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The influence of a single water molecule on the reaction of BrO + HO$_2$

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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$_2$ ($^1\Delta_g$) and HBr + O$_3$, and the channel of generation of HOBr + O$_2$ ($^1\Delta_g$) dominated 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$_2$O with BrO, H$_2$O···HO$_2$ with BrO, BrO···H$_2$O with HO$_2$, H$_2$O···BrO with HO$_2$ are researched. The most feasible channels, stemming from H$_2$O···HO$_2$ with BrO, and BrO···H$_2$O 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.

Methyl bromide stems from nature and humanity. It is the main precursor of active bromine involved in stratospheric ozone chemistry[1,2]. Bromine containing molecules, 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 their concentration being much lower than that of chlorine containing molecules. Such destruction takes place passing through catalytic cycles, 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 of these 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 complete 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].

$$BrO + HO_2 \rightarrow HOBr + O_2 \tag{1}$$

$$HOBr + h\nu \rightarrow OH + Br \tag{2}$$

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{3}$$

$$Br + O_3 \rightarrow BrO + O_2 \tag{4}$$

$$Net: 2O_3 \rightarrow 3O_2 \tag{5}$$

The mechanism and kinetics for the reaction of HO$_2$ + BrO have been researched within a certain temperature and pressure range 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 value of the rate constants 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 values of $(3.4 \pm 1.0) \times 10^{-11}$ and $(3.3 \pm 0.5) \times 10^{-11}$

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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 studied again by the Larichev et al.[4] at 233–344 K, and they obtained the Arrhenius expression 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 and demonstrated the negative dependence of the rate constant on temperature. The reported values of the reaction rate constant at 298 K were significantly lower in these studies than in earlier 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 $k = (9.28 \pm 5.61) \times 10^{-12} \exp{[(2.63 \pm 1.31)/RT]}$ cm^3 molecule^{-1} s^{-1}. In the computational work, Guha and Francisco[14] researched the geometries and relative energies of the HOOBrO and HOOOBr generated from the BrO + HO$_2$ reaction, and showed that 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. In 2019, Tsona, Tang and Du researched "Impact of water on the BrO + HO$_2$ gas-phase reaction: mechanism, kinetics and products[15]. The obtained results revealed significant differences from those published earlier on this reaction by Chow et al.[16] In 2021, Chow et al.[17] performed further calculation for this present work, combined with higher level calculations published by Chow et al.[16], demonstrate that the work of Tsona et al. is flawed because the integration grid size used in their lowest singlet and triplet calculations is too small, and a closed-shell wavefunction, rather than an open-shell wavefunction, has been used for the singlet surface. The major conclusion in the work of Tsona et al. that the lowest singlet and triplet channels are barrierless is shown to be incorrect. Moreover, the calculated rate constants by Tsona et al. showed a positive temperature dependence, which is inconsistent with the experimentally observed negative temperature dependence, whereas the singlet rate constants for the BrO + HO$_2$ → HOBr + O$_2$ reaction which produces singlet O$_2$ computed by Chow et al.[16] revealed a negative temperature dependence consistent with experiment.

As is well known, there are a great quantity of water and water clusters in the atmosphere. Water could act as acceptor and donor in a hydrogen bond, and could form a hydrogen bond with active radicals and polar molecules. Hence, it could easily generate stable cyclic compounds with other species[18]. In recent years, more and more attention has been paid to the influence of water on the gas-phase reaction.[19–26] Numerous theoretical and experimental studies have found that water molecules could decrease the reaction energy barrier[26–35]. Moreover, some researches revealed that water dimer could also take an significant catalytic role in H-abstraction reaction at 298 K at the atmospheric concentration of 9.0 $\times$ 10^{14} molecular cm$^{336-39}$. 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 this must also be borne in mind. Quantum chemical calculation can provide theoretical guidance for the study of such species.

In this work, the detailed channels of BrO + HO$_2$ reaction on the singlet potential energy surface (PES) without water and containing water are researched using theoretical methods to establish the reaction mechanism and the influence of water according to the detailed potential energy surface.

Computational method

Gaussian 09 program package[40] was used to obtain all the results of the quantum chemical computations. B3LYP[41,42] 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[43,44] was used to guarantee the linkage of the transition state between reactants and expected products. CCSD(T)[45]/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[46], which is based on the Transition State Theory (TST) with Wigner tunneling correction. According to the study of Shiroudi[47], the detailed calculation process of rate coefficient is in the supporting information. In the following discussion, the B3LYP/6-311 + + G(d,p) optimized geometric parameters and CCSD(T)/aug-cc-pVTZ + ZPE energies are used unless otherwise stated.

