The influence of a single water molecule on the reaction of BrO + HO_2

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Abstract

The influence of a single water molecule on the BrO + HO_2 hydrogen extraction reaction has been explored by taking advantage of CCSD(T)/aug-cc-pVTZ//B3LYP/6-311++G(d,p) method. The reaction in the absence of water have two distinct kinds of H-extraction channels to generate HOBr + O_2 and HBr + O_3, and the channel of generation of HOBr + O_2 occupied the BrO + HO_2 reaction. The rate coefficient of the most feasible channel for the BrO + HO_2 reaction in the absence of water is estimated to be 1.44 ´ 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298.15 K, which is consistent with the experiment. The introduction of water made the reaction more complex, but the products are unchanged. Four distinct channels, beginning with HO_2···H_2O with BrO, H_2O···HO_2 with BrO, BrO···H_2O with HO_2, H_2O···BrO with HO_2 are researched. The most feasible channels, stemming from H_2O···HO_2 with BrO, and BrO···H_2O with HO_2, are much slower than the reaction of BrO + HO_2 without water, respectively. Thus, the existence of water molecule takes a negative catalytic role for BrO + HO_2 reaction.

1. Introduction

Methyl bromide stems from nature and humanity. It is the main precursor of active bromine involved in stratospheric ozone chemistry[1, 2]. Bromine, especially bromine oxide species are known to play a significant role in stratospheric ozone destruction and polar ozone hole chemistry[3, 4], in spite of its concentration being much lower than that of chlorine. Such destruction takes place passing through catalytic circles, in which the active substances are regenerated. In order to comprehend and simulate atmospheric ozone concentration, it is necessary to obtain the parameters describing the kinetics and photochemistry including such cycles.

Because the reaction of BrO + HO_2 is of great significance in evaluating the influence of bromine on the damage of O_3, it has attracted great interest of many research groups[3–10]. Yung et al [5]. researched that the reaction of BrO + HO_2 could induce ozone destruction cycle through synergistic coupling, and result in the generation of HOBr. The photolysis of HOBr could produce OH, and then OH reacts with ozone to finish the cycle (1–4). Interestingly, this cycle does not require the participation of oxygen atoms. Thus, the cycle of HO_2 + BrO is of special importance in the lower stratosphere[3, 5].

$$BrO + HO_2 \longrightarrow HOBr + O_2 \quad (1)$$

$$HOBr + h\nu \longrightarrow OH + Br \quad (2)$$

$$OH + O_3 \longrightarrow HO_2 + O_2 \quad (3)$$

$$Br + O_3 \longrightarrow BrO + O_2 \quad (4)$$

$$\text{Net: } 2O_3 \longrightarrow 3O_2 \quad (5)$$

The mechanism and kinetics for the reaction of HO_2 + BrO have been researched within a certain temperature and pressure range in experimentally and theoretically. In the point of view of experiment, Cox and Sheppard [6] measured the kinetics of the BrO + HO_2 by means of the modulated photolysis and molecular modulation/UV-visible absorption resulting in the data of $0.5^{+0.5}_{-0.3} \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at 303 K, 760 Torr. Bridier et al. [7] and Poulet et al. [3] respective obtained the higher datas of $(3.4 \pm 1.0) \cdot 10^{-11}$ and $(3.3 \pm 0.5) \cdot 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} taking advantaging of the flash photolysis/UVvisible absorption method and the discharge flow reactor and mass spectrometry techniques. The HO_2 + BrO reaction was discussed again by the Larichev et al [4] at 233–344 K, with the Arrhenius formula of $k = (4.8 \pm 0.3) \times 10^{-12} \exp[(580 \pm 100)/T]$ cm^3 $molecule^{-1}$ s^{-1}. In 1996, Elrod et al [8] and in 1997, Li, et al [11] also implemented in a discharge flow reactor with a mass spectrometer, demonstrate the negative dependence on temperature. Despite the activation energies consistent well, the reported datas of the reaction rate at 298 K were significantly lower in these studies. Finally, Results from the three most recent research of Cronkhite et al. [12], Bloss et al [9] and Ward et al[13] where the HO_2 + BrO reaction was investigated by means of the laser flash photolysis/UV absorption/IR tunable diode laser absorption, resulting in the rate constants at 296 K ($(2.0 \pm 0.6) \times 10^{-11}$$cm^3$ $molecule^{-1}$ s^{-1}), flash photolysis/time resolved UV absorption spectroscopy with the obtained rate constants at 298 K 760 Torr ($(2.35 \pm 0.82) \times 10^{-11}$$cm^3$ $molecule^{-1}$ s^{-1}), and by means of flash photolysis/Vis-UV absorption at 246–314 K with the Arrhenius formula of $k = (9.28 \pm 5.61) \times 10^{-12} \exp[(2.63 \pm 1.31)/\mathrm{RT}]$$cm^3$ $molecule^{-1}$ s^{-1}. In theory, Guha and Francisco [14] researched the geometries and relative energies of the HOOBrO and HOOOBr generated from the BrO + HO_2 reaction, and then HOOBrO and HOOOBr dissociated to HOBr + O_2 and HBr + O_3 with the barrier of 2.8 and 26.40 kcal/mol, respectively, which is consistent with the computed results in this work.

