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Theoretical Study on Impact of Single Water Molecule on OH+O₃ Reaction

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Quantum chemical calculations are performed to study the reactions of OH and ozone with-out and with water to estimate whether the single water molecule can decrease the energy barrier of the OH radical reaction with ozone. The calculated results demonstrate that the single water molecule can reduce the activated barrier of the naked OH+O₃ reaction with the value of about 4.18 kJ/mol. In addition, the transition state theory is carried out to determine whether the single water molecule could enhance the rate constant of the OH+O₃ reaction. The computed kinetic data indicate that the rate of the ozone reaction with the formed complexes between OH and water is much slower than that of the OH+O₃ reaction, whereas the rate constant of OH reaction with the formed H₂O···O₃ complex is 2 times greater than that of the naked OH radical with ozone reaction. However, these processes in the atmosphere are not important because the reactions can not compete well with the naked reaction of OH with ozone under atmospheric condition.

Key words: Ozone, OH, H₂O, Atmospheric chemistry, Quantum chemical calculation

I. INTRODUCTION

The reaction of hydroxyl radical with ozone is of key significance in the atmosphere because it has an influence on the concentrations of many trace gases and plays a crucial role in the stratospheric ozone destruction [1–7]. Due to the importance of the reaction of OH with ozone in the Earth's chemistry, there have been many experimental and theoretical reports [7–18] on the reaction mechanisms and kinetics of the OH+O₃ reaction. The rate constant is calculated to be $7.37 \times 10^{14} \text{ cm}^3/(\text{molecule s})$ [18], which is in close agreement with the experimental value of $7.25 \times 10^{14} \text{ cm}^3/(\text{molecule s})$ at 298 K [7].

On the other hand, water is of great abundance in the Earth's atmosphere and can form hydrogen bonded complexes with other molecules such as O₃···H₂O [19], HNO₃···H₂O [20], OCIO···H₂O [21, 22], and H₂SO₄···H₂O [23], which have impacts on the photochemistry of atmosphere. Moreover, very recently, some theoretical and experimental reports [24–42] have been demonstrated that the single water molecule can enhance or decrease the reaction constants and change the reaction mechanisms. For example, a single wa-

ter molecule can promote the oxidation of acetaldehyde [24], glyoxal [40], and sulfuric acid [42] via the OH radical, the HO₂-self reaction [28] leading to the formation of H₂O₂ and O₂ and the decomposition of CF₃OH [41] by the HO₂ radical. The water vapor can not only accelerate the reaction [25, 26] of HCOOH with OH but also change the reaction mechanisms responsible for the influence of the product distributions. In addition, the water dimer or water cluster plays a significant role in reactions of carbonyl oxides [29, 30] with water, the decomposition of gas phase peroxyacetyl nitrate (PAN) [31] and SO₃ [32–34] with water responsible for the formation of sulfuric acid. Additionally, the water molecule can also hamper the reactions of CH₄ [38], HNO₃ [39] with OH.

In the present work, the reactions of ozone with the formed OH···H₂O complex Eq.(1) and the formed O₃···H₂O complex with OH Eq.(2) are investigated using quantum chemical methods and transition state theory.



As for the reactions studies herein, it is the first theoretical study on the reaction of ozone with the OH radical and the single water molecule. In addition, to the best of our knowledge, it is also the first investigation on the OH addition reaction in the presence of the

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single water molecule, which is different from the hydrogen atom abstracted by OH radical with the single water added. In this work, we elucidate the reaction mechanisms and evaluate whether the reactions are kinetically favored, compared with the naked reaction of ozone with the OH radical.

