

# Formic Acid Catalyzed Gas-Phase Reaction of H<sub>2</sub>O with SO<sub>3</sub> and the Reverse Reaction: A Theoretical Study

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The formic acid catalyzed gas-phase reaction between H<sub>2</sub>O and SO<sub>3</sub> and its reverse reaction are respectively investigated by means of quantum chemical calculations at the CCSD(T)//B3LYP/cc-pv(T+d)z and CCSD(T)//MP2/aug-cc-pv(T+d)z levels of theory. Remarkably, the activation energy relative to the reactants for the reaction of H<sub>2</sub>O with SO<sub>3</sub> is lowered through formic acid catalysis from 15.97 kcal mol<sup>-1</sup> to -15.12 and -14.83 kcal mol<sup>-1</sup> for the formed H<sub>2</sub>O...SO<sub>3</sub> complex plus HCOOH and the formed H<sub>2</sub>O...HCOOH complex plus SO<sub>3</sub>, respectively, at the CCSD(T)//MP2/aug-cc-pv(T+d)z level. For the reverse reaction, the energy barrier for decomposition of sulfu-

ric acid is reduced to -3.07 kcal mol<sup>-1</sup> from 35.82 kcal mol<sup>-1</sup> with the aid of formic acid. The results show that formic acid plays a strong catalytic role in facilitating the formation and decomposition of sulfuric acid. The rate constant of the SO<sub>3</sub> + H<sub>2</sub>O reaction with formic acid is 10<sup>5</sup> times greater than that of the corresponding reaction with water dimer. The calculated rate constant for the HCOOH + H<sub>2</sub>SO<sub>4</sub> reaction is about 10<sup>-13</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> in the temperature range 200–280 K. The results of the present investigation show that formic acid plays a crucial role in the cycle between SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in atmospheric chemistry.

## 1. Introduction

Sulfuric acid is of major importance and continuous interest in the Earth's chemistry because of its major contribution to the formation of acid rain<sup>[1,2]</sup> and its role in the formation of atmospheric aerosols,<sup>[3–7]</sup> which affect clouds, precipitation, and radiation balance. In particular, cycling of SO<sub>2</sub> and sulfuric acid has been investigated by field measures combined with model calculations to illustrate the stratospheric aerosol.<sup>[8–11]</sup> In the atmosphere, sulfuric acid is mainly produced by reactions (1)–(3), where M represents a collision partner. On the other hand, H<sub>2</sub>SO<sub>4</sub> is also decomposed into SO<sub>3</sub>, which is subsequently photolyzed to SO<sub>2</sub>.



For reaction (3), there have been some theoretical and experimental reports<sup>[12–18]</sup> on the elementary process occurring in the atmosphere. The first suggested atmospheric mechanism of reaction (3) is the reaction of SO<sub>3</sub> with small water clusters.<sup>[17]</sup> In an alternative mechanism, recently proposed by Anglada et al.,<sup>[18]</sup> an HO<sub>2</sub> radical acts as a catalyst to accelerate the reaction of SO<sub>3</sub> with H<sub>2</sub>O. As the ratio of the rate constant<sup>[18]</sup> of the reaction SO<sub>3</sub> + HO<sub>2</sub>...H<sub>2</sub>O to that of SO<sub>3</sub> + H<sub>2</sub>O...H<sub>2</sub>O is 10<sup>6</sup> and the ratio between the HO<sub>2</sub>...H<sub>2</sub>O complex and the H<sub>2</sub>O...H<sub>2</sub>O complex is 10<sup>-6</sup>, the process competes well with the water dimer to lead to formation of sulfuric acid. In addition, since the barrier of unimolecular decomposition of sulfuric acid into SO<sub>3</sub> and H<sub>2</sub>O is high (36.0 kcal mol<sup>-1</sup><sup>[19]</sup>), direct decomposition of H<sub>2</sub>SO<sub>4</sub> into SO<sub>3</sub> and H<sub>2</sub>O is improbable. It

was proposed that H<sub>2</sub>SO<sub>4</sub> and its hydrate are photolyzed to SO<sub>3</sub> via overtone excitation of the OH stretch in sulfuric acid.<sup>[20–25]</sup> However, dynamic calculations<sup>[26]</sup> show that the H<sub>2</sub>SO<sub>4</sub>...H<sub>2</sub>O complex is not dissociated into SO<sub>3</sub> and water. Furthermore, photolysis<sup>[27]</sup> of H<sub>2</sub>SO<sub>4</sub> is not adequate to yield the amount of SO<sub>2</sub> in the upper atmosphere. Thus, exploring whether the barrier can be significantly lowered by a catalytic reaction with other species provides new insight into the dissociation of sulfuric acid.

