

# Theoretical Studies on Gas-Phase Reactions of Sulfuric Acid Catalyzed Hydrolysis of Formaldehyde and Formaldehyde with Sulfuric Acid and $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$ Complex

Bo Long,<sup>\*,†,‡</sup> Xing-Feng Tan,<sup>‡</sup> Chun-Ran Chang,<sup>⊥</sup> Wei-Xiong Zhao,<sup>||</sup> Zheng-Wen Long,<sup>§</sup> Da-Sen Ren,<sup>‡</sup> and Wei-Jun Zhang<sup>\*,†,||</sup>

<sup>†</sup>Key Laboratory of Atmospheric Composition and Optical Radiation, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China

<sup>‡</sup>College of Information Engineering, Guizhou Minzu University, Guiyang 550025, China

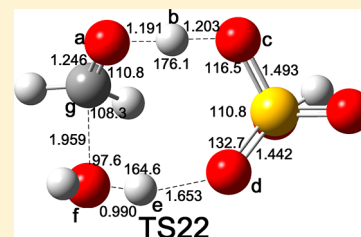
<sup>§</sup>Laboratory for Photoelectric Technology and Application, College of Science, Guizhou University, Guiyang 550025, China

<sup>||</sup>Laboratory of Atmospheric Physico-Chemistry, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China

<sup>⊥</sup>School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China

## S Supporting Information

**ABSTRACT:** The gas-phase reactions of sulfuric acid catalyzed hydrolysis of formaldehyde and formaldehyde with sulfuric acid and  $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$  complex are investigated employing the high-level quantum chemical calculations with M06-2X and CCSD(T) theoretical methods and the conventional transition state theory (CTST) with Eckart tunneling correction. The calculated results show that the energy barrier of hydrolysis of formaldehyde in gas phase is lowered to 6.09 kcal/mol from 38.04 kcal/mol, when the sulfuric acid is acted as a catalyst at the CCSD(T)/aug-cc-pv(T+d)z//M06-2X/6-311++G(3df,3pd) level of theory. Furthermore, the rate constant of the sulfuric acid catalyzed hydrolysis of formaldehyde combined with the concentrations of the species in the atmosphere demonstrates that the gas-phase hydrolysis of formaldehyde of sulfuric acid catalyst is feasible and could be of great importance for the sink of formaldehyde, which is in previously forbidden hydrolysis reaction. However, it is shown that the gas-phase reactions of formaldehyde with sulfuric acid and  $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$  complex lead to the formation of  $\text{H}_2\text{C}(\text{OH})\text{OSO}_3\text{H}$ , which is of minor importance in the atmosphere.



## 1. INTRODUCTION

Formaldehyde ( $\text{HCHO}$ ) is one of the most abundant carbonyl-containing compounds<sup>1</sup> in the atmosphere, which is produced via the atmospheric oxidation of volatile organic compounds (VOCs) and primary emissions from industrial processes, combustion, and fossil fuels.<sup>1–4</sup> It plays a key role in atmospheric chemistry because  $\text{HCHO}$  participates in some important atmospheric processes such as interactions of formaldehyde with aqueous acid surfaces<sup>5–7</sup> or water droplet,<sup>8–10</sup> and formation of secondary organic aerosol.<sup>11</sup> In addition,  $\text{HCHO}$  is also closely related to  $\text{HO}_x$  ( $\text{HO}_x = \text{HO}_2 + \text{HO}$ ) radical.<sup>12</sup> The  $\text{HO}_x$  radical is a primary contributor to catalytic ozone destruction.<sup>13</sup> Therefore, understanding the sink and reactivity of formaldehyde is of great necessity to elucidate the effects of formaldehyde in the atmosphere.

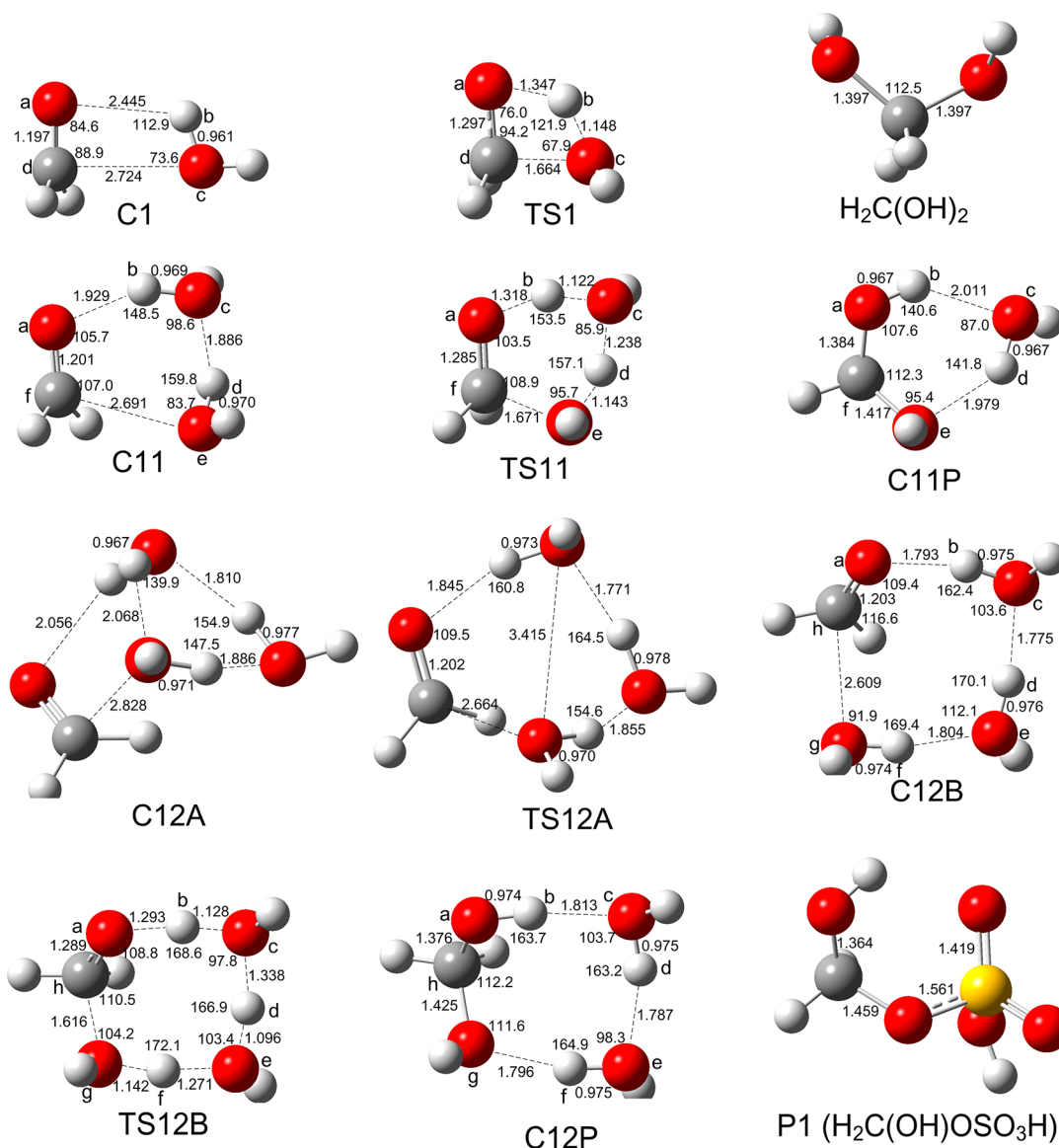
The atmospheric lifetime of  $\text{HCHO}$  is fairly short within the order of a few hours.<sup>14,15</sup> The accepted point is that the primary removal process of formaldehyde in the gas phase is  $\text{HCHO}$  reaction with  $\text{OH}$  and gas-phase photolysis.<sup>1,16</sup> Additionally, formaldehyde easily reacts with water to lead to the formation of methylene glycol ( $\text{HOCH}_2\text{OH}$ )<sup>17</sup> in the water or sulfuric acid solution, which is extensively studied both experimentally

