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ARTICLE

Quantum Chemical Study of Potential Energy Surface in the Formation of Atmospheric Sulfuric Acid[†]

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A new potential energy surface (PES) for the atmospheric formation of sulfuric acid from $OH+SO_2$ is investigated using density functional theory and high-level *ab initio* molecular orbital theory. A pathway focused on the new PES assumes the reaction to take place between the radical complex $SO_3{\cdot}HO_2$ and H_2O. The unusual stability of $SO_3{\cdot}HO_2$ is the principal basis of the new pathway, which has the same final outcome as the current reaction mechanism in the literature but it avoids the production and complete release of SO_3. The entire reaction pathway is composed of three consecutive elementary steps: (1) $HOSO_2+O_2 \rightarrow SO_3{\cdot}HO_2$, (2) $SO_3{\cdot}HO_2+H_2O \rightarrow SO_3{\cdot}H_2O{\cdot}HO_2$, (3) $SO_3{\cdot}H_2O{\cdot}HO_2 \rightarrow H_2SO_4+HO_2$. All three steps have small energy barriers, under 10 kcal/mol, and are exothermic, and the new pathway is therefore favorable both kinetically and thermodynamically. As a key step of the reactions, step (3), HO_2 serves as a bridge molecule for low-barrier hydrogen transfer in the hydrolysis of SO_3. Two significant atmospheric implications are expected from the present study. First, SO_3 is not released from the oxidation of SO_2 by OH radical in the atmosphere. Second, the conversion of SO_2 into sulfuric acid is weakly dependent on the humidity of air.

Key words: Quantum chemistry, Atmospheric chemistry, Sulfur dioxide, Sulfuric acid, Computational chemistry, Density functional theory, *Ab initio* methods

I. INTRODUCTION

Atmospheric reactions of sulfur compounds, particularly for the formation of sulfuric acid, have been a topic of considerable study in recent years [1, 2]. Sulfuric acid, a major component of acid rain, is also known to influence atmospheric nucleation processes for the formation of atmospheric aerosols [3−6]. Because virtually all sulfur in the atmosphere is either emitted as or eventually converted into sulfur dioxide (SO_2), many studies focus on the oxidation of SO_2 as an initial step for sulfuric acid formation. The general reaction process of sulfur dioxide oxidation is fairly well-established, beginning with the reaction of SO_2 with hydroxyl radical (OH) [1, 2, 7]. Sulfur compounds emitted to the atmosphere are oxidized to form SO_2, which reacts first with OH to form the $HOSO_2$ radical. The $HOSO_2$ radical then forms SO_3 and HO_2 through collisions with O_2. Finally SO_3 goes on to react with water via a water/acid catalyzed reaction to form sulfuric acid:

(1) $SO_2 + OH + M \rightarrow HOSO_2 + M$
(2) $HOSO_2 + O_2 \rightarrow SO_3 + HO_2$
(3) $SO_3 + H_2O \rightarrow H_2SO_4$

The first step of this mechanism has been more or less confirmed by theoretical and experimental evidence; its product, the $HOSO_2$ radical, has been detected directly in the atmosphere [1]. Step (2) has been proposed as a dominant channel for the reaction of the $HOSO_2$ radical in the atmosphere [7]. While both the thermochemical estimation [8] and theoretical calculation [9−11] showed that the reaction was endothermic with an energy change of 8 kcal/mol or larger, a recent study revealed it to be slightly exothermic with an enthalpy of −2.3 kcal/mol [12]. Some studies propose an alternate step involving the formation of a $HOSO_4$ radical instead of SO_3 and HO_2 [13]. However, this step, while a likely atmospheric process, is of little importance in the overall reaction mechanism because the $HOSO_4$ radical may form SO_3 and HO_2 on its own through a fast hydrogen transfer step [2].

Reaction (3) also has been a subject of several theoretical studies [14, 15]. Sulfuric acid is unlikely to form directly from an elementary reaction of SO_3 and H_2O due to the high energy barrier involved (about 30 kcal/mol) [16]. Although various studies [15, 17] show that reaction of SO_3 in a cluster of two, three, or four waters significantly lowers the barrier, making this step appear more favorable, clusters of multiple waters are in fact highly unstable in the gas phase under

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normal atmospheric conditions. Therefore, it is still uncertain that such a process actually occurs in the atmosphere, and an alternate reaction pathway should be considered.