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In this investigation, we estimate that the catalytic role which formic acid plays makes cycling between  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  in the atmosphere much easier. Although some recent reports<sup>[28–37]</sup> have demonstrated that water or acid can greatly reduce the activation barrier for various reactions, this is the first study on formic acid catalyzed hydration of  $\text{SO}_3$  in the gas phase. Our results also confirm that this process is competitive with the reaction of  $\text{SO}_3$  with the water dimer responsible for the formation of sulfuric acid and provide deeper insight into dissociation of the ground state of sulfuric acid, previously considered to be forbidden.

## Computational Details

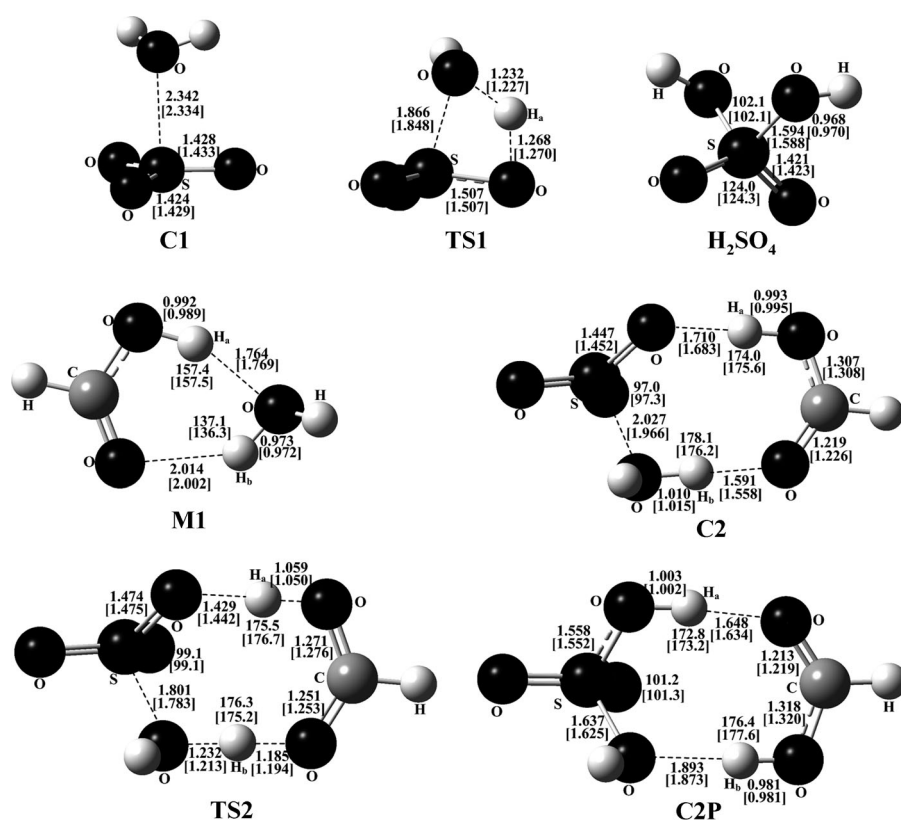
All electronic-structure calculations were carried out with the Gaussian 09<sup>[38]</sup> suite of software. Test calculations estimate the reliability of used methods and the uncertainty related to those energies. The geometrical structures of all reactants, prereactive complexes, transition states, and products were optimized by utilizing the hybrid density functional B3LYP method<sup>[39]</sup> with cc-pv(T+d)z<sup>[40]</sup> basis set and MP2<sup>[41]</sup> approach with aug-cc-pv(T+d)z basis set, because their reliability and efficiency were confirmed by previous studies on reactions<sup>[13, 17, 18, 30, 42]</sup> and clusters<sup>[43–49]</sup> involving sulfuric acid. Moreover, it is also proven<sup>[50, 51]</sup> that the cc-pv(T+d)z and aug-cc-pv(T+d)z basis sets can produce more accurate results for sulfur-containing compounds. Corresponding frequencies of the optimized geometries were computed at these levels to verify the characters of transition states with one imaginary frequency and stationary points without imaginary frequency and obtain the zero-point vibrational energy (ZPE). Additionally, anharmonic corrections were done to evaluate the contribution to the zero-point vibrational energy by using the second-order perturbative treatment (VPT2)<sup>[52, 53]</sup> at the B3LYP/cc-pv(T+d)z level. To obtain reliable relative energies, single-point energies were refined by using the CCSD(T)<sup>[54–56]</sup>/cc-pv(T+d)z and CCSD(T)/aug-cc-pv(T+d)z methods at the B3LYP and MP2 optimized geometries, respectively, whereby the CCSD(T)/aug-cc-pv(T+d)z theoretical approach is also executed with GAMESS<sup>[57]</sup> software. The basis-set superposition error (BSSE) is not considered here because the common counterpoise (CP) correction<sup>[58]</sup> is not adequate for large basis sets involving multiple diffuse basis functions. Furthermore, Kurtén et al.<sup>[48, 49]</sup> showed that basis-set effects have relatively small influences on binding energies of clusters containing sulfuric acid. In addition, the intrinsic reaction coordinate (IRC)<sup>[59, 60]</sup> was calculated at the B3LYP/cc-pv(T+d)z level to examine the given transition states connected with the designated reactants and products.