and theoretically.<sup>9,18–25</sup> However, the gas-phase reaction of  $\text{HCHO}$  with the single water molecule<sup>26,27</sup> is forbidden due to the extreme high energy barrier in the atmosphere. Furthermore, when the second water molecule is introduced into the reaction  $\text{HCHO} + \text{H}_2\text{O}$ , the reaction barrier is lowered to be 0.8 kcal/mol with respect to the isolated reactants. The first calculations only were done at the low-level. Thus, high-level ab initio calculations are needed to clarify whether the gas-phase reactions of  $\text{HCHO}$  with  $\text{H}_2\text{O}$ , water dimer, and water trimer are significant atmospheric processes for the sink of formaldehyde. In addition, very recently, there are some reports on the acid catalyzed gas-phase reaction<sup>28,29</sup> of  $\text{H}_2\text{O}$  with  $\text{SO}_3$  and the hydrogen transfer in the  $\text{CH}_3\text{O}^{30}$  isomerization and keto–enol tautomerizations,<sup>31</sup> which are of great importance in the atmosphere. Therefore, it is worth studying whether the atmospheric acids can catalyze the  $\text{H}_2\text{O} + \text{HCHO}$  reaction in the gas phase.

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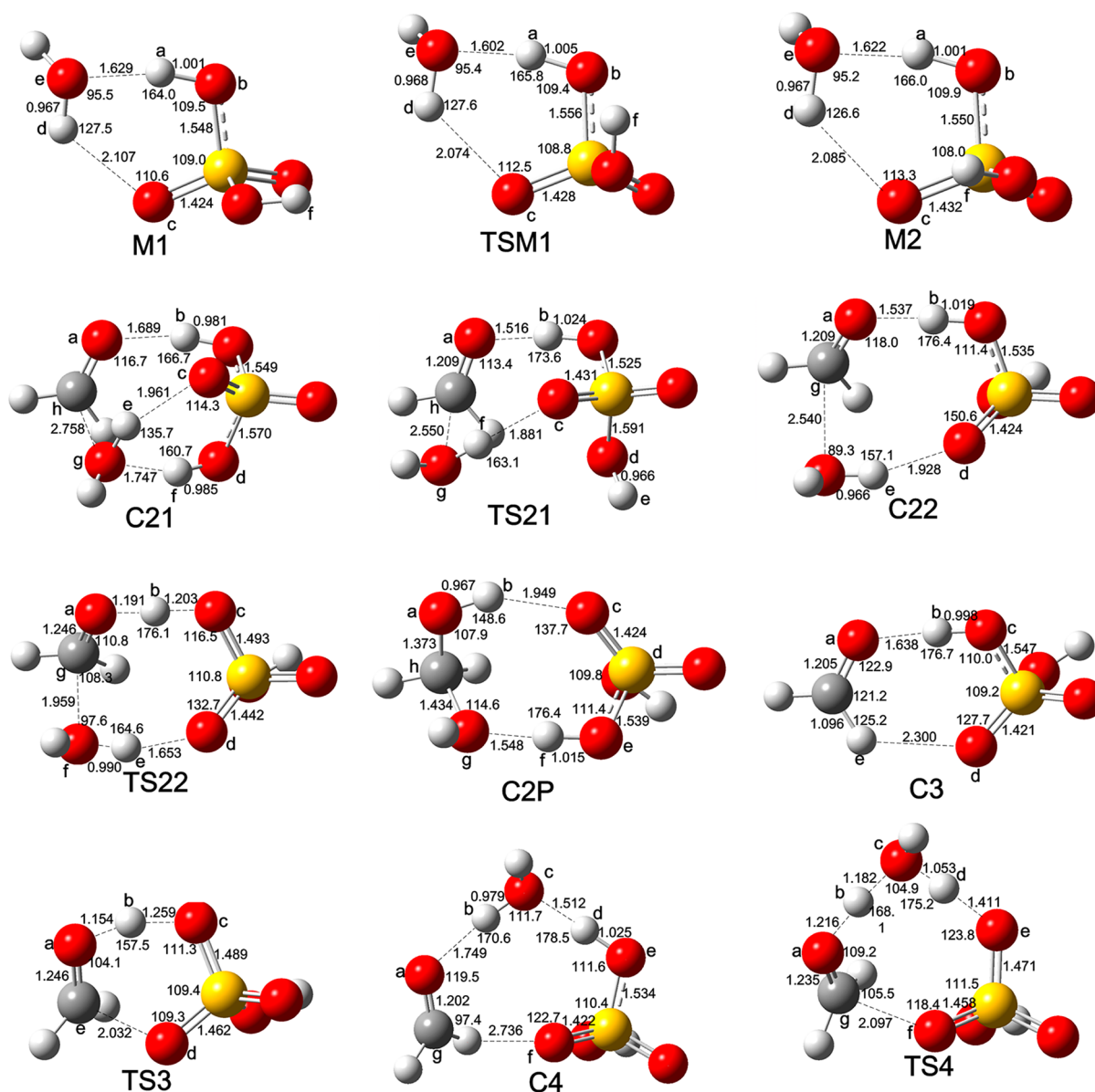
**Figure 1.** Selected geometrical parameters of the optimized reactants, products, and complexes at the M06-2X/6-311++G(3df,3pd) level of theory (bond distances in angstroms and angles in degrees).

