

Sulfuric Acid as Autocatalyst in the Formation of Sulfuric Acid

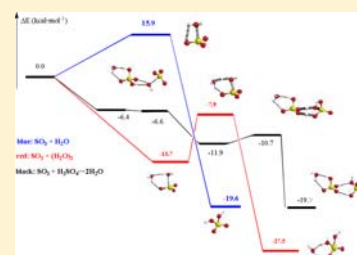
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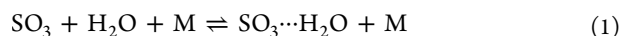
S Supporting Information

ABSTRACT: Sulfuric acid can act as a catalyst of its own formation. We have carried out a computational investigation on the gas-phase formation of H₂SO₄ by hydrolysis of SO₃ involving one and two water molecules, and also in the presence of sulfuric acid and its complexes with one and two water molecules. The hydrolysis of SO₃ requires the concurrence of two water molecules, one of them acting as a catalyzer, and our results predict an important catalytic effect, ranging between 3 and 11 kcal·mol⁻¹ when the catalytic water molecule is substituted by a sulfuric acid molecule or one of its hydrates. In these cases, the reaction products are either bare sulfuric acid dimer or sulfuric acid dimer complexed with a water molecule. There are broad implications from these new findings. The results of the present investigation show that the catalytic effect of sulfuric acid in the SO₃ hydrolysis can be important in the Earth's stratosphere, in the heterogeneous formation of sulfuric acid and in the formation of aerosols, in H₂SO₄ formation by aircraft engines, and also in understanding the formation of sulfuric acid in the atmosphere of Venus.



1. INTRODUCTION

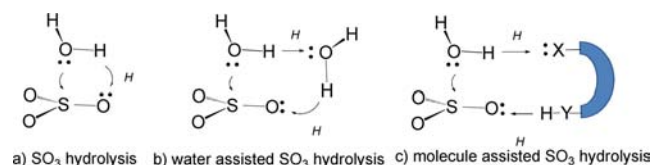
Sulfuric acid has become of renewed interest in the past few years because of its importance in the chemistry of the atmosphere. It contributes to acid rain^{1–3} and to atmospheric nucleation processes,^{4–9} which consequently have a great impact on the environment, on human health, and in climate change. The formation of sulfuric acid, and in particular its atmospheric formation, has received much attention from both experimental^{10–17} and theoretical groups.^{18–24} The atmospheric formation of sulfuric acid occurs following two main steps. The first step corresponds to gas-phase oxidation of SO₂ to SO₃, which can be done involving hydroxyl radical and molecular oxygen²⁵ or other species like carbonyl oxides.²⁶ The second step corresponds to hydrolysis of SO₃ to produce sulfuric acid. Regarding the reaction of SO₃ with water vapor, Castleman and co-workers^{10,11} proposed that sulfur trioxide first forms a complex with one water molecule and this adduct rearranges to form H₂SO₄ via reactions 1 and 2. The mechanism involves addition of the oxygen atom of water to the sulfur atom of SO₃ and simultaneous transfer of one hydrogen atom of water to one oxygen atom of sulfur trioxide, as shown in Scheme 1a.



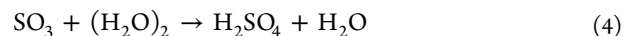
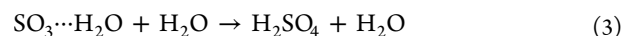
However, Hofmann and Schleyer¹⁸ and Morokuma and Muguruma¹⁹ showed that the process involving a single water molecule does not occur because the corresponding transition structure has a very high energy barrier.

Later studies from the literature showed that, in order for the reaction to be feasible, the participation of a second water molecule is required.^{15,19} Both experimental and theoretical results,

Scheme 1. Pictorial Representation of (a) Gas-Phase Hydrolysis of SO₃, (b) Water-Assisted Gas-Phase Hydrolysis of SO₃, and (c) Molecule-Assisted Gas-Phase Hydrolysis of SO₃



consistent with reactions 3 and 4, suggest that either SO₃ first forms a complex with a water molecule and then reacts with a second water molecule or SO₃ reacts with a water dimer, in both cases forming sulfuric acid plus water.¹⁶



Morokuma and Muguruma¹⁹ first pointed out the importance of a second water molecule by studying reaction 4 and showed that the participation of two water molecules makes the energy barrier almost negligible. Later studies also showed that the presence of additional water molecules further reduces the energy barrier.^{21,22,24,27} In fact, the second water molecule acts as a catalyst, making a bridge in the hydrogen transfer from water to SO₃. This process is depicted in Scheme 1b, which shows that the hydrogen atom of the water being added to sulfur trioxide is transferred to the second water molecule and,

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Table 1. Entropies, Relative Energies, Energies plus ZPE, Enthalpies, and Free Energies Calculated for Formation of the Water Complexes (H₂O)₂ and SO₃⋯H₂O (Reactions 5 and 6)^a

compd	method ^b	S, eu	ΔE, kcal·mol ⁻¹	Δ(E + ZPE), kcal·mol ⁻¹	ΔH(298), kcal·mol ⁻¹	ΔG(298), kcal·mol ⁻¹
H ₂ O + H ₂ O → (H ₂ O) ₂						
H ₂ O + H ₂ O	A, B	90.2	0.0	0.0	0.0	0.0
(H ₂ O) ₂	A	70.6	-5.9	-3.8	-4.2	1.6
(H ₂ O) ₂	B	70.6	-5.0	-2.9	-3.3	2.5
SO ₃ + H ₂ O → SO ₃ ⋯H ₂ O						
SO ₃ + H ₂ O	A, B	106.4	0.0	0.0	0.0	0.0
SO ₃ ⋯H ₂ O	A	79.7	-9.9	-7.7	-8.2	-0.2
SO ₃ ⋯H ₂ O	B	79.7	-9.8	-7.6	-8.1	-0.1

^aZPE, S, and enthalpic and entropic corrections correspond to calculations at the B3LYP/cc-pV(T+d)Z level of theory. ^bMethod A stands for CCSD(T)/cc-pV(T+d)Z//B3LYP/cc-pV(T+d)Z; method B stands for CCSD(T)/CBS//B3LYP/cc-pV(T+d)Z. The CBS extrapolation has been done over single-point energy calculations at CCSD(T)/aug-cc-pV(T+d)Z and CCSD(T)/aug-cc-pV(Q+d)Z levels of theory.

simultaneously, one hydrogen atom of the second water molecule is transferred to one oxygen atom of SO₃.

Knowledge of the role played by the second water in the gas-phase hydrolysis of SO₃ molecule has led to new studies investigating whether other atmospheric molecules can play the same role. Thus, for instance, Gonzalez et al.²⁸ showed that hydroperoxyl radical significantly reduces the energy barrier of the SO₃ hydrolysis, whereas Hazra and Sinha²⁹ and Long et al.³⁰ reported that formic acid plays the same role. These two species, hydroperoxyl radical and formic acid, act in the same way as the second water molecule described above; namely, they borrow one hydrogen atom of the water to be added to SO₃ and, simultaneously, they transfer one hydrogen atom to one oxygen atom of SO₃, as shown in Scheme 1c, so that they act as a catalyst in the gas-phase SO₃ hydrolysis. These reported results^{28–30} also suggest that “other atmospheric molecules” are, from an energetic point of view, even more effective than the “second” water molecule that was needed to make the process feasible.

In the present work we investigate the effect of sulfuric acid acting as a catalyst in the hydrolysis of SO₃. In other words, we address the question of whether and how sulfuric acid catalyzes its own formation. Recently, it has been shown in the literature that, in the atmosphere, sulfuric acid form complexes with several water molecules and the atmospheric concentration of such complexes depends on the relative humidity.^{31,32} Therefore, in the present work, we consider the formation of sulfuric acid catalyzed by sulfuric acid itself, by sulfuric acid complexes with one water molecule, and by sulfuric acid forming a complex with two water molecules. In all cases, the processes correspond to that described in Scheme 1c and the reaction product is either a sulfuric acid dimer or a sulfuric acid dimer forming a complex with one water molecule. For completeness we have also investigated the hydrolysis of SO₃ and the equilibrium constants of water dimer and four sulfuric acid hydrates at different altitudes of the Earth and Venus atmospheres.

