

Theoretical Study on the Gas Phase Reaction of Sulfuric Acid with Hydroxyl Radical in the Presence of Water

Bo Long,^{*,†} Wei-jun Zhang,[‡] Xing-feng Tan,[§] Zheng-wen Long,^{||} Yi-bo Wang,[⊥] and Da-sen Ren[†]

[†]College of Computer and Information Engineering, Guizhou University for Nationalities, Guiyang, China 550025

[‡]Laboratory of Environment Spectroscopy, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei, China 230031

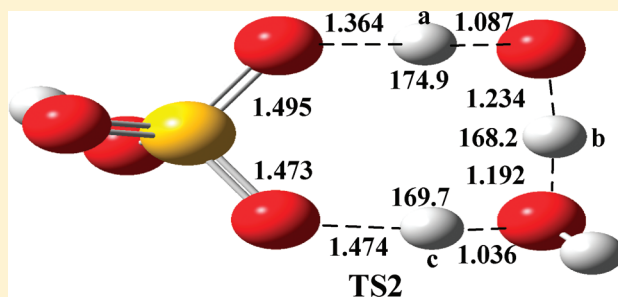
[§]College of Photo-Electronics, Chongqing University of Posts and Telecommunications, Chongqing, China 400065

^{||}Department of Physics, Guizhou University, Guiyang, China 550025

[⊥]Key Laboratory of Guizhou High Performance Computational Chemistry, Department of Chemistry, Guizhou University, Guiyang, China 550025

S Supporting Information

ABSTRACT: The reactions of H₂SO₄ with the OH radical without water and with water are investigated employing the quantum chemical calculations at the B3LYP/6-311+G(2df,2p) and MP2/aug-cc-pv(T+d)z levels of theory, respectively. The calculated results show that the reaction of H₂SO₄ with OH and H₂O is a very complex mechanism because of the formation of the prereactive complex prior to the transition state and product. There are two prereactive complexes with stabilization energies being −20.28 and −20.67 kcal/mol, respectively. In addition, the single water can lower the energy barriers of the hydrogen abstraction and the proton transfer to 7.51 and 6.37 kcal/mol, respectively from 13.79 and 8.82 kcal/mol with respect to the corresponding prereactive complex. The computed rate constants indicate that the water-assisted reaction of sulfuric acid with OH radical is of greater importance than the reaction of the naked sulfuric acid with the OH radical because the rate constant of the water-assisted process is about 10³ faster than that of the reaction sulfuric acid with OH. Therefore, the conclusion is obtained that the water-assisted process plays an important role in the sink for the gaseous sulfuric acid in the clean area.



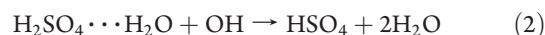
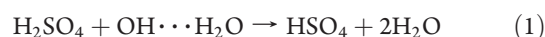
1. INTRODUCTION

Sulfuric acid (H₂SO₄) is of great importance and interest in the Earth's chemistry because it makes the main contribution to the formation of acid rain^{1,2} and plays an important role in the formation of the sulfate aerosols,^{3–7} which affect clouds, precipitation, and radiation balance.^{8,9} Sulfur dioxide (SO₂) is the precursor of H₂SO₄, which is emitted into the atmosphere from both natural and anthropogenic sources in the amount of 100 Tg year^{−1}. Although the main sinks for sulfuric acid are aerosol deposition and wet precipitation in the atmosphere, the reaction¹⁰ of H₂SO₄ with OH has been theoretically investigated recently, which shows that the process could be an important sink for gaseous sulfuric acid.

Water is of great abundance in the Earth's atmosphere and can form hydrogen bonded complexes with other molecules such as O₃···H₂O,¹¹ HNO₃···H₂O,¹² OClO···H₂O,^{13,14} and H₂SO₄···H₂O.¹⁵ Therefore it has an important impact on the photochemistry of atmosphere. Moreover, very recently, there are some theoretical and experimental reports^{16–32} demonstrated that the single water not only can enhance the reaction constants and change the reaction mechanisms but also can decrease the rate constants. For example, a single water

molecular can promote the oxidation of acetaldehyde¹⁶ and glyoxal³² via the OH radical, the HO₂-self-reaction²⁰ leading to the formation of H₂O₂ and O₂. The water vapor can not only accelerate the reaction^{17,18} of HCOOH with OH but also change the reaction mechanisms responsible for the influence of the product distribution. In addition, the water dimer or water clusters play a significant role in the reactions of carbonyl oxides^{21,22} with water and the decomposition of gas phase peroxyacetyl nitrate²³ (PAN) and SO₃^{24–26} with H₂O responsible for the formation of sulfuric acid. On the other hand, the single water molecule also hampers the reactions of the hydrogen abstraction of CH₄ and ³⁰HNO₃³¹ by OH.