In this investigation, the hydrolysis of HCHO catalyzed by sulfuric acid, water, and water dimer is studied using quantum chemical calculations to determine whether the gas phase hydrolysis of formaldehyde is feasible and important in the atmosphere. Here, the sulfuric acid<sup>32</sup> is selected due to the importance of the formation of secondary organic aerosol. In particular, the uptake<sup>7</sup> of formaldehyde on the sulfuric acid films is reported, which has potential implication in the atmosphere. In addition, the reactions of formaldehyde with sulfuric acid and  $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$  complex are considered herein because the single water molecule can affect the atmospheric reaction processes.<sup>33–60</sup> The single water molecule plays a crucial role in the  $\text{CH}_3\text{CHO} + \text{OH}$ ,<sup>35,37</sup>  $\text{OH} + \text{HOCl}$ ,<sup>47</sup>  $\text{H}_2\text{SO}_4 + \text{OH}$ ,<sup>49</sup>  $\text{HCOOH} + \text{OH}$ ,<sup>36,39</sup> and  $\text{SO}_3 + \text{HO}$ ,<sup>42</sup> reactions.

## 2. COMPUTATIONAL METHODS

All the geometrical structures reported in this investigation were optimized using the M06-2X<sup>61</sup> functional at the 6-311++G(3df,3pd)<sup>62,63</sup> basis set. The method was chosen because the recent calculations<sup>64</sup> showed that the utilization of M06-2X

functional with the 6-311++G(3df,3pd) basis set can obtain more reliable results than other functionals for the sulfuric acid-containing clusters. The corresponding frequencies of the structures were estimated at the same level of theory to check the stationary points without imaginary frequencies and the transition states with only one imaginary frequency. Additionally, the intrinsic reaction coordinate (IRC)<sup>65</sup> approach was performed to ensure that the given transition state connects with the corresponding reactants and products. Furthermore, single-point energies of optimized geometries were refined using the CCSD(T)<sup>66,67</sup> theoretical method with the aug-cc-pv(T+d)<sup>68,69</sup> basis set to represent the improved results. In these calculations, the number of T<sub>1</sub> diagnostic<sup>70</sup> for the CCSD wave function was taken into account to estimate the reliability of these computations relative to a possible multireference feature of the wave function at the reported structures in this article. If the value of T<sub>1</sub> diagnostic in the CCSD wave functions is larger than 0.02 for the closed-shell molecular compounds, the CCSD wave functions are thought to be unreliable.<sup>70</sup> Here, T<sub>1</sub> diagnostic values do not exceed the



**Figure 2.** Selected geometrical parameters of the optimized reactants, products, and complexes at the M06-2X/6-311++G(3df,3pd) level of theory (bond distances in angstroms and angles in degrees).

upper limit of 0.02 from Table S1 (Supporting Information), reflecting that the CCSD wave functions of the stationary points could be reliable. Finally, the conventional transition state theory (TST)<sup>71–73</sup> combined with Eckart correction<sup>74</sup> was employed to investigate the rate constant of every elementary reaction. The method can provide reliable data, which is extensively utilized in the atmospheric reactions.<sup>30,39,42,47,75,76</sup> The electronic calculations were executed using Gaussian09 code,<sup>77</sup> while the rate constant was performed on the TheRate code.<sup>78,79</sup>

### 3. RESULTS AND DISCUSSION

The optimized geometries are depicted in Figures 1 and 2 at the M06-2X basis set. The electronic energies ( $\Delta E$ ) and the corresponding thermodynamics values ( $\Delta H$  and  $\Delta G$ ) involve the zero-point energies correction at the M06-2X/6-311++G(3df,3pd) and CCSD(T)/aug-cc-pv(T+d)//M06-2X/6-311++G(3df,3pd) levels, respectively, as represented in Tables 1 and 2. The corresponding potential profile is shown in

Figures 3–7 at the CCSD(T)/aug-cc-pv(T+d)// M06-2X/6-311++G(3df,3pd) level of theory.

**3.1. Hydrolysis of Formaldehyde Catalyzed by Water, Water Dimer, and Water Trimer.** The formaldehyde reaction with the single water molecule begins with the formation of hydrogen-bonded complex (C1) and proceeds through a transition state (TS1) to lead to the formation of  $\text{H}_2\text{C}(\text{OH})_2$  as characterized in Figure 1. The prereactive complex between formaldehyde and water has been extensively investigated by both experimental and theoretical methods<sup>43,80–87</sup> in the literature. Herein, we report that the precomplex structure (C1) is taken into account as the initial step of the  $\text{HCHO} + \text{H}_2\text{O}$  reaction because the C1 is connected with the corresponding transition state TS1 along the reaction coordinate. The C1 is a local minima with the binding energy of  $-1.62$  kcal/mol. The transition state (TS1) as reported in the previous study<sup>24,26,27</sup> is a four-ring structure with the bond distances of  $\text{O}_\text{a}\text{H}_\text{b} = 1.347$  Å,  $\text{H}_\text{b}\text{O}_\text{c} = 1.148$  Å,  $\text{O}_\text{c}\text{O}_\text{d} = 1.664$  Å, and  $\text{C}_\text{d}\text{O}_\text{a} = 1.297$  Å at the M06-2X/6-311++

**Table 1.** Binding, Activated, and Reaction Enthalpies ( $\Delta H$ ), Free Energies ( $\Delta G$ ), and Energies ( $\Delta E$ ) for the Reactions of HCHO with H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>, and H<sub>2</sub>SO<sub>4</sub>⋯H<sub>2</sub>O with Zero-Point Correction (ZPE) Included at 298 K (in kcal/mol)