2. METHODS

All quantum chemistry calculations reported in this work have been carried out with the Gaussian 03 program package.³³ We have used the hybrid density functional B3LYP method³⁴ with the cc-p-V(T+d)Z basis set^{35,36} to optimize and characterize all stationary points investigated in this work. At this level of theory we have also calculated the harmonic vibrational frequencies to verify the nature of the corresponding stationary points (minima or transition state), to provide the zero-point vibrational energy (ZPE) and the thermodynamic contributions to the enthalpy and free energy. Moreover, to ensure that the transition states connect to the desired reactants and products, we have performed intrinsic reaction coordinate calculations (IRC).^{37–39}

With the aim to get more accurate relative energies, we have performed single-point CCSD(T)^{40–43} calculations at the optimized geometries using the cc-pV(T+d)Z basis set.^{35,36} In order to check the reliability of single-determinant-based methods, we have looked at spin eigenvalue of the unrestricted Hartree–Fock wave function (before and after annihilation) and at the T1 diagnostic⁴⁴ of the CCSD wave function with regard to the multireference character of the wave function. The reliability of the theoretical approach employed has been also checked by doing additional single-point CCSD(T) calculations at the optimized geometries of reactions 3 and 4, using the aug-cc-pV(T+d)Z, aug-cc-pV(Q+d)Z^{35,36} and considering the extrapolation to the complete basis set limit (CBS) according to the extrapolation scheme by Helgaker et al.⁴⁵ Details of the geometrical parameters of the stationary points investigated, complementary potential energy surfaces, equilibrium constants, rate constants, absolute energies, and Cartesian coordinates of all stationary points investigated are reported as Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Reaction between SO₃ and Water. The reaction between SO₃ and water has been extensively investigated, and our results agree qualitatively with those previously reported in the literature.^{19–22,24,27} Therefore, we will discuss only the main trends regarding the reaction involving two water molecules. We have considered the reaction of SO₃⋯H₂O complex with H₂O, and the reaction of SO₃ with (H₂O)₂ (reactions 3 and 4), both leading to the formation of H₂SO₄ + H₂O. The reaction of sulfur trioxide with a single water molecule is reported in the Supporting Information. Prior to the study of these reactions, we calculated the stability of water dimer and SO₃⋯H₂O complex (reactions 5 and 6), and the corresponding results are displayed in Table 1. These calculations allow us to check the reliability of our results, to calculate its equilibrium constants, and consequently to estimate the concentration of these complexes in the atmosphere of either Earth or Venus; these complexes in turn are the reactants of the reactions investigated.



The results displayed in Table 1 show that, at our best level of theory, the binding energy of water dimer is computed to be 2.9 kcal·mol⁻¹. This is in good agreement with the experimental *D*₀ value of 3.15 ± 0.03 kcal·mol⁻¹ obtained by velocity map imaging.⁴⁶ Our computed binding enthalpy (3.3 kcal·mol⁻¹) also compares very well with the Δ*H*⁰ of 3.59 ± 0.50 kcal·mol⁻¹ obtained by increase in thermal conductivity at *T* = 358–386 K;⁴⁷ Δ*H*⁰ values of 3.98 ± 0.90 and 3.58 ± 0.72 kcal·mol⁻¹ obtained by measurements of integrated IR absorption at

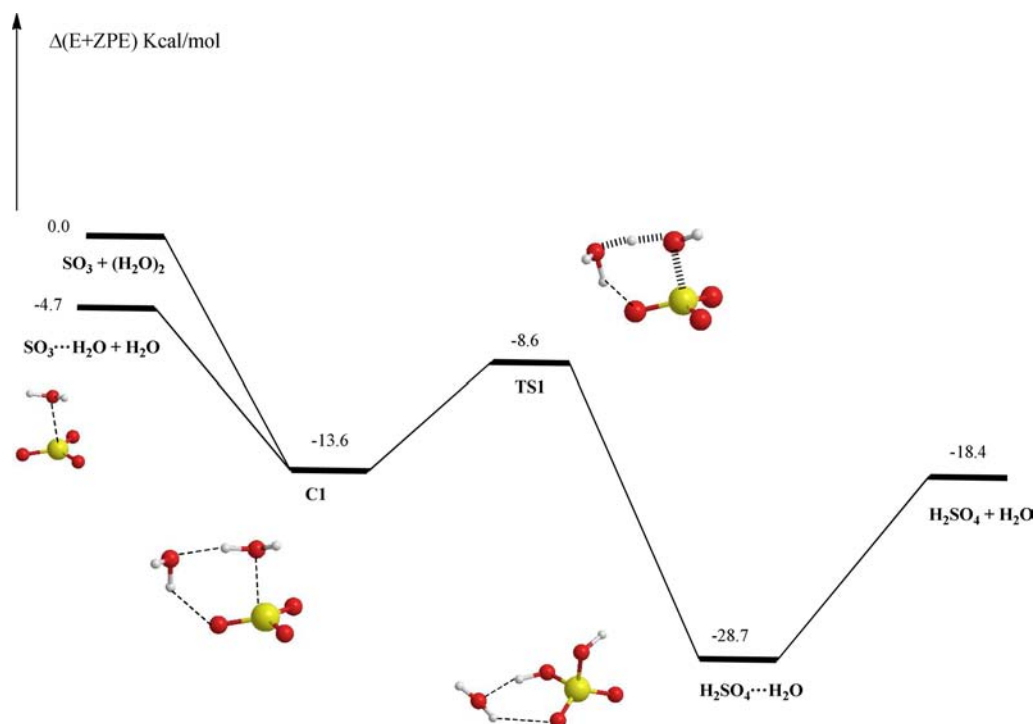


Figure 1. Schematic potential energy surface for the hydrolysis of SO_3 (reactions 3 and 4).

$T = 573\text{--}723$ K and $373\text{--}673$ K, respectively;^{48,49} or ΔH° of 3.24 ± 0.95 kcal·mol⁻¹ obtained by pressure broadening.⁵⁰ Our computed value agrees with theoretical estimates of binding energy reported in the literature (in kilocalories per mol): 3.30,⁵¹ 3.01–3.12;⁵² 2.99–3.15;⁵³ and 2.86⁵⁴. All these results let us to conclude an error bar of 0.3 kcal·mol⁻¹ for our computed value of the binding energy.

For the $\text{SO}_3\cdots\text{H}_2\text{O}$ complex we have computed a binding energy of 7.6 kcal·mol⁻¹, which is in very good agreement with 7.4 and 7.7 kcal·mol⁻¹ theoretical results reported by Standard et al.⁵⁵ and by Fliegl et al.,²³ respectively, from the literature. Fliegl et al.²³ estimated an error bar of 0.5 kcal·mol⁻¹ based on geometry relaxation effects, basis set corrections, and relativistic effects, whereas experimentally, an upper limit in the bond enthalpy of 13 kcal·mol⁻¹ for the bonding enthalpy has been reported.¹⁷

At room temperature, the computed equilibrium constants for $(\text{H}_2\text{O})_2$ and $\text{SO}_3\cdots\text{H}_2\text{O}$ are 2.34×10^{-21} and 1.01×10^{-19} cm³·molecule⁻¹, respectively. When a water concentration of 7.64×10^{17} molecules·cm⁻³ is considered (that corresponds to 100% relative humidity at 298 K), the atmospheric concentration of water dimer is predicted to be 1.35×10^{15} molecule·cm⁻³, in good agreement with 1.01×10^{15} to 1.22×10^{15} molecules·cm⁻³ experimental estimates derived from the reported equilibrium constants^{56–58} and with 9×10^{14} molecules·cm⁻³ theoretical results.⁵² Our calculations also predict that 7.7% of SO_3 forms a complex with one water molecule. These results assert the importance of these complexes as reactants in the atmospheric gas-phase formation of sulfuric acid. Equilibrium constants for these complexes computed at different temperatures are found in the Supporting Information.

Figure 1 shows the schematic potential energy surface for reactions 3 and 4, and Table 2 contains their energetic results. Our CCSD(T)/CBS calculations indicate that, at 0 K, $\text{SO}_3\cdots\text{H}_2\text{O} + \text{H}_2\text{O}$ is more stable than $\text{SO}_3 + (\text{H}_2\text{O})_2$ by 4.7 kcal·mol⁻¹. Both entry channels lead to the formation of a common prereactive

complex C1, before the transition state TS1 and the formation of sulfuric acid forming a complex with a water molecule. Table 2 shows that C1 has a binding energy of 13.6 kcal·mol⁻¹ relative to the $\text{SO}_3 + (\text{H}_2\text{O})_2$ entry channel but 8.9 kcal·mol⁻¹ relative to the $\text{SO}_3\cdots\text{H}_2\text{O} + \text{H}_2\text{O}$ entry channel. TS1 lies below the two sets of reactants (by -8.6 and -3.9 kcal·mol⁻¹, respectively), which implies that both reactions are barrierless with respect to the reactants.