This study attempts to find an alternate pathway to better describe the sulfuric acid formation mechanism. One possible pathway for consideration is the direct reaction of a water molecule with the intermediate product $SO_3{\cdot}HO_2$ from reaction (2), rather than releasing the separate intermediate products SO_3 and HO_2. The reaction steps can be revised as follows.

(4) $HOSO_2 + O_2 \rightarrow SO_3{\cdot}HO_2$
(5) $SO_3{\cdot}HO_2 + H_2O \rightarrow H_2SO_4 + HO_2$

The $SO_3{\cdot}HO_2$ complex is known to be highly stable. A binding energy of 12.5 kcal/mol was found for $SO_3{\cdot}HO_2$ with respect to the separate SO_3 and HO_2 species [11]. Water, abundant under normal atmospheric conditions, is widely available to facilitate the hydrolysis of $SO_3{\cdot}HO_2$ to form sulfuric acid and HO_2. The final outcome of the new mechanism is identical to that of the original mechanism in the literature, except that the production and complete release of SO_3 is avoided in the new mechanisms. Other possible pathways could also be considered. For example, a radical complex $HOSO_2{\cdot}H_2O$ could be formed prior to the reaction with O_2. The radical complex $HOSO_2{\cdot}H_2O$ is also very stable with a binding energy of 10.6 kcal/mol [18].

In this study, the atmospheric reaction mechanism for the production of sulfuric acid from SO_2 is investigated with quantum chemical calculations using density functional theory and high-level *ab initio* molecular orbital theory. The new reaction pathway outlined above is the main focus of this study. All reactant complexes, transition states, reaction intermediates, product complexes, and separate products are characterized for their molecular and thermodynamic properties. A new reaction mechanism will be established based on the results, and the atmospheric implications will be discussed.

II. THEORETICAL METHODS

Equilibrium geometries and energies of the reactant complexes, transition states, and reaction intermediates involved in reactions (1) to (5) were calculated using density functional theory (DFT) and *ab initio* molecular orbital theory. These geometries and energies represent the stationary points on a new potential energy surface in the atmospheric formation of H_2SO_4 from $OH+SO_2$. The DFT method in this study employed Becke's three-parameter functional with nonlocal correlation provided by Lee, Yang, and Parr (B3LYP) [19, 20], along with three different basis sets, 6-31+G* [21], aug-cc-pVDZ [22], and aug-cc-pVTZ [22]. Two *ab initio* methods for different levels of electron correlation involving valence electrons only were employed: second-order Møller-Plesset perturbation approximation (MP2) [23] and coupled-cluster method with single, double, and non-iterative triple excitations (CCSD(T)) [24−27], both using the aug-cc-pVDZ basis set. The CCSD(T) calculations were carried out using single-point energy calculations on the MP2/aug-cc-pVDZ geometries. Frozen-core approximation was used in both MP2 and CCSD(T) calculations. Level of consistency in the results from the diverse theoretical methods and basis sets may indicate the accuracy and reliability in the results of calculation. Transition state geometries were found using the synchronous transit-guided quasi-Newton (STQN) method [28, 29]. Transition states were verified by harmonic frequency calculations and by Intrinsic Reaction Coordinate (IRC) calculations [30, 31].

Relative electronic energy (ΔE), enthalpy (ΔH), and Gibbs free energy (ΔG) were determined as the difference between the energy of the given molecular complex (or transition state) and the sum of the energies of the respective reactant monomers $HOSO_2$, H_2O, and O_2 (in the triplet ground state), that is,

$$\Delta E = E - (E_{\mathrm{HOSO_2}} + E_{\mathrm{H_2O}} + E_{\mathrm{O_2}}) \qquad (1)$$

$$\Delta H = H - (H_{\mathrm{HOSO_2}} + H_{\mathrm{H_2O}} + H_{\mathrm{O_2}}) \qquad (2)$$

$$\Delta G = G - (G_{\mathrm{HOSO_2}} + G_{\mathrm{H_2O}} + G_{\mathrm{O_2}}) \qquad (3)$$

where E, H, and G are the total electronic energy, enthalpy, and Gibbs free energy of the molecular complex (or transition state), and E_m, H_m, and G_m are the corresponding energies of the reactant monomer ($HOSO_2$, H_2O, or O_2) which the molecular complex is composed of. The relative enthalpy (ΔH) and Gibbs free energy (ΔG), reported at 298.15 K and 1 atm, were calculated using harmonic vibrational frequencies. All calculations in this study were carried out on the Gaussian 09 computational chemistry program [32] running on a UNIX computer cluster.