As we all know, there are a great quantity of water and water clusters in the atmosphere. Water could act as acceptor and donor of hydrogen bond, and could generate hydrogen bond with active radicals and polar molecules. Hence, it could easily generate stable cyclic compounds with other species[15]. In recent years, more and more attention was paid to the influence of water on the gas-phase reaction.[16–23] Numerous theoretical and experimental studies have found that water molecules could decrease the reaction energy barrier.[23–32] Moreover, some researches revealed that water dimer could also take an significant catalytic role in H-abstraction reaction at 298 K under the atmospheric concentration of 9.0×10^{14} molecular cm^3[33–36]. Thus, to fully comprehend this atmospheric process, it is necessary to further study the influence of water on BrO + HO_2 reaction. High temperature reduces the stability of weak bond complexes in the lower troposphere, so it is difficult for the empirical study. Quantum chemical calculation can provide theoretical guidance for the study of such species. Unfortunately, no theoretical and experimental investigation on the reaction of HO_2 + BrO to investigate the influence of water.

In this work, the detailed channels of BrO + HO_2 reaction without water and containing water are researched in theory to expound the reaction mechanism and the influence of water according to the detailed potential energy surface (PES).

2. Computational Method

Gaussian 09 program package[37] was used to obtain all the results of the quantum chemical computations. B3LYP[38, 39] method combined with the 6-311 + + G(d,p) basis set were employed to optimize and characterize all the species on the PESs. Harmonic vibrational frequencies were also gained at the same level to testify that transition states only possesses one imaginary frequency and other speices possess no imaginary frequencies, and the thermodynamic dedication to the free energy and enthalpy and the value of the zero-point energy (ZPE) at the identical level. Intrinsic reaction coordinate (IRC) computations[40, 41] was used to guarantee the linkage of the transition state between reactants and expected products. CCSD(T)[42]/aug-cc-pVTZ method was used to gained more accurate energy on account of the geometric configuration at B3LYP method. The rate coefficients of the BrO + HO_2 reaction were employed by the KisThelP program[43], which is based on the Transition State Theory (TST) with Wigner tunneling correction. According to the study of Shiroudi [44], the detailed calculation process of rate coefficient is in the supporting information.

3. Results And Discussion

3.1 The H-abstraction of the BrO + HO_2 reaction with water-free

Similar to the previous investigations on the H-extraction reaction of BrO + HO_2 [14], two distinct products channels of the generation of HBr + O_3 and HOBr + O_2 were simulated located for the anhydrous BrO + HO_2 reaction (see Fig. 1). Complex intermediate will be generated at the entrance and exit of these two pathways. As for the pathway of generation of HOBr and O_2, Channel 1 results in the generation of pre-reactive complex COMR1, and subsequently proceeds via TS1 with the forecasted energy of 2.80 kcal/mol (see Table 1) below BrO + HO_2, to generate post-reactive complex COMP1. The barrier of COMR1→TS1→COMP1 is 3.68 kcal/mol, which is consistent with the results obtained by Guha and Francisco (2.80 kcal/mol)[14]. The energy of COMP1 with respect to the reactant are − 20.72 kcal/mol. In the channel of generation of HBr + O_3 (Channel 2), pre-reactive complex COMR2 will be generated with no barrier from the combination of BrO with HO_2. With respect to COMR2, the barrier of the generation of HBr + O_3 is 24.85 kcal/mol, which is consistent with the results obtained by Guha and Francisco (26.40 kcal/mol). Stemming from COMR2, the reaction goes through TS2 to generate post-reactive complex COMP2 before generating the final products HBr and O_3. COMP2 is steadied through the interaction of the hydrogen bond with the binding energy of 7.92 kcal/mol below BrO + HO_2. The Channel 1 is superior to the Channel 2 owning to the higher barrier height.

Table 1
Relative energies (ΔE), enthalpies (ΔH) and Gibbs free energies (ΔG) for the $BrO + HO_2$ reaction. All energies are computed with respect to the energy of $BrO + HO_2$, (units: kcal/mol)

Species	ΔE_{298K}	ΔH_{298K}	ΔG_{298K}
$BrO + HO_2$	0.00	0.00	0.00
COMR1	-6.48	-7.11	3.23
TS1	-2.80	-3.93	7.58
COMP1	-20.72	-20.51	-14.19
COMR2	-17.71	-18.58	-7.65
TS2	7.14	6.02	17.18
COMP2	-7.92	-7.74	-1.07
$HBr + O_3$	-6.35	-6.36	-4.98
$HOBr + O_2$	-18.65	-18.62	-17.36