In the present work, the reaction of sulfuric acid with OH and a single water (reactions 1 and 2)



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is studied to explore the reaction mechanisms and to judge whether this reaction is of great importance in atmospheric chemistry. This investigation is of great necessity because the $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$ complex may be a precursor for sulfate aerosols as well as nucleation of particles is strongly dependent on the concentration of sulfuric acid.^{3,33} Furthermore, the $\text{H}_2\text{O} \cdots \text{HO}$ complex should be considered because its concentration³⁰ was reported to be 5.5×10^4 molecules cm^{-3} in the troposphere.

2. THEORETICAL METHODS

The electronic structure calculations are performed using the Gaussian 03³⁴ software. The geometries of all the reactants, prereactive complexes, transition states, and products are optimized at the B3LYP/6-311+G(2df,2p) level of theory, and the corresponding frequencies of the optimized geometries are computed at the same level to prove the characters of the transition states with one imaginary frequency and the stationary points without imaginary frequency. In order to obtain the reliable relative energies, single point energies are refined using the MP2(full)/aug-cc-pv(T+d)z method at the B3LYP-optimized geometries because the method^{35,36} has been used to describe the sulfuric acid containing cluster reliably and the calculation cost is inexpensive, compared with the higher-level CCSD(T) theoretical method. To clarify the selected theoretical methods reliably herein, the test calculations are accomplished. The basis set superposition error (BSSE) is not computed here because the common counterpoise (CP) correction³⁷ is not adequate enough for the large basis sets involving multiple diffuse basis functions. In addition, the H-bond natures in this investigation are analyzed in terms of the atoms in molecules (AIM) theory by Bader,³⁸ which has been executed in AIM2000.^{39–41} If necessary, the intrinsic reaction coordinate (IRC)^{42,43} is employed at the B3LYP/6-311+G(2df,2p) level of theory to verify the transition states connected with the desired reactants and products. Finally, the rate constant is calculated using the transition state theory with Wigner correction, which is executed in the TheRate program.⁴⁴

3. RESULTS AND DISCUSSION

The reaction of OH with sulfuric acid is reproduced to examine the selected methods. It is compared to the H_2SO_4 reaction with OH and the water molecule. The transition states and stationary points of the reaction of sulfuric acid with the OH radical are optimized using the same theoretical method reported by Anglada.¹⁰ Thus, the optimized parameters are not listed herein. However, the calculated results are provided in Table S1 (see the Supporting Information), which indicates that the MP2/aug-cc-pv(T+d)z//B3LYP/6-311+(2df,2p) theoretical method can exactly produce the binding energy of the $\text{H}_2\text{SO}_4 \cdots \text{OH}$ complex obtained at the CCSD(T)/cc-pvtz//B3LYP/6-311+(2df,2p) theoretical approach. In addition, it is noted that although the energy barriers change about 1–2 kcal/mol at the MP2/aug-cc-pv(T+d)z//B3LYP/6-311+(2df,2p) and CCSD(T)/cc-pvtz//B3LYP/6-311+(2df,2p) levels of theory, the reaction mechanisms can be well characterized because the double proton-transfer mechanism is still the dominant pathway. Therefore, the theoretical methods utilized herein are able to describe the reaction system reliably.

3.1. The $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$, $\text{H}_2\text{O} \cdots \text{HO}$, and $\text{HO} \cdots \text{H}_2\text{O}$ Complexes. The hydrogen bonded complex M1 ($\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$) between sulfuric acid and water was extensively investigated^{35,45–52}

from theoretical and experimental points of view and is presented in Figure 1, which shows a six-membered ring structure with two hydrogen bonds. One is formed by the hydrogen atom of OH group in sulfuric acid and the central oxygen of water with the calculated bond of 1.680 Å, which is around 0.030 Å longer than the experimental value.⁵² The other is formed via the oxygen of sulfuric acid and the hydrogen of water with the computed hydrogen-bonded distance of 2.224 Å, which is about 0.074 Å longer than the experimental value.⁵² From Table 1, the calculated binding energy of the M1 ($\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$) is −11.55 kcal/mol, which is in good agreement with the value⁵¹ of −12.07 obtained at the CCSD(T)/cc-pv(∞+d)z level. Additionally, from Table S2 (Supporting Information) topological properties compare well with the results reported in the literature.⁵¹ There are two complexes M2 ($\text{H}_2\text{O} \cdots \text{HO}$) and M3 ($\text{HO} \cdots \text{H}_2\text{O}$) between OH and H_2O as presented in Figure 1. Their stabilized energies are −3.76 and −2.18 kcal/mol, respectively, at the B3LYP/6-311+G(2df,2p) level of theory, which agrees well with the experimental and theoretical results reported in the literature.^{30,31,53–59}