The natures of these complexes in this investigation were analyzed in terms of the atoms in molecules (AIM) theory by Bader,<sup>[61]</sup> which was executed in AIM2000.<sup>[62–64]</sup> Finally, rate constants were calculated by using transition state theory with Wigner correction, which was performed with the TheRate program.<sup>[65, 66]</sup>

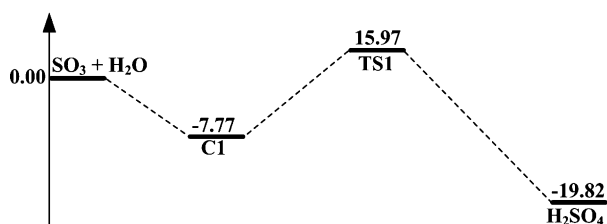
## 2. Results and Discussion

### 2.1. Reaction of $\text{SO}_3$ with $\text{H}_2\text{O}$ and the Reverse Reaction

Although the reaction of  $\text{SO}_3$  with water has been extensively investigated,<sup>[12–13, 67, 68]</sup> the goal of our study is to estimate the reliability of the selected theoretical methods and the role of catalysis in reducing the activation barrier for the reaction  $\text{SO}_3 + \text{H}_2\text{O}$ . The optimized geometries are displayed in Figure 1, and the potential-energy profile in Figure 2. Our calculation results indicate that the binding energy  $D_e$  of **C1** ( $\text{SO}_3 \cdots \text{H}_2\text{O}$ ) without zero-point energy correction is  $-9.90 \text{ kcal mol}^{-1}$  at the CCSD(T)//B3LYP/cc-pv(T+d)z level and  $-9.81 \text{ kcal mol}^{-1}$  at the CCSD(T)//MP2/aug-cc-pv(T+d)z level (Table S1, Supporting Information). The results are in excellent agreement with the value of  $-9.8 \pm 0.2 \text{ kcal mol}^{-1}$ <sup>[69]</sup> obtained by high-level evaluation. The binding enthalpy of **C1** is  $-8.37 \text{ kcal mol}^{-1}$  at the B3LYP/cc-pv(T+d)z level and  $-8.11 \text{ kcal mol}^{-1}$  at the MP2/tug-cc-pv(T+d)z level (Table 1), close to the reported value of  $-8.3 \pm 0.1 \text{ kcal mol}^{-1}$ <sup>[69]</sup> at 298 K. The activation barrier of the reaction  $\text{H}_2\text{O} + \text{SO}_3$  is  $23.33 \text{ kcal mol}^{-1}$  at the CCSD(T)//B3LYP/cc-pv(T+d)z level, and  $23.64 \text{ kcal mol}^{-1}$  at the CCSD(T)//MP2/



**Figure 1.** Complexes, transition states, and products at the B3LYP/cc-pv(T+d)z and MP2/aug-cc-pv(T+d)z (in brackets) levels of theory (bond lengths in angstroms and angles in degrees).



**Figure 2.** Potential-energy profile [kcal mol<sup>-1</sup>] of the reaction SO<sub>3</sub> + H<sub>2</sub>O at the CCSD(T)//MP2/aug-cc-pv(T+d)z level of theory.

**Table 1.** Binding, activation, and reaction enthalpies  $\Delta H$  [kcal mol<sup>-1</sup>], free energies  $\Delta G$  [kcal mol<sup>-1</sup>], and energies  $\Delta E$  [kcal mol<sup>-1</sup>] for the reactions of SO<sub>3</sub> with H<sub>2</sub>O and with H<sub>2</sub>O and HCOOH relative to the free reactants with zero-point correction at 298 K.