3.2 The H-abstraction of the $BrO + HO_2$ reaction with a water molecule

To assess the influence of a single water molecule on the H-extraction for the $BrO + HO_2$ reaction in the atmosphere, distinct pathways have been investigated. Analogue to the aforementioned naked reaction, a pre-reactive complex will be generated at the beginning of each reaction channel with water. It should be mentioned that since it is impossible for the collision of three isolated molecules (including HO_2, BrO and H_2O) simultaneously, they will firstly generate a two-body complex, and then generate a three-body complex by the collision between the third specie and the two-body complex. Hence, in the existence of one water molecule, both BrO and HO_2 could combine with the water molecule through hydrogen bond to firstly generate corresponding binary complexes before combining with the third species. Four hydrogen bonded complexes have been located, namely as $BrO\cdots H_2O$, $H_2O\cdots BrO$, $H_2O\cdots HO_2$ and $HO_2\cdots H_2O$. The water moiety in $BrO\cdots H_2O$ and $HO_2\cdots H_2O$ serve as a hydrogen bond donor, and water acts as both the H-bond acceptor and donor in $H_2O\cdots HO_2$, as well as there exist one halogen bonded complex in $H_2O\cdots BrO$. The complex $H_2O\cdots HO_2$, with a binding energy of -6.79 kcal/mol, presents a five-membered-ring structure by generating two hydrogen bonds (2.641 Å and 1.773 Å), which are more stable than $HO_2\cdots H_2O$, $BrO\cdots H_2O$ and $H_2O\cdots BrO$ by 4.84, 3.95 and 3.05 kcal/mol, respectively. Subsequently, these four binary complexes

could further combine with the third species to generate three body complexes, and generate post-reactive complexes by surmounting corresponding transition state and then released to the final products. When a water molecule participates in the reaction, we found that, the reaction products are the same compared with anhydrous reaction, but the potential energy surface (PES) is complicated. In this paper, four pathways in the existence of water are employed to describe the influence of water molecule on the generation of $HBr + O_3$ and $HOBr + O_2$ from the reaction of $BrO + HO_2$ under atmospheric conditions.

3.2.1 The reactions of $BrO + HO_2\cdots H_2O$ and $BrO + H_2O\cdots HO_2$

In the existence of water, the channels on the PES for the generation of $HOBr + O_2$ and $HBr + O_3$ taking place by through the reactions of $H_2O\cdots HO_2 + BrO$ (Channel 1W1) and $HO_2\cdots H_2O + BrO$ (Channel 1W2) are displayed in Fig. 2. The $H_2O\cdots HO_2 + BrO$ reaction starts from the generation of the pre-reactive complex COMRW1, and the stable energy with respect to the separate molecules is -17.21 kcal/mol (see Table 2). Considering the geometry, complex COMRW1 is a seven-membered-ring consisted of two parts, which are bound together through two hydrogen bonds (1.731 Å and 1.916 Å). Beginning with the complex COMRW1, the reaction proceeds through the transition state TS1W1 involving the O atom of the BrO part extracting the H atom of HO_2 to generate the post-reactive complex COMPW1, and then COMPW1 quickly decomposes into $HOBr + O_2 + H_2O$. the energy of COMRW1 and TS1W1 in the existence of water decreased by 10.73 and 2.07 kcal/mol, respectively. The barrier of COMRW1→TS1W1→COMPW1 is 12.34 kcal/mol with respect to COMRW1. From the perspective of the generated product, water hardly takes part in Channel 1W1, because its presence increases the potential barriers of the Channel 1 by 8.66 kcal/mol. This shows that water molecule creates adverse effect on the generation of $HOBr + O_2$ for the $BrO + HO_2$ reaction.

Table 2
Relative energies (ΔE), enthalpies (ΔH), and Gibbs free energies (ΔG) for the $BrO + HO_2 + H_2O$ reaction taking place via $HO_2\cdots H_2O + BrO$, $H_2O\cdots HO_2 + BrO$, $BrO...H_2O + HO_2$ and $H_2O...BrO + HO_2$. All energies are computed with respect to the energy of $BrO + HO_2 + H_2O$ (units: kcal/mol)

Species	ΔE_{298K}	ΔH_{298K}	ΔG_{298K}
$HO_2 + BrO + H_2O$	0.00	0.00	0.00
$HO_2\cdots H_2O + BrO$	-1.95	-1.98	3.46
$H_2O\cdots HO_2 + BrO$	-6.79	-7.46	0.40
$BrO...H_2O + HO_2$	-2.84	-2.94	2.42
$H_2O...BrO + HO_2$	-3.74	-3.66	2.48
COMRW1	-17.21	-18.70	1.60
TS1W1	-4.87	-5.86	12.54
COMPW1	-26.18	-26.96	-8.76
COMRW2	-24.05	-25.16	-6.56
TS1W2	4.33	3.61	20.80
COMPW2	-11.65	-12.46	5.22
COMRW3	-17.04	-18.46	1.64
TS2W1	-4.86	-5.86	12.55
COMPW3	-25.97	-26.72	-8.56
COMRW4	-24.34	-25.39	-7.09
TS2W2	5.62	4.83	22.68
COMPW4	-25.37	-25.93	-8.67
$HBr + O_3 + H_2O$	-6.35	-6.36	-4.98
$HOBr + O_2 + H_2O$	-18.65	-18.62	-17.36

As for the route initiating the $HO_2...H_2O + BrO$, the reaction primitively generates hydrogen bond complex COMRW2, whose structure is analogue to the above-mentioned COMRW1. According to the relative

energy, the generation of three-body complexes COMRW2 through between BrO and HO_2···H_2O is superior to the generation of COMRW1 through combination between BrO and H_2O···HO_2. Similar to TS1W1, water molecule acts as the role of bystander for TS1W2. The barrier of generating of HBr + O_3 through TS1W2 in the existence of water is 3.53 kcal/mol higher than that without water. Similar to the way of generating HOBr + O_2, the existence of water molecules raises the barrier height, resulting in a negative effect on the whole reaction.