| compd   | $\Delta H^a$ | $\Delta G^a$ | $\Delta E^a$ | $\Delta H^b$ | $\Delta G^b$ | $\Delta E^b$ |
|---|--------------|--------------|--------------|--------------|--------------|--------------|
| HCHO + H <sub>2</sub> O → H <sub>2</sub> C(OH) <sub>2</sub>   |              |              |              |              |              |              |
| HCHO + H <sub>2</sub> O   | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| C1 (HCHO⋯H <sub>2</sub> O)  | −2.42        | 4.75         | −2.19        | −1.85        | 5.32         | −1.62        |
| TS1   | 32.00        | 43.10        | 33.97        | 34.44        | 45.55        | 36.42        |
| H <sub>2</sub> C(OH) <sub>2</sub>   | −13.70       | −2.84        | −11.89       | −10.09       | 0.78         | −8.27        |
| HCHO + H <sub>2</sub> O + H <sub>2</sub> O → H <sub>2</sub> C(OH) <sub>2</sub> + H <sub>2</sub> O                                       |              |              |              |              |              |              |
| HCHO + H <sub>2</sub> O + H <sub>2</sub> O  | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| HCHO + H <sub>2</sub> O⋯H <sub>2</sub> O  | −3.63        | 3.06         | −2.95        | −3.42        | 3.27         | −2.74        |
| C11   | −11.12       | 5.73         | −9.96        | −9.88        | 6.97         | −8.72        |
| TS11  | 6.31         | 28.33        | 9.80         | 11.42        | 33.44        | 14.91        |
| C11P  | −21.31       | −1.30        | −18.79       | −16.92       | 3.09         | −14.41       |
| H <sub>2</sub> C(OH) <sub>2</sub> + H <sub>2</sub> O  | −13.70       | −2.84        | −11.89       | −10.09       | 0.78         | −8.27        |
| HCHO + H <sub>2</sub> O + H <sub>2</sub> O + H <sub>2</sub> O → H <sub>2</sub> C(OH) <sub>2</sub> + H <sub>2</sub> O + H <sub>2</sub> O |              |              |              |              |              |              |
| HCHO + H <sub>2</sub> O + H <sub>2</sub> O + H <sub>2</sub> O   | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| HCHO + H <sub>2</sub> O⋯H <sub>2</sub> O⋯H <sub>2</sub> O   | −13.74       | 3.13         | −11.80       | −12.45       | 4.42         | −10.51       |
| C12A  | −19.58       | 7.21         | −17.52       | −17.20       | 9.59         | −15.14       |
| TS12A   | −19.51       | 7.91         | −17.17       | −18.05       | 9.37         | −15.71       |
| C12B  | −19.77       | 5.80         | −17.86       | −18.46       | 7.11         | −16.55       |
| TS12B   | −8.75        | 23.57        | −4.12        | −1.45        | 30.87        | 3.18         |
| C12P  | −30.65       | −1.44        | −27.40       | −26.47       | 2.74         | −23.22       |
| H <sub>2</sub> C(OH) <sub>2</sub> + H <sub>2</sub> O + H <sub>2</sub> O   | −13.70       | −2.84        | −11.89       | −10.09       | 0.78         | −8.27        |
| H <sub>2</sub> SO <sub>4</sub> + HCHO + H <sub>2</sub> O → H <sub>2</sub> SO <sub>4</sub> + H <sub>2</sub> C(OH) <sub>2</sub>           |              |              |              |              |              |              |
| H <sub>2</sub> SO <sub>4</sub> + HCHO + H <sub>2</sub> O  | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| C1 (HCHO⋯H <sub>2</sub> O) + H <sub>2</sub> SO <sub>4</sub>   | −2.42        | 4.75         | −2.19        | −1.85        | 5.32         | −1.62        |
| M1  | −12.35       | −3.25        | −11.56       | −11.44       | −2.33        | −10.64       |
| TSM1  | −9.96        | −0.33        | −8.86        | −8.87        | 0.76         | −7.77        |
| M2  | −11.28       | −2.77        | −10.62       | −10.32       | −1.82        | −9.67        |
| C21   | −20.88       | −1.19        | −19.86       | −19.61       | 0.08         | −18.58       |
| TS21  | −18.18       | 2.07         | −16.89       | −16.96       | 3.30         | −15.67       |
| C22 (HCHO⋯H <sub>2</sub> O⋯H <sub>2</sub> SO <sub>4</sub> )   | −18.74       | −0.19        | −17.93       | −17.58       | 0.97         | −16.77       |
| TS22  | −15.90       | 6.14         | −13.77       | −12.82       | 9.22         | −10.68       |
| C2P   | −29.85       | −8.14        | −27.81       | −25.83       | −4.12        | −23.79       |
| P1 (H <sub>2</sub> C(OH) <sub>2</sub> ) + H <sub>2</sub> SO <sub>4</sub>  | −13.70       | −2.84        | −11.89       | −10.09       | 0.78         | −8.27        |

<sup>a</sup> $\Delta H$ ,  $\Delta G$ , and  $\Delta E$  are computed at the M06-2X/6-311++G(3df,3pd) level of theory. <sup>b</sup> $\Delta H$ ,  $\Delta G$ , and  $\Delta E$  are calculated at the CCSD(T)/aug-cc-pv(T+d)z//M06-2X/6-311++G(3df,3pd) level of theory.

**Table 2.** Binding, Activated, and Reaction Enthalpies ( $\Delta H$ ), Free Energies ( $\Delta G$ ), and Energies ( $\Delta E$ ) for the Reactions of HCHO with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>⋯H<sub>2</sub>O with Zero-Point Correction (ZPE) Included at 298 K, Respectively (in kcal/mol)

| compd  | $\Delta H^a$ | $\Delta G^a$ | $\Delta E^a$ | $\Delta H^b$ | $\Delta G^b$ | $\Delta E^b$ |
|--|--------------|--------------|--------------|--------------|--------------|--------------|
| H <sub>2</sub> SO <sub>4</sub> + HCHO → P1 (H <sub>2</sub> C(OH)OSO <sub>3</sub> H)                                  |              |              |              |              |              |              |
| H <sub>2</sub> SO <sub>4</sub> + HCHO  | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| C3 (H <sub>2</sub> SO <sub>4</sub> ⋯HCHO)  | −11.34       | −2.09        | −11.22       | −11.39       | −2.15        | −11.27       |
| TS3  | −0.05        | 12.12        | 1.14         | 1.49         | 13.65        | 2.67         |
| P1(H <sub>2</sub> C(OH)OSO <sub>3</sub> H)   | −17.50       | −5.34        | −16.37       | −14.76       | −2.60        | −13.62       |
| H <sub>2</sub> SO <sub>4</sub> + HCHO + H <sub>2</sub> O → H <sub>2</sub> O + H <sub>2</sub> C(OH)OSO <sub>3</sub> H |              |              |              |              |              |              |
| H <sub>2</sub> SO <sub>4</sub> + HCHO + H <sub>2</sub> O   | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         | 0.00         |
| M1 (H <sub>2</sub> SO <sub>4</sub> ⋯H <sub>2</sub> O) + HCHO   | −12.35       | −3.25        | −11.56       | −11.44       | −2.33        | −10.64       |
| C4 (HCHO⋯H <sub>2</sub> SO <sub>4</sub> ⋯H <sub>2</sub> O)   | −20.41       | −1.84        | −19.58       | −19.48       | −0.91        | −18.64       |
| TS4  | −14.09       | 7.95         | −11.92       | −11.00       | 11.04        | −8.83        |
| P1 (H <sub>2</sub> C(OH)OSO <sub>3</sub> H) + H <sub>2</sub> O   | −17.50       | −5.34        | −16.37       | −14.76       | −2.60        | −13.62       |

