***Ab initio* study on the paths of oxygen abstraction of hydrogen trioxide (HO₃) molecule in the HO₃ + SO₂ reaction**

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Abstract. The reaction paths of hydrogen trioxide (HO₃) with sulphur dioxide (SO₂) have been investigated on the doublet potential energy surface, theoretically. All species of the title reaction have been optimized at the PMP2(FC)/cc-pVDZ computational level. Energetic data have been obtained at the CCSD(T)//PMP2 level employing the cc-pVDZ basis set. No stable collision complexes have been found between the SO₂ and HO₃ molecules. Therefore, the SO₂ + HO₃ reaction starts without initial associations. The four possible paths, P₁ through P₄, have been obtained for the formation of SO₃ (D_{3h}) + HOO• product. Our results show that these four paths include relatively high energy barriers to produce the final product of the SO₃ (D_{3h}) + HOO•. Therefore, the SO₂ + HO₃ → SO₃ (D_{3h}) + HOO• reaction is difficult to perform under atmospheric conditions. This means that the importance of SO₂ + HO₃ → SO₃ (D_{3h}) + HOO• reaction increases with increasing temperature and, this reaction plays an important role in the SO₃ (D_{3h}) production as the main molecule of the formation of acid rain at high temperatures.

Keywords. *Ab initio* calculations; atmospheric chemistry; hydrogen trioxide; acid rain.

1. Introduction

Processes such as volcanic eruptions, biogenic activity, and the combustion of fossil fuels are resources for the emission of sulphur gases into the atmosphere. Sulphur has been recognized as an important constituent of atmospheric aerosols and its compounds are major pollutants of the environment.¹ The 16 molecular species of type S_nO_m (*m* = 1–4 and *n* = 1–12), (SO, SO₂, SO₃, SO₄, S₂O₂, etc.), have been detected, experimentally.² Among these species, the sulphur dioxide (SO₂) and sulphur trioxide (SO₃ (D_{3h})) play an important role in the atmospheric formation of sulphuric acid which is a primary constituent of acid rain.^{3,4} Accepted mechanism for the formation of sulphuric acid has attracted considerable attention in recent years. It has been shown as follows.^{5–8}

In the above mechanism, OH• radical attacks SO₂ molecule to form the HOSO₂ intermediate. Subsequently, the HOSO₂ intermediate reacts with O₂ and the SO₃ (D_{3h}) + HOO• product appears. The SO₃ (D_{3h}) is a well-known molecule in the atmosphere and its vibrational spectra in the gaseous phase or isolated in a matrix were reported by numerous investigators.^{9–16} In the third reaction, the SO₃ (D_{3h}) molecule reacts with two water molecules or a water dimer^{17,18} to produce sulphuric acid. Note that the SO₃ (D_{3h}) molecule is the main factor of the formation of acid rain and the reaction of SO₃ (D_{3h}) + H₂O is very important. The many experimental and theoretical studies have been performed on the reaction of SO₃ (D_{3h}) with H₂O.^{17–20}

In the present study, we have deleted OH• radical and O₂ molecule from steps (1) and (2) of the above mechanism and have replaced them with one hydrogen trioxide molecule, HO₃. Subsequently, the mechanism of the atmospheric reaction of SO₂ + HO₃ → SO₃ (D_{3h}) + HOO• has been investigated to produce the SO₃ (D_{3h}) molecule as the main factor of the formation of acid rain (SO₂ + HO₃ → SO₃ (D_{3h}) + HOO•).

The HO₃ molecule has been assumed to be an important intermediate in atmospheric and combustion chemistry.²¹ In the past decades, because of lack of direct experimental evidence, numerous theoretical

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investigations have been performed on the stability of the HO₃ molecule. These theoretical studies included conflicting results.^{22–29} Finally, the stability problem of the HO₃ molecule has been solved by two experimental measurements.^{21,30} The Fourier-transform ion cyclotron resonance mass spectrometry study³⁰ shows that the HO₃ molecule is relatively stable at 10 ± 5 kcal/mol with respect to OH• + O₂. In turn, Cacace *et al.*²¹ detected directly a stable HO₃ molecule using neutralization–reionization and neutralization–reionization/collisionally activated dissociation mass spectrometry.