3.2.2 The reactions of BrO···H_2O + HO_2 and H_2O···BrO + HO_2

Expect for the above described reaction channels with water, the other two channels were located to generate HOBr + O_2 from the reactions of BrO···H_2O + HO_2 (Channel 1W3) and H_2O···BrO + HO_2 (Channel 1W4), which are displayed in Fig. 3. The energy of the halogen bonded complex H_2O···BrO is stable than the hydrogen bond complex BrO···H_2O by 0.90 kcal/mol. Two distinct reaction channels starting from the complexes BrO···H_2O and H_2O···BrO were located.

The complex BrO...H_2O with HO_2 reaction starts with the generation of the COMRW3 complex possess a lower barrier (12.18 kcal/mol). With respect to BrO...H_2O + HO_2, the binding energy of complex COMRW3, which have two hydrogen bond structure, is 17.04 kcal/mol below the reactants. Stemming from COMRW3, the O atom in the moiety of BrO in BrO···H_2O extracts the H atom of HO_2 through TS1W3 (-4.86 kcal/mol) to generate post-reactive complex COMPW3 (-25.97 kcal/mol). In addition, the channel beginning with the generation of COMRW4 proceeds via TS1W4 surmounting a higher barrier (29.96 kcal/mol), which is 17.78 kcal/mol higher than the Channel 1W3. Thus, the H-extraction of Channel 1W4 is much more difficult than that of Channel 1W3. Although Channel 1W3 is the most feasible channel among the BrO + HO_2 + H_2O reaction. the barrier of COMRW3→TS1W3→COMPW3 in Channel 1W3 is 8.50 kcal/mol higher than the analogous channel without water, which manifested that the introduction of water molecule inhibited the reaction through raising the barrier. In order to validly understand the influence of water, it is necessary to further research the kinetics of BrO + HO_2 reaction with and without water molecule.

3.3 Kinetics Computations

The above-mentioned mechanism manifested that the existence of a water molecule takes a negative catalytic influence on the BrO + HO_2 reaction. Water restrains the generation of HOBr + O_2 and also raises the barrier when the reaction occurs via generation of a transition state. In this work, we execute rate coefficient computations to research the influence of water molecule on the BrO + HO_2 reaction. The rate coefficients and the effective rate coefficients for the representative channel of the BrO + HO_2 reaction both with and without water are listed in Table 3 and Table 4, respectively. Table 3 listed the computed data of the rate coefficient for the channel of generation of HOBr + O_2 and HBr + O_3 for the BrO + HO_2 reaction by employing the KisThelP program. The computed rate coefficients for the Channel 1 and Channel 2 in the temperature region of 216.69–298.15 K are 7.16 ×10^{-11}-1.44 ×10^{-11} cm^3 $molecule^{-1}$ s^{-}

^{1} and 2.05 ×10^{-23}-2.62 ×10^{-21} cm^3 $molecule^{-1}$ s^{-1}, respectively. For the BrO + HO_2 reaction, the datas of 7.16 ×10^{-11}-1.44 ×10^{-11} cm^3 $molecule^{-1}$ s^{-1} in the researched temperature region are agreement with the previous experimental results[4, 10–13]. Larichev et al, Li et al, Bedjanian et al and Ward and Rowley [4, 10, 11, 13] measured the rate coefficients at 300 K are 3.29 ×10^{-11}, 1.86 ×10^{-11}, 2.97 ×10^{-11} and 2.66 ×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, and Cronkhite et al [12] measured the rate coefficient at 296 K is 2.01 ×10^{-11} cm^3 $molecule^{-1}$ s^{-1}. Our computed results indicated that the rate coefficients of generating of HOBr + O_2 is 12□9 orders of magnitude faster than that of generation of HBr + O_3, manifesting that the channel of generating of HOBr + O_2 occupied the BrO + HO_2 reaction under researched conditions.

Table 3

Rate coefficient (in cm^3 $molecule^{-1}$ s^{-1}) for the BrO + HO_2 reaction without and with one water molecule.