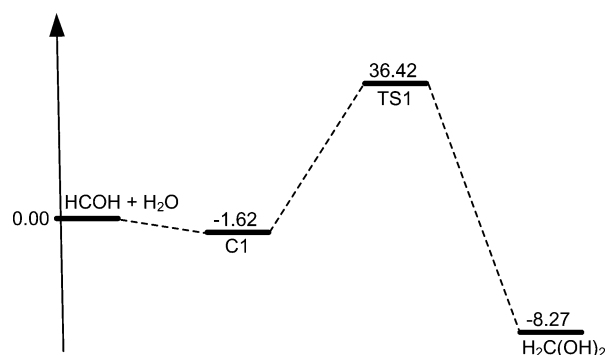
<sup>a</sup> $\Delta H$ ,  $\Delta G$ , and  $\Delta E$  are computed at the M06-2X/6-311++G(3df,3pd) level of theory. <sup>b</sup> $\Delta H$ ,  $\Delta G$ , and  $\Delta E$  are calculated at the CCSD(T)/aug-cc-pv(T+d)z//M06-2X/6-311++G(3df,3pd) level of theory.

+G(3df,3pd) level of theory, which is in good agreement with the reported values<sup>26</sup> at the MP2(full)/6-31(d) level. The energy barrier is calculated to be 38.04 kcal/mol with respect to the prereactive complex consistent with the suggested value of about 40 kcal/mol,<sup>24</sup> which is so high that the process is

impossible to occur in the atmosphere. The product H<sub>2</sub>C(OH)<sub>2</sub> is formed with release energy of 8.27 kcal/mol.

When the second molecule is introduced into the reaction HCHO + H<sub>2</sub>O, the reactants are regarded as HCHO and water dimer. The interaction energy of water dimer is estimated to be





**Figure 3.** Calculated potential energy profile for the HCHO reaction with  $\text{H}_2\text{O}$  at the CCSD(T)/aug-cc-pv(T+d)z//M06-2X/6-311++G-(3df,3pd) level of theory (in kcal/mol).

$-2.74$  kcal/mol, which compares well with the experimental value and previously theoretical results in the literature  $3.15 \pm 0.03$ ,<sup>88</sup>  $2.9$ ,<sup>89</sup>  $2.91$ ,<sup>90</sup>  $3.30$ ,<sup>91</sup>  $3.01$ – $3.12$ ,<sup>92</sup>  $2.99$ – $3.15$ ,<sup>93</sup> and  $2.86$  kcal/mol,<sup>94</sup> respectively. Also, the dissociation energy ( $D_e$ ) of water dimer without zero-point vibrational energy involved is  $21.83$  kJ/mol, which agrees reasonably with the best estimate of  $21.007$  kJ/mol by Lane<sup>95</sup> and previous benchmark results of  $20.97$ ,<sup>91</sup>  $20.99$ ,<sup>96</sup>  $21$ ,<sup>97</sup> and  $20.88$ <sup>90</sup> kJ/mol, respectively. The reported binding enthalpy of  $-3.42$  kcal/mol at  $298$  K is reasonably consistent with the experimental values of  $-3.59 \pm 0.50$ <sup>98</sup> at  $358$ – $386$  K,  $-3.98 \pm 0.90$ <sup>99</sup> at  $573$ – $723$  K,  $-3.58 \pm 0.72$ <sup>100</sup> at  $373$ – $673$  K, and  $-3.24 \pm 0.95$ <sup>101</sup> kcal·mol<sup>-1</sup> and theoretical results of  $-3.3$ <sup>89</sup> and  $-3.34$ <sup>90</sup> kcal/mol, respectively.

The reaction between formaldehyde and water dimer occurs via a six-membered cyclic prereactive complex (C11) before the formation of the transition state (TS11). The corresponding potential energy profile is presented in Figure 4. The prereactive complex C11 involved two weak hydrogen bonded interactions and one van der Waals interaction. The computed binding energy is  $-5.98$  kcal/mol with respect to HCHO and water dimer. It is worth noting that the activated barrier of HCHO with water dimer is reduced to  $17.65$  kcal/mol from  $36.42$  kcal/mol in the reaction  $\text{HCHO} + \text{H}_2\text{O}$  relative to the respective reactants.

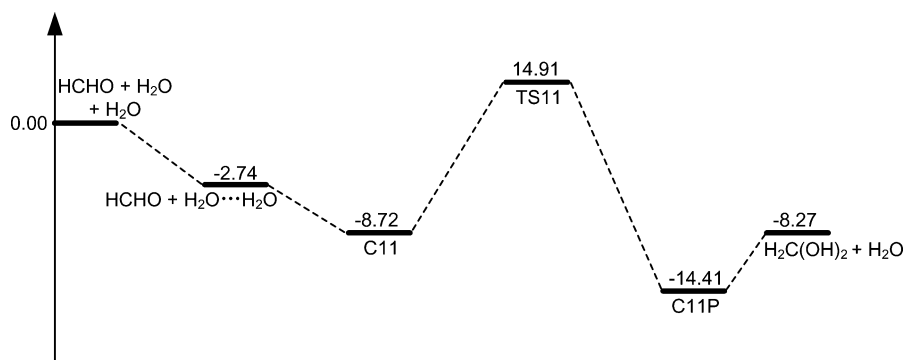
When the third water molecule is added into the reaction of formaldehyde with water dimer, the reaction process is similar to the reactions of formaldehyde with water and water dimer mentioned above, which is displayed in Figure 5. The reactants are considered to be formaldehyde and water trimer. The reaction takes place by the prereactive complex C12A and

transition state TS12A and proceeds to the formation of complex C12B with an eight-ringlike structure formation prior to the transition state TS12B. The binding energy of C12A is  $-4.63$  kcal/mol from Table 1. It is noted that the complex C12A is transferred to C12B through the transition state TS12A almost without an energy barrier, which is similar to the hydrolysis of  $\text{SO}_3$  catalyzed by sulfuric acid.<sup>89</sup> The complex C12B contains three hydrogen bonds and one van der Waals bond. Obviously, the hydrogen bonding strength in C12B is stronger than that of C11 because the hydrogen-bonded distances in C12B are shorter than those in C11. It is also noted that the barrier of TS12B is  $13.69$  kcal/mol, only about  $4$  kcal/mol lower than that of TS11 related to the respective reactants in Table 1. Although the third water molecule can further decrease the activated barrier of formaldehyde with water dimer, the catalytic role is not more obvious than that in the reaction of formaldehyde with the single water molecule, which is similar to that in other reactions.<sup>102</sup>