Compound	$\Delta H^{[a]}$	$\Delta G^{[a]}$	$\Delta E^{[a]}$	$\Delta E^{[b]}$	$\Delta H^{[c]}$	$\Delta G^{[c]}$	$\Delta E^{[c]}$	$\Delta E^{[d]}$
HCOOH + H <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HCOOH...H <sub>2</sub> O (M1)	-10.13	-0.78	-9.29	-9.41	-8.80	0.39	-8.04	-8.06
SO <sub>3</sub> + H <sub>2</sub> O → H <sub>2</sub> SO <sub>4</sub>								
SO <sub>3</sub> + H <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO <sub>3</sub> ...H <sub>2</sub> O (C1)	-8.37	0.62	-7.87	-7.36	-8.11	0.01	-7.74	-7.77
TS1	14.32	26.02	15.97	15.97	13.71	25.45	15.38	15.97
H <sub>2</sub> SO <sub>4</sub>	-19.32	-8.06	-17.96	-19.85	-19.10	-7.78	-17.71	-19.82
HCOOH + SO <sub>3</sub> + H <sub>2</sub> O → H <sub>2</sub> SO <sub>4</sub> + HCOOH								
SO <sub>3</sub> + H <sub>2</sub> O + HCOOH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO <sub>3</sub> + HCOOH...H <sub>2</sub> O (M1)	-10.13	-0.78	-9.29	-9.41	-8.80	0.39	-8.04	-8.06
HCOOH + SO <sub>3</sub> ...H <sub>2</sub> O (C1)	-8.37	0.62	-7.87	-7.36	-8.11	0.01	-7.74	-7.77
SO <sub>3</sub> ...H <sub>2</sub> O...HCOOH (C2)	-23.49	-1.91	-22.18	-22.35	-23.88	-1.98	-22.46	-22.61
TS2	-23.30	0.30	-21.22	-22.14	-24.83	-0.95	-22.60	-22.89
H <sub>2</sub> SO <sub>4</sub> ...HCOOH (C2P)	-30.46	-8.26	-28.96	-32.34	-31.82	-9.54	-30.29	-32.41
H <sub>2</sub> SO <sub>4</sub> + HCOOH	-19.32	-8.06	-17.96	-19.85	-19.10	-7.78	-17.71	-19.82

[a] Computed at the B3LYP/cc-pv(T+d)z level of theory. [b] Obtained at the CCSD(T)//B3LYP/cc-pv(T+d)z level of theory plus anharmonic corrections at the B3LYP/cc-pv(T+d)z level of theory. [c] Calculated at the MP2/aug-cc-pv(T+d)z level of theory. [d] The relative energies are reported at the CCSD(T)//MP2/aug-cc-pv(T+d)z level of theory plus the zero-point vibrational energies.

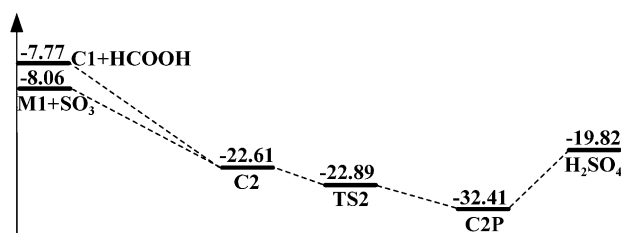
aug-cc-pv(T+d)z level with respect to the prereactive complex C1, which is accordance with values in the range of 23.2–29.0 kcal mol<sup>-1</sup> in prior studies<sup>[12,13,67,68]</sup>. The activation energy of decomposition of sulfuric acid into SO<sub>3</sub> and H<sub>2</sub>O is 35.82 and 35.81 kcal mol<sup>-1</sup> at the CCSD(T)//B3LYP/cc-pv(T+d)z and CSD(T)//MP2/aug-cc-pv(T+d)z levels, respectively. These values are closely consistent with the calculated value of 36.0 kcal mol<sup>-1</sup>.<sup>[19]</sup> Therefore, these test calculations show that both of the theoretical methods produce consistent results for the binding and activation energies of the reaction between SO<sub>3</sub> and H<sub>2</sub>O. From the geometrical point of view, according to the microwave spectrum of gaseous sulfuric acid,<sup>[70]</sup> the equivalent S=O (1.422 Å), S–O (1.574 Å), and O–H (0.970 Å) bond lengths agree well with the calculated geometrical parameters of S=O (1.423 Å, 1.421 Å), S–O (1.588, 1.594 Å), and O–H (0.970, 0.968 Å) at the MP2/aug-cc-pv(T+d)z and B3LYP/cc-pv(T+d)z levels, respectively. The results reveal that the two methods also agree well with each other in computing relative energies and geometrical parameters. For the sake of simplicity, the discussion is based on the CCSD(T)//MP2/aug-cc-pv(T+d)z level.