T (K)	k_{COMR1} Channel 1	k_{COMR2} Channel 2	k_{COMRW1} Channel 1W1	k_{COMRW2} Channel 1W2	k_{COMRW3} Channel 1W3	k_{COMRW4} Channel 1W4
298.15	1.44×10^{-11}	2.62×10^{-21}	1.29×10^{-17}	1.99×10^{-21}	3.83×10^{-16}	1.98×10^{-21}
288.19	1.66×10^{-11}	1.67×10^{-21}	1.12×10^{-17}	1.33×10^{-21}	4.16×10^{-16}	1.11×10^{-21}
275.21	2.03×10^{-11}	8.90×10^{-22}	9.12×10^{-18}	7.61×10^{-22}	4.72×10^{-16}	4.89×10^{-22}
262.23	2.55×10^{-11}	4.42×10^{-22}	7.30×10^{-18}	4.11×10^{-22}	5.38×10^{-16}	2.00×10^{-22}
249.25	3.28×10^{-11}	2.06×10^{-23}	5.73×10^{-18}	2.09×10^{-22}	6.26×10^{-16}	7.47×10^{-23}
236.27	2.36×10^{-11}	8.84×10^{-23}	4.40×10^{-18}	9.87×10^{-23}	7.45×10^{-16}	2.51×10^{-23}
223.29	3.60×10^{-11}	3.46×10^{-23}	3.27×10^{-18}	4.28×10^{-23}	9.00×10^{-16}	7.44×10^{-24}
216.69	7.16×10^{-11}	2.05×10^{-23}	2.79×10^{-18}	2.30×10^{-23}	1.01×10^{-15}	3.80×10^{-24}

Table 4

Effective rate coefficients for the BrO + HO_2 + H_2O reaction at216.69-298.15 K (cm^3 $molecule^{-1}$ s^{-1})

T (K)	[H_2O]	k'_{COMR1}	k'_{COMR2}	k'_{COMR3}	k'_{COMR4}
298.15	7.79×10^{17}	8.52×10^{-21}	7.55×10^{-27}	8.14×10^{-21}	3.90×10^{-26}
288.19	4.34×10^{17}	6.12×10^{-21}	3.15×10^{-27}	5.99×10^{-21}	1.51×10^{-26}
275.21	1.89×10^{17}	3.79×10^{-21}	9.22×10^{-28}	3.74×10^{-21}	3.96×10^{-27}
262.23	7.43×10^{16}	2.21×10^{-21}	2.33×10^{-28}	2.17×10^{-21}	8.92×10^{-28}
249.25	2.64×10^{16}	1.21×10^{-21}	5.13×10^{-29}	1.19×10^{-21}	1.72×10^{-28}
236.27	8.15×10^{15}	6.10×10^{-22}	9.25×10^{-30}	5.99×10^{-22}	2.70×10^{-29}
223.29	2.15×10^{15}	2.78×10^{-22}	1.34×10^{-30}	2.71×10^{-22}	3.36×10^{-30}
216.69	1.01×10^{15}	1.77×10^{-22}	3.90×10^{-31}	1.74×10^{-22}	1.04×10^{-30}

k'_{COMR2}, k'_{COMR1}, k'_{COMR3} and k'_{COMR4} are the effective rate coefficients of Channel 1W1, Channel 1W2, Channel 1W3 and Channel 1W4, respectively.

With the introduction of water, the rate coefficients for the Channel 1W1, Channel 1W2 and Channel 1W4 reveal positive temperature dependence, and the rate coefficients for the Channel 1W3 displays negative temperature dependence. The rate coefficients for the Channel 1W2 and Channel 1W4 are lower than that of Channel 1W1 and Channel 1W3. Moreover, Table 3 indicates that the rate coefficients for Channel 1W1 and Channel 1W3 are much smaller than that for the generation of HOBr + O_2 in the absence of water at 216.69–298.15 K.

Taking the concentration of the binary complexes HO_2···H_2O, H_2O···HO_2, BrO···H_2O and H_2O···BrO into account, it is necessary to compare the effective rate coefficients of the BrO + HO_2 reaction in the existence of water with that of in the absence water to fully comprehend the influence of water on the BrO + HO_2 reaction. The rate coefficients for the BrO + HO_2 reaction in the absence of water could be written as

$$\nu_{\mathrm{COMR1(or\ 2)}} = k_{\mathrm{COMR1\,(or2)}}[\mathrm{BrO}]\left[\mathrm{HO_2}\right]$$

whereas the rate coefficients for the generation of HOBr + O_2 of the BrO + HO_2 reaction in the existence of water can be written as