Included in our calculations are all species involved in reactions (1), (2), and (3), particularly the reactant complex $HOSO_2{\cdot}O_2$, product complex $SO_3{\cdot}HO_2$, and the corresponding transition state TS0. Instead of the dissociation channel of $SO_3{\cdot}HO_2$ into SO_3 and the HO_2 radical, our focus is on the continuing reaction of $SO_3{\cdot}HO_2$ with water which is abundant in the atmosphere. As a new reaction pathway on the potential energy surface, a water molecule is introduced to the complex $SO_3{\cdot}HO_2$, resulting in the trimolecular complex $SO_3{\cdot}HO_2{\cdot}H_2O$ as involved in reaction (5). It should be noted that several conformations are expected for the complex $SO_3{\cdot}HO_2{\cdot}H_2O$ and the present study primarily focuses on the most stable conformation as well as the one which would directly facilitate the hydrolysis reaction to form sulfuric acid in the following step.

III. RESULTS AND DISCUSSION

FIG. 1 shows the equilibrium geometries of all complexes and transition states at the stationary points

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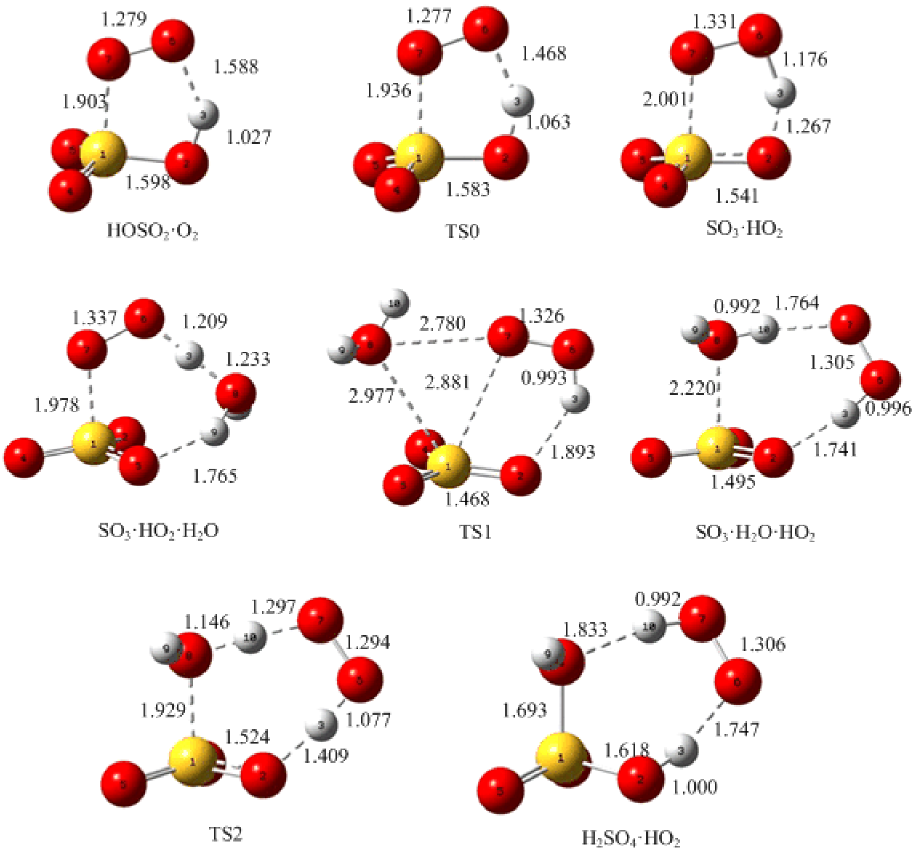

FIG. 1 Optimized geometries from MP2/aug-cc-pVDZ calculations. Selected bond lengths are in Å.