Results and discussion

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$_2$ ($^1\Delta_g$) 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 singlet 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
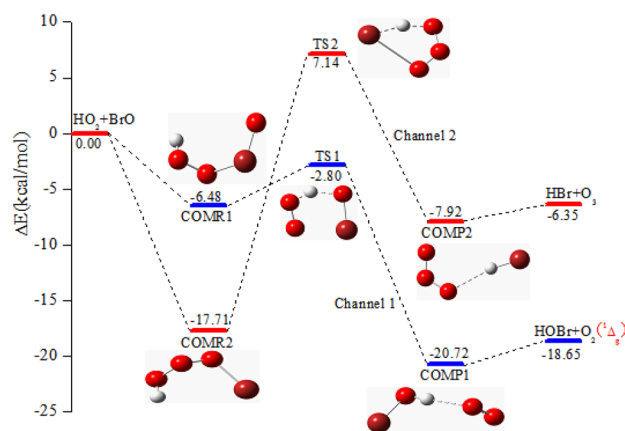
Figure 1. The potential energy surface for the HO$_2$ and BrO reaction in the absence of water are calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311 + + G(d,p) level.

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$_2$ ($^1\Delta_g$)	− 18.65	− 18.62	− 17.36

Table 1. Relative energies (ΔE), enthalpies (ΔH) and Gibbs free energies (ΔG) for the BrO + HO$_2$ reaction are calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311 + + G(d,p) level. All energies are computed with respect to the energy of BrO + HO$_2$, (units: kcal/mol).

hydrogen bond wth 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. In addition, the pathway on the triplet surface contribute less to the BrO + HO$_2$ reaction due to the higher barrier height. Thus we have no further consideration in here.

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$_2$O) 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···H$_2$O, H$_2$O···BrO, H$_2$O···HO$_2$ and HO$_2$···H$_2$O. The energies of BrO···H$_2$O, H$_2$O···HO$_2$ and HO$_2$···H$_2$O are − 2.84, − 6.79 and − 1.95 kcal/mol, which are consistent with the obtained results by Tsona et al. (− 2.51, − 6.51 and − 1.31 kcal/mol). The water moiety in BrO···H$_2$O and HO$_2$···H$_2$O serve as a hydrogen bond donor, and water acts as both the H-bond acceptor and donor in H$_2$O···HO$_2$, as well as there exist one halogen bonded complex in H$_2$O···BrO. The complex H$_2$O···HO$_2$ presents a five-membered-ring structure by generating two hydrogen bonds (2.641 Å and 1.773 Å, see Fig. S1), which are more stable than HO$_2$···H$_2$O, BrO···H$_2$O and H$_2$O···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$_2$ ($^1\Delta_g$) from the reaction of BrO + HO$_2$ under atmospheric conditions.

The reactions of BrO + HO₂···H₂O and BrO + H₂O···HO₂. In the existence of water, the channels on the PES for the generation of HOBr + O₂ ($^1\Delta_g$) and HBr + O₃ taking place by through the reactions of H₂O···HO₂ + BrO (Channel 1W1) and HO₂···H₂O + BrO (Channel 1W2) are displayed in Fig. 2. The H₂O···HO₂ + 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 HO₂ to generate the post-reactive complex COMPW1, and then COMPW1 quickly decomposes into HOBr + O₂ ($^1\Delta_g$) + H₂O. 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
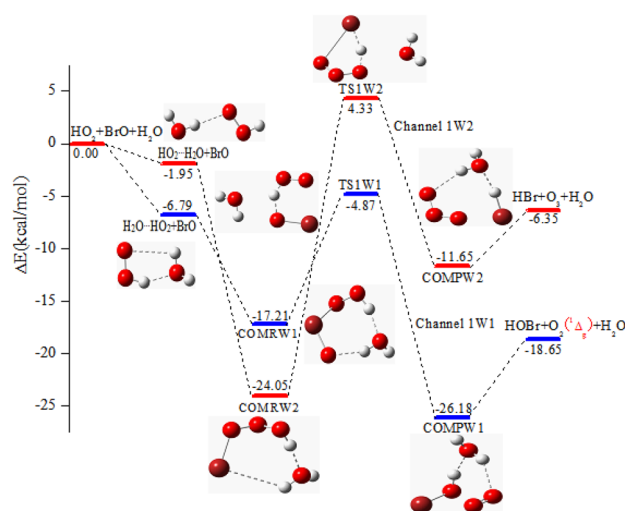
Figure 2. The potential energy surface for the HO₂ and BrO reaction in the existence of water taking place via H₂O···HO₂ + BrO and HO₂···H₂O + BrO pathways are calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311 + + G(d,p) level.