$$\nu_{COMR1W1} = k_{COMRW1}[H_2O\cdots HO_2][BrO] = k'_{COMRW1}[HO_2][BrO]$$

$$\nu_{COMR1W1} = k_{COMRW2}[HO_2\cdots H_2O][BrO] = k'_{COMRW2}[HO_2][BrO]$$

$$\nu_{COMR1W1} = k_{COMRW3}[BrO\cdots H_2O][HO_2] = k'_{COMRW3}[HO_2][BrO]$$

$$\nu_{COMR1W1} = k_{COMRW4}[H_2O\cdots BrO][HO_2] = k'_{COMRW4}[HO_2][BrO]$$

In above equations, $k'_{COMRW1} = k_{COMRW1}K_{eq1}[H_2O]$, $k'_{COMRW2} = k_{COMRW2}K_{eq2}[H_2O]$, $k'_{COMRW3} = k_{COMRW3}K_{eq3}[H_2O]$ and $k'_{COMRW4} = k_{COMRW4}K_{eq4}[H_2O]$. K_{eq1}, K_{eq2},$K_{eq3}$and K_{eq4} are the rate coefficients for the generation of the complexes $H_2O\cdots HO_2$, $HO_2\cdots H_2O$, $BrO\cdots H_2O$ and $H_2O\cdots BrO$, respectively. K_{eq1}, K_{eq2},$K_{eq3}$and K_{eq4} are listed in Table S1. The effective rate coefficients of k'_{COMRW1}, k'_{COMRW2}, k'_{COMRW3} and k'_{COMRW4} are decided by the concentration of water to compare the rate coefficient in the absence of water ($k_{COMR1}$and k_{COMR2}), which are given in Table 4. The effective rate coefficients of k'_{COMRW1}, k'_{COMRW2}, k'_{COMRW3} and k'_{COMRW4} at 216.69–298.15 K are 1.77×10^{-22}-8.52×10^{-21} cm^3 $molecule^{-1}$ s^{-1}, 3.90×10^{-31}-7.55×10^{-27} cm^3 $molecule^{-1}$ s^{-1}, 1.74×10^{-22}-8.14×10^{-21} cm^3 $molecule^{-1}$ s^{-1} and 1.04×10^{-30}-3.90×10^{-26} cm^3 $molecule^{-1}$ s^{-1}, respectively. The computed results reveal that the BrO + HO_2 reaction in the existence of water are much slower with respect to the feasible channels of the BrO + HO_2 reaction. In a word, under atmospheric conditions, the above findings manifest that a single water molecule possesses negative influence on the BrO + HO_2 reaction.

4. Conclusion

HOBr is generated through the atmospheric reaction of BrO + HO_2, which is the temporary storage of BrOx substances. It is great interest to research the influence of water molecule on the mechanism and kinetics of the BrO + HO_2 reaction. In the present work, the probable catalytic influence of water molecule on the reaction BrO + HO_2 was researched from the perspective of mechanism and kinetics taking advantage of quantum chemical calculation. The rate coefficients at 216.69-298.15 K were obtained by employing the KisThelP program based on the Transition State Theory (TST) with Wigner tunneling correction for the BrO + HO_2 reaction in the absence and existence water. There exist two distinct channels for the BrO + HO_2 reaction in the absence water, and the channel of generation of HOBr + O_2 dominant the reaction. With the introduction of water, the influence of a single water was researched through taking into account four distinct types of reactions: $HO_2\cdots H_2O$ with BrO, $H_2O\cdots HO_2$ with BrO, $BrO\cdots H_2O$ with HO_2, $H_2O\cdots BrO$ with HO_2. Owning to the higher barrier height, the channel taking place by $BrO\cdots H_2O$ with HO_2 may be significant with respect to other channels. The effective rate coefficients of Channel 1W2 and Channel 1W4 are much lower than the reaction in te absence of water. These results come to the conclusion that

water molecule inhibits the BrO + HO_2 reaction through increasing the stability of the pre-reactive complex and raising the barrier. In a word, the present work might contribute to a better comprehending of the influence of water on radical- radical reaction in troposphere.

Declarations

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Conflict of interest The authors declare no competing interests.

Availability of data and material: (data transparency) Not applicable

Code availability: (software application or custom code) Yes.

Author contribution Ma Lu contributed to the conception of the study, performed the computations and wrote the manuscript; Bing He, Meilian Zhao, Yongguo Liu, Ruojing Song, Huaming Du and Huirong Li contributed to the execution and analysis of calculations. Yunju Zhang contributed significantly to analysis and wrote the manuscript; All authors have reviewed the manuscript.

