Influence of Water on the Gas-Phase Reaction of Dimethyl Sulfide with BrO in the Marine Boundary Layer

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ABSTRACT: The effect of a single water molecule on the reaction of dimethyl sulfide (DMS) with BrO reaction has been investigated using quantum chemical calculations at the CCSD(T)/6-311++G**//BH&HLYP/aug-cc-pVTZ level of theory. Two reaction mechanisms have been considered both in the absence and the presence of water, namely, oxygen atom transfer and hydrogen abstraction, among which the oxygen atom transfer was predominant. Five reaction channels were found in the absence of water, in which the channels starting from the cis-configuration of the pre-reaction complexes were more favorable because of the low energy barrier. The inclusion of water slightly decreased the energy barrier height of the pre-reaction complexes were more favorable because of the low energy barrier. The effective rate coefficients for the oxygen atom transfer paths are found to have decreased by 3−7 orders of magnitude in the presence of water relative to the water-free reactions, the negligible fraction of reactants that are effectively clustered with water does not significantly change the overall rate of the formation of dimethyl sulfoxide and Br. The present results show that the overall mechanism and rate of the DMS + BrO reaction may not be affected by humidity under atmospheric conditions.

1. INTRODUCTION

Chemical reactions occurring in the ocean’s atmospheric boundary layer profoundly affect climate change. A significant difference of characteristics between ocean atmospheric boundary layer and land atmospheric boundary layer chemistry lies in the existence of dimethyl sulfide (DMS), which is naturally emitted from the ocean to the troposphere by oceanic phytoplankton.1 Approximately half of the global flux of natural sulfur to the atmosphere consists of DMS volatilized from the oceans, while the main source of terrestrial atmospheric sulfur is SO2.2−6 DMS is the most important natural sulfur compound in the marine troposphere, where its production forms a negative feedback mechanism with climate change, as described by the “CLAW” hypothesis in 1987.1 DMS emitted into the atmosphere is oxidized to non-sea-salt sulfate, which is known to be an important precursor of marine sulfate aerosols. DMS and its oxidation products play a major role in regulating the climate through formation of cloud condensation nuclei.1 It is therefore necessary to understand the transformation mechanisms of DMS in order to assess its atmospheric importance.7−9

In the troposphere, reactive halogenated hydrocarbons emitted by marine organisms could release halogen atoms (X, X = Cl, Br and I) and halogenated oxide radicals (XO) through photochemical reactions, thus changing the oxidation power of the atmosphere and the concentration of some greenhouse gases like O3, CH4, and N2O. Halogenated oxide radicals play an important role in the ozone depletion cycle. Almost 1/3 of the photochemical loss of ozone is due to the reactions involving ClO and BrO, which have been widely investigated in laboratory and field studies.10−12 BrO has been known to react with various atmospheric species, such as CH3SO, HO2, NOx, and CH2O, producing active halogen atoms, reservoir species, or other reactive halogen species, greatly affecting the atmospheric chemistry and climate change.13−18 It has been shown that the rate of DMS oxidation depends on the oxidability of the atmosphere. During the daytime, the gaseous DMS reacts with OH, halogen atoms, and halogenated oxide radicals, while it reacts with NO3 at night.19 The studies of Barnes et al. and Sayin and McKee have also shown that tropospheric DMS emitted from the ocean could react with halogen monoxide radicals (XO) in the catalytic ozone loss cycle in the marine atmosphere.20,21

DMS + XO → DMSO + X  (X = Cl, Br and I)  

(1)  

DMS + XO → CH3SCH2 + HOX

(2)
O₃ + X → O₂ + XO  \hspace{2cm} (3)