II. COMPUTATIONAL DETAILS

All the calculations have been carried out using the Gaussian 03 software [43]. The geometries of all the reactants, pre-reactive complexes, transition states and products are optimized at the MP2/6-311+G(d, p) level of theory. The corresponding frequencies of the optimized geometries are computed at the same level to prove the characters of the transition states with one imaginary frequency and the stationary points with positive frequencies. In order to obtain relative energies reliably, single point energies have been refined using the CCSD(T)/6-311++G(3df, 3pd) theoretical method at the MP2-optimized geometries. To estimate the selected theoretical methods reliably, test calculations have been performed and analyzed. In these computations, the values of $T1$ diagnostic in the CCSD wave function are considered to evaluate the reliability of these computations with respect to a possible multireference feature of the wave function at the stationary points and transition states [44, 45]. The $T1$ diagnostic are up to 0.045, which do not exceed the upper limit of the criteria [45], unraveling that the calculations could be considered to be reliable. Moreover, as for the complexes founded in this work, the basis set superposition error (BSSE) is calculated using the counterpoise method by Boys and Bernardi at the CCSD(T)/6-311++G(3df, 3pd) level [46].

The rate constant is evaluated using the conventional transition state theory (CTST) [47–52] as written

$$k(T) = \kappa \sigma \frac{k_B T}{h} \frac{Q_{TS}}{Q_R} \exp\left(-\frac{E_{TS} - E_R}{k_B T}\right) \quad (3)$$

where Q_{TS} and Q_R are, respectively, the partition functions of the transition states and the reactants, k_B is the Boltzmann's constant, κ is the transmission coefficient, and σ is the symmetry factor. The E_{TS} and E_R stand for the energy of the transition state and the reactant with zero point energy correction involved, respectively. The tunneling factor is calculated in terms of the one-dimensional Eckart [53] correction carried out in the TheRate program [54].

III. RESULTS AND DISCUSSION

A. $\text{HO}\cdots\text{H}_2\text{O}$, $\text{H}_2\text{O}\cdots\text{HO}$, and $\text{H}_2\text{O}\cdots\text{O}_3$ complexes

As for the water molecule interaction with OH, there are two hydrogen bonded complexes $\text{H}_2\text{O}\cdots\text{HO}$ (M1)

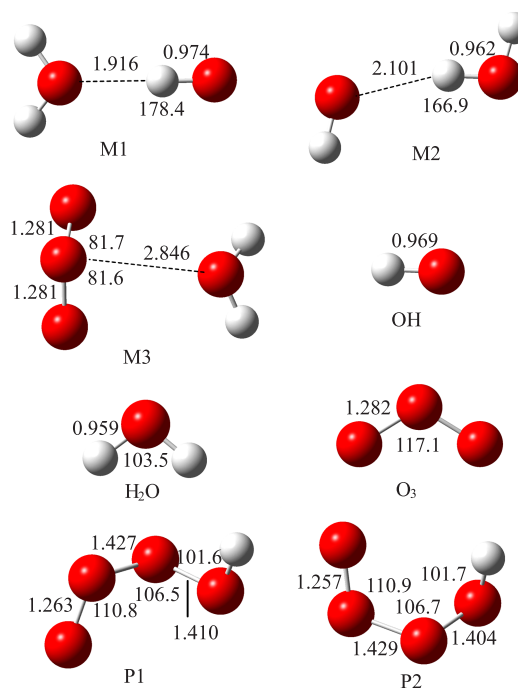


FIG. 1 The optimized geometries of the reactants, the complexes and products at the MP2/6-311+G(d, p) level of theory, bond distances in Å and angles in ($^{\circ}$).

and $\text{HO}\cdots\text{H}_2\text{O}$ (M2) located herein as presented in Fig.1. In addition, the binding energies between OH and H_2O are provided to compare our results with the previously experimental and theoretical results in Table I. From Table I, the interaction energies of the M1 and M2 are found to be -15.84 and -9.36 kJ/mol respectively at the CCSD(T)/6-311++G(3df, 3pd)/MP2/6-311+G(d, p) level without BSSE correction and with zero-point energy correction involved, which is in good agreement with the experimental and theoretical data in the literature [39, 55–62].