The formation of $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$ is computed to be exothermic by 28.7 kcal·mol⁻¹, relative to the $\text{SO}_3 + (\text{H}_2\text{O})_2$ entry channel. In order to check the reliability of these results, we have also performed geometry optimizations at the QCISD/cc-pV(T+d)Z level of theory and single-point energy calculations with the optimized geometries at the CCSD(T) level using the same basis set. The results, displayed in footnote *b* of Table 2, differ by less than 0.5 kcal·mol⁻¹ from those obtained at the CCSD(T)/B3LYP level using the same basis set, which gives us confidence in the accuracy of the B3LYP geometries. Table 2 also shows that the computed energy values obtained at the CCSD(T)/cc-pV(T+d)Z level differ between 0.3 and 2.4 kcal·mol⁻¹ with respect to the more accurate results [obtained at CCSD(T)/CBS level], with the computed energy barrier being only 0.8 kcal·mol⁻¹ higher. Our results compare qualitatively with other theoretical data from the literature, with differences around 6 kcal·mol⁻¹ in the relative stability of C1 complex and the energy barrier as well.^{22,27} This reflects the importance of employing high-level calculations with a flexible enough basis set, as already suggested by Morokuma and Muguruma.¹⁹

Finally, analysis of the potential energy surface (Figure 1) and the fact that the two entry channels share the same pre-reactive complex (C1) opens the possibility of a new reaction, which is the interchange between the two reactant channels, namely, $\text{SO}_3 + (\text{H}_2\text{O})_2$ and $\text{SO}_3\cdots\text{H}_2\text{O} + \text{H}_2\text{O}$. According to the free energy values displayed in Table 2, TS1 lies above the free energies of the two entry channels by 4.2 and 6.0 kcal·mol⁻¹,

Table 2. Entropies, Relative Energies, Energies plus ZPE, Enthalpies, and Free Energies Calculated for Reactions 3 and 4

compd	method ^a	S, eu	$\Delta E,^b$ kcal·mol ⁻¹	$\Delta(E + ZPE)$, kcal·mol ⁻¹	$\Delta H(298)$, kcal·mol ⁻¹	$\Delta G(298)$, kcal·mol ⁻¹
SO ₃ + (H ₂ O) ₂	A	132.0	0.0	0.0	0.0	0.0
SO ₃ + (H ₂ O) ₂	B		0.0	0.0	0.0	0.0
SO ₃ ⋯H ₂ O + H ₂ O	A	124.7	-4.0	-3.8	-3.9	-1.8
SO ₃ ⋯H ₂ O + H ₂ O	B		-4.8	-4.7	-4.7	-2.6
C1	A	90.2	-17.0	-13.7	-14.9	-2.5
C1	B		-16.8	-13.6	-14.8	-2.3
TS1	A	80.4	-9.6	-7.9	-10.4	5.0
TS1	B		-10.4	-8.6	-11.1	4.2
H ₂ SO ₄ ⋯H ₂ O	A	86.6	-31.2	-27.5	-29.1	-15.6
H ₂ SO ₄ ⋯H ₂ O	B		-32.4	-28.7	-30.3	-16.8
H ₂ SO ₄ + H ₂ O	A	116.1	-17.2	-15.8	-16.8	-12.0
H ₂ SO ₄ + H ₂ O	B		-19.8	-18.4	-19.3	-14.9

^aMethod A stands for energies computed at the CCSD(T)/cc-pV(T+d)Z//B3LYP/cc-pV(T+d)Z level of theory, and method B stands for relative energies computed at the CCSD(T)/CBS//B3LYP/cc-pV(T+d)Z level of theory. In both cases, ZPE, S, and enthalpic and entropic corrections correspond to calculations at the B3LYP/cc-pV(T+d)Z level of theory. ^bFor comparison, relative energies computed at the CCSD(T)/cc-pV(T+d)Z//QCISD/cc-pV(T+d)Z level of theory are -4.1 kcal·mol⁻¹ for SO₃⋯H₂O + H₂O; -17.3 kcal·mol⁻¹ for C1; -10.1 kcal·mol⁻¹ for TS1; -31.4 kcal·mol⁻¹ for H₂SO₄⋯H₂O; and -17.4 kcal·mol⁻¹ for H₂SO₄ + H₂O.

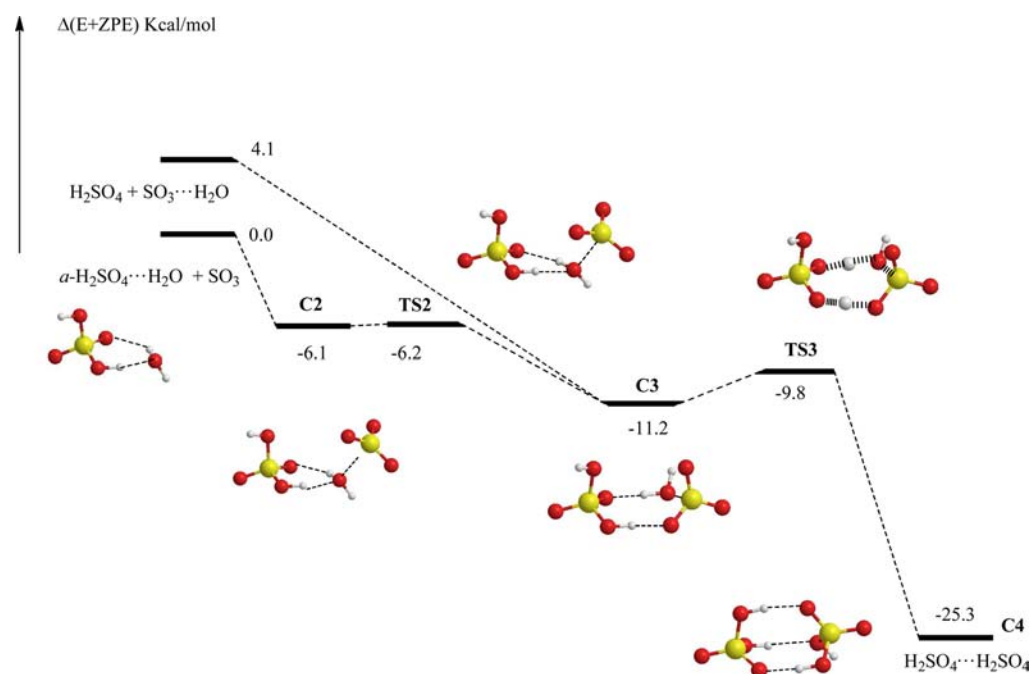


Figure 2. Schematic potential energy surface for reactions 7 and 8.

which makes the interchange between the two entry channels very plausible.

3.2. Sulfuric Acid as Catalyst. The role of sulfuric acid acting as a catalyst to its own formation has not been taken into account in the literature to date, and it is considered in the present work by examining reactions 7–10. The reaction products are sulfuric acid dimer (reactions 7 and 8) or sulfuric acid dimer forming a complex with a water molecule (reactions 9 and 10):

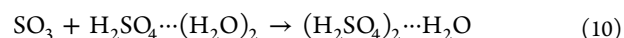
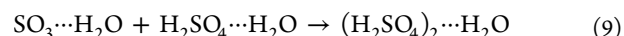
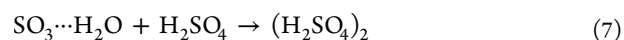


Figure 2 shows that reactions 7 and 8 share the same potential energy surface, and the corresponding energy values are contained in Table 3. In fact, there is an equivalent potential energy surface to that of Figure 2 that differentiates the orientation of the dangling hydrogen atom in all structures (minima and transition states).

Table 3. Entropies, Relative Energies, Energies plus ZPE, Enthalpies, and Free Energies Calculated for Reactions 7 and 8^a

compd	S, eu	ΔE , kcal·mol ⁻¹	$\Delta(E + ZPE)$, kcal·mol ⁻¹	$\Delta H(298)$, kcal·mol ⁻¹	$\Delta G(298)$, kcal·mol ⁻¹
<i>anti</i> -H ₂ SO ₄ ···H ₂ O + SO ₃	147.7	0.0	0.0	0.0	0.0
SO ₃ ···H ₂ O + H ₂ SO ₄	152.0	4.1	4.1	4.3	3.0
C2	120.4	-7.2	-6.1	-5.8	2.4
TS2	113.3	-7.1	-6.2	-6.3	3.9
C3	111.4	-13.1	-11.2	-11.5	-0.6
TS3	103.0	-7.8	-9.8	-11.0	2.3
C4	103.3	-28.0	-25.3	-26.2	-13.0
2H ₂ SO ₄	144.4	-9.1	-7.9	-8.6	28.0
<i>syn</i> -H ₂ SO ₄ ···H ₂ O + SO ₃	148.0	0.0	0.0	0.0	0.0
C2a	120.8	-6.9	-5.7	-5.4	2.8
TS2a	114.1	-6.4	-5.5	-5.6	4.5
C3a	110.6	-13.1	-11.2	-11.6	-0.4
TS3a	102.6	-8.1	-10.0	-11.3	2.3
C4a	103.3	-28.0	-25.3	-26.3	-12.9

^aEnergies were computed at the CCSD(T)/cc-pV(T+d)Z//B3LYP/cc-pV(T+d)Z level of theory. ZPE, S, and enthalpic and entropic corrections correspond to calculations at the B3LYP/cc-pV(T+d)Z level of theory.