along the new reaction pathway on the potential energy surface. It should be noted that selected bond lengths in the figure were obtained from MP2/aug-cc-pVDZ calculations. The equilibrium geometries from B3LYP calculations with the three basis sets, 6-31+G*, aug-cc-pVDZ, and aug-cc-pVQZ respectively, are similar to those from MP2/aug-cc-pVDZ calculations. The reaction pathway is composed of three reaction steps: (i) the radical complex $HOSO_2$ reacts with O_2 to form the radical complex $SO_3{\cdot}HO_2$, (ii) $SO_3{\cdot}HO_2$ combines H_2O to form the radical complex $SO_3{\cdot}HO_2{\cdot}H_2O$ which is rearranged to $SO_3{\cdot}H_2O{\cdot}HO_2$, and (iii) $SO_3{\cdot}H_2O{\cdot}HO_2$ reacts to form the product complex $H_2SO_4{\cdot}HO_2$. Each of the reaction steps involves a transition state. For reaction step (i), the reactant complex, transition state, and the product complex are denoted $HOSO_2{\cdot}O_2$, TS0, and $SO_3{\cdot}HO_2$, respectively. Similarly, the corresponding species for step (ii) are $SO_3{\cdot}HO_2{\cdot}H_2O$, TS1, and $SO_3{\cdot}H_2O{\cdot}HO_2$, and those for step (iii) are $SO_3{\cdot}H_2O{\cdot}HO_2$, TS2, and $H_2SO_4{\cdot}HO_2$.

The total electronic energies of the species of all species at the stationary points along the reaction pathways on the potential energy surface, including those of separate reactant and product molecules, are available from the authors directly. These energies are from B3LYP/6-31+G*, B3LYP/aug-cc-pVDZ, B3LYP/ aug-cc-pVTZ, MP2/aug-cc-pVDZ, and CCSD(T)/aug-cc-pVDZ calculations, respectively. Table I gives the relative electronic energies (ΔE), relative enthalpies (ΔH), and relative Gibbs free energies (ΔG) with respect to the separate reactants, $HOSO_2$, O_2, and H_2O. Note that only electronic energies (ΔE) are available from CCSD(T)/aug-cc-pVDZ calculations. FIG. 2 shows a schematic of the corresponding potential energy profile for the reactions of $HOSO_2$, O_2, and H_2O to form H_2SO_4 and HO_2.

As shown in Table I and FIG. 2, the reaction $HOSO_2+O_2\rightarrow SO_3+HO_2$ has a very small energy barrier from the reactant complex $HOSO_2{\cdot}O_2$: about 4.0, 0.1, and 1.4 kcal/mol at the B3LYP, MP2, and CCSD(T) levels, respectively. The corresponding activation energies are either slightly negative or near zero, which would suggest the reaction is fast and kinetically favorable. However, the separate products SO_3 and HO_2 are about 10 kcal/mol higher in energy than the reactants $HOSO_2$ and O_2. The result is consistent with the thermal estimation [8] and the reported theoretical calculations [9−11]. It indicates that the reaction $HOSO_2+O_2\rightarrow SO_3+HO_2$ is not thermodynamically favorable. The similar, positive values of ΔG at the various levels confirm the thermodynamic un-favorability of the reaction. The strong intermolecular energy between

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TABLE I Relative electronic energies (ΔE), enthalpies (ΔH), and Gibbs free energies (ΔG) (all in kcal/mol) from B3LYP, MP2, and CCSD(T) calculations with different basis sets.

Complex	B3LYP/6-31+G*			B3LYP/aug-cc-pVDZ			B3LYP/aug-cc-pVTZ			MP2/aug-cc-pVDZ			CCSD(T)
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	ΔE
$HOSO_2 \cdot O_2$	−1.1	−0.1	5.5	−0.2	1.5	12.5	−5.2	−3.9	7.1	−0. 8	2.1	13.5	−1.8
TS0	2.7	1.7	13.9	4.3	3.3	15.5	−1.6	−2.5	9.8	0.8	1.2	13.4	−0.4
$SO_3 \cdot HO_2$	−1.8	0.1	10.9	1.5	3.2	14.3	−5.1	−3.2	7.8	−4.0	7.9	20.1	1.7
SO_3+HO_2	9.3	9.6	9.5	12.5	12.8	12.8	5.9	6.2	6.2	10.4	10.6	10.5	9.7
$SO_3 \cdot HO_2.H_2O$	−14.1	−10.5	9.8	−8.2	−5.0	15.3	−14.8	−11.5	8.9	−15.3	6.3	28.7	−9.6
TS1	−14.2	−10.5	9.8	4.6	7.0	24.3	−1.4	1.1	18.2	−1.6	0.9	18.7	−2.7
$SO_3 \cdot H_2O \cdot HO_2$	−13.8	−10.3	11.5	−6.9	−3.2	17.0	−14.1	−10.9	11.0	−10.6	−6.8	13.2	−11.6
TS2	−5.6	−5.8	17.1	−0.5	−1.0	21.7	−8.6	−8. 8	13.9	−6.8	−6.2	16.5	−4.7
$H_2SO_4 \cdot HO_2$	−18.0	−14.0	7.5	−11.1	−7.4	13.9	−19.9	−16.0	5.2	−13.4	−9.5	11.7	−17.3
$H_2SO_4+HO_2$	−6.3	−4.1	6.2	−1.0	1.2	11.3	−10.3	−8.1	2.0	−0.9	1.3	11.4	−5.0