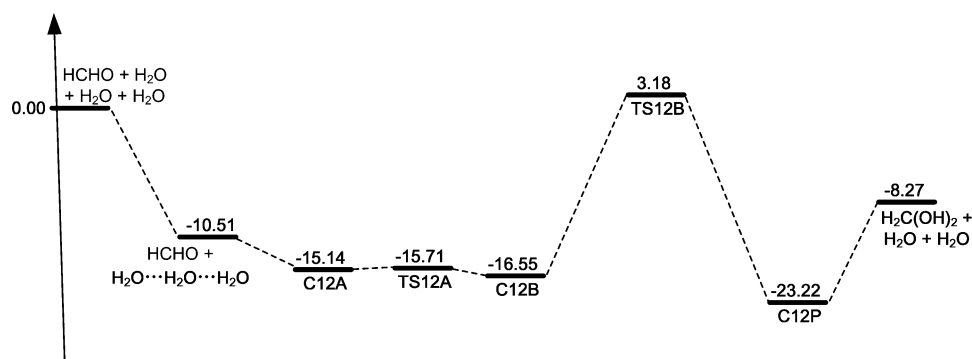
### 3.2. Hydrolysis of Formaldehyde Catalyzed Sulfuric Acid.

As for the hydrolysis of formaldehyde catalyzed by sulfuric acid, we take into account the reactions of C1 ( $\text{HCHO} \cdots \text{H}_2\text{O}$ ) with  $\text{H}_2\text{SO}_4$  and M2 with HCHO. The corresponding potential energy profile is listed in Figure 6. The M2 is an isomer of the formed M1 ( $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$ ) complex as shown in Figure 2. The binding energy of M1 ( $\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}$ ) complex is  $-10.64$  kcal/mol, which agrees well with the reported value<sup>89</sup> of  $-10.3$  kcal/mol at the CCSD(T)/CBS//B3LYP/cc-pv(T+d)Z level of theory. The complex M2 is formed by the transition state TSM1. The computed barrier is  $2.87$  kcal/mol with respect to M1. Table 2 tells us that the binding energy of M2 is higher than that of M1 by about  $1$  kcal/mol.

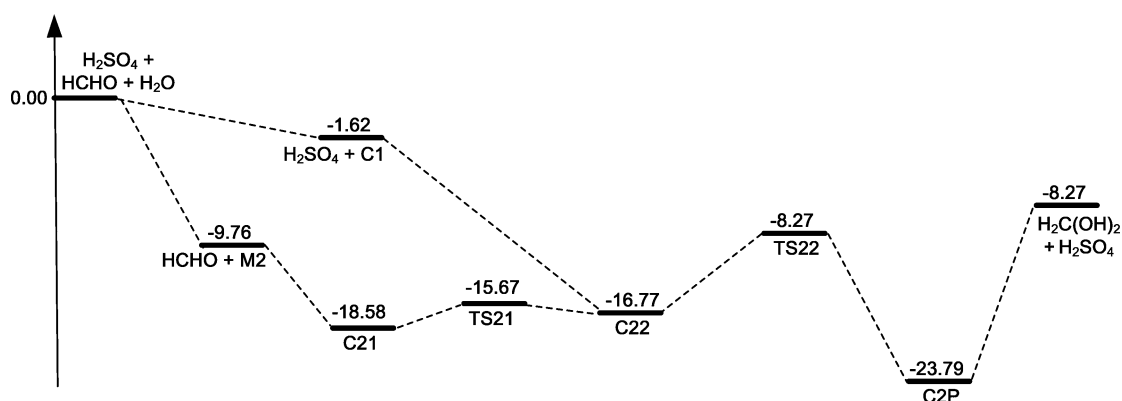
When the reactants are regarded as M2 and HCHO, the reaction starts with the formation of the complex C21 and undergoes the transition state TS21 responsible for the formation of C22. In complex C21, there are three hydrogen-bonded interactions and a van der Waals interaction with binding energy of  $-8.82$  kcal/mol. The complex C21 is transformed into its isomer C22 with the barrier of about  $2$  kcal/mol. However, as for the reactants C1 ( $\text{HCHO} \cdots \text{H}_2\text{O}$ ) with  $\text{H}_2\text{SO}_4$ , the reaction  $\text{H}_2\text{SO}_4 + \text{HCHO} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{H}_2\text{C}(\text{OH})_2$  proceeds through an eight-cyclic structure prereactive complex C22 and undergoes the corresponding transition state TS22 and postreactive complex C2P before the formation of the products  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{C}(\text{OH})_2$ , where the sulfuric acid is acted as a catalyst. In complex C22, two



**Figure 4.** Calculated potential energy profile for the HCHO reaction with water dimer at the CCSD(T)/aug-cc-pv(T+d)z//M06-2X/6-311++G-(3df,3pd) level of theory (in kcal/mol).



**Figure 5.** Calculated potential energy profile for formaldehyde reaction with water trimer at the CCSD(T)/aug-cc-pv(T+d)z//M06-2X/6-311++G(3df,3pd) level of theory (in kcal/mol).



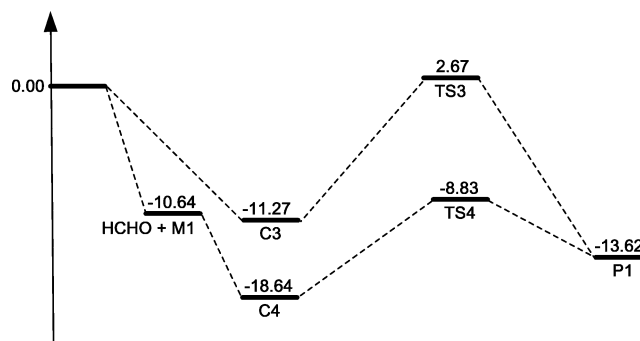
**Figure 6.** Calculated potential energy profile for hydrolysis of formaldehyde catalyzed by sulfuric acid at the CCSD(T)/aug-cc-pv(T+d)z//M06-2X/6-311++G(3df,3pd) level of theory (in kcal/mol).

hydrogen bonds  $O_a \cdots H_b O_c$  and  $O_d \cdots H_e O_f$  are calculated to be 1.537 and 1.928 Å, respectively, in Figure 2, reflecting that the hydrogen bond  $O_a \cdots H_b O_c$  is very strong because the  $O_a \cdots H_b O_c$  bond is shorter than the counterpart in complex<sup>49</sup>  $H_2SO_4$  with water. The tendency is also confirmed by the binding energy of  $-7.01$  kcal/mol as listed in Table 1 relative to the reactants  $M2 + HCHO$ . The corresponding transition state is a concerted mechanism that the hydrogen atom  $H_b$  of OH group in sulfuric acid is transferred to  $O_a$  in HCHO, the  $H_e$  atom is migrated to  $O_d$  in sulfuric acid, and simultaneously, the OH group in water is added to  $C_g$  in HCHO as characterized in TS22 of Figure 2. It is noted that the concerted mechanism of hydrolysis of formaldehyde in gas phase is different from that of the stepwise nucleophilic addition of water to carbonyl group<sup>103–105</sup> in aqueous phase. The calculated energy barrier is  $-1.49$  kcal/mol with respect to the corresponding reactants  $M2$  and HCHO. The unprecedented results show that the sulfuric acid exerts a strong catalytic effect on the hydration of HCHO because the barrier is about 32 kcal/mol lower than that of the reaction  $H_2O$  with HCHO.