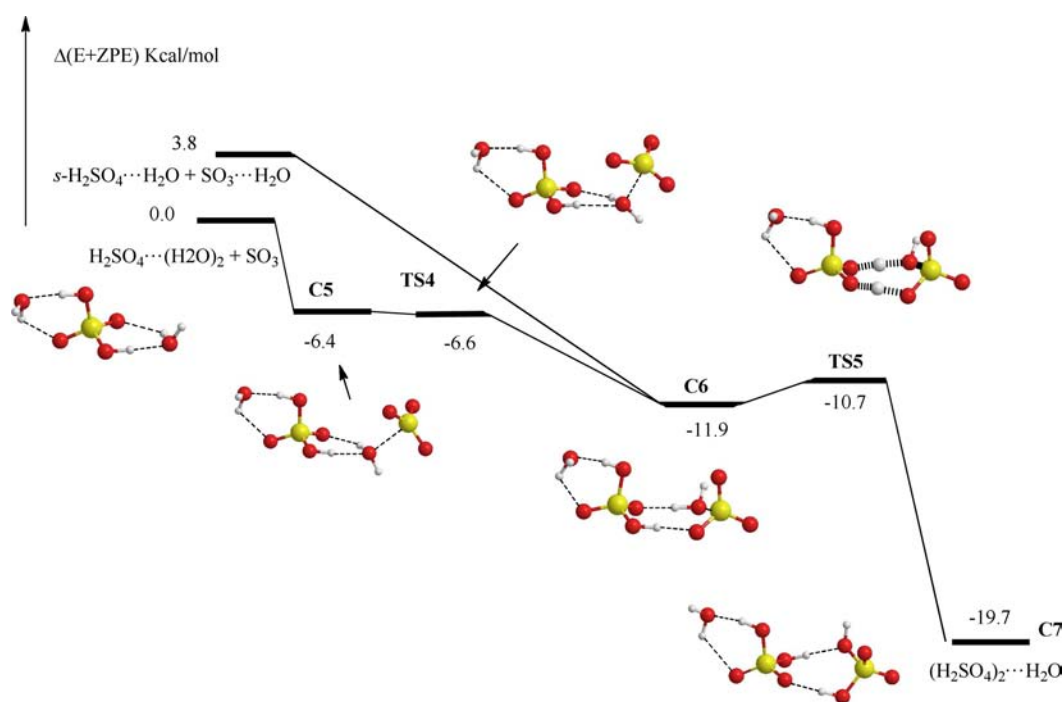


Figure 3. Schematic potential energy surface for reactions 9 and 10.

The stationary points are named with the same acronym as those of Figure 2 but appending the letter a. The corresponding potential energy surface is displayed in Figure S4 of the Supporting Information, while the energetic values are also contained in Table 3. Since both potential energy surfaces run parallel to each other energetically, we will restrict the discussion to the surface displayed in Figure 2.

Starting with the H₂SO₄ + SO₃···H₂O entry channel, the reaction proceeds with formation of the C3 complex, with a computed binding energy of 15.3 kcal·mol⁻¹. This is a three-body complex, which is held together by two hydrogen bonds and one van der Waals interaction. The first hydrogen bond is formed between one oxygen atom of sulfuric acid and one hydrogen atom of water, the second hydrogen bond is formed between one hydrogen atom of the H₂SO₄ moiety and one oxygen atom of SO₃ moiety, whereas the van der Waals interaction takes

place between the oxygen atom of water and the sulfur atom of SO₃. Please note that the last interaction already occurs on one of the reactants. The reaction goes on to the formation of sulfuric acid dimer (C4) through TS3, in which, simultaneously, the hydrogen atom of water moves to the sulfuric acid moiety, the oxygen atom of water adds to the sulfur atom of the SO₃ moiety, and one hydrogen atom from the sulfuric acid is transferred to one oxygen atom of the SO₃ moiety. The geometric features of TS3 (see Figure 2 and Supporting Information) show clearly how sulfuric acid assists SO₃ hydrolysis according to Scheme 1c discussed above.

Figure 2 and Table 3 show that TS3 lies only 1.4 kcal·mol⁻¹ above C3 and 13.9 kcal·mol⁻¹ below H₂SO₄ + SO₃···H₂O reactants. Comparing these results with those of reaction 3 discussed above, (where TS1 lies 5.0 kcal·mol⁻¹ above C1 and 3.9 kcal·mol⁻¹ below SO₃···H₂O + H₂O; see Figure 1 and Table 2),

Table 4. Entropies, Relative Energies, Energies plus ZPE, Enthalpies, and Free Energies Calculated for Reactions 9 and 10^a

compd	S, eu	ΔE , kcal·mol ⁻¹	$\Delta(E + \text{ZPE})$, kcal·mol ⁻¹	$\Delta H(298)$, kcal·mol ⁻¹	$\Delta G(298)$, kcal·mol ⁻¹
H ₂ SO ₄ ··(H ₂ O) ₂ + SO ₃	160.5	0.0	0.0	0.0	0.0
<i>syn</i> -H ₂ SO ₄ ··H ₂ O + SO ₃ ··H ₂ O	166.5	4.0	3.8	4.0	2.2
C5	134.9	-7.3	-6.4	-6.0	1.6
TS4	128.3	-7.3	-6.6	-6.6	3.0
C6	126.0	-13.6	-11.9	-12.2	-1.9
TSS	120.2	-8.6	-10.7	-11.8	0.2
C7	124.6	-21.7	-19.7	-20.2	-9.5
<i>anti</i> -H ₂ SO ₄ ··H ₂ O + SO ₃ ··H ₂ O	166.3	4.0	3.8	4.0	2.2
C5a	134.6	-7.3	-6.3	-5.9	1.8
TS4a	128.7	-7.0	-6.2	-6.3	3.1
C6a	125.2	-13.6	-11.9	-12.2	-1.7
TSSa	119.5	-8.7	-10.8	-12.0	0.3
C7a	123.4	-23.2	-21.2	-21.7	-10.6

^aEnergies were computed at the CCSD(T)/cc-pV(T+d)Z//B3LYP/cc-pV(T+d)Z level of theory. ZPE, S, and enthalpic and entropic corrections correspond to calculations at the B3LYP/cc-pV(T+d)Z level of theory.

we observe an additional and very important catalytic effect (close to 10 kcal·mol⁻¹) as a result of substituting the catalytic water molecule as reactant in reaction 3 by a sulfuric acid molecule as reactant in reaction 7. A similar stabilization has been reported in the literature as a result of substituting the catalytic water molecule by hydroperoxyl radical or formic acid.^{28–30}

Starting with SO₃ + H₂SO₄··H₂O reactants, the reaction proceeds to the formation of prereactive complex C2 and transition state TS2 before the formation of complex C3 and its subsequent conversion to sulfuric acid dimer already discussed. Figure 2 and Table 3 show that C2 has a binding energy of 6.1 kcal·mol⁻¹. In this complex, the SO₃ reactant forms a van der Waals interaction with the oxygen atom of the water moiety in the H₂SO₄··H₂O reactant and, almost without an energy barrier, this complex is rearranged to C3 through TS2 setting free 5.1 kcal·mol⁻¹ (the energy difference between C3 and C2). Along this process, the hydrogen bond between the hydrogen atom of sulfuric acid and the oxygen atom of water in C2 is replaced by the hydrogen bond between the hydrogen atom of sulfuric acid and the oxygen atom of SO₃ in C3, a replacement that is necessary in order for the reaction to proceed to the formation of sulfuric acid dimer through TS3.

Reactions 9 and 10 share also the same potential energy surface, as shown in Figure 3. Indeed, reactions 9 and 10 have exactly the same features as those for reactions 7 and 8 just discussed. The only difference is in the fact that the last reactions have an additional water molecule forming two hydrogen bonds with the sulfuric acid molecule acting as a catalyst, although this additional water molecule does not participate in the reactions. The discussion carried out for reactions 7 and 8 is thus also valid for reactions 9 and 10. Thus, the sequence of steps H₂SO₄··H₂O + SO₃··H₂O → C6 → TSS → C7 (reaction 9, Figure 3), has exactly the same features as the sequence H₂SO₄ + SO₃··H₂O → C3 → TS3 → C4 described for reaction 7. Likewise, the sequence H₂SO₄··(H₂O)₂ + SO₃ → C5 → TS4 → C6 (reaction 10; after C6 the reaction goes on as reaction 9, see Figure 3) has exactly the same features as reaction 8 (H₂SO₄··H₂O + SO₃ → C2 → TS2 → C3). Even the relative energies of both sets of reactions are very similar, with differences in the corresponding stationary points being smaller than 0.9 kcal·mol⁻¹. Only the sulfuric acid dimer (C4) is much more stable than the sulfuric acid dimer forming a complex with a single water molecule (C7), because the

former is stabilized by three hydrogen bonds and the latter by two (see the structures in Figures 2 and 3 and in the Supporting Information).