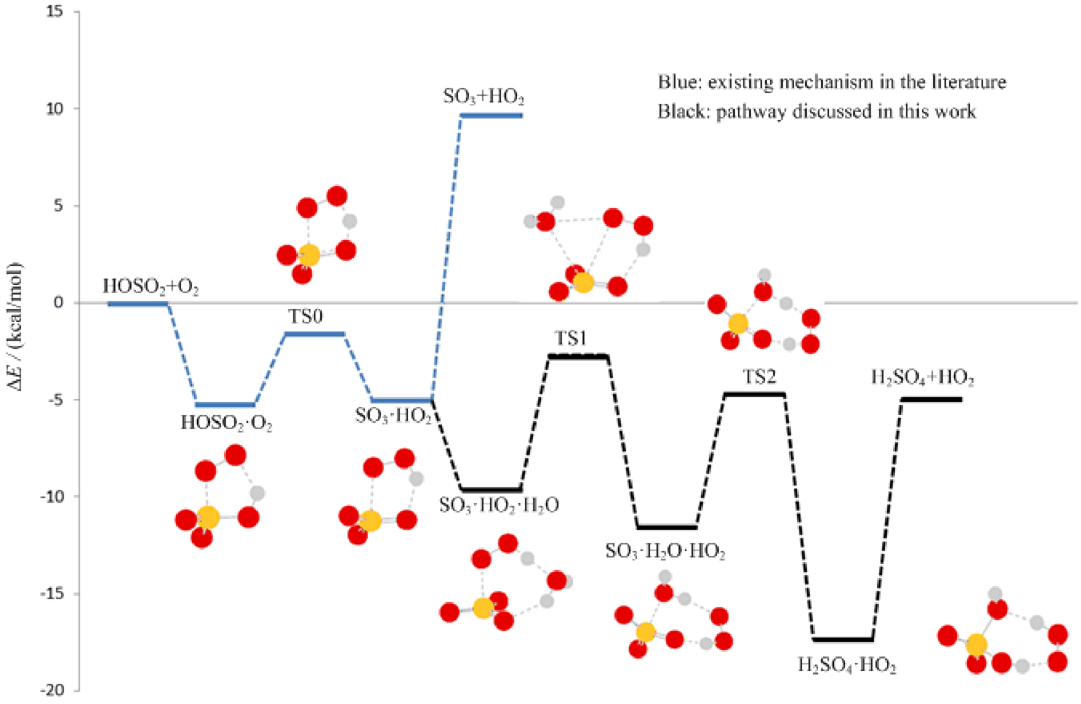

FIG. 2 Schematic of the potential energy profile for the reaction $HOSO_2+O_2+H_2O \rightarrow H_2SO_4+HO_2$.

SO_3 and HO_2, as in the product complex $SO_3 \cdot HO_2$, is mainly responsible for this result. It can thus be concluded that the reaction $HOSO_2+O_2$ may take place, but it only produces the $SO_3 \cdot HO_2$ complex.