The postcomplex C2P is formed by two hydrogen bonds  $O_a \cdots H_b O_c$  and  $O_e \cdots H_f O_g$ , where the  $O_e \cdots H_f O_g$  bond is very strong with the bond distance of 1.537 Å, while the  $O_a \cdots H_b O_c$  bond is a weak interaction with the bond length of 1.949 Å. The feature of the geometrical structure of C2P is demonstrated with the reported binding energy of  $-15.52$  kcal/mol relative to the free products sulfuric acid and  $H_2C(OH)_2$ .

The formaldehyde with sulfuric acid reaction takes place via the prereactive complex C3, transition state TS3, and product

P1 as shown in Figures 1 and 2. The calculated potential energy profile is described in Figure 7. The complex C3 in which there



**Figure 7.** Calculated potential energy profile for the reactions of HCHO with  $H_2SO_4$  and  $H_2SO_4 \cdots H_2O$  at the CCSD(T)/aug-cc-pv(T+d)z//M06-2X/6-311++G(3df,3pd) level of theory (in kcal/mol).

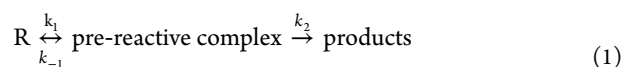
are two hydrogen bonds  $R_{O_a H_b} = 1.638$  Å and  $R_{O_d H_e} = 2.300$  Å are bound to be  $-11.27$  kcal/mol. The transition state TS3 occurs via a concerted mechanism that the  $H_b$  atom of OH group in sulfuric acid is transferred to the  $O_a$  atom of carbonyl group in HCHO, and simultaneously, the  $O_d$  atom in sulfuric acid is added to the  $C_e$  in HCHO. It is noted as well that energy height of TS3 is 2.67 kcal/mol, which indicates that the reaction is feasible in the atmospheric chemistry. The product P1 ( $H_2C(OH)OSO_3H$ ) is formed by the transition state TS3 with release energy of  $-13.62$  kcal/mol as in Table 2.

Table 3. Equilibrium Constant ( $K_{eq}$ , molecules  $\text{cm}^{-3}$ ) between  $\text{HCHO}\cdots\text{H}_2\text{O}$  Complex, the Free Reactants  $\text{H}_2\text{O}$  and  $\text{HCHO}$ , M1 ( $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$ ), M2 (anti- $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$ ) Complex, and Reactants  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , and the Total Rate Constant ( $k$ ,  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for the Individual Reaction Pathway with the Temperature Range 200–298 K

| reaction   | 200 K                  | 220 K                  | 240 K                  | 260 K                  | 280 K                  | 298 K                  |
|--|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| $K_{eq} (\text{HCHO}\cdots\text{H}_2\text{O})$                           | $3.62 \times 10^{-23}$ | $2.47 \times 10^{-23}$ | $1.83 \times 10^{-23}$ | $1.44 \times 10^{-23}$ | $1.18 \times 10^{-23}$ | $1.03 \times 10^{-23}$ |
| $K_{eq} \text{ M1 } (\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O})$     | $1.82 \times 10^{-14}$ | $1.45 \times 10^{-15}$ | $1.79 \times 10^{-16}$ | $3.06 \times 10^{-17}$ | $6.77 \times 10^{-18}$ | $2.08 \times 10^{-18}$ |
| $K_{eq} \text{ M2 (anti-}\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O})$ | $3.09 \times 10^{-15}$ | $3.18 \times 10^{-16}$ | $4.83 \times 10^{-17}$ | $9.85 \times 10^{-18}$ | $2.54 \times 10^{-18}$ | $8.81 \times 10^{-19}$ |
| $k_{\text{TS1}}$   | $6.96 \times 10^{-44}$ | $7.02 \times 10^{-43}$ | $8.35 \times 10^{-42}$ | $1.13 \times 10^{-40}$ | $1.70 \times 10^{-39}$ | $2.04 \times 10^{-38}$ |
| $k_{\text{TS11}}$  | $6.44 \times 10^{-32}$ | $3.04 \times 10^{-31}$ | $1.77 \times 10^{-30}$ | $1.05 \times 10^{-29}$ | $5.73 \times 10^{-29}$ | $2.34 \times 10^{-28}$ |
| $k_{\text{TS12}}$  | $1.31 \times 10^{-29}$ | $1.10 \times 10^{-26}$ | $7.51 \times 10^{-28}$ | $4.10 \times 10^{-27}$ | $1.82 \times 10^{-26}$ | $5.92 \times 10^{-26}$ |
| $k_{\text{TS2}} (\text{C1} + \text{H}_2\text{SO}_4)$                     | $2.49 \times 10^{-6}$  | $2.49 \times 10^{-7}$  | $3.66 \times 10^{-8}$  | $7.22 \times 10^{-9}$  | $1.79 \times 10^{-9}$  | $6.01 \times 10^{-10}$ |
| $k'_{\text{TS1}} (\text{M2} + \text{HCHO})$                              | $3.38 \times 10^{-13}$ | $1.43 \times 10^{-13}$ | $7.03 \times 10^{-14}$ | $3.87 \times 10^{-14}$ | $2.32 \times 10^{-14}$ | $1.56 \times 10^{-14}$ |
| $k_{\text{TS3}}$   | $3.96 \times 10^{-17}$ | $4.72 \times 10^{-17}$ | $5.89 \times 10^{-17}$ | $7.37 \times 10^{-17}$ | $9.22 \times 10^{-17}$ | $1.11 \times 10^{-16}$ |
| $k_{\text{TS4}}$   | $1.83 \times 10^{-17}$ | $2.27 \times 10^{-17}$ | $2.76 \times 10^{-17}$ | $3.28 \times 10^{-17}$ | $3.84 \times 10^{-17}$ | $4.36 \times 10^{-17}$ |

The single water molecule is added into the reaction  $\text{HCHO} + \text{H}_2\text{SO}_4$  as the water molecule is of great interest in the atmospheric chemistry, and the  $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$  complex is about 95% pure sulfuric acid. When the reaction of formaldehyde with sulfuric acid with the single water molecule is added, the single water molecule complexes with sulfuric acid to result in the formation of M1 ( $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$ ). The reaction proceeds via the prereactive complex C4 and the transition state TS4. The activated barrier is reported to be  $-1.81 \text{ kcal/mol}$  with respect to the reactants  $\text{HCHO}$  and M1, which is  $4.48 \text{ kcal/mol}$  lower than that of the bare reaction  $\text{HCHO} + \text{H}_2\text{SO}_4$ . The calculated prediction shows that the single water molecule can reduce the energy barrier of the  $\text{HCHO} + \text{H}_2\text{SO}_4$  reaction.