Furthermore, there is also an equivalent potential energy surface to that of Figure 3 that differentiates in the orientation of the dangling hydrogen atom in all structures (minima and transition states). The corresponding potential energy surface is displayed in Figure S6 of the Supporting Information, while the energetic values are contained in Table 4.

Finally, the facts that (a) the mono- and dihydrates of sulfuric acid can contribute to the formation of sulfuric acid with a very similar catalytic effect and (b) both reaction mechanisms have the same electronic and geometric features, clearly suggests that higher hydrates of H₂SO₄ may have a very similar effect on the SO₃ hydrolysis.

3.3. H₂SO₄··(H₂O)_n, n = 1–4 Hydrates. The existence of several hydrates of sulfuric acid has been reported in the literature,^{31,32,59–72} and it has been shown that the atmospheric abundance of these hydrates strongly depends on atmospheric conditions like temperature and relative humidity.^{31,32} We refer to these studies for a detailed discussion on these complexes and on their atmospheric implications.

In the present investigation, and for completeness, we have also investigated the formation of hydrates of sulfuric acid up to four water molecules, in a similar way as reported by Kurten et al.³¹ Figure 4 displays the most relevant geometrical parameters, and Table 5 contains the computed relative energies. The optimized geometries were obtained at the B3LYP/aug-cc-pVTZ level of theory and the final energies were computed at CCSD(T)/aug-cc-pV(T+d)Z level of theory. For the monohydrates we have also performed calculations at the CCSD(T)/aug-cc-pV(Q+d)Z level of theory and we have considered the extrapolation to the CBS basis set. The energy differences between CCSD(T)/aug-cc-pV(T+d)Z and CCSD(T)/CBS levels are smaller than 0.23 kcal·mol⁻¹, and we conclude that the CCSD(T)/aug-cc-pV(T+d)Z approach provide accurate energies for the formation of these complexes.

Our computed hydrogen-bond distances for the monohydrate cluster differ by 0.03–0.10 Å from other theoretical results^{31,32,65,66,68,73} and by less than 0.14 Å from experiments.⁶² For higher hydrates, our hydrogen-bond lengths differ by less than 0.08 Å from those reported on the literature.^{31,66,73}

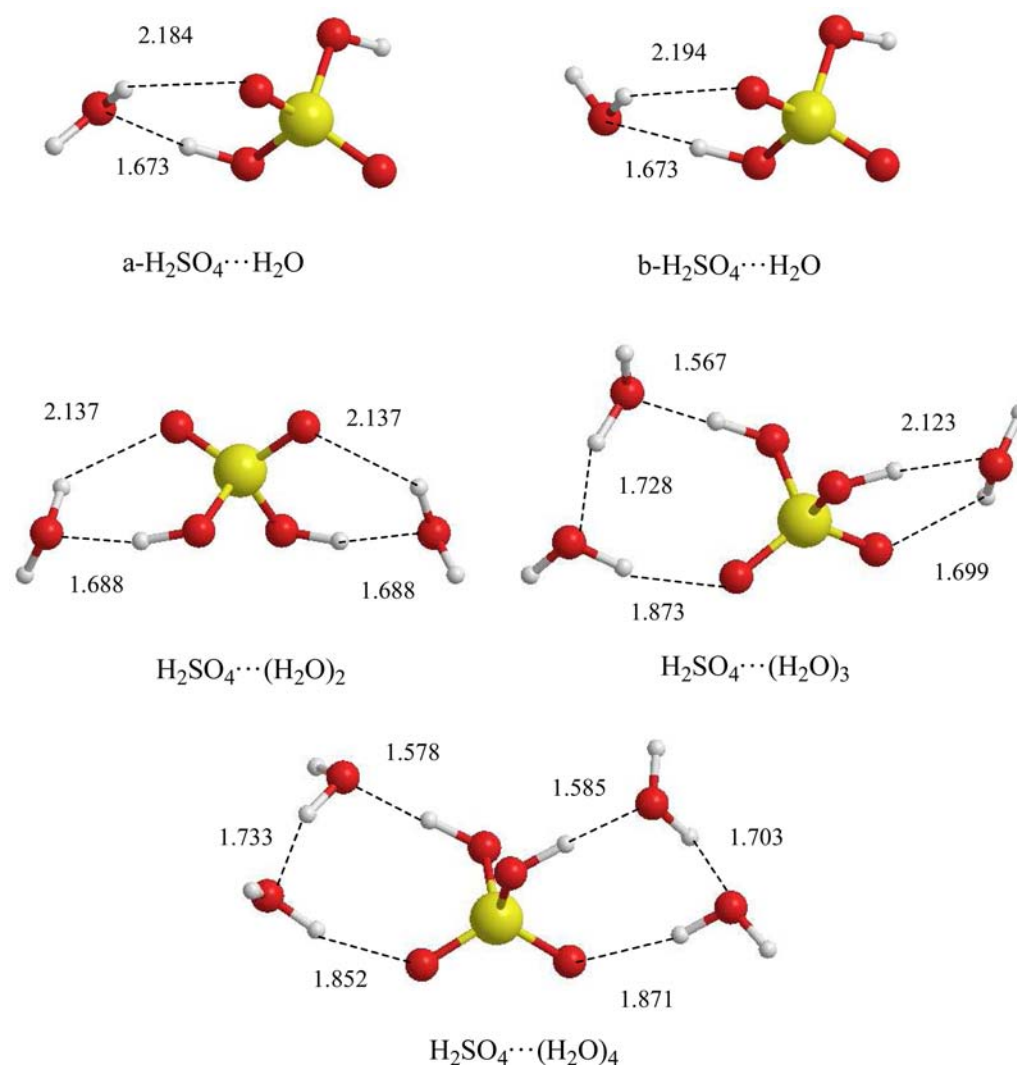


Figure 4. Most relevant geometrical parameters (hydrogen-bond distances, in angstroms) for the H₂SO₄⋯(H₂O)_{*n*}, *n* = 1–4 complexes investigated in this work.

Table 5. Entropies, Relative Energies, Energies plus ZPE, Enthalpies, and Free Energies Calculated for Formation of H₂SO₄ + *n*H₂O (*n* = 1–4) Complexes

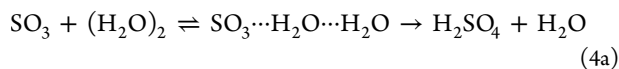
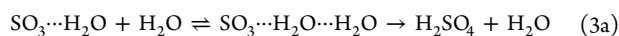
compd	method ^a	ZPE	S, eu	Δ <i>E</i> , kcal·mol ⁻¹	Δ(<i>E</i> + ZPE), kcal·mol ⁻¹	Δ <i>H</i> (298), kcal·mol ⁻¹	Δ <i>G</i> (298), kcal·mol ⁻¹
H ₂ SO ₄ + H ₂ O	A	37.5	116.5	0.00	0.00	0.00	0.00
a-H ₂ SO ₄ ·H ₂ O	A	39.7	87.6	-12.94	-10.72	-11.33	-2.72
a-H ₂ SO ₄ ·H ₂ O	B	39.7	87.7	-12.79	-10.56	-11.20	-2.57
a-H ₂ SO ₄ ·H ₂ O	C	39.7	87.7	-12.72	-10.49	-11.13	-2.50
b-H ₂ SO ₄ ·H ₂ O	A	39.8	87.1	-13.02	-10.74	-11.42	-2.65
b-H ₂ SO ₄ ·H ₂ O	B	39.8	87.1	-12.88	-10.59	-11.27	-2.50
b-H ₂ SO ₄ ·H ₂ O	C	39.8	87.1	-12.81	-10.53	-11.20	-2.43
H ₂ SO ₄ ·H ₂ O + H ₂ O	A	53.1	132.7	0.00	0.00	0.00	0.00
H ₂ SO ₄ ·(H ₂ O) ₂	A	55.4	101.6	-12.81	-10.42	-11.15	-1.87
H ₂ SO ₄ ·2H ₂ O + H ₂ O	A	68.8	146.7	0.00	0.00	0.00	0.00
H ₂ SO ₄ ·(H ₂ O) ₃	A	71.1	114.9	-12.47	-10.11	-10.93	-1.46
H ₂ SO ₄ ·3H ₂ O + H ₂ O	A	84.4	160.0	0.00	0.00	0.00	0.00
H ₂ SO ₄ ·(H ₂ O) ₄	A	86.9	127.2	-12.66	-10.21	-11.07	-1.30

^aMethod A stands for CCSD(T)/aug-cc-pV(T+d)Z//B3LYP/aug-cc-pVTZ; method B stands for CCSD(T)/aug-cc-pV(Q+d)Z//B3LYP/aug-cc-pVTZ; and method C stands for CCSD(T)/CBS//B3LYP/aug-cc-pVTZ.