## 2.2. Reaction of SO<sub>3</sub> with H<sub>2</sub>O and the Reverse Reaction with Formic Acid Catalysis

When formic acid is introduced into the H<sub>2</sub>O + SO<sub>3</sub> reaction, the reactants may be the H<sub>2</sub>O...SO<sub>3</sub> complex (C1) and HCOOH or the H<sub>2</sub>O...HCOOH complex (M1) and SO<sub>3</sub>, because the probability of a simultaneous collision of three molecules is very low under atmospheric conditions. The process is similar to the reactions of OH with compounds in the presence of water.<sup>[28,30,34]</sup> Based on previous theoretical and experimental

studies,<sup>[34,71–73]</sup> the major features of the hydrogen-bonded complexes between formic acid and water are discussed here. Although there are three distinguishable complexes formed between formic acid and water, the most stable complex (M1) is shown in Figure 1 because of its contribution to the reaction mechanism. The stabilization energy of M1 is -8.06 kcal mol<sup>-1</sup> at the CCSD(T) MP2/aug-cc-pvTz level, which agrees well with the reported values of -8.06 and -8.08 kcal mol<sup>-1</sup> at the CCSD(T)aug-cc-pvTz/B3LYP/6-311 + G(2df,2p) and CCSD(T)aug-cc-pvTz/MP2/6-311 + G(2df,2p) levels, respectively.<sup>[34]</sup> From the geometrical viewpoint, the main change is that the interaction distance between H<sub>a</sub> and O is 2.002 Å at the MP2/aug-cc-pvTz level, which is shorter than the corresponding value<sup>[34]</sup> at the MP2/6-311 + G(2df,2p) level by 0.030 Å.

The reaction of H<sub>2</sub>O with SO<sub>3</sub> and HCOOH occurs via pre-reactive complex C2 prior to transition state TS2 and precedes post-reactive complex C2P in Figure 1. The calculated potential-energy profile (Figure 3) reflects the reaction process. Complex C2 is an eight-membered ring structure with two hydrogen bonds and an O...S bond, whereby formic acid acts as both hydrogen-bond acceptor and donor simultaneously. One hydrogen bond is formed by interaction between an oxygen atom in SO<sub>3</sub> and the H<sub>a</sub> of the HO group in formic acid with a short bond length of 1.683 Å. The other hydrogen-bonding distance, between the oxygen atom of the C=O group in HCOOH and H<sub>b</sub> in water, is computed to be 1.558 Å, which is shorter than that of the H<sub>a</sub>...O bond by 0.125 Å. The short interaction distances of the two hydrogen bonds reveal strong interactions, confirmed by the topological properties listed in Table S2 of the Supporting Information. The total electronic energy densities  $H_{H_aO}$  and  $H_{H_bO}$  at the bond critical points are found to be negative ( $H_{H_aO} = -0.0111$  a.u. and  $H_{H_bO} = -0.0226$  a.u.), and represent partial covalent and partial electrostatic nature.<sup>[61]</sup> Therefore, the strong hydrogen-bonding interaction facilitates hydrogen transfer between SO<sub>3</sub> and HCOOH



**Figure 3.** Potential-energy profile [kcal mol<sup>-1</sup>] of the reaction SO<sub>3</sub> + H<sub>2</sub>O in the presence of formic acid at the CCSD(T)//MP2/aug-cc-pv(T+d)z level of theory.

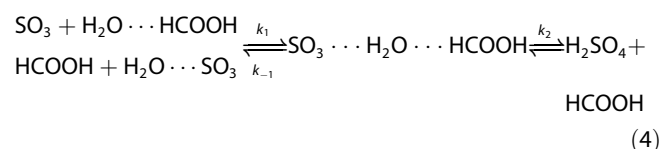
and between HCOOH and H<sub>2</sub>O. In addition, the distance between the oxygen atom of water and the sulfur atom of SO<sub>3</sub> is contracted to 1.966 Å in **C2** from 2.334 Å in **C1**. The stabilization energy is computed to be -22.61 kcal mol<sup>-1</sup> with respect to the separate reactants SO<sub>3</sub>, HCOOH, and H<sub>2</sub>O, that is, the interaction in complex **C2** is very strong.