To the best of our knowledge, the reaction mechanism of SO₂ + HO₃ → SO₃ (D_{3h}) + HOO• is ambiguous and the location of its transition states has not been reported in literature. In view of the lack of information and theoretical investigations for this system, theoretical studies of mechanism have been carried out on the doublet potential energy surface (PES) to reveal the details of reaction mechanism to explain the role of SO₂ + HO₃ → SO₃ (D_{3h}) + HOO• reaction in the formation of the SO₃ (D_{3h}) molecule as the main factor in the formation of acid rain.

2. Computational methods

Calculations were performed using the Gaussian 03 system of codes.³¹ Geometries of all the species fully optimized at the second-order Møller–Plesset perturbation method (MP2)³² in conjunction with the Dunning's cc-pVDZ³³ (correlation-consistent polarized valence double-zeta) basis set. In order to remove spin contamination from higher spin states, spins were projected out of the spin contaminant of the unrestricted wave function. The resulting energies were denoted as PMP2. The core orbitals (1s for O atom and 1s, 2s and 2p for S atom) were not included in the correlation treatment (Frozen-Core (FC) approach). To gain reliable energies of each stationary state, calculations of single-point energy at the spin unrestricted at the CCSD(T)^{34–38} (coupled-cluster single and double excitation model augmented with a non-iterative triplet excitation correction) level were carried out on the optimized geometries of the PMP2 level. The cc-pVDZ basis set was employed for the energetic calculations (CCSD(T)/cc-pVDZ//PMP2).

Vibrational frequencies characterize the nature of the stationary points, i.e., minimum or saddle point, according to the number of negative eigenvalues of the Hessian matrix at the PMP2(FC)/cc-pVDZ level. All the stationary points were identified as local minima (number of imaginary frequencies (NIMAG) is zero) or

transition states (NIMAG = 1). Finally, the calculation of intrinsic reaction coordinates (IRC)³⁹ was performed at the PMP2 (FC) level to confirm connection of the transition states with intermediates.

3. Results and discussion

Optimized geometries of the reactants, intermediates (INs), transition states (TSs) and products at the PMP2(FC)/cc-pVDZ level are shown in figure 1. Note that the optimized geometries of the HO₃, SO₂, HOO• and SO₃ (D_{3h}) in the present study are in good agreement with available experimental^{40,41} and theoretical⁴² data as shown in figure 1. Total energies (E_T) and relative energies (ΔE_T) have been listed in table 1 for the PMP2 and CCSD(T) levels. Note that the $\langle S^2 \rangle$ values of the INs and TSs are listed in table 1 (where S stands for electron spin angular momentum in unit of $\hbar$). These values are predicted to be in the range of 0.751–0.798 which is close to that of a pure doublet state (0.750). Therefore, the theoretical results of the present study do not include a serious problem regarding spin contamination.

Finally, the potential energy diagram of the SO₂ + HO₃ reaction at the CCSD(T) level is plotted in figure 2. Where, the reaction energy of SO₂ + HO₃ is set to zero as reference and, the paths containing the formation of the S–O1 bond and the decomposition of O1–O2 bond have been shown through dashed and solid lines, respectively.

3.1 Reaction mechanism

In spite of numerous attempts, no stable collision complexes have been found between SO₂ and HO₃ molecules. Therefore, the SO₂ + HO₃ reaction starts without initial associations. Our calculations led to the identification of a simple mechanism for the reaction between SO₂ and HO₃ molecules. There are four possible paths for the formation of SO₃ (D_{3h}) + HOO• product, which can be written as follows:

The overall mechanism of paths P₁, P₂, P₃ and P₄ is similar to one another. In these four paths, the first

Figure 1. Optimized geometries of the reactants, INs, TSs and products at the PMP2 level. (The bond lengths are in angstrom.) The values in square brackets and parentheses are the experimental^{40,41} and theoretical⁴² data, respectively.

transition states (TS₁ through TS₄) include S–O1 bond which is between S-atom of the SO_2 and terminal O-atom of the HO_3 molecule (approaching of S to O1). The second transition states (TS₅ through TS₈) show decomposition of O1–O2 bond in the IN1, IN2, IN3 and IN4 intermediates.