The calculated results prove that the BSSE has little influence on the binding energies of the complexes. Thus, the BSSE is not taken into account. Regarding the complexes between ozone and H_2O , there are three stationary points reported [63]. However, in this investigation, the most stable complex $\text{HO}\cdots\text{O}_3$ (M3) is depicted in Fig.1, which contributes to the elementary reaction of M3 with OH. The calculated binding energy without the zero-point correction is -10.45 kJ/mol, which is consistent with the reported value of -9.99 kJ/mol at the QCISD(T)/6-311++G(3df, 3pd)/QCISD/6-311++G((d, p) level [63]. In addition, the energy barriers of OH with ozone are calculated here to be 6.48 and 8.57 kJ/mol with respect to the separated reactants, respectively, which are in reasonable agreement with the reported values 7.52 and 9.45 kJ/mol by Anglada *et al.* [18]. Therefore, the test results above reflect that the selected methods can describe the reaction system reliably.

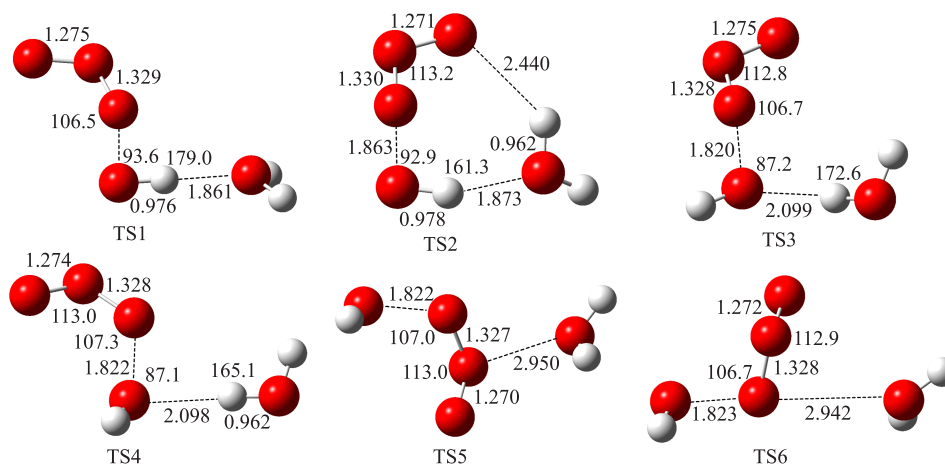


FIG. 2 The optimized geometries of the transition states at the MP2/6-311+G(d, p) level of theory, bond distances in Å and angles in ($^{\circ}$).

TABLE I The binding, reaction, and activated energy ΔH , enthalpy ΔG , and free energy ΔE for the reactions of OH with ozone and H_2O with zero-point correction at 298 K.

Compound	ΔH^a /(kJ/mol)	ΔG^a /(kJ/mol)	ΔE^a /(kJ/mol)	ΔE^b /(kJ/mol)	$T1^c$
OH+ H_2O	0.00	0.00	0.00	0.00	0.010, 0.010
M1	-21.61	6.60	-18.56	-15.84	0.010
M2	-10.70	12.25	-9.53	-9.36	0.010
$\text{H}_2\text{O}+\text{O}_3$	0.00	0.00	0.00	0.00	0.010, 0.029
M3	-10.28	17.93	-11.04	-5.73	0.025
OH+ $\text{H}_2\text{O}+\text{O}_3$	0.00	0.00	0.00	0.00	0.010, 0.010, 0.029
TS1	139.32	205.99	143.71	-9.28	0.044
TS2	134.60	210.21	140.74	-13.75	0.044
TS3	153.41	218.82	157.63	-3.85	0.044
TS4	152.40	218.45	156.62	-4.93	0.044
TS5	156.29	218.03	158.55	0.13	0.044
TS6	158.13	220.37	160.60	2.05	0.044
P1+ H_2O	7.27	47.32	12.46	-74.11	0.030
P2+ H_2O	3.43	44.10	8.78	-79.71	0.031

^a ΔH , ΔG , and ΔE are computed at the MP2/6-311+G(d, p) level of theory.

^b ΔE is calculated at the CCSD(T)/6-311++G(3df, 3pd)//MP2/6-311+G(d, p) level of theory.