Transition-state structure **TS2** for the SO<sub>3</sub> + H<sub>2</sub>O reaction with the formic acid catalysis is shown in Figure 1. The reaction takes place by simultaneous transfer of the hydrogen atom of the HO group of HCOOH (H<sub>a</sub>) to an oxygen atom in SO<sub>3</sub> and hydrogen atom H<sub>b</sub> of water to the oxygen atom of the C=O bond of formic acid, as well as addition of OH of water to the central sulfur atom of the SO<sub>3</sub>, responsible for the formation of sulfuric acid. In **TS2**, to facilitate the double hydrogen transfer from water to formic acid and from formic acid to SO<sub>3</sub>, the H<sub>a</sub>...O and H<sub>b</sub>...O bond lengths are shortened to 1.442 Å from 1.683 Å and 1.194 Å from 1.558 Å in **C2**, respectively. Additionally, the C–O bond of the HCOOH in **TS2** is further contracted to 1.276 Å from 1.308 Å in **C2**, while the C=O bond is stretched to 1.253 Å from 1.226 Å in complex **C2**. Interestingly, the contraction of 0.032 Å for the C–O single bond of HCOOH is approximately equal to the elongation of 0.033 Å for the C–O double bond in HCOOH with respect to prereactive complex **C2**. From the energetic viewpoint, the activation barrier of the H<sub>2</sub>O + SO<sub>3</sub> reaction is reduced from 15.97 kcal mol<sup>-1</sup> to -15.12 kcal mol<sup>-1</sup> and -14.83 kcal mol<sup>-1</sup> for reaction of the H<sub>2</sub>O...SO<sub>3</sub> complex with HCOOH and of H<sub>2</sub>O...HCOOH complex with SO<sub>3</sub>, respectively. These results reflect that formic acid plays a remarkable catalytic role in the formation of sulfuric acid. The energy barrier is even lower than that of the reaction of SO<sub>3</sub> with HO<sub>2</sub>...H<sub>2</sub>O,<sup>[18]</sup> by about 6 kcal mol<sup>-1</sup>. Additionally, a negative free energy of ΔG = -0.95 kcal mol<sup>-1</sup> at 298 K indicates that the reaction via **TS2** is thermodynamically driven. The formed post-reactive complex **C2P** is -32.41 kcal mol<sup>-1</sup> below the free reactants SO<sub>3</sub>, H<sub>2</sub>O, and HCOOH.

In the reverse reaction, formic acid and sulfuric acid serve as reactants. The barrier for decomposition of sulfuric acid into SO<sub>3</sub> and H<sub>2</sub>O<sup>[63]</sup> is reduced from 35.82 kcal mol<sup>-1</sup> to -3.07 kcal mol<sup>-1</sup> with the aid of formic acid. The low energy barrier shows that HCOOH promotes splitting of ground-state sulfuric acid in the atmosphere, whereas unimolecular decomposition of sulfuric acid was previously considered to be forbidden.

### 2.3. Kinetics and Potential Importance in Atmospheric Chemistry

To estimate the importance of the catalytic effect of formic acid in the reaction between H<sub>2</sub>O and SO<sub>3</sub> and the reverse reaction in the atmosphere, kinetics were calculated in the framework of canonical transition-state theory. Since the reactions start with formation of the pre-reactive complex before the transition state and release the product, the reaction mechanism is characterized by Equation (4).



Assuming that the pre-reactive complex is in equilibrium with the reactants and applying steady-state conditions, the overall rate constant is obtained as Equation (5).

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

If  $k_2 \ll k_{-1}$ , the rate constant is rewritten as Equation (6)

$$k = \frac{k_1}{k_{-1}} k_2 = K_{\text{eq}} k_2 \quad (6)$$

where  $K_{\text{eq}}$  is the equilibrium constant of the first step and  $k_2$  the rate constant of the second step. The process is similar to radical-molecule reactions<sup>[74]</sup> in the atmosphere, for which these quantities are calculated via Equations (7) and (8)

$$K_{\text{eq}}(T) = \sigma \frac{Q_{\text{complex}}}{Q_{\text{R1}} \times Q_{\text{R2}}} \exp[-(E_c - E_R)/RT] \quad (7)$$

$$k_2(T) = \kappa \sigma \frac{k_B T}{h} \frac{Q_{\text{TS}}}{Q_{\text{complex}}} \exp[-(E_{\text{TS}} - E_R)/RT] \quad (8)$$

where  $Q_{\text{TS}}$ ,  $Q_{\text{R}}$  and  $Q_c$  stand for products of translational, rotational, vibrational, and electronic partition functions of the transition states, the reactants, and the pre-reactive complex, and  $k_B$ ,  $\kappa$ , and  $\sigma$  are the Boltzmann constant, the transmission coefficient, and the symmetry factor. Total energies  $E_{\text{TS}}$ ,  $E_R$ , and  $E_c$  of the transition states, the reactants and the complexes involve zero-point energy corrections. If  $k_{-1}$  is not much larger than  $k_2$ , the overall rate constant approaches  $k_1$ , which is evaluated by hard-sphere collision theory. Finally, the overall rate constant is obtained by Equation (5). Rate constant  $k_{-1}$  is computed from equilibrium constant  $K_{\text{eq}}$  and  $k_1$ . This method was used to compute the rate constant for low energy barriers in our previous studies.<sup>[30,75]</sup> Additionally, the rate constant of the reaction H<sub>2</sub>O with SO<sub>3</sub> in the presence of HCOOH was evaluated by using the pseudo-second order method proposed by Alvarez-Idaboy et al.<sup>[76]</sup> Detailed calculated results are provided in