In paths P₁, P₂, P₃ and P₄, the initial reactants of the SO_2 and HO_3 transform to the intermediates of IN1, IN2, IN3 and IN4 via TS1, TS2, TS3 and TS4, respectively. The energy barrier for the conversions of $\text{SO}_2 + \text{HO}_3 \rightarrow \text{IN1}$, $\text{SO}_2 + \text{HO}_3 \rightarrow \text{IN2}$, $\text{SO}_2 + \text{HO}_3 \rightarrow \text{IN3}$ and, $\text{SO}_2 + \text{HO}_3 \rightarrow \text{IN4}$ is 29.45, 28.08, 27.63 and 24.95 kcal/mol at the CCSD(T) level, respectively. In this step, the reaction mechanism is the formation of S–O1 bond as shown in figure 2 (through dashed

lines). The IN1, IN2, IN3 and IN4 intermediates are 21.87, 21.66, 21.34 and 19.65 kcal/mol above the initial reactants of the SO_2 and HO_3 , respectively. Therefore, IN4 is the most stable intermediate in the $\text{SO}_2 + \text{HO}_3$ reaction.

Finally, the IN1, IN2, IN3 and IN4 intermediates can transform to final product of $\text{SO}_3 (\text{D}_{3h}) + \text{HOO}\cdot$ through TS8, TS6, TS5 and TS7, respectively. In this step, the reaction mechanism is the decomposition of O1–O2 bond of IN1, IN2, IN3 and IN4 intermediates as shown in figure 2 (through solid lines). The energy barrier for the conversions of $\text{IN1} \rightarrow \text{SO}_3 (\text{D}_{3h}) + \text{HOO}\cdot$, $\text{IN2} \rightarrow \text{SO}_3 (\text{D}_{3h}) + \text{HOO}\cdot$, $\text{IN3} \rightarrow \text{SO}_3 (\text{D}_{3h}) + \text{HOO}\cdot$ and $\text{IN4} \rightarrow \text{SO}_3 (\text{D}_{3h}) + \text{HOO}\cdot$ is 24.24, 34.35, 36.11 and 31.35 kcal/mol at the CCSD(T) level, respectively.

Table 1. Total energies (E_T) and relative energies (ΔE_T) obtained in the $\text{SO}_2 + \text{HO}_3$ reaction.

Species	PMP2/cc-pVDZ		CCSD(T)/cc-pVDZ//PMP2	
	E_T	$\langle S^2 \rangle$	E_T	ΔE_T
$\text{SO}_2 (^1\text{A}_1) + \text{HO}_3 (^2\text{A})$	-773.17240		-773.23146	0.00
IN1 (^2A)	-773.15010	0.792	-773.19661	21.87
IN2 (^2A)	-773.15165	0.798	-773.19695	21.66
IN3 (^2A)	-773.15229	0.798	-773.19746	21.34
IN4 (^2A)	-773.15359	0.797	-773.20015	19.65
$\text{SO}_3 (^1\text{A}') + \text{HOO}\cdot (^1\text{A}'')$	-773.20370		-773.24915	-11.10
TS1 (^2A)	-773.12834	0.760	-773.18453	29.45
TS2 (^2A)	-773.12907	0.760	-773.18671	28.08
TS3 (^2A)	-773.12941	0.760	-773.18743	27.63
TS4 (^2A)	-773.13102	0.758	-773.19170	24.95
TS5 (^2A)	-773.12323	0.751	-773.13991	57.45
TS6 (^2A)	-773.12347	0.769	-773.14220	56.01
TS7 (^2A)	-773.12878	0.772	-773.15019	51.00
TS8 (^2A)	-773.13239	0.770	-773.15798	46.11

Total energies (E_T) and relative energies (ΔE_T) are in hartree and kcal/mol, respectively

$$E_T = E_{\text{elec}} + E_{\text{NN}} + \text{ZPE}$$

Spectroscopic symbols are in parentheses

In $\langle S^2 \rangle$, S stands for electron spin angular momentum in unit of $\hbar$

The S^2 value for a pure doublet state is 0.750

3.2 Thermodynamic data for the $\text{SO}_2 + \text{HO}_3 \rightarrow \text{SO}_3 + \text{HOO}\cdot$ reaction

The change of thermodynamic characteristics for each reaction step is the difference between corresponding thermodynamic properties of products and reactants. Thermodynamic data are corrected by ZPE at the PMP2 level. The relative internal energies (ΔU), enthalpies (ΔH), Gibbs free energies (ΔG), and entropies (ΔS)

of the $\text{SO}_2 + \text{HO}_3 \rightarrow \text{SO}_3 + \text{HOO}\cdot$ reaction have been summarized in table 2 at 298.15 K.

Table 2 shows that ΔH for steps (1), (3), (5) and (7) is positive (endothermic), while that of steps (2), (4), (6) and (8) is negative (exothermic). Also, the investigation of ΔG values implies that steps (1), (3), (5) and (7) should be non-spontaneous ($\Delta G > 0$) and the other steps in table 2 are spontaneous ($\Delta G < 0$).