Our predicted binding energies are 10.49 and 10.53 kcal·mol⁻¹ for the monohydrates, 10.42 kcal·mol⁻¹ for the dihydrates, 10.11 kcal·mol⁻¹ for the trihydrates, and 10.21 kcal·mol⁻¹ for the tetrahydrates. Our results also compare quite well with those reported in the literature, with differences in $\Delta H(298)$ between 0.07 and 0.17 kcal·mol⁻¹ and in $\Delta G(298)$ between 0.09 and 1.07 kcal·mol⁻¹ with respect to the values reported by Kurten et al.;³¹ with differences in $\Delta H(298)$ between 0.22 and 0.70 kcal·mol⁻¹ and in $\Delta G(298)$ between 0.00 and 1.24 kcal·mol⁻¹ with respect to the values reported by Temelso et al.;³² and with differences in $\Delta H(298)$ between 0.10 and 0.90 kcal·mol⁻¹ and in $\Delta G(298)$ between 0.00 and 0.6 kcal·mol⁻¹ with respect to the values reported by Re et al.⁷³ Finally, Hanson and Eisele,⁶⁴ from experimental determination of the rate constants of successive formation of the first and second hydrates of sulfuric acid, have estimated $\Delta G(298)$ values of $-3.6 (\pm 1)$ and $-2.3 (\pm 0.3)$ kcal·mol⁻¹, which are in a quite good agreement with our computed results displayed in Table 5.

3.4. Relevance of the Results. The results of the present study suggest that *sulfuric acid will significantly impact the gas-phase hydrolysis of SO₃. The impact is a catalytic effect.* The results displayed in Tables 2, 3, and 4 and in Figures 2 and 3 show a stabilization between 2 and 3 kcal·mol⁻¹ when the water dimer of reaction 4 is replaced by H₂SO₄·H₂O in reaction 8 or by H₂SO₄·(H₂O)₂ in reaction 10. The stabilization is even greater when the single water molecule in reaction 3 is replaced by H₂SO₄ in reaction 7 (by 10.0 kcal·mol⁻¹) or by H₂SO₄·H₂O in reaction 9 (by 10.6 kcal·mol⁻¹). In addition, and taking into account the electronic structure features of the processes investigated, as discussed in the previous section, we suggest that higher hydrates of sulfuric acid should play a similar catalytic role. This fact is especially important because it has been shown that, depending on the relative humidity, different hydrates of sulfuric acid have distinct populations in the atmosphere,^{31,32} and consequently, they can play an important role in the atmospheric hydrolysis of SO₃ catalyzed either by sulfuric acid and/or by the different water complexes of sulfuric acid.

Given the ability of sulfuric acid and/or the different water complexes of sulfuric acid to lower the barrier for SO₃ hydrolysis, and given also its potential to play an important role in the formation of atmospheric H₂SO₄, it is useful to examine the possible atmospheric impact of the reactions investigated in this work by comparing their rate constants relative to that for the water-assisted reaction. This comparison will provide some important insights into the significance of this work. The details of the kinetic study can be found in the Supporting Information, and here it is worth mentioning that we assume that reactants are in equilibrium with the prereactive complexes and steady-state conditions apply. Furthermore, the rate constants of the unimolecular reactions are obtained by conventional transition-state theory (TST). In all cases, the energies employed are computed at the CCSD(T)/cc-pV(T+d)Z level of theory, whereas the partition functions and Hessians are obtained at the B3LYP/cc-pV(T+d)Z level of theory. For the formation of sulfuric acid, and assuming that reaction 4a is the sole H₂SO₄-producing reaction, we have calculated a rate constant of 1.28×10^{-10} cm³·molecule⁻¹·s⁻¹ at 300 K, which is slightly smaller than the 2.1×10^{-10} cm³·molecule⁻¹·s⁻¹ estimated experimentally at 300 K as an upper limit for this reaction.¹⁶



Assuming reaction 3a to be the primary sulfuric acid generator, we have calculated a rate constant of 1.84×10^{-11} cm³·molecule⁻¹·s⁻¹ at 300 K, which is 15.3 times faster than the value computed by Jayne et al.¹⁶ (1.2×10^{-12} cm³·molecule⁻¹·s⁻¹ at 300 K). These authors have taken the thermodynamic values computed by Morokuma and Muguruma,¹⁹ who concluded that higher-level calculations would be necessary to obtain a more quantitative evaluation of the potential energy surface. The difference with our values is mainly due to the better quality of the calculations employed.

At 300 K, the rate constants calculated for reactions 8 and 10 are estimated to be 1.16×10^{-10} cm³·molecule⁻¹·s⁻¹ and 6.58×10^{-10} cm³·molecule⁻¹·s⁻¹, respectively, whereas the calculations show that the rates for reactions 7 and 9 are gas kinetic. Similar catalytic effects have been reported for the hydrolysis of SO₃ catalyzed by formic acid.^{29,30} Note that the relative low values for the rate constants of reactions 8 and 10 are due to the reorganization in the prereactive complex region necessary for the reaction to occur, as is discussed in section 3.2 (see also Supporting Information).

The reactions investigated in this work may have relevance in the Earth and Venus atmospheres, since in both atmospheres sulfuric acid plays an important role. In order to assess the real impact, it is necessary to compare reaction rates rather than reaction rate constants. Therefore, a first insight can be obtained by comparing, for instance, reactions 4a and 8; 4a and 10; 3a and 7; and 3a and 9. The reaction rates can be written as

$$v_{4a} = k_{4a}[\text{SO}_3][(\text{H}_2\text{O})_2] \quad (11)$$

$$v_8 = k_8[\text{SO}_3][\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}] \quad (12)$$

$$v_{10} = k_{10}[\text{SO}_3][\text{H}_2\text{SO}_4 \cdots (\text{H}_2\text{O})_2] \quad (13)$$

$$v_{3a} = k_{3a}[\text{SO}_3 \cdots \text{H}_2\text{O}][\text{H}_2\text{O}] \quad (14)$$

$$v_7 = k_7[\text{SO}_3 \cdots \text{H}_2\text{O}][\text{H}_2\text{SO}_4] \quad (15)$$

$$v_9 = k_9[\text{SO}_3 \cdots \text{H}_2\text{O}][\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}] \quad (16)$$

and the relative rates are

$$\frac{v_8}{v_{4a}} = \frac{k_8[\text{SO}_3][\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}]}{k_{4a}[\text{SO}_3][(\text{H}_2\text{O})_2]} = \frac{k_8[\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}]}{k_{4a}[(\text{H}_2\text{O})_2]} \quad (17)$$

$$\begin{aligned} \frac{v_{10}}{v_{4a}} &= \frac{k_{10}[\text{SO}_3][\text{H}_2\text{SO}_4 \cdots (\text{H}_2\text{O})_2]}{k_{4a}[\text{SO}_3][(\text{H}_2\text{O})_2]} \\ &= \frac{k_{10}[\text{H}_2\text{SO}_4 \cdots (\text{H}_2\text{O})_2]}{k_{4a}[(\text{H}_2\text{O})_2]} \end{aligned} \quad (18)$$

$$\frac{v_7}{v_{3a}} = \frac{k_7[\text{SO}_3 \cdots \text{H}_2\text{O}][\text{H}_2\text{SO}_4]}{k_{3a}[\text{SO}_3 \cdots \text{H}_2\text{O}][\text{H}_2\text{O}]} = \frac{k_7[\text{H}_2\text{SO}_4]}{k_{3a}[\text{H}_2\text{O}]} \quad (19)$$

$$\begin{aligned} \frac{v_9}{v_{3a}} &= \frac{k_9[\text{SO}_3 \cdots \text{H}_2\text{O}][\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}]}{k_{3a}[\text{SO}_3 \cdots \text{H}_2\text{O}][\text{H}_2\text{O}]} \\ &= \frac{k_9[\text{H}_2\text{SO}_4 \cdots \text{H}_2\text{O}]}{k_{3a}[\text{H}_2\text{O}]} \end{aligned} \quad (20)$$

Thus, the importance of sulfuric acid and its hydrates as reactants in their own formation depends not only on the rate constants but also on the relative concentrations of H₂O and H₂SO₄, or water dimer and sulfuric acid hydrates, respectively.