3.2. The Hydrogen Abstraction Reaction. The OH radical attack on the M1 ($\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$) complex or the M2 ($\text{H}_2\text{O} \cdots \text{HO}$) complex attack on the sulfuric acid occurs, which is similar to the reaction of HCOOH ^{17,18} with OH and H_2O and the water-assisted HNO_3 ³¹ reaction with OH. There are three reaction types: the hydrogen abstraction, two or three proton transfers, and a proton coupled electron transfer. To elucidate reaction mechanism, the three reaction processes are discussed in terms of the reaction type. The hydrogen in sulfuric acid abstracted by the OH radical and the M2 ($\text{H}_2\text{O} \cdots \text{HO}$) complex occurs via the prereactive complexes C1 ($\text{H}_2\text{SO}_4 \cdots \text{OH} \cdots \text{H}_2\text{O}$) and C2 ($\text{HO} \cdots \text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$) as depicted in Figure 1. The corresponding transition states TS1 and TS5 responsible for the formation of HSO_4 and water dimer are depicted in Figure 2. As for TS1, the reactants may be sulfuric acid and the $\text{H}_2\text{O} \cdots \text{HO}$ complex, or the $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$ complex and the OH radical, while the reactants in TS5 are the $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$ complex and the OH radical, which is described in the potential energy profile presented in Figure 3.

The complex C1 ($\text{H}_2\text{SO}_4 \cdots \text{OH} \cdots \text{H}_2\text{O}$) is an eight-membered ring structure with three hydrogen bonds, which is similar to the hydrogen-bonded complexes between formic acid¹⁷ and $\text{H}_2\text{O} \cdots \text{HO}$, HNO_3 ,³¹ and $\text{H}_2\text{O} \cdots \text{HO}$. The hydrogen atom of the OH group in the sulfuric acid interacts with the oxygen of the OH radical with the computed hydrogen-bonded distance of 1.655 Å. The H_b interaction with the central oxygen of water is computed to be the bond distance of 1.689 Å and the H_c atom bridged with the oxygen of O=S bond responsible for the weak hydrogen bond formation with the bond distance of 1.915 Å. The optimized parameters clearly show that H_aO interaction is strongest in complex C1, which is proved by the topological properties as listed in Table S2 (Supporting Information). In addition, as for the hydrogen-bonding interaction, Table S2 (Supporting Information) shows that the total electronic energy densities of $H_{\text{H}_a\text{O}}$ and $H_{\text{H}_b\text{O}}$ at the bond critical points ($H_{\text{H}_a\text{O}} = -0.0079$ and $H_{\text{H}_b\text{O}} = -0.0041$) are found to be negative, indicating a partially covalent and partially electrostatic nature, whereas the value of the H_cO bond ($H_{\text{H}_c\text{O}} = 0.0021$) is positive for the weak and medium hydrogen bond, showing that the bond is only electrostatic interactions. The stabilization energy is computed to be −20.28 kcal/mol relative to the separate reactants H_2SO_4 , OH, and H_2O , revealing again that the interaction in complex C1 is very strong.