In the new reaction pathway, a water molecule is added to the $SO_3 \cdot HO_2$ complex formed from the reaction between $HOSO_2$ and O_2. At least two conformations were found for the $SO_3 \cdot HO_2 \cdot H_2O$ complex. In the most stable conformation, H_2O accepts a hydrogen bond from HO_2 while donating a hydrogen bond to an oxygen atom of SO_3. In the second conformation, $SO_3 \cdot H_2O \cdot HO_2$, the water is inserted between the O atom of HO_2 and the S atom of SO_3. In other words, HO_2 and H_2O exchange positions on SO_3. The $SO_3 \cdot H_2O$ unit is an electron donor-acceptor complex involved as a pre-reaction complex for reaction (3). There is a transition state, TS1, for the conversion between the two complexes, $SO_3 \cdot HO_2 \cdot H_2O$ and $SO_3 \cdot H_2O \cdot HO_2$. The fairly low value of the relative energy at TS1, −1.6 kcal/mol at the MP2 level or −2.7 kcal/mol at CCSD(T), indicates that the conversion should be kinetically favorable. The further next step of the reaction is the hydrolysis of SO_3 in the complex $SO_3 \cdot H_2O \cdot HO_2$. The transition state, TS2, involves the transfer of an H atom from H_2O to HO_2 as the latter returns its own H atom to SO_3. The relative energy at TS2, −6.8 kcal/mol at the MP2 level or −4.7 kcal/mol at CCSD(T), is again very low, and so the reaction

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is also expected to be fast. The product complex $H_2SO_4{\cdot}HO_2$ is highly stable with a low relative energy of −13.4 kcal/mol at the MP2 level or −17.3 kcal/mol at CCSD(T). Finally, the $H_2SO_4{\cdot}HO_2$ complex is dissociated into the separate products H_2SO_4 and HO_2. The overall reaction, $HOSO_2+O_2+H_2O\rightarrow SO_3+HO_2$, has a value of $\Delta E=-5.0$ kcal/mol at the CCSD(T) level. The reaction is expected to be slightly endothermic or exothermic as shown by small values of ΔH, −8.1 and 1.3 kcal/mol from B3LYP/aug-cc-pVTZ and MP2/aug-cc-pVDZ calculations, respectively.

The hydrolysis of SO_3, with the transition state TS2, is a critical step in the reaction pathway. The relative energy of the transition state is surprisingly low. The corresponding energy barrier, about 6 kcal/mol from both MP2 and CCSD(T) methods, is much smaller than the energy barriers for the hydrolysis of SO_3 in small water clusters $SO_3{\cdot}(H_2O)_n$, ca. 21 and 14 kcal/mol with one and two waters, respectively [14, 15]. The barrier height is comparable to the one found for the cluster of three water molecules [15]. Clearly, HO_2 plays a more efficient role in transferring the proton/hydrogen atom in the hydrolysis reaction than a single H_2O molecule or a water dimer $(H_2O)_2$. At the transition state TS2, the $H\cdots O{-}O\cdots H$ chain appears to be equivalent to a stable molecule of hydrogen peroxide (H_2O_2), which might be responsible for the stability of TS2 and the low energy barrier for the hydrolysis of SO_3 in the complex $SO_3{\cdot}H_2O{\cdot}HO_2$. Note that the progressively large unit of the hydrated proton was responsible for the step-wise decrease in the energy barrier in the clusters $SO_3{\cdot}(H_2O)_n$ [15].

The results should be reliable as shown by generally consistent values of the relative energies (ΔE, ΔH, and ΔG) from different methods and basis sets in Table I. There are some noticeable fluctuations in these values at the B3LYP level among the three basis sets, 6-31+G*, aug-cc-pVDZ, and aug-cc-pVTZ. It appears that the proposed new reactions are more favored by the use of the largest basis set (aug-cc-pVTZ). On the other hand, MP2 and B3LYP calculations using the same basis set (aug-cc-pVDZ) give surprisingly consistent results despite of the two very different theoretical methods. Furthermore, CCSD(T) calculations using the same basis set have nearly reproduced the results from MP2 calculations. It is expected that the energetic values for the proposed reactions would become more favorable if CCSD(T) calculations were performed using a larger basis set beyond aug-cc-pVDZ. Such calculations were attempted but were not complete because of limitations in our computer resources.

Finally, it is important to point out that the spin-contamination problem is very mild throughout the calculations and it does not severely affect the reliability of the results in the present study. Typically unrestricted DFT methods such as B3LYP are subject to less spin contamination than molecular orbital methods such as UHF and UMP2. Coupled-cluster theory is even more effective in reducing the spin-contamination problem and CCSD(T) nearly completely eliminates the two major contaminants (S+1 and S+2). This is another reason why three different methods, B3LYP, MP2, and CCSD(T), were performed in our calculations. Almost all molecular species (reactant complexes, transition states, and product complexes) in the study are open-shell with the exact expectation eigenvalue of 0.75 for the spin-squared expectation operator $\langle S^2\rangle$. The unrestricted B3LYP, MP2, and CCSD(T) procedures were used for the calculations of these open-shell species. The B3LYP calculations with the different basis sets give the $\langle S^2\rangle$ values between 0.7550 and 0.7563 before annihilation (0.7500 after annihilation). The MP2 calculations give the values between 0.7639 and 0.7816 before annihilation (0.7501−0.7507 after annihilation). As expected, no spin-contamination problems were found in the CCSD(T) calculations. It is clear that the results in the present study are not affected by the spin-contamination problem.