**Table 2.** Calculated equilibrium constants  $K_{\text{eq1}}$  and  $K_{\text{eq2}}$  [cm<sup>3</sup> molecule<sup>-1</sup>] and the overall rate constants  $k_{\text{T52}}$  and  $k_{-\text{T52}}$  [cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>] for every elementary process in the temperature range 200–320 K.<sup>[a]</sup>

Reaction		200 K	220 K	240 K	260 K	280 K	298 K	320 K
SO <sub>3</sub> ...H <sub>2</sub> O ( <b>C1</b> )	$K_{\text{eq1}}$	$3.98 \times 10^{-17}$	$6.56 \times 10^{-18}$	$1.48 \times 10^{-18}$	$4.24 \times 10^{-19}$	$1.47 \times 10^{-19}$	$6.44 \times 10^{-20}$	$2.61 \times 10^{-20}$
HCOOH...H <sub>2</sub> O ( <b>M1</b> )	$K_{\text{eq2}}$	$1.12 \times 10^{-17}$	$1.62 \times 10^{-18}$	$3.26 \times 10^{-19}$	$8.47 \times 10^{-20}$	$2.69 \times 10^{-20}$	$1.10 \times 10^{-20}$	$4.24 \times 10^{-21}$
HCOOH + SO <sub>3</sub> + H <sub>2</sub> O → H <sub>2</sub> SO <sub>4</sub> + HCOOH								
HCOOH + SO <sub>3</sub> ...H <sub>2</sub> O	$k_{\text{T52}}$	$1.87 \times 10^{-10}$	$1.96 \times 10^{-10}$	$2.05 \times 10^{-10}$	$2.13 \times 10^{-10}$	$2.21 \times 10^{-10}$	$2.28 \times 10^{-10}$	$2.37 \times 10^{-10}$
HCOOH + SO <sub>3</sub> ...H <sub>2</sub> O	$k_{\text{T52}}^*$	$1.74 \times 10^2$	$7.56 \times 10^{-1}$	$8.25 \times 10^{-3}$	$1.83 \times 10^{-4}$	$7.09 \times 10^{-6}$	$5.58 \times 10^{-7}$	$3.74 \times 10^{-8}$
SO <sub>3</sub> + HCOOH...H <sub>2</sub> O	$k_{\text{T52}}$	$1.76 \times 10^{-10}$	$1.84 \times 10^{-10}$	$1.92 \times 10^{-10}$	$2.00 \times 10^{-10}$	$2.08 \times 10^{-10}$	$2.14 \times 10^{-10}$	$2.22 \times 10^{-10}$
SO <sub>3</sub> + HCOOH...H <sub>2</sub> O	$k_{\text{T52}}^*$	$1.39 \times 10^1$	$4.63 \times 10^{-2}$	$4.02 \times 10^{-4}$	$7.30 \times 10^{-6}$	$2.37 \times 10^{-7}$	$1.62 \times 10^{-8}$	$9.30 \times 10^{-10}$
H <sub>2</sub> SO <sub>4</sub> + HCOOH → HCOOH + SO <sub>3</sub> + H <sub>2</sub> O								
H <sub>2</sub> SO <sub>4</sub> + HCOOH	$k_{-\text{T52}}$	$4.66 \times 10^{-12}$	$2.18 \times 10^{-12}$	$1.17 \times 10^{-12}$	$6.95 \times 10^{-13}$	$4.50 \times 10^{-13}$	$3.22 \times 10^{-13}$	$2.27 \times 10^{-13}$

[a]  $k_{\text{T52}}$ ,  $k_{\text{T52}}^*$  were calculated in terms of Equation (5);  $k_{\text{T52}}^*$ ,  $k_{-\text{T52}}^*$  were computed by the pseudo-second-order method.

Tables S4–S7 of the Supporting Information. The overall rate constant is represented in Table 2.