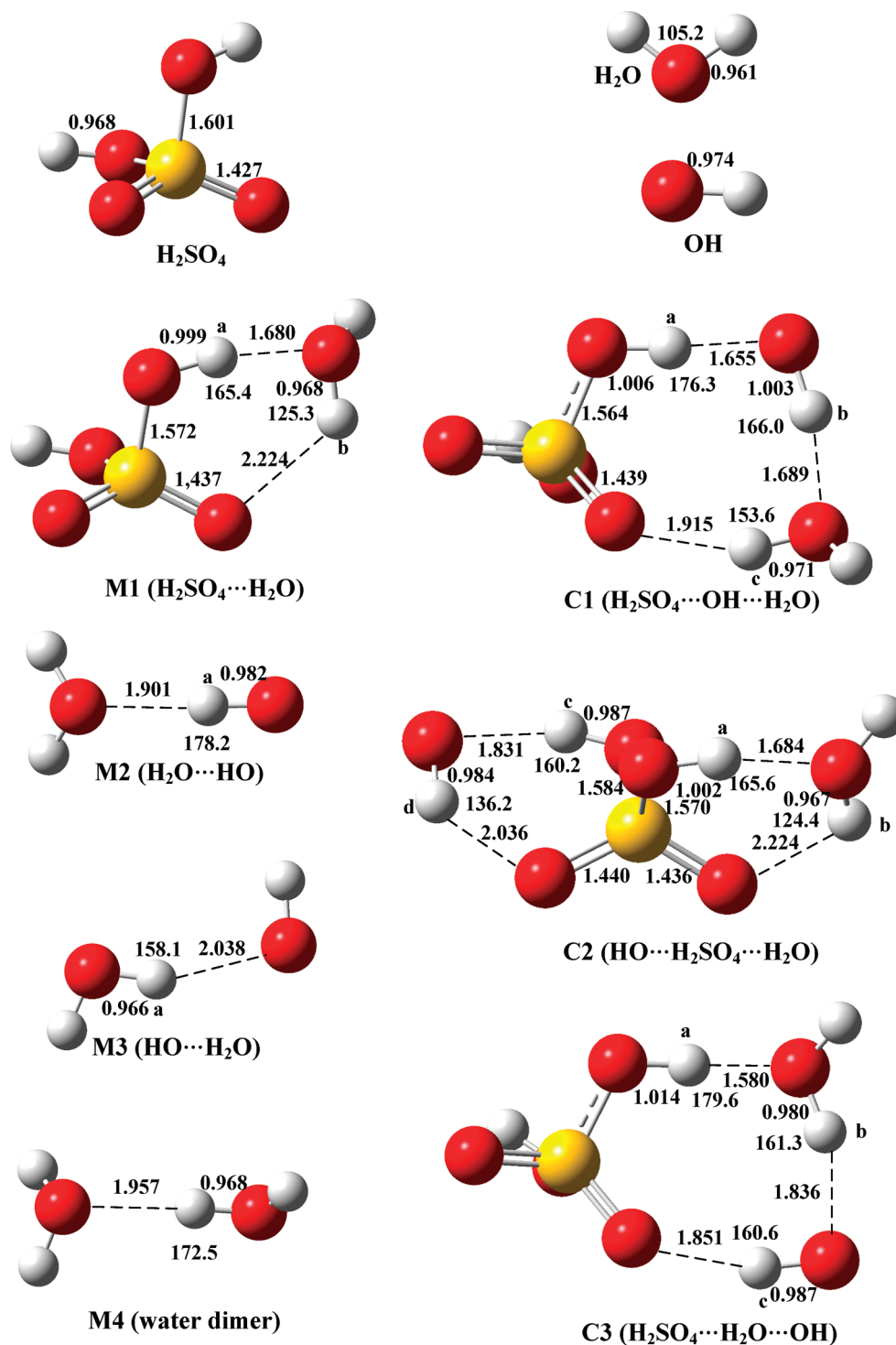


Figure 1. The optimized reactants and complexes at the B3LYP/6-311+G(2df,2p) level of theory (bond distances in angstroms and angles in degrees).

The complex C2 (HO...H₂SO₄...H₂O) involves two six-membered ring structures with four hydrogen bonds. The first ring structure (H_aOH_bOSO) is formed via water approaching near sulfuric acid. The calculated geometrical parameters indicate that the hydrogen-bonded ring structure is approximately equal to the complex M1 (H₂SO₄...H₂O). The topological properties of the corresponding bond critical points in C2 and M1 also clearly reveal that the ring structures in C2 and M1 change

very slightly. The second ring structure (OH_cOH_dOS) is similar to the OH radical interaction with sulfuric acid¹⁰ (C1' in Table S1, Supporting Information). It is worth noting that the binding energy C2 is −20.67 kcal/mol, which approximately equals to the sum of the stabilized energy of C1' 9.11 kcal/mol and M1 11.55 kcal/mol, indicating that the formed two hydrogen-bonded rings in C2 have little influence on each other.

Table 1. The Reaction and Activated Energies, Enthalpies, And Free Energies for the Reaction of H₂SO₄ with OH and H₂O with Zero-Point Correction (ZPE) Included at 298 K (kcal/mol)

compound	ΔH^a	ΔG^a	ΔE^a	ΔE^b	$\Delta(E^b + \text{ZPE})$
H ₂ SO ₄ + H ₂ O	0.00	0.00	0.00	0.00	0.00
M1 (H ₂ SO ₄ ···H ₂ O)	−9.72	−1.17	−9.11	−13.76	−11.55
OH + H ₂ O	0.00	0.00	0.00	0.00	0.00
M2 (H ₂ O···HO)	−4.47	1.83	−3.76	−6.44	−4.35
M3 (HO···H ₂ O)	−2.43	2.50	−2.18	−4.00	−2.7
H ₂ SO ₄ + OH + H ₂ O	0.00	0.00	0.00	0.00	0.00
C1 (H ₂ SO ₄ ···OH···H ₂ O)	−18.11	−0.84	−16.74	−24.31	−20.28
TS1	−14.84	3.45	−13.07	−13.56	−12.77
TS2	−13.73	5.34	−11.36	−14.70	−14.30
C2 (HO···H ₂ SO ₄ ···H ₂ O)	−17.44	−0.45	−16.23	−24.58	−20.67
C3 (H ₂ SO ₄ ···H ₂ O···OH)	−18.60	−1.43	−17.27	−25.08	−21.11
TS3	−14.06	4.29	−12.20	−9.18	−7.04
TS4	−13.77	4.64	−11.90	−9.02	−6.89
TS5	−12.13	5.17	−10.67	−6.91	−6.20
TS6	−9.52	9.35	−7.35	−12.14	−11.91
M5 (H ₂ SO ₄ ···H ₂ O) + H ₂ O	−21.93	−15.56	−21.77	−17.36	−15.57
M6 (HSO ₄) + M4 (water dimer)	−15.55	−10.79	−15.26	−9.27	−7.34

^a ΔH , ΔG , and ΔE are computed at the B3LYP/6-311+G(2df,2p) level of theory. ^b ΔE is calculated at the MP2(full)/aug-cc-pv(T+d)z//B3LYP/6-311+G(2df,2p) level of theory.