^c $T1$ is diagnostic value.

B. Reaction between $\text{HO}\cdots\text{H}_2\text{O}$, $\text{H}_2\text{O}\cdots\text{HO}$ and ozone

The ozone attacks the $\text{H}_2\text{O}\cdots\text{HO}$ complex via the corresponding transition states TS1 and TS2 from the two different directions as displayed in Fig.2. The potential energy profile reveals the elementary process as provided in Fig.3, which is similar to the reaction of ozone with OH [18]. In the two transition states TS1 and TS2, it is noted that the bond distances between the H atom in the OH radical and the oxygen of the water are shorter than the corresponding $\text{HO}\cdots\text{H}_2\text{O}$ complex by 0.055 and 0.043 Å, respectively, whereas the O–O bonds in the ozone approaching the OH radical are stretched to 1.329 and 1.330 Å, respectively. Ad-

ditionally, in the TS2, it is also worth noting that the hydrogen atom of water interaction with the terminal oxygen in the ozone leads to the decrease of the activated barrier of TS2 because the energy barrier of TS2 is lower than the corresponding TS1 by 4.47 kJ/mol as seen Table I. Furthermore, the energy barrier via TS2 is lower than that of the correspondingly naked OH reaction with O_3 [18] by ~ 5.43 kJ/mol relative to the corresponding reactants, indicating that the single water can reduce the energy barrier of the OH+ O_3 reaction. As for the reaction $\text{O}_3+\text{M2}$, the reaction mechanism is similar to the $\text{O}_3+\text{M1}$ and the corresponding transition states TS3 and TS4 are given in Fig.2. From the geometrical point of view, in the TS3 and TS4, the terminal

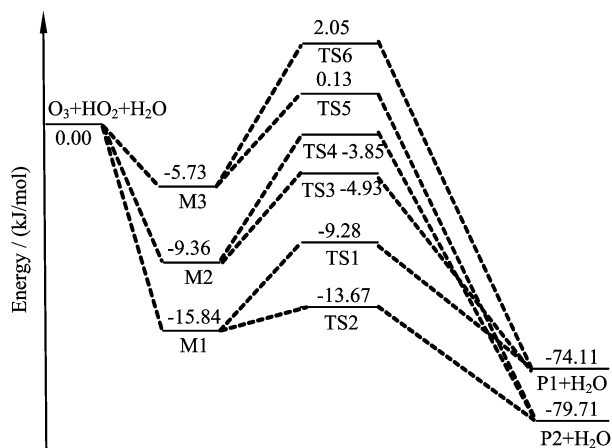


FIG. 3 The calculated potential energy profile at the CCSD(T)6-311++G(3df, 3pd)//MP2/6-311+G(d, p) level of theory.

oxygens of the ozone approach the oxygen of OH with the distances of 1.820 and 1.822 Å, respectively, which are about 0.4 Å shorter than those of the corresponding transition states TS1 and TS2. The barriers of TS3 and TS4 are computed to be 5.52 and 4.43 kJ/mol with respective to M2 and ozone, respectively. The calculated results show that the single water molecule accelerates the reaction of ozone with OH from the energetic point of view because the barriers of the naked reaction $\text{OH} + \text{O}_3$ are 7.52 and 9.45 kJ/mol [18].

C. Reaction between $\text{H}_2\text{O} \cdots \text{O}_3$ and OH

Due to the water molecule in the atmosphere, the single water molecule can form the complexes between water and ozone. Although there are three complexes formed between water and ozone reported in Ref.[63], there is only the most stable M3 contributed to the elementary process, where the corresponding transition states TS5 and TS6 (Fig.2) are located herein. In the transition states TS5 and TS6, the bond distances of the terminal oxygen of ozone approaching the oxygen atom of the OH radical are approximately equal to the corresponding bond distances in transition states TS3 and TS4. Additionally, the bond lengths of the oxygen atom of ozone interaction with the central oxygen of water are stretched with respect to the corresponding complex M3. The energy barrier via TS5 is calculated to be 5.85 kJ/mol, relevant to the M3 and OH, which is slightly lower than that of the TS6 by 1.93 kJ/mol, which is very similar to the value (1.92 kJ/mol) of the barrier difference in the reaction of ozone with OH [18]. Furthermore, the activated barrier of TS5 is lower than that of the corresponding reaction of OH with ozone by 1.67 kJ/mol [18]. Therefore, from the energetical point of view, the energy barriers of the reaction of ozone with OH and the single water molecule are lowered because there are weak interactions existing in the transition