The positive ΔS values of steps (2), (4), (6) and (8) show that entropy (S) increases in these steps, while it decreases in remaining steps. Finally, the results show that the $\text{SO}_2 + \text{HO}_3 \rightarrow \text{SO}_3 + \text{HOO}\cdot$ reaction is exothermic ($\Delta H < 0$), exergonic and spontaneous ($\Delta G < 0$). Note that the ΔU value of the $\text{SO}_2 + \text{HO}_3 \rightarrow \text{SO}_3 + \text{HOO}\cdot$ reaction is similar to its corresponding ΔH value ($\Delta U = \Delta H = 18.41$ kcal/mol). This result is not surprising because, the number of gaseous moles of input ($\text{SO}_2 + \text{HO}_3$) and output ($\text{SO}_3 + \text{HOO}\cdot$) is exactly equivalent in the $\text{SO}_2 + \text{HO}_3 \rightarrow \text{SO}_3 + \text{HOO}\cdot$ reaction.

As a result, the paths obtained from the $\text{SO}_2 + \text{HO}_3$ reaction (P_1 through P_4) include relatively high energy barriers to produce the final product of $\text{SO}_3 + \text{HOO}\cdot$. This means that paths P_1 through P_4 are not suitable, kinetically. In contrast, the study on thermodynamics of the $\text{SO}_2 + \text{HO}_3$ reaction shows which this reaction should be exothermic ($\Delta H < 0$), exergonic and spontaneous ($\Delta G < 0$). Therefore, the importance of the $\text{SO}_2 + \text{HO}_3 \rightarrow \text{SO}_3 + \text{HOO}\cdot$ reaction

Figure 2. Potential energy profile of the $\text{SO}_2 + \text{HO}_3$ reaction at the CCSD(T) level.

Table 2. Thermodynamic data for the SO₂ + HO₃ → SO₃(D_{3h}) + HOO• reaction at the PMP2 level.

Steps		ΔU	ΔH	ΔG	$T \Delta S$
(1)	SO ₂ + HO ₃ → IN1	18.61	18.01	29.8	−11.79
(2)	IN1 → SO ₃ (D _{3h}) + HOO•	−37.01	−36.42	−47.70	11.28
(3)	SO ₂ + HO ₃ → IN2	18.09	17.50	29.23	−11.72
(4)	IN2 → SO ₃ (D _{3h}) + HOO•	−36.50	−35.90	−47.11	11.21
(5)	SO ₂ + HO ₃ → IN3	17.73	17.13	28.17	−11.59
(6)	IN3 → SO ₃ (D _{3h}) + HOO•	−36.13	−35.53	−46.62	11.08
(7)	SO ₂ + HO ₃ → IN4	16.61	16.01	28.32	−12.31
(8)	IN4 → SO ₃ (D _{3h}) + HOO•	−35.01	−34.42	−46.22	11.81
	SO ₂ + HO ₃ → SO ₃ (D _{3h}) + HOO•	−18.41	−18.41	−17.90	−0.51

All energies are in kcal/mol and the temperature is 298.15 K

$$\Delta U = E_{\text{elec}} + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{NN}}$$

increases with increasing temperature and, this reaction plays an important role in the SO₃ (D_{3h}) production as main factor of acid rain formation at high temperatures.

4. Conclusion

Details of the reaction mechanism of SO₂ + HO₃ → SO₃ (D_{3h}) + HOO• on the doublet PES have been investigated at PMP2 and CCSD(T) levels, theoretically. In spite of numerous attempts, no stable collision complexes have been found between the SO₂ and HO₃ molecules. Therefore, the SO₂ + HO₃ reaction starts without initial associations. The four possible paths, P₁ through P₄, have been obtained for the formation of the SO₃ (D_{3h}) + HOO• product. These paths include relatively high energy barriers to produce the final product of SO₃ (D_{3h}) + HOO•. The result of our calculations shows that the SO₂ + HO₃ → SO₃ (D_{3h}) + HOO• reaction is exothermic and spontaneous, thermodynamically. However, this reaction is difficult to perform under ordinary conditions, kinetically. Therefore, the importance of the SO₂ + HO₃ → SO₃ (D_{3h}) + HOO• reaction increases with increasing temperature and, this reaction plays an important role in the SO₃ (D_{3h}) production as main factor of the acid rain formation at high temperatures.

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