The transition state TS1 is listed in Figure 2, which is an eight-membered ring structure with two hydrogen bonds. The OH_a bond of OH group in the sulfuric acid is lengthened from 1.006 Å in C1 to 1.255 Å in TS1, and the S=O in the sulfuric acid is stretched to 1.446 Å. It is noted that the H_bO hydrogen bond in TS1 is 1.599 Å, which is very short, indicating strong bond strength. The energy barrier is found to be 7.41 kcal/mol relative to the corresponding prereactive complex C1, which is about 6.00 kcal/mol lower than that of the corresponding reaction¹⁰ OH with sulfuric without water (see TS3' in the Supporting Information). Moreover, the barrier is −1.22 kcal/mol, −8.35 kcal/mol with respect to the separated reactants M1 (H₂SO₄···H₂O) + OH or H₂SO₄ + M2 (H₂O···HO), respectively. The calculated results show that the single water exerts strong effects on the reaction barrier, comparing with HNO₃³¹ reaction with OH, HCOOH³⁰ reaction with OH with water molecule added because the barriers are positive relative to the corresponding reactants. However, the barrier in TS5 is obtained to be 5.35 kcal/mol relative to the separated reactants M1 (H₂SO₄···H₂O) + OH, which is about 1.00 kcal/mol higher than that of the reaction of OH with sulfuric acid (See Supporting Information of TS3'), indicating the single water has negative influences on the reaction barrier.

3.3. The Double or Three Proton Transfer. The double proton transfer process begins with the prereactive complex C2 and proceeds through the transition state TS6 leading to the formation of the complex C3, which is similar to the corresponding process in the reactions of HCOOH + OH,⁶⁰ H₂SO₄ + OH,¹⁰ and HNO₃ + OH.^{31,61} As a result, the reactants and the products are the same compounds. However, the reaction may be experimentally measured via the deuterated isotope. From Figure 2, the geometrical parameters show that the two S=O bonds (1.501 and 1.502 Å) are approximately equal; the OH_d bond of 1.310 Å is equal to the OH_c bond and H_dO bond is also equal to the H_cO bond, which is different from the corresponding transition state TS4' (see Figure S1 in the Supporting

Information). In addition, the six atoms (OH_dOH_cOS) lie in the same plane. The barrier is 9.76 kcal/mol with respect to the prereactive complex C2, indicating that the single water molecule cannot lower the reaction barrier because the barrier without water is 8.82 kcal/mol relative to the reaction complex (See TS4' in Table S1, Supporting Information).

The complex C1 is regarded as the incipient step of the three proton transfer process. The reaction takes place via the simultaneous hydrogen transfer of the OH group in sulfuric acid to oxygen in OH, the hydrogen of the OH radical to the central oxygen of water, and the hydrogen of water to oxygen of S=O bond in sulfuric acid. It is noted that the postreactive complex C3 (H₂SO₄···H₂O···OH) is different from the complex C1. Moreover, the complex C3 is formed via the M3 (HO···H₂O) interaction with sulfuric acid. Therefore, the reverse process also occurs. The corresponding transition state is an eight-membered ring structure as given in Figure 2. The eight atoms approximately lie in the same plane because the dihedral angle in the ring varies in the range of 10.0°. Additionally, the OH bond length in the ring changes from 1.036 to 1.474 Å and the two S=O bonds change in the opposite way: One is stretched to 1.473 Å from 1.446 Å in complex C1. The other is shortened to 1.495 Å from 1.527 Å in C1. It is noted that the lengthening distance of the first S=O bond of 0.034 Å is about equal to the contracted distance of the second S=O bond of 0.032 Å. The barrier of the three proton transfer is estimated to be 5.98 kcal/mol relative to the prereactive complex C1, which is lower than that of the corresponding reaction of OH with sulfuric acid (see TS4' in Table S1, Supporting Information) by 2.84 kcal/mol, reflecting that single water plays an important role in the energy barrier lowering.