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Figures

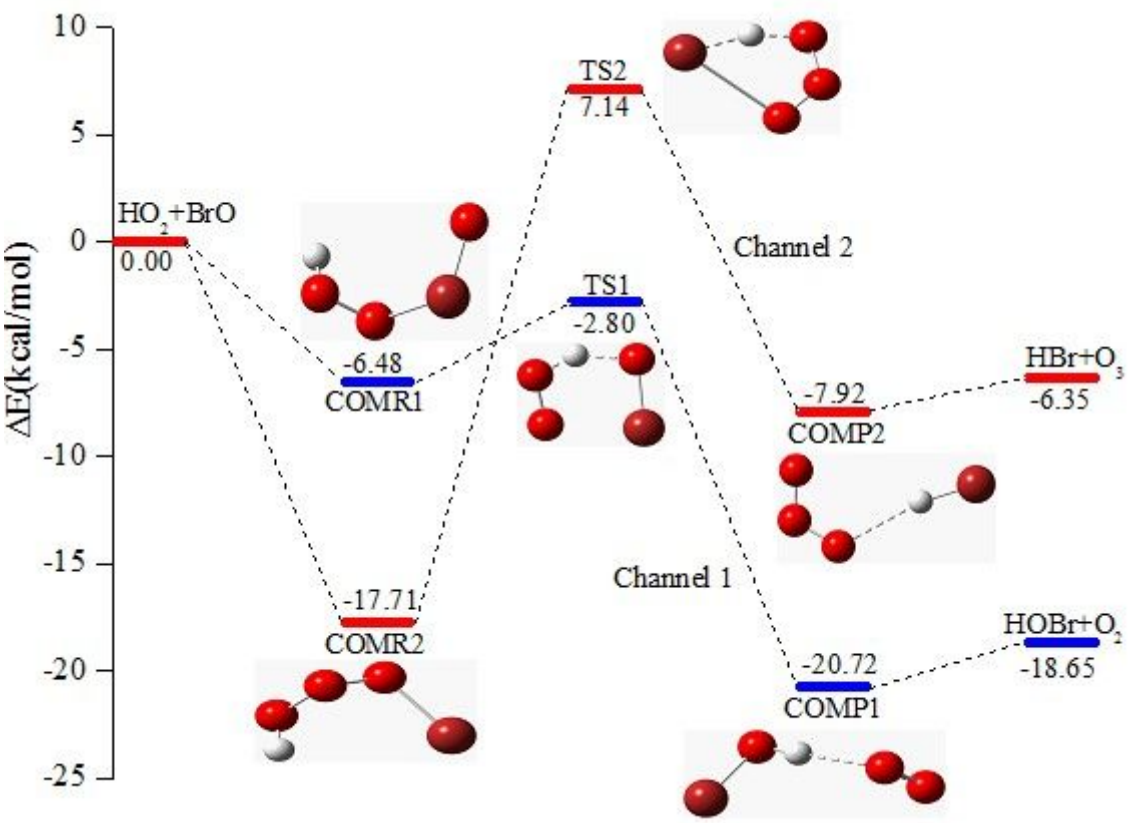

Figure 1

The potential energy surface for the HO_2 and BrO reaction in the absence of water