Table 6. Calculated Equilibrium Constants for the Formation of (H₂O)₂ and (SO₃⋯H₂O), Concentrations of H₂O and (H₂O)₂, and Fraction of the SO₃⋯H₂O Complex at Different Heights in the Atmospheres of Earth and Venus

<i>H</i> , km	<i>T</i> , K	<i>P</i> , atm	$K_{\text{eq}}(\text{H}_2\text{O})_2$, cm ³ ·molecule ⁻¹	[H ₂ O], molecules·cm ³	[(H ₂ O) ₂], molecules·cm ³	$K_{\text{eq}}(\text{SO}_3\cdots\text{H}_2\text{O})$, cm ³ ·molecule ⁻¹	[SO ₃ ⋯H ₂ O]/ [SO ₃]
Earth Atmosphere ^a							
0	298.1	1.000	2.34×10^{-21}	5.18×10^{17}	6.28×10^{14}	1.01×10^{-19}	5.23×10^0
5	259.3	0.535	4.75×10^{-21}	2.41×10^{16}	2.77×10^{12}	6.71×10^{-19}	1.62×10^0
10	229.7	0.266	9.89×10^{-21}	4.92×10^{15}	2.40×10^{11}	4.55×10^{-18}	2.24×10^0
15	212.6	0.120	1.68×10^{-20}	1.96×10^{13}	6.45×10^6	1.77×10^{-17}	3.47×10^{-2}
20	215.5	0.054	1.53×10^{-20}	9.56×10^{12}	1.40×10^6	1.39×10^{-17}	1.33×10^{-2}
25	218.6	0.025	1.38×10^{-20}	5.21×10^{12}	3.74×10^5	1.07×10^{-17}	5.57×10^{-3}
30	223.7	0.011	1.18×10^{-20}	2.62×10^{12}	8.10×10^4	7.15×10^{-18}	1.87×10^{-3}
35	235.1	0.005	8.52×10^{-21}	1.31×10^{12}	1.47×10^4	3.09×10^{-18}	4.06×10^{-4}
40	249.9	0.003	5.87×10^{-21}	6.44×10^{12}	2.44×10^3	1.17×10^{-18}	7.54×10^{-5}
Venus Atmosphere ^b							
0	740	94.350	3.18×10^{-22}			1.16×10^{-22}	
30	490	7.106	4.90×10^{-22}			9.20×10^{-22}	
40	410	2.665	7.36×10^{-22}			3.57×10^{-21}	
50	340	0.987	1.35×10^{-21}			2.16×10^{-20}	
60	270	0.138	3.87×10^{-21}			3.80×10^{-19}	
66	250	0.069	5.94×10^{-21}			1.18×10^{-18}	
70	230	0.025	9.81×10^{-21}			4.45×10^{-18}	

^a*T* and *P* values and water vapor concentration are taken from ref 74. ^b*T* and *P* values are taken from ref 75.

Table 7. Equilibrium Constants for the H₂SO₄⋯(H₂O)_{*n*}, *n* = 1–4 Complexes at Different Heights in the Atmospheres of Earth and Venus

<i>H</i> (km)	<i>T</i> (K)	<i>P</i> (atm)	equilibrium constants, ^a cm ³ ·molecule ⁻¹			
			$K_{\text{eq}1}$	$K_{\text{eq}2}$	$K_{\text{eq}3}$	$K_{\text{eq}4}$
Earth Atmosphere ^b						
0	298.1	1.000	1.39×10^{-17}	2.35×10^{-18}	7.65×10^{-18}	5.99×10^{-18}
5	259.2	0.535	2.18×10^{-16}	3.43×10^{-17}	1.06×10^{-16}	8.63×10^{-17}
10	229.7	0.266	3.34×10^{-15}	4.90×10^{-16}	1.44×10^{-15}	1.21×10^{-15}
15	212.6	0.120	2.32×10^{-14}	3.23×10^{-15}	9.13×10^{-15}	7.87×10^{-15}
20	215.5	0.054	1.63×10^{-14}	2.29×10^{-15}	6.54×10^{-15}	5.61×10^{-15}
25	218.6	0.025	1.14×10^{-14}	1.61×10^{-15}	4.62×10^{-15}	3.95×10^{-15}
30	223.7	0.011	6.37×10^{-15}	9.18×10^{-16}	2.66×10^{-15}	2.26×10^{-15}
35	235.1	0.005	1.92×10^{-15}	2.86×10^{-16}	8.50×10^{-16}	7.10×10^{-16}
40	249.9	0.003	4.80×10^{-16}	7.40×10^{-17}	2.26×10^{-16}	1.85×10^{-16}
Venus Atmosphere ^c						
0	740	94.35	4.71×10^{-22}	1.06×10^{-22}	3.93×10^{-22}	2.60×10^{-22}
30	490	7.106	1.31×10^{-20}	2.68×10^{-21}	9.62×10^{-21}	6.78×10^{-21}
40	410	2.665	1.03×10^{-19}	1.98×10^{-20}	6.95×10^{-20}	5.06×10^{-20}
50	340	0.987	1.48×10^{-18}	2.67×10^{-19}	8.98×10^{-19}	6.82×10^{-19}
60	270	0.138	9.33×10^{-17}	1.50×10^{-17}	4.73×10^{-17}	3.80×10^{-17}
66	250	0.069	4.75×10^{-16}	7.33×10^{-17}	2.24×10^{-16}	1.84×10^{-16}
70	230	0.025	3.24×10^{-15}	4.74×10^{-16}	1.40×10^{-15}	1.17×10^{-15}

^a $K_{\text{eq}1}$, equilibrium constant for $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_4\cdots\text{H}_2\text{O}$. $K_{\text{eq}2}$, equilibrium constant for $\text{H}_2\text{SO}_4\cdots\text{H}_2\text{O} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_4\cdots(\text{H}_2\text{O})_2$. $K_{\text{eq}3}$, equilibrium constant for $\text{H}_2\text{SO}_4\cdots(\text{H}_2\text{O})_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_4\cdots(\text{H}_2\text{O})_3$. $K_{\text{eq}4}$, equilibrium constant for $\text{H}_2\text{SO}_4\cdots(\text{H}_2\text{O})_3 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_4\cdots(\text{H}_2\text{O})_4$.
^b*T* and *P* values are taken from ref 74. ^c*T* and *P* values are taken from ref 75.

Our calculations predict that the ratio of the rate constants in eq 17 is almost 1 and in eq 18 is close to 5. Since reactions 7 and 9 are gas kinetic, we estimate a ratio of rate constants of 2 orders of magnitude for eqs 19 and 20. Thus, in order for these reactions to play a role, it is necessary that the ratio between sulfuric acid and water or the hydrates of sulfuric acid and water dimer be of the same order of magnitude or even greater than the ratio of rate constants. It is thus necessary to have an estimation of the concentrations of water, water dimer, sulfuric acid, and its hydrates.

In Table 6 we have collected the computed equilibrium constants for (H₂O)₂ and SO₃⋯H₂O as a function of height in

the atmospheres of Earth and Venus. This table also includes water vapor concentration (taken from ref 74), calculated concentration of water dimer, and the computed value of the fraction of SO₃ forming a complex with a water molecule. At ground level the computed equilibrium constant of water dimer (2.34×10^{-21} cm³·molecule⁻¹) agrees very well with the 1.75×10^{-21} to 2.12×10^{-21} cm³·molecule⁻¹ experimental values^{56–58} and with the 1.21×10^{-21} cm³·molecule⁻¹ theoretical value from the literature.⁵²

It is also interesting to observe that the value of both equilibrium constants increases with the altitude of the Earth

Table 8. Percentage of Sulfuric Acid Hydrates Calculated at Different Altitudes of the Earth's Atmosphere^a

H (km)	T (K)	P (atm)	[H ₂ O]	percentage of sulfuric acid hydrates ^b				
				A	B	C	D	E
Earth Atmosphere								
0	298.1	1	7.80×10^{17}	0.0 ^c	1.5	2.8	16.8	78.7
5	259.2	0.535	2.41×10^{16}	0.4	11.7	9.7	24.8	51.6
10	229.7	0.266	4.92×10^{15}	0.0 ^c	0.8	2.0	14.0	83.2
15	212.6	0.120	1.96×10^{13}	67.4	30.5	1.9	0.3	0.1
20	215.5	0.053	9.56×10^{12}	86.3	13.4	0.3	0.02	0.0 ^c
25	218.6	0.025	5.21×10^{12}	94.3	5.6	0.05	0.0 ^c	0.0 ^c
30	223.7	0.011	2.62×10^{12}	98.4	1.6	0.0 ^c	0.0 ^c	0.0 ^c
35	235.1	0.005	1.31×10^{12}	99.7	0.3	0.0 ^c	0.0 ^c	0.0 ^c
40	249.9	0.003	6.44×10^{11}	99.9	0.03	0.0 ^c	0.0 ^c	0.0 ^c

^aT and P values and water vapor concentration are taken from ref 74. ^bPercentages are relative to the total sulfuric acid of (A) H₂SO₄, (B) H₂SO₄·H₂O, (C) H₂SO₄·(H₂O)₂, (D) H₂SO₄·(H₂O)₃, and (E) H₂SO₄·(H₂O)₄. ^cPercentage smaller than 10⁻².

atmosphere, reaching its maximum close to 15 km of altitude and then decreasing, in the same way as reported by Vaida and co-workers^{70,76} for the water dimer. The behavior is different in the Venus atmosphere, where both equilibrium constants increase with the altitude.