3.4. A Single Proton Coupled Electron Transfer. Although the reaction mechanism plays a significant role in the reactions HCOOH + OH⁶⁰ and HNO₃ + OH,³¹ it is of minor importance in the reaction of sulfuric acid with the OH radical.¹⁰ The reaction occurs via the transition states (TS3, TS4) in Figure 2

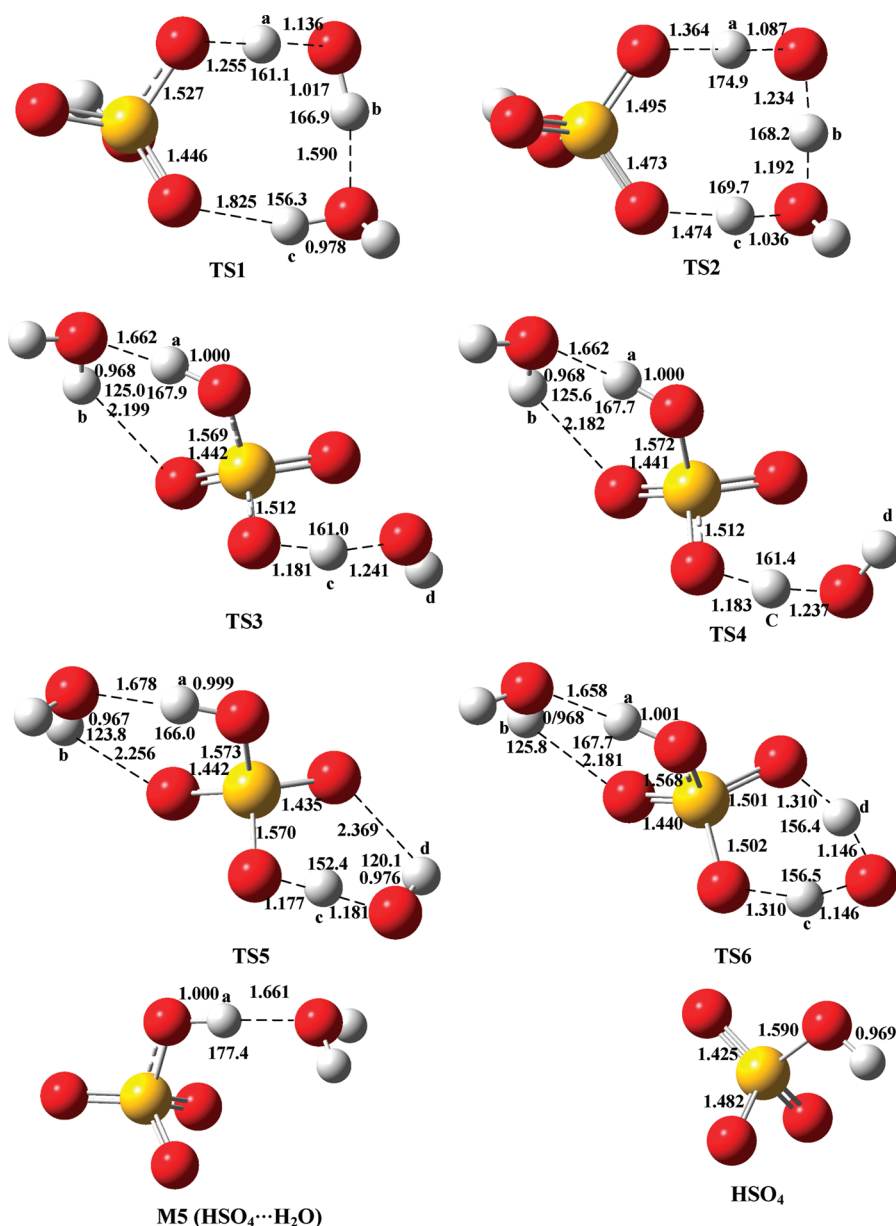
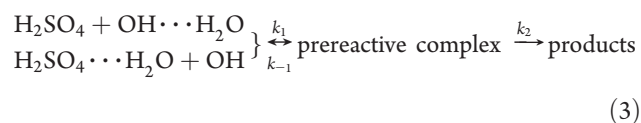


Figure 2. The optimized transition states and complexes at the B3LYP/6-311+G(2df,2p) level of theory.

with the reactants M1 and the OH radical. From Table 1, the calculated results show that the single water molecule cannot reduce the reaction energy barrier because the energy barriers are 4.51 and 5.67 kcal/mol with respect to the reactants, respectively, whereas the energy barriers in reaction of sulfuric acid with OH are 3.95 and 4.12 kcal/mol in Table S1 (Supporting Information).

3.5. Kinetics and the Potential Applications in Atmospheric Chemistry. To estimate the effects of the single water molecule added, the kinetic is carried out in terms of the canonical transition state theory. As the reactions start with the formation of the prereactive complexes before the transition states and release the products, the reaction mechanism can be characterized by the eq 3.