Species	ΔE_{298K}	ΔH_{298K}	ΔG_{298K}
HO₂ + BrO + H₂O	0.00	0.00	0.00
HO₂···H₂O + BrO	− 1.95	− 1.98	3.46
H₂O···HO₂ + BrO	− 6.79	− 7.46	0.40
BrO···H₂O + HO₂	− 2.84	− 2.94	2.42
H₂O…BrO + HO₂	− 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
TS1W3	− 4.86	− 5.86	12.55
COMPW3	− 25.97	− 26.72	− 8.56
COMRW4	− 24.34	− 25.39	− 7.09
TS1W4	5.62	4.83	22.68
COMPW4	− 25.37	− 25.93	− 8.67
HBr + O₃ + H₂O	− 6.35	− 6.36	− 4.98
HOBr + O₂ ($^1\Delta_g$) + H₂O	− 18.65	− 18.62	− 17.36

Table 2. Relative energies (Δ*E*), enthalpies (Δ*H*), and Gibbs free energies (Δ*G*) for the BrO + HO₂ + H₂O reaction taking place via HO₂···H₂O + BrO, H₂O···HO₂ + BrO, BrO···H₂O + HO₂ and H₂O···BrO + HO₂ are calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311 + + G(d,p) level. All energies are computed with respect to the energy of BrO + HO₂ + H₂O (units: kcal/mol).

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 $HOBr + O_2$ ($^1\Delta_g$) for the $BrO + HO_2$ reaction.

As for the route initiating the $HO_2 \cdots H_2O + BrO$, 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 $HO_2 \cdots H_2O$ is superior to the generation of COMRW1 through combination between BrO and $H_2O \cdots HO_2$. 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 $HOBr + O_2$ ($^1\Delta_g$), the existence of water molecules raises the barrier height, resulting in a negative effect on the whole reaction.

The reactions of BrO$\cdots$H$_2$O + HO$_2$ and H$_2$O$\cdots$BrO + HO$_2$. Expect for the above described reaction channels with water, the other two channels were located to generate $HOBr + O_2$ ($^1\Delta_g$) from the reactions of $BrO \cdots H_2O + HO_2$ (Channel 1W3) and $H_2O \cdots BrO + HO_2$ (Channel 1W4), which are displayed in Fig. 3. The energy of the halogen bonded complex $H_2O \cdots BrO$ is stable than the hydrogen bond complex $BrO \cdots H_2O$ by 0.90 kcal/mol. Two distinct reaction channels starting from the complexes $BrO \cdots H_2O$ and $H_2O \cdots BrO$ were located.

The complex $BrO \cdots H_2O$ with HO_2 reaction starts with the generation of the COMRW3 complex possess a lower barrier (12.18 kcal/mol). With respect to $BrO \cdots H_2O + HO_2$, 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 $BrO \cdots H_2O$ extracts the H atom of HO_2 through TS1W3 (− 4.86 kcal/mol) to generate post-reactive complexe 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 identificate the influence of water, it is necessary to further research the kinetics of $BrO + HO_2$ reaction with and without water molecule.

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 $HOBr + O_2$ ($^1\Delta_g$) and also raises the barrier when the reaction occurs via generationn 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. At different altitudes, the rate coefficients and the effective rate coefficients for the representative channel of the $BrO + HO_2$ reaction both with and without water are summaried in Tables 3 and 4, respectively. Table 3 listed the computed data of the rate coefficient for the channel of generation of $HOBr + O_2$ ($^1\Delta_g$) 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 $HOBr + O_2$ ($^1\Delta_g$) is 12–9 orders of magnitude faster
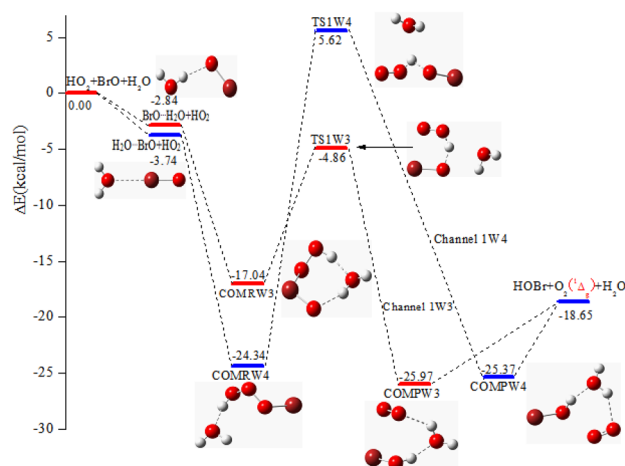
Figure 3. The potential energy surface for the HO_2 and BrO reaction in the existence of water taking place via $BrO \cdots H_2O + HO_2$ and $H_2O \cdots BrO + HO_2$ pathway are calculated at the CCSD(T)/aug-cc-pVTZ//B3LYP/6-311 + + G(d,p) level.