Table 7 contains the equilibrium constants of the H₂SO₄·(H₂O)_n (n = 1–4) complexes investigated, and Table 8 displays the computed percentage of these complexes relative to the total concentration of H₂SO₄ at different conditions of T, P, and water vapor concentration. The equilibrium constants have been calculated by use of the CCSD(T)/aug-cc-pV(T+d)Z energies and the B3LYP/aug-cc-pVTZ partition functions, without consideration of anharmonic effects. As far as we know, the only experimental estimates of equilibrium constants of successive hydration of sulfuric acid have been reported by Hanson and Eisele⁶⁴ for H₂SO₄·H₂O and H₂SO₄·(H₂O)₂, with values of 1.7×10^{-17} and 2.0×10^{-18} cm³·molecule⁻¹, respectively, which are in a very good agreement with the values computed in this work at 298 K and 1 atm (1.39×10^{-17} and 2.35×10^{-18} cm³·molecule⁻¹, respectively; see Table 7). It is also interesting to observe that the behavior of the four equilibrium constants with altitude in the Earth's atmosphere is similar than those described for water dimer and SO₃·H₂O, namely, an increase with a maximum close to 15 km and then a decrease. Similar behavior has been described by Vaida et al.⁷⁰ for the monohydrated complexes, although our computed values for K_{eq1} between 30 and 40 km of altitude differ by 57–60 times from those reported in that work.⁶⁹ In the Venus atmosphere the values of the four equilibrium constants increase with altitude.

On the other hand, the fraction of sulfuric acid hydrates estimated in this work, at 298 K, 1 atm, and 100% relative humidity, differs quantitatively but agrees qualitatively with the values reported by Kurten et al.³¹ and by Temelso et al.³² These differences may be due to the differences in the computed free energies of up to 1.24 kcal·mol⁻¹. It is also worth pointing out from our calculations that, up to 10 km of altitude in the Earth's atmosphere, the contributions of tri- and tetrahydrates are very important. Between 15 and 25 km, almost all sulfuric acid should be found either nonhydrated or as a complex with one water molecule, whereas from 30 km upward less than 2% of sulfuric acid is hydrated.

Knowing the abundance profiles of water dimer and sulfuric acid hydrates in the atmospheres of Earth and Venus, we are now able to assess the impact of the reactions investigated in this work in these environments.

Table 6 shows that in the troposphere, and up to a high of 10 km, the concentration of water vapor ranges between 5.18×10^{17} and 4.92×10^{15} molecules·cm⁻³, the concentration of water dimer ranges between 6.28×10^{14} and 2.40×10^{11} molecules·cm⁻³, and the percentage of SO₃ forming a complex with one water molecule ranges between 5.23% and 2.24%. Regarding the sulfuric acid hydrates, the results of Table 8 indicate that almost all sulfuric acid is hydrated with 2–4 water molecules. The gas-phase concentration of sulfuric acid ranges between 10⁴ and 4 × 10⁸ molecules·cm⁻³,^{77,78} which is about 10⁹ times smaller than the atmospheric water vapor concentration, and according to eqs 17–20, the catalytic effect of a maximum 2 orders of magnitude for the reactions investigated in this work is not enough to compensate for the very high difference in the concentration of sulfuric acid (or its hydrates) and water vapor (or water vapor dimer). Consequently, the H₂SO₄-catalyzed SO₃ conversion to sulfuric acid is negligible in the troposphere of Earth. This result agrees with the measurements by Jayne et al.,¹⁶ who have considered the possibility of secondary reactions of SO₃ with acid hydrates in the formation of sulfuric acid and concluded that they do not contribute significantly to the measurements of SO₃ decay.

However, in the stratosphere the situation is quite different. It has been reported that sulfuric acid can be efficiently produced up to 39 km high and the H₂SO₄ concentration reaches its maximum (just close to 5×10^6 molecules·cm⁻³) near 36 km.⁷⁹ Table 6 shows that from 15 km upward the fraction of SO₃ forming a complex with one water molecule is negligible, so the processes involving SO₃·H₂O as reactants (reactions 3, 7, and 10) will not play any role in the formation of sulfuric acid. In addition, the concentration of water dimer drops to 1.47×10^4 molecules·cm⁻³ at 35 km of altitude (see Table 6), which is almost the same concentration than H₂SO₄·H₂O complex (estimated to be close to 1.25×10^4 molecule·cm⁻³ when the values from Table 8 are taken into account). Consequently, we expect that sulfuric acid as reactant will catalyze its own formation in the stratosphere. *This becomes the major mechanism for sulfuric acid generation in the stratosphere rather than via water hydrolysis.*

Gaseous sulfuric acid is also formed in aircraft engines and the reactions investigated in this work have also potential importance in understanding its formation in this environment. H₂SO₄ is formed at the end and outside the engine,^{80,81} and flight measurements in the exhaust plume have measured sulfuric acid abundances up to a value of 600 pptv.⁸² When an average flight altitude of 10 km is considered, this corresponds

to a concentration of 5.1×10^9 molecules·cm⁻³, which is only 47 times smaller than the concentration of water dimer (2.40×10^{11} molecules·cm⁻³; see Table 6). According to the results in Table 8, close to 10 km of altitude in the Earth's atmosphere, almost all sulfuric acid will form complexes with water [for instance, 4.2×10^9 molecules·cm⁻³ for the H₂SO₄·(H₂O)₄ complex], with density numbers smaller by 2 orders of magnitude than that of the estimated water dimer concentration. Consequently, the reactions investigated in this work may play a role as catalyzers in the formation of sulfuric acid from aircraft engines. In addition, at the inside end of the engine, where sulfuric acid is also formed, the H₂SO₄ concentration may be even greater, and consequently, the role of sulfuric acid acting as a catalyst of its own formation cannot be ruled out.

The results reported in this work also have relevance in the heterogeneous formation of sulfuric acid. Recently, sulfuric acid molecular hydrated complexes have been detected in sulfuric acid aerosols.^{72,83} The fact that the products of reactions 7–10 are sulfuric acid dimers or sulfuric acid complexes with water also enhances their atmospheric importance. It has been recently reported in the literature that sulfuric acid dimers play a key role in atmospheric aerosol formation,^{63,84,85} and consequently these reactions, or reactions of SO₃ with further sulfuric acid–water complexes, or even reactions of SO₃ with sulfuric acid dimers may contribute to the atmospheric formation of aerosols.

Finally, the H₂SO₄-catalyzed conversion of SO₃ to sulfuric acid can be also important in the atmosphere of Venus, where the concentration of sulfuric acid may be even greater than the concentration of water vapor.^{86–89} It has been proposed that sulfuric acid is formed in a narrow layer with a peak at 66 km,⁹⁰ and although there is some debate about the water vapor and sulfuric acid concentrations, we could consider a concentration of H₂O of 25 ppm at 68 km (close to 5×10^{13} molecules·cm⁻³) and a concentration of sulfuric acid of 3.6×10^{12} molecules·cm⁻³.^{87,90,91} According to the results of Tables 7 and 8, we estimate concentrations of water dimer and H₂SO₄·H₂O of 1.5×10^7 and 8.3×10^{10} molecules·cm⁻³, respectively, which would suggest a possible catalytic effect of the reactions investigated in this work.

4. CONCLUSIONS

The important finding of this work is that sulfuric acid can act as a catalyst in the hydrolysis of sulfur trioxide. Sulfuric acid itself and its hydrates can react with SO₃ or with SO₃·H₂O, leading to the formation of sulfuric acid dimer or sulfuric acid dimer complexed with a water molecule. Our calculations predict a catalytic effect of up to 10 kcal·mol⁻¹ as a result of substituting a water molecule as a reactant in the hydrolysis of SO₃ by a H₂SO₄ molecule, and in this way, sulfuric acid can act as an autocatalyst. Our calculations also predict that sulfuric acid hydrates play a similar role, and we estimate an increase in the rate constants between 5 times and 2 orders of magnitude for the H₂SO₄-catalyzed SO₃ hydrolysis compared to the water-catalyzed hydrolysis.

We have also investigated the successive formation for hydrated clusters of sulfuric acid [H₂SO₄·(H₂O)_n, n = 1–4] and their possible role in the atmospheres of Earth and Venus. Our calculations predict that in Earth's atmosphere the corresponding equilibrium constants increase with altitude, with a maximum close to 15 km, and then decrease. Moreover, the formation of higher hydrates is important only in the troposphere, whereas from 30 km upward, less than 2% of sulfuric acid is hydrated

The results of the present investigation show that the real impact of the reactions investigated in this work depends not only on the rate constants but also on the relative concentrations of H₂O, H₂SO₄, water dimer, and sulfuric acid hydrates. The autocatalytic ability of sulfuric acid does not play any role in the troposphere but can be important in the Earth's stratosphere, in heterogeneous formation of sulfuric acid in the formation of aerosols, in H₂SO₄ formation by aircraft engines, and in sulfuric acid formation in the atmosphere of Venus.

■ ASSOCIATED CONTENT

Supporting Information

Additional text, six figures, and eight tables containing data regarding the reaction between SO₃ and H₂O and equilibrium constants, rate constants, absolute energies, and Cartesian coordinates of all stationary points investigated in this work. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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