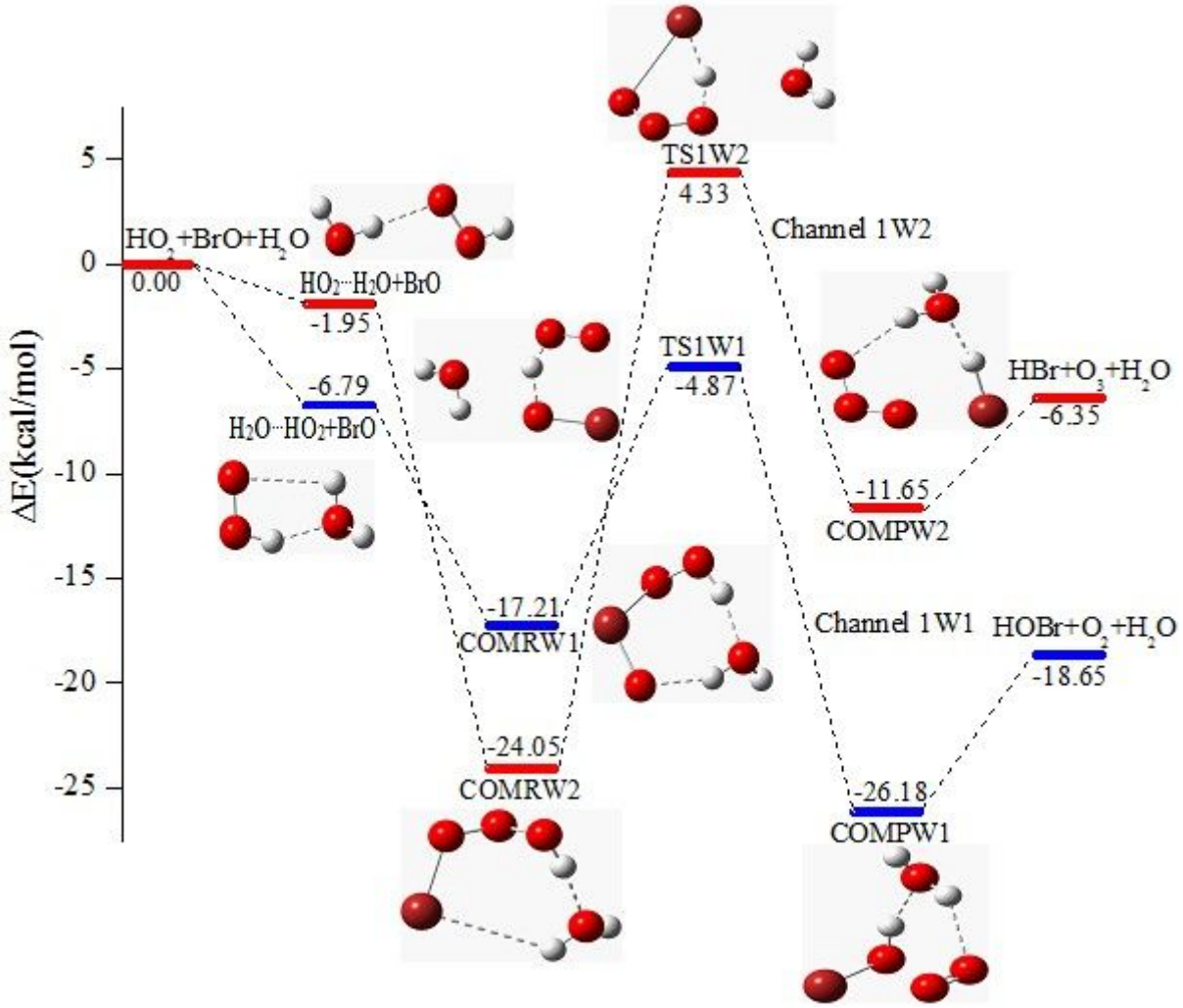

Figure 2

The potential energy surface for the HO_2 and BrO reaction in the existence of water taking place via $H_2O\cdots HO_2$ + BrO and $HO_2\cdots H_2O$ + BrO pathways

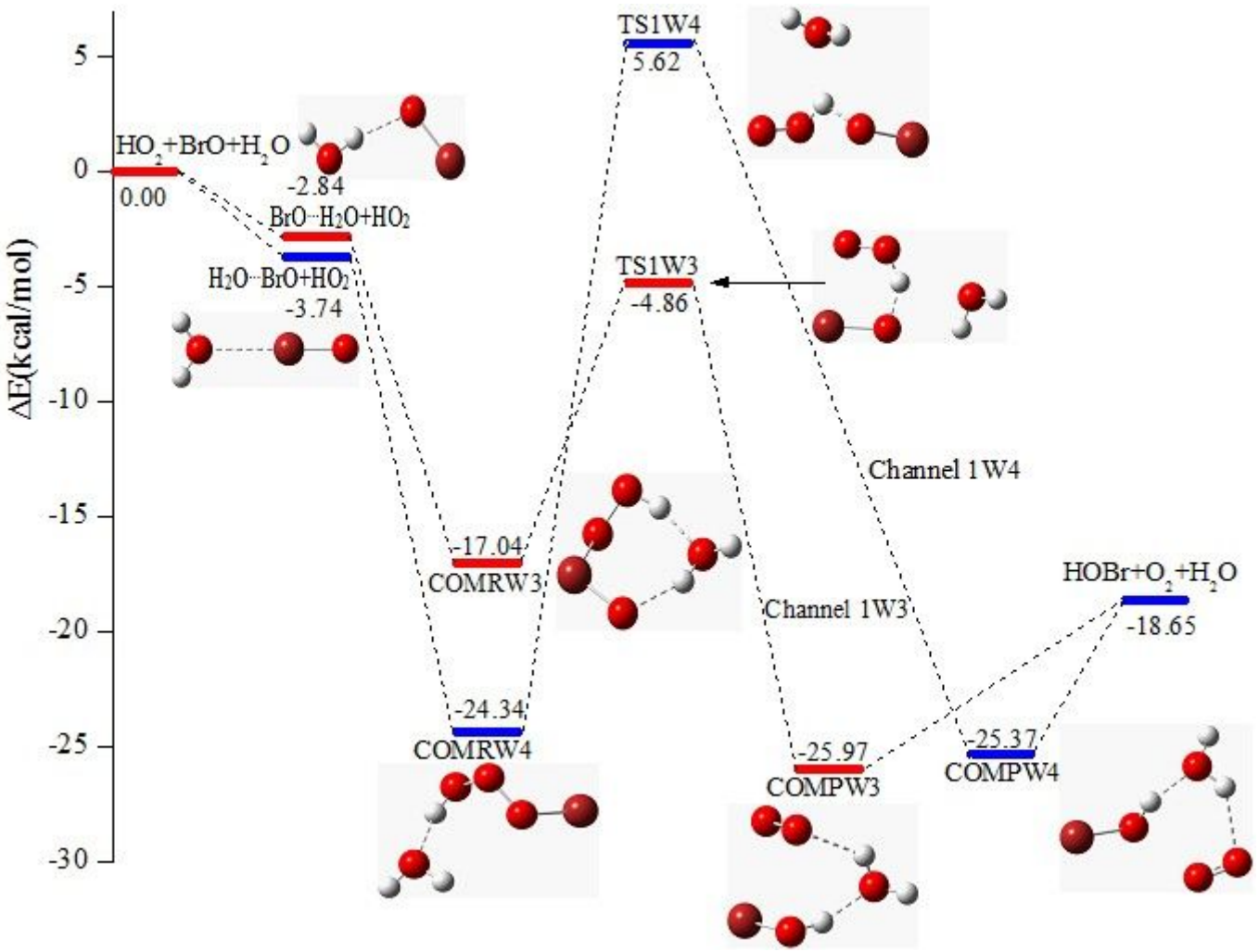

Figure 3

The potential energy surface for the HO_2 and BrO reaction in the existence of water taking place via BrO···H_2O + HO_2 and H_2O···BrO + HO_2 pathway

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