h (km)[a]	T (K)[a]	k_{COMR1} Channel 1	k_{COMR2} Channel 2	k_{COMRW1} Channel 1W1	k_{COMRW2} Channel 1W2	k_{COMRW3} Channel 1W3	k_{COMRW4} Channel 1W4
0	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}
0	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}
2	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}
4	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}
6	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}
8	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}
10	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}
12	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 3. Rate coefficient (in cm³ molecule⁻¹ s⁻¹) for the BrO + HO₂ reaction without and with one water molecule at different heights (h). [a]The values are taken from Ref.[48].

h (km)[a]	T (K)[a]	[H₂O][b]	k'_{COMR1}	k'_{COMR2}	k'_{COMR3}	k'_{COMR4}
0	298.15	7.79×10^{17}	8.52×10^{-21}	7.55×10^{-27}	8.14×10^{-21}	3.90×10^{-26}
0	288.19	4.34×10^{17}	6.12×10^{-21}	3.15×10^{-27}	5.99×10^{-21}	1.51×10^{-26}
2	275.21	1.89×10^{17}	3.79×10^{-21}	9.22×10^{-28}	3.74×10^{-21}	3.96×10^{-27}
4	262.23	7.43×10^{16}	2.21×10^{-21}	2.33×10^{-28}	2.17×10^{-21}	8.92×10^{-28}
6	249.25	2.64×10^{16}	1.21×10^{-21}	5.13×10^{-29}	1.19×10^{-21}	1.72×10^{-28}
8	236.27	8.15×10^{15}	6.10×10^{-22}	9.25×10^{-30}	5.99×10^{-22}	2.70×10^{-29}
10	223.29	2.15×10^{15}	2.78×10^{-22}	1.34×10^{-30}	2.71×10^{-22}	3.36×10^{-30}
12	216.69	1.01×10^{15}	1.77×10^{-22}	3.90×10^{-31}	1.74×10^{-22}	1.04×10^{-30}

Table 4. Effective rate coefficients for the BrO + HO₂ + H₂O reaction at 216.69–298.15 K (cm³ molecule⁻¹ s⁻¹). 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. [a]The values are taken from Ref.[48]. [b]Water concentrations are taken from Ref.[49].

than that of generation of HBr + O₃, manifesting that the channel of generating of HOBr + O₂ ($^1\Delta_g$) occupied the BrO + HO₂ reaction under researched conditions.

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 + O₂ in the absence of water at 216.69–298.15 K.

Taking the concentration of the binary complexes HO₂···H₂O, H₂O···HO₂, BrO···H₂O and H₂O···BrO into account, it is nessary to compare the effective rate coefficients of the BrO + HO₂ reaction in the exitence of water with that of in the absence water to fully acquaintancing the influence of water on the BrO + HO₂ reaction. The rate coefficients for the BrO + HO₂ reaction in the absence of water could be written as

$$\nu_{COMR1(or\ 2)} = k_{COMR1(or\ 2)}[BrO][HO_2]$$

whereas the rate coefficients for the generation of HOBr + O₂ of the BrO + HO₂ 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 H₂O···HO₂, HO₂···H₂O, BrO···H₂O and H₂O···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} cm³ molecule⁻¹ s⁻¹, 3.90×10^{-31}–7.55×10^{-27} cm³ molecule⁻¹ s⁻¹, 1.74×10^{-22}–8.14×10^{-21} cm³ molecule⁻¹ s⁻¹ and 1.04×10^{-30}–3.90×10^{-26} cm³ molecule⁻¹ s⁻¹, respectively. The computed results reveal that the BrO + HO₂ reaction in the existence of water are much slower with respect to the feasible channels of the BrO + HO₂ reaction. In a word, under atmospheric conditions, the above findings manifest that a single water molecule possesses negative influence on the BrO + HO₂ reaction.

Conclusion

HOBr is generated through the atmospheric reaction of BrO + HO₂, 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 + HO₂ reaction. In the present work, the probable catalytic influence of water molecule on the reaction BrO + HO₂ was reaearched 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 + HO₂ reaction in the absence and existence water. There exist two distinct channels for the BrO + HO₂ reaction in the absence water, and the channel of generation of HOBr + O₂ ($^1\Delta_g$) 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: HO₂···H₂O with BrO, H₂O···HO₂ with BrO, BrO···H₂O with HO₂, H₂O···BrO with HO₂. Owning to the higher barrier height, the channel taking palce by BrO···H₂O with HO₂ may be significant with respect to other channels. The effective rate coefficients of Channle 1W2 and Channle 1W4 are much lower than the reacton in te absence of water. These results come to the conclusion that water molecule inhibits the BrO + HO₂ 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.

Data availability

The data that support the findings of this study are available on request from the corresponding author.

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