Two possible reaction pathways were considered: oxygen atom transfer from XO to DMS and hydrogen abstraction by XO. For X = Cl, Br, and I, the order of reactivity is ClO < BrO < IO at 298 K and 760 Torr.²¹ The mechanism and kinetics of the reaction between DMS and XO have been studied extensively using experimental techniques and theoretical calculations.²²⁻²⁴ Breider et al. have studied the impact of BrO on DMS in the remote marine boundary layer, using a global three-dimensional chemical transport model coupled to a detailed size-resolved aerosol microphysics module. The modeled results indicated that BrO contributes to 16% of the global annual DMS oxidation sink.²⁰ In 2018, a series of gas-phase and multiphase mechanisms were implemented into a Goddard Earth Observing System-Chemistry global chemical transport model to study the sulfur cycle in the global marine troposphere.²⁵ They found that the DMS oxidation by BrO accounts for 12% of its gas-phase oxidation globally. The DMS + BrO reaction is important for the model’s ability to reproduce the observed seasonality of the surface DMS mixing ratio in the Southern Hemisphere. In terms of experimental research, different facilities have been used to get a better understanding of the DMS + BrO reaction. For example, the discharge-flow mass spectrometry technique was used to monitor the kinetics of the reactions of halogen oxide radicals and a rate coefficient of \((2.7 \pm 0.5) \times 10^{-13}\) cm³ molecule⁻¹ s⁻¹ was obtained for the DMS + BrO reaction.²² Nakano et al. determined a rate coefficient of \(4.2 \times 10^{-13}\) cm³ molecule⁻¹ s⁻¹ at 298 K for the same reaction using cavity ring-down spectroscopy in 100 Torr of \(N₂\) diluent at 278–333 K.²³ Using a different experimental technique, based on the laser photolysis absorption, Ingham et al. determined a rate coefficient of \((4.4 \pm 0.7) \times 10^{-13}\) cm³ molecule⁻¹ s⁻¹ for this reaction.²⁴ Theoretical calculations assessing the importance of the oxygen atom transfer and H-abstraction reaction pathways in the DMS + BrO reaction led to a \(8.7 \times 10^{-13}\) cm³ molecule⁻¹ s⁻¹ rate coefficient for the oxygen atom transfer, which was consistent with the experimental results.²¹ These studies provide important information for the chemistry of DMS in the atmosphere.

Water is a significant component of the atmosphere that actively takes part in various chemical processes in Earth’s atmosphere. The possible reactions inside the hydrated particles have aroused great interest among researchers.²²⁻³⁴ The importance of water in atmospheric processes has always been concerned, but its role as a catalyst in chemical reactions is not completely elucidated and remains highly uncertain. Water could participate in atmospheric reactions by forming hydrogen bonds with reactive species, thereby having a decisive effect on their gas-phase chemistry.³⁵⁻³⁸ The study of Vöhringer-Martinez et al. was one of the first to elucidate that a single water molecule could catalyze the molecule–radical reactions involving OH.³⁹ Aloisio and Francisco first proposed that the photochemical properties of molecule–water complexes are different from those of individual molecules.⁴⁰ These complexes significantly affect chemical processes in the atmosphere, especially the heterogeneous removal of atmospheric species and the formation of aerosol particles.³⁷,⁴¹,⁴² However, previous studies of the DMS + BrO reaction did not take into account the impact of ubiquitous atmospheric water, though it is known to alter the reaction mechanism and kinetics.

Here, we investigated the effect of a single water molecule on the oxygen atom transfer and H-abstraction reaction between DMS and BrO, using quantum chemical calculations. The two mechanisms were compared both in the water-free and water-containing reactions. In addition, rate coefficients for the most favorable paths have been calculated, to further confirm the effect of atmospheric water on DMS oxidation by BrO in the marine troposphere.

2. RESULTS AND DISCUSSION

The energy profiles of different pathways of the DMS + BrO reaction at the CCSD(T)/aug-cc-pVTZ//BH&HLYP/aug-cc-pVTZ level of theory are depicted in Figures 1–4, while Tables 1–4 list the corresponding electronic energy, including ZPE-corrected \(\Delta E\) and \(\Delta(E + ZPE)\), enthalpy \(\Delta H\), and Gibbs

![Figure 1. Schematic energy diagrams for the reaction of DMS with BrO, proceeding through the trans configuration of the formed reactive complex.](https://dx.doi.org/10.1021/acsomega.0c05945)

![Figure 2. Schematic energy diagrams of the DMS + H₂O + BrO reaction channel.](https://dx.doi.org/10.1021/acsomega.0c05945)
and white for hydrogen. Brown for bromine, yellow for sulfur, red for oxygen, gray for carbon, and white for hydrogen.

**Figure 3.** Schematic energy diagrams of the BrO−H₂O + DMS reaction channel. Energies are in kcal mol⁻¹. The color coding is brown for bromine, yellow for sulfur, red for oxygen, gray for carbon, and white for hydrogen.

**Figure 