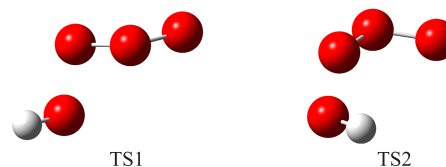


FIG. 4 The optimized geometries of the transition states at the MP2/6-311+G(d, p) level of theory.

TABLE II The calculated rate constant with Eckart correction for every elementary process in 220–320 K.

	$k/10^{-15}$ ($\text{cm}^3/(\text{molecule s})$)						
	220 K	240 K	260 K	280 K	298 K	300 K	320 K
TS1	2.26	3.23	4.44	5.91	7.50	7.67	9.75
TS2	1.62	1.78	1.95	2.14	2.32	2.34	2.56
TS3	2.05	2.60	3.22	3.91	4.61	4.68	5.53
TS4	2.86	3.47	4.13	4.84	5.55	5.62	6.47
TS5	61.7	79.8	100	124	147	149	178
TS6	19.9	27.7	37.2	48.4	60.1	61.3	7.61

states mentioned above.

D. Kinetics

In order to demonstrate whether the single water molecule can enhance the rate constant of OH reaction with ozone, the rate constant of every elementary process discussed above is computed in terms of the transition state theory as reported in Table II. The rate constants of the naked reaction of OH with ozone via TS01 and TS02 (Fig.4) are computed to be 2.67×10^{-14} and $2.49 \times 10^{-14} \text{ cm}^3/(\text{molecule s})$ at 298 K, which reasonably agree with the theoretical and experimental data [7, 18]. Table II indicates that the rate constants via TS5 ($1.47 \times 10^{-14} \text{ cm}^3/(\text{molecule s})$) and TS6 ($6.01 \times 10^{-14} \text{ cm}^3/(\text{molecule s})$) are about two times larger than those of the naked reaction of OH with ozone, which shows that the single water molecule can accelerate the $\text{OH} + \text{O}_3$ reaction, whereas other reaction pathways decrease the rate constants of the OH reaction with ozone. Regarding the importance of the reactions via TS5 and TS6 in the atmosphere, the TS5 and TS6 may play a minor role in the atmosphere because the rate coefficients via TS5 and TS6 are about 2 times greater than the naked $\text{OH} + \text{O}_3$ reaction and the concentration of the $\text{H}_2\text{O} \cdots \text{O}_3$ complex is quite small, compared with the concentration of ozone. These similar results are also reported in Refs.[64, 65].

IV. CONCLUSION

The reactions of ozone with the formed $\text{HO} \cdots \text{H}_2\text{O}$ and $\text{H}_2\text{O} \cdots \text{HO}$ complexes and OH with the $\text{H}_2\text{O} \cdots \text{O}_3$ complex are studied using the quantum chemical meth-

ods and the transition state theory. To check the reliability of the theoretical methods selected here, we reinvestigate the reaction $\text{OH} + \text{O}_3$ at the CCSD(T)/6-311++G(3df, 3pd)//MP2/6-311+G(d, p) level of theory. The test calculations show that the theoretical approaches used here are reliable to study the title reaction. As for the single water molecule introduced to the reaction $\text{OH} + \text{O}_3$, although the barriers of these elementary processes are slightly decreased, the computed rate constants show that OH reaction with the $\text{H}_2\text{O} \cdots \text{O}_3$ complex is kinetically favored. However, the rate is enhanced so small that the process is unlikely to play an important role in the ozone depletion.

V. ACKNOWLEDGMENTS

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