**3.3. Kinetics and Applications in Atmospheric Chemistry.** The rate coefficient is evaluated herein to judge whether the hydrolysis of formaldehyde catalyzed sulfuric acid and the reactions of  $\text{HCHO}$  with sulfuric acid and  $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$  complex could play an important role in the atmosphere. In terms of the theoretical results discussed above, the reactions begin with the formation of the pre-reactive complexes before the transition states, which can be characterized by eq 1. Assuming that the



prereactive complexes and the corresponding reactants are at equilibrium and according to the steady-state conditions, the rate constant is formulated as

$$k_1 = \frac{K_1}{K_{-1}} k_2 = K_{eq} k_2 \quad (2)$$

and  $K_{eq}$  and  $k_2$  are the equilibrium constant of the first step and the rate constant of the second step in the reactions, respectively. The computed data is shown in Table 3, and the detailed information is provided in Tables S2–S5, Supporting Information.

The kinetic data also demonstrates the conclusion that the reaction  $\text{HCHO} + \text{H}_2\text{O}$  is extremely minor in the gas phase because the rate constant is very low, about  $10^{-44}$ – $10^{-38} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with the temperature range 200–298 K. As for the sulfuric acid-catalyzed hydrolysis of formaldehyde, the reactions are regarded as  $\text{HCHO}\cdots\text{H}_2\text{O}$  complex and  $\text{H}_2\text{SO}_4$ . It is noted that the reported rate constant  $k_2$  of the hydrolysis of formaldehyde catalyzed by sulfuric acid is quite interesting, especially at low temperature. The concentrations<sup>43</sup> of formaldehyde and water at 50% relative humidity are about  $8.00 \times 10^{11}$  and  $3.97 \times 10^{17} \text{ molecules cm}^{-3}$ , respectively,

combined with the equilibrium constant of  $\text{HCHO}\cdots\text{H}_2\text{O}$  complex  $10^{-23} \text{ cm}^3 \text{ molecule}^{-1}$ . It is noted that the equilibrium constant of the complex C1 ( $\text{HCHO}\cdots\text{H}_2\text{O}$ ) is lower than that of the reported value<sup>43</sup> by about 1 order because the discussed complex C1 is not a global minima but a local minima relative to the reaction coordinate. The concentration of  $\text{HCHO}\cdots\text{H}_2\text{O}$  complex is about  $10^{-4}$  times lower than that of the pure  $\text{HCHO}$ . However, the rate constant of  $\text{HCHO}\cdots\text{H}_2\text{O}$  complex with sulfuric acid is  $10^5$  higher than the rate constant<sup>106</sup> of  $\text{HCHO}$  with  $\text{OH}$  by about  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  with the temperature range 200–220 K. When the reactants are M2 ( $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$ ) and  $\text{HCHO}$ , the calculated rate constant  $k'_2$  is in the range of  $3.38 \times 10^{-13}$  to  $3.87 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at the temperature 200–260 K. M2 (anti- $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$ ) can be formed from M1 ( $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$ ) through TSM1. From Table 3, it is suggested that about 17–40% M1 ( $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$ ) is transferred to M2 (anti- $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$ ) from the calculated equilibrium constant. It is also noted that the equilibrium constant of M1 ( $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$ ) is less than that of the reported value<sup>89,107</sup> in the literature by several times because the binding Gibbs free energy  $\Delta G_{298} = -2.33 \text{ kcal/mol}$  is higher than the corresponding value of  $-2.72 \text{ kcal/mol}$ .<sup>89</sup> Although the sulfuric acid can form successive hydrates<sup>108,109</sup> and its tri- and tetrahydrates are of great importance at altitude below 10 km, the concentration of M1 is about 30% of the pure sulfuric acid at altitudes of 15 km. However, the concentration<sup>110</sup> of sulfuric acid is higher than that of  $\text{OH}$  in some areas. Furthermore, the rate constant of  $\text{M2} + \text{HCHO}$  reaction is  $10^{-1}$  lower than that of  $\text{HCHO} + \text{OH}$ . Therefore, the process of the sulfuric acid catalyzed  $\text{H}_2\text{O} + \text{HCHO}$  could play a critical role in the sink of  $\text{HCHO}$  at low temperature. As for the reactions  $\text{HCHO} + \text{H}_2\text{SO}_4$  and  $\text{HCHO} + \text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$ , the rate constants are quite slow, which is minor in the atmosphere.

## 4. CONCLUSIONS

The gas-phase hydrolysis of formaldehyde catalyzed by water, water dimer, and sulfuric acid and the  $\text{HCHO}$  reaction with  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$  complexes are theoretically investigated using the quantum chemical methods and the canonical transition state theory, which results in the following conclusions. (1) The sulfuric acid exerts a strong catalytic role in the gas-phase hydrolysis of formaldehyde relative to atmospheric chemistry, which makes the reaction of gas-phase hydrolysis of formaldehyde occur at a faster rate at lower temperature. The process could compete well with the reaction  $\text{HCHO} + \text{OH}$  under certain atmospheric conditions. (2) Although the reaction of  $\text{H}_2\text{SO}_4$  with  $\text{HCHO}$  is calculated with

a lower energy barrier of 2.67 kcal/mol related to the free reactants, the elementary process is of no importance from the kinetic point of view in atmospheric chemistry. (3) The important conclusions mentioned above should not only give insight into the new mechanism of gas-phase hydrolysis of formaldehyde and catalytic role of sulfuric acid in previously forbidden reaction but it is also likely to be a important channel for hydrolysis of carbonyl groups in gas-phase atmospheric chemistry.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Tables S1–S6 listing the  $T_1$  diagnostic value, the total energies of the stationary points, the detailed information of rate constant, and Cartesian coordinates of the optimized geometries. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [longbo@gzmu.edu.cn](mailto:longbo@gzmu.edu.cn) (B.L.); [wjzhang@aiofm.ac.cn](mailto:wjzhang@aiofm.ac.cn) (W.-J.Z.).

### Notes

The authors declare no competing financial interest.

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