 before the formation of post-reactive complex C3P, and subsequently form sulfuric acid and nitric acid. The binding energy of complex C3 is -17.17 kcal/mol relative to the free molecules water, nitric acid, and sulfur trioxide in Table 1. In complex C3, there are two hydrogen-bonded interactions and one $\text{O} \cdots \text{S}$ bonding interaction. The energy barrier of TS3 lies about 3.7 kcal/mol above C3, which is about 20 kcal/mol, 1.8 kcal/mol lower than those of the corresponding reaction SO_3 with water, water dimer, respectively, reflecting that nitric acid plays a strong catalytic effect on the hydrolysis of SO_3 . It is also noted that the reaction barrier of TS3 relative to C3 is higher than that of the corresponding hydrolysis of SO_3 by HO_2 [22], HCOOH [21,23], and H_2SO_4 [24] by about 1 kcal/mol, 3.7 kcal/mol, 2.5 kcal/mol, respectively.

The reaction of hydrolysis of SO_3 catalyzed by nitric acid begins with the $\text{SO}_3 + \text{H}_2\text{O} \cdots \text{HNO}_3$, undergo the pre-reactive complex C2 and transition state TS2 before the formation of complex C3 responsible for the formation of sulfuric acid and nitric acid discussed below. From Table 1 and Figure 2, C2 has a binding energy of -13.58 kcal/mol, where the sulfur atom of SO_3 interacts with the oxygen atom of water in the formed $\text{H}_2\text{O} \cdots \text{HNO}_3$ complex. In Figure 2, C3 is formed by the rearrangement from C2 through the transition state TS2 almost with a barrierless process, which is very similar to the sulfuric acid [24] as autocatalyst in the formation of sulfuric acid. In this process, the hydrogen bonding between the

oxygen atom of H_2O and the hydrogen atom in HNO_3 in formed $\text{H}_2\text{O} \cdots \text{HNO}_3$ complex is broken to lead to the formation of new hydrogen bonding between the oxygen atom of SO_3 and the hydrogen atom in HNO_3 . C3 is more stable than C2 by 3.59 kcal/mol.

3.3. Kinetics and application in atmospheric chemistry

The rate constant is calculated using the conventional transition theory to determine whether the hydrolysis of SO_3 catalyzed by nitric acid could compete well with the corresponding hydrolysis by water. The conventional transition theory has extensively utilized to study the rate constants of gas-phase reactions of atmosphere in the literature [46–48]. The computed rate constants are provided in Table 2. The first two rows in Table 2 list the rate constants of $\text{SO}_3 + \text{H}_2\text{O} \cdots \text{H}_2\text{O}$, $\text{SO}_3 + \text{H}_2\text{O} \cdots \text{HNO}_3$, respectively, while the next rows involve the rate constants $\text{H}_2\text{O} + \text{H}_2\text{O} \cdots \text{SO}_3$, $\text{HNO}_3 + \text{H}_2\text{O} \cdots \text{SO}_3$, respectively at 298 K. From Table 2, it is noted that the rate constant of SO_3 reaction with the formed $\text{H}_2\text{O} \cdots \text{HNO}_3$ complex is far less than that of SO_3 reaction with water dimer, unraveling that the process of $\text{SO}_3 + \text{H}_2\text{O} \cdots \text{HNO}_3$ is of minor importance in formation of sulfuric acid in the atmospheric chemistry. However, the rate constant of the reaction of HNO_3 with $\text{H}_2\text{O} \cdots \text{SO}_3$ is slightly larger than that of $\text{H}_2\text{O} + \text{H}_2\text{O} \cdots \text{SO}_3$. Furthermore, the concentration of water [49] is up to 10^{17} molecule cm^{-3} , which is 10^8 times more than that of nitric acid (10^9 molecule cm^{-3}) in the atmospheric chemistry. Therefore, the process of hydrolysis of

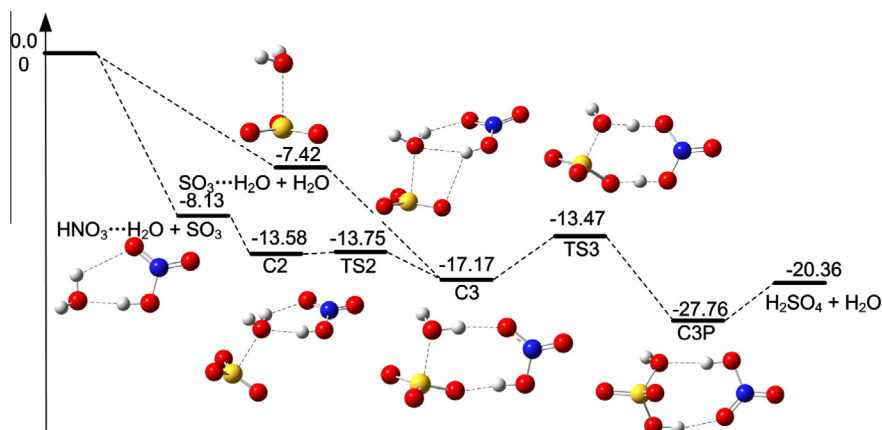


Figure 2. Schematic potential energy surface for the hydrolysis of SO_3 catalyzed by HNO_3 (in kcal/mol).

Table 2

The calculated rate constant (k , $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) for the individual reaction pathway with the temperature range 298 K.

Reactions	298 K
$k_{\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}}$	2.45×10^{-10}
$k_{\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{HNO}_3}$	3.00×10^{-13}
$k_{\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{SO}_3}$	4.41×10^{-12}
$k_{\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{SO}_3}$	5.26×10^{-12}

SO_3 catalyzed by nitric acid is of minor importance responsible for the formation of sulfuric acid.

4. Conclusions

The conclusions are obtained from the extraction of the results based on this investigation.

(1) The activated barrier of hydrolysis of SO_3 catalyzed by nitric acid is reduced to about 3.7 kcal/mol, which is about 20 kcal/mol lower than that of the SO_3 reaction with water relative to the respective pre-reactive complex. The result shows that nitric acid can play a strong catalytic role in the reaction of SO_3 with H_2O responsible for the formation of sulfuric acid.

(2) Although the rate constant of $\text{HNO}_3 + \text{H}_2\text{O} \cdots \text{SO}_3$ is accelerated, compared with the corresponding $\text{H}_2\text{O} + \text{H}_2\text{O} \cdots \text{SO}_3$, the concentration of nitric acid is far less than that of water. Therefore, the process in the atmosphere is of minor significance. The theoretical results also provide a new understanding of formation of sulfuric acid in the atmosphere. However, of possible interest in the present work is relative to hydrolysis of other atmospheric molecules with nitric acid as catalyst.

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