IV. CONCLUSION AND ATMOSPHERIC IMPLICATIONS

Density functional theory and high-level *ab initio* molecular orbital theory have been used to explore the new potential energy surface for the atmospheric formation of sulfuric acid from $OH+SO_2$ by simultaneous inclusion of O_2 and H_2O molecules. Instead of producing the separate products of SO_3 and HO_2, as for the reaction $HOSO_2+O_2$ discussed in the literature, the intermediate complex $SO_3{\cdot}HO_2$ directly reacts with a water molecule and produces the final products H_2SO_4 and HO_2. The entire reaction pathway is composed of three consecutive elementary steps: (1) $HOSO_2+O_2\rightarrow SO_3{\cdot}HO_2$, (2) $SO_3{\cdot}HO_2+H_2O\rightarrow SO_3{\cdot}H_2O{\cdot}HO_2$, (3) $SO_3{\cdot}H_2O{\cdot}HO_2\rightarrow H_2SO_4+HO_2$. Molecular geometries at the stationary points of PES were calculated using B3LYP and MP2 methods with several basis sets, corresponding to the reactant complex, transition state, and product complex involved in each reaction step. The results consistently show that all three elementary steps have very low activation energies and are exothermic or nearly exothermic. It implies that the reactions are favorable both kinetically and thermodynamically. The results have been further confirmed by single-point energy calculations with high-level CCSD(T) method using MP2 geometries.

The new reaction pathway for the formation of sulfuric acid from SO_2 is more direct and favorable than existing mechanisms in the literature which assume the release of SO_3 from the initial steps of reaction. No additional species are required in the new pathway to initiate or complete the reaction other than OH, O_2, and H_2O, which are abundant in the atmosphere and known to be the principal ingredients in the conversion of SO_2

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into sulfuric acid. There are several major advantages of the new pathway over existing mechanisms in the literature. First, the hydrolysis of SO_3 takes place before SO_3 is released from the $SO_3{\cdot}HO_2$ complex. In other words, no release of SO_3 is necessary in the new reaction pathway. There is very strong intermolecular binding in the $SO_3{\cdot}HO_2$ complex, about 10 kcal/mol, which is thermodynamically unfavorable to dissociate into SO_3 and HO_2. Second, the radical HO_2 in the $SO_3{\cdot}HO_2$ complex assists the hydrolysis by exchanging its hydrogen between H_2O and an O atom of SO_3 and lowering the energy barrier of reaction; without HO_2, additional water molecules, at least two, must be added to serve the same purpose of lowering the energy barrier. Third, the hydrogen of HO_2 generated in the new mechanism originates from the water molecule was directly used for the hydrolysis of SO_3, instead of coming from $HOSO_2$ (originally the OH radical). Note that the production of HO_2 is important to the overall chemistry of SO_2 oxidation [1]. In the presence of NO, the HO_2 reacts to regenerate OH by the reaction $HO_2+NO\rightarrow OH+NO_2$. As a result, the oxidation of SO_2 is a chain reaction without a net loss of OH. The production of HO_2 is predicted in the new mechanism as well as in existing mechanisms in the literature.

Clearly, there are several significant atmospheric implications with the new mechanism. First, no SO_3 is released or can be observed in the conversion of SO_2 into sulfuric acid. As an intermediate, SO_3 is predicted in the existing mechanism. To our best knowledge, however, no direct evidence has been reported in support of the generation of SO_3 in the oxidation of SO_2 by the OH radical in the atmosphere. Second, the rate of conversion in the new mechanism is expected to weakly depend on the humidity of air because only one water molecule is required for each SO_2. In contrast, the rate of conversion in the existing mechanism would be strongly dependent on the humidity because multiple water molecules are required for the conversion process of each SO_2.

V. ACKNOWLEDGMENTS

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