Assuming that the prereactive complex is in equilibrium with the reactants and in terms of the steady-state conditions, the overall rate constant is expressed as

$$k = \frac{k_1}{k_{-1} + k_2} k_2 \quad (4)$$

If $k_2 \ll k_{-1}$, the rate constant is rewritten as

$$k = \frac{k_1}{k_{-1} + k_2} k_2 = K_{\text{eq}} k_2 \quad (5)$$

where the K_{eq} and k_2 are the equilibrium constant of the first step and the rate constant of the second step in the reactions, respectively, which is calculated by eqs 5 and 6

$$K_{\text{eq}}(T) = \sigma \frac{Q_{\text{complex}}}{Q_{\text{R1}} Q_{\text{R2}}} \exp[-(E_{\text{C}} - E_{\text{R}})/RT] \quad (6)$$

Table 2. The Calculated Equilibrium Constant (K_{eq} , in $\text{cm}^3 \text{ molecule}^{-1}$), Tunneling Factor (κ), Collision Rate (k_1 , in $\text{cm}^3 \text{ molecule}^{-1}$), Unimolecular Rate Constant (k_2 , s^{-1}), and the Overall Rate Constant ($k_{\text{TS1}}, k_{\text{TS2}}, k_{\text{TS1}}'$ and k_{TS2}' , in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for Every Elementary Process in the Temperature Range 260–320 K

reaction		260 K	270 K	280 K	290 K	298 K	310 K	320 K
$\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O} + \text{OH}$	K_{eq}	2.69×10^{-18}	1.42×10^{-18}	7.83×10^{-19}	4.51×10^{-19}	2.98×10^{-19}	1.68×10^{-19}	1.06×10^{-19}
	κ	4.45	4.20	3.97	3.77	3.63	3.43	3.28
	k_2	1.03×10^6	1.79×10^6	2.99×10^6	4.82×10^6	6.89×10^6	1.24×10^7	1.68×10^7
	k_{TS1}	1.23×10^{-11}	1.07×10^{-11}	9.29×10^{-12}	8.20×10^{-12}	7.45×10^{-12}	7.15×10^{-12}	5.84×10^{-12}
	K_{eq}	2.69×10^{-18}	1.42×10^{-18}	7.83×10^{-19}	4.51×10^{-19}	2.98×10^{-19}	1.68×10^{-19}	1.06×10^{-19}
	κ	1.53	1.49	1.46	1.43	1.40	1.37	1.35
	k_2	1.19×10^7	1.79×10^7	2.60×10^7	3.68×10^7	4.77×10^7	6.86×10^7	9.01×10^7
$\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \cdots \text{HO}$	k_{TS2}	4.90×10^{-11}	3.79×10^{-11}	2.97×10^{-11}	2.37×10^{-11}	1.99×10^{-11}	1.58×10^{-11}	1.29×10^{-11}
	K_{eq}	2.82×10^{-14}	8.93×10^{-15}	3.07×10^{-15}	1.14×10^{-15}	5.40×10^{-16}	1.90×10^{-16}	8.46×10^{-17}
	κ	4.45	4.20	3.97	3.77	3.63	3.43	3.28
	k_1	4.43×10^{-10}	4.52×10^{-10}	4.60×10^{-10}	4.68×10^{-10}	4.75×10^{-10}	4.84×10^{-10}	4.92×10^{-10}
	k_{-1}	1.57×10^4	5.06×10^4	1.50×10^5	4.11×10^5	8.79×10^5	2.55×10^6	5.81×10^6
	k_2	1.03×10^6	1.79×10^6	2.99×10^6	4.82×10^6	6.89×10^6	1.24×10^7	1.68×10^7
	k_{TS1}'	4.37×10^{-10}	4.39×10^{-10}	4.38×10^{-10}	4.32×10^{-10}	4.21×10^{-10}	4.02×10^{-10}	4.65×10^{-10}
	K_{eq}	2.82×10^{-14}	8.93×10^{-15}	3.07×10^{-15}	1.14×10^{-15}	5.40×10^{-16}	1.90×10^{-16}	8.46×10^{-17}
	κ	1.53	1.49	1.46	1.43	1.40	1.37	1.35
	k_1	4.43×10^{-10}	4.52×10^{-10}	4.60×10^{-10}	4.68×10^{-10}	4.75×10^{-10}	4.84×10^{-10}	4.92×10^{-10}
	k_{-1}	1.57×10^4	5.06×10^4	1.50×10^5	4.11×10^5	8.79×10^5	2.55×10^6	5.81×10^6
	k_2	1.19×10^7	1.79×10^7	2.60×10^7	3.68×10^7	4.77×10^7	6.86×10^7	9.01×10^7
	k_{TS2}'	4.43×10^{-10}	4.51×10^{-10}	4.58×10^{-10}	4.63×10^{-10}	4.66×10^{-10}	4.67×10^{-10}	4.62×10^{-10}

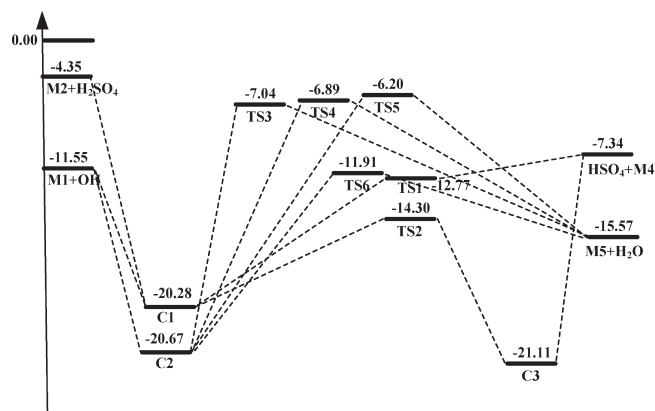


Figure 3. The calculated potential energy profile at the MP2(full)/aug-cc-pv(T+d)z//B3LYP/6-311+G(2df,2p) level of theory (kcal/mol).