As the reactants may be HCOOH...H<sub>2</sub>O (**M1**) and SO<sub>3</sub> or SO<sub>3</sub>...H<sub>2</sub>O (**C1**) and HCOOH in the formic acid catalyzed H<sub>2</sub>O reaction with SO<sub>3</sub>, the equilibrium constants of the **M1** and **C1** were computed at the CCSD(T)//MP2/aug-cc-pvTz level (Table 2). The equilibrium constant of **C1** is slightly larger than that of **M1**, which shows that the reactants are HCOOH...H<sub>2</sub>O (**M1**) and SO<sub>3</sub> or SO<sub>3</sub>...H<sub>2</sub>O (**C1**) and HCOOH. In addition, the calculated value of **M1** at 298 K is  $1.10 \times 10^{-20}$  cm<sup>3</sup> molecule<sup>-1</sup>, which is reasonably close to the value reported by Anglada and Gonzales.<sup>[34]</sup> In atmospheric chemistry, it is important to determine whether the reaction studied here can compete with the reaction of SO<sub>3</sub> with H<sub>2</sub>O. From Table 2, we note that the rate constant obtained by using the pseudo-second-order method is erroneous, because the estimated rate constant extends the limit rate constant of hard-sphere collision in the atmosphere. Therefore, analysis of the rate constant is based on the results obtained via Equation (5). The reported upper limit of the rate constant for the reaction of SO<sub>3</sub> with H<sub>2</sub>O is  $2.4 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K,<sup>[77,78]</sup> which is about  $10^{-5}$  smaller than that for the reaction of SO<sub>3</sub> with **M1** reaction ( $2.14 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). However, further experimental results show that the gas-phase formation reaction of sulfuric acid involves the reaction of water dimer with SO<sub>3</sub>.<sup>[12–16]</sup> The ratio between water dimer and the formed HCOOH...H<sub>2</sub>O complex is reported to be about  $10^5$ .<sup>[79–81]</sup> Therefore, the reaction investigated here is well competitive with the reaction of SO<sub>3</sub> with water dimer. For the reaction of HCOOH and H<sub>2</sub>O...SO<sub>3</sub>, the calculated rate is  $2.13 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at the typical atmospheric temperature of 260 K, which is about  $10^5$  times greater than the corresponding rate constant of SO<sub>3</sub> + H<sub>2</sub>O...H<sub>2</sub>O. The concentration of the formed complex H<sub>2</sub>O...SO<sub>3</sub> is 16.3% of that of pure SO<sub>3</sub> with the concentration of water ( $3.85 \times 10^{17}$  molecules cm<sup>-3</sup>) at 50% relative humidity. Moreover, the concentration<sup>[80,81]</sup> of HCOOH is about  $10^{11}$  molecules cm<sup>-3</sup>. Therefore, the reaction process (HCOOH + H<sub>2</sub>O...SO<sub>3</sub>) can compete well with SO<sub>3</sub> + H<sub>2</sub>O...H<sub>2</sub>O. Another significant point is the reverse reaction relative to the Earth's chemistry. The presented results reveal that the rate constant is  $3.22 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at 298 K. The lifetime of sulfuric acid is about 15 s at an HCOOH concentration of  $2.00 \times$

$10^{-11}$  molecule cm<sup>-3</sup>. The results indicate that decomposition of sulfuric acid is feasible and fast in the presence of HCOOH under atmospheric conditions.

### 3. Conclusions

From both electronic and kinetic viewpoints, we have studied reactions between SO<sub>3</sub> and H<sub>2</sub>O with and without the presence of formic acid, and came to the following conclusions.

- 1) Barriers for formation and decomposition of the sulfuric acid are reduced to about  $-15.12$  kcal mol<sup>-1</sup> from about  $15.97$  kcal mol<sup>-1</sup> and to  $-3.07$  kcal mol<sup>-1</sup> from  $35.82$  kcal mol<sup>-1</sup>, respectively. Therefore, formic acid plays an important role in lowering activation barriers of the reaction between water and SO<sub>3</sub> and the decomposition of sulfuric acid.
- 2) Reactions of carboxylic acids with sulfuric acid merit further studies, because our results show that the sulfuric acid rapidly dissociates into **C2** in the presence of HCOOH. It is necessary to explore the lifetime of complex **C2**. If **C2** can decompose into SO<sub>3</sub>, due to photolysis of SO<sub>3</sub> to SO<sub>2</sub>, the reaction of HCOOH with sulfuric acid provides a new insight into sources of SO<sub>2</sub> in the atmosphere. Furthermore, organic acids and sulfuric acid are considered to be precursors for nucleation.<sup>[82,83]</sup> Since sulfuric acid condenses onto existing particles and takes part in nucleation responsible for the formation of new particles in the time range of one second, as reported by Pierce and Adams,<sup>[84]</sup> the process investigated here is not competitive with nucleation of sulfuric acid, because the lifetime of sulfuric acid is 15 s in our work. However, it is likely that other organic acids react with sulfuric acid faster than HCOOH. Therefore, the nucleation process may be affected.
- 3) The conclusion that formic acid plays a major role in the cycle between SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> could stimulate other investigations on similarly structured, surrounding molecules that catalyze the reaction of H<sub>2</sub>O and SO<sub>3</sub>, such as nitric acid, carbonic acid, acetic acid, and oxalic acid.

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