$$k_2(T) = \kappa \sigma \frac{k_B T}{h} \frac{Q_{\text{TS}}}{Q_{\text{complex}}} \exp[-(E_{\text{TS}} - E_{\text{C}})/RT] \quad (7)$$

where Q_{TS} , Q_{R} , and Q_{C} denote the partition functions of the transition states, the reactants, and the prereactive complex, k_B is Boltzmann's constant, κ is the transmission coefficient, and σ is the symmetry factor. The E_{TS} , E_{R} , and E_{C} stand for the total energy of the transition states, the reactants, and the complexes with zero point energy correction involved. If the k_{-1} is not much bigger than k_2 , the overall rate constant approaches k_1 , which is obtained by hard-sphere collision theory. Finally, the overall rate constant is evaluated in terms of eq 4. k_{-1} is computed from the equilibrium constant K_{eq} and k_1 .

According to results of the energy analysis, the elementary processes via TS1 and TS2 are more important than other

processes reported here. Therefore, the rate constants through TS1 and TS2 are calculated and given in Table 2. Table 2 tells that the rate constants by TS1 and TS2 have negative temperature dependence. It is noted that the rate constants of k_{TS1} and k_{TS2} ($\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O} + \text{OH}$) are 7.45×10^{-12} and $1.99 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K respectively, which is about an order of 10^3 greater than those of the corresponding transition states in the reaction of sulfuric acid with OH,¹⁰ whereas the rate constants k_{TS1}' and k_{TS2}' ($\text{H}_2\text{SO}_4 + \text{HO} \cdots \text{H}_2\text{O}$) are 10^4 greater than the corresponding rate constant without water.¹⁰ Thus, the estimated rate constants indicate that the reaction $\text{H}_2\text{SO}_4 + \text{OH}$ with water is well competed with the reaction of sulfuric acid with OH without water because the concentration of the $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$ complex is much higher, up to 90–95% of the pure sulfuric acid by the previous calculations.³⁵ In addition, the lifetime of sulfuric acid is about 40 min with the OH concentration of $10^6 \text{ molecules cm}^{-3}$. Thus, the title reaction investigated here is of minor importance in the polluted area where the sulfuric acid condenses into existing particles or takes part in nucleation responsible for the formation of new particles in the time range of a second reported by Pierce and Adams.⁶¹ The reaction may play an important role in the clean area where the lifetime of H_2SO_4 is on the order of hours. Additionally, the calculated results would also provide a new insight on the very recent experiment,⁶² which reports that the OH radical concentration in the range $(4-300) \times 10^5 \text{ molecules cm}^{-3}$ has no influence on the nucleation process because the reaction $\text{OH} + \text{H}_2\text{SO}_4$ in the presence of water cannot compete well with H_2SO_4 nucleation described above.

4. CONCLUSIONS

The reactions of OH with sulfuric acid without added water and with added water are investigated from the electronic

and kinetic points of view, which leads to the following conclusions.

- (1) The reaction mechanism of sulfuric acid with the OH radical is not changed with the single water added.
- (2) The single water molecule can promote the decomposition of sulfuric acid with the aid of the OH radical, which is demonstrated from the energetic and kinetic points of view.
- (3) The lifetime of the formed HSO_4 in the atmosphere is further studied, which is of great necessity because of organic compound or water is extracted by HSO_4 , resulting in the formation of H_2SO_4 . Thus, the reaction $\text{OH} + \text{H}_2\text{SO}_4$ in the presence of water is not a net loss of H_2SO_4 . Additionally, whether HSO_4 can decompose into SO_3 and OH via the OH-overtone induced excitation or not is interesting, which provides a new pathway for the transformation of H_2SO_4 to SO_3 . HSO_4 also provides a pathway to form the organosulfates, recently reported by Ehn et al.⁶³ It is worth noting that the uncertainty related to the energy values is possibly on the order of 1–2 kcal/mol, which leads to the computed rate constants with the uncertainty of around 1 order of magnitude somewhere. However, extra inaccuracy is introduced here, which does not influence the conclusions described above.

■ ASSOCIATED CONTENT

S Supporting Information. Table S1 listing reaction and activated energies, enthalpies, and free energies for the reaction of OH with sulfuric acid, Table S2 representing the topological properties of the bond critical points of the complexes discussed in the paper, and Figure S1 showing the prereactive complex and transition states for the reaction of sulfuric acid with the OH radical. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: wwwlcommon@sina.com (Dr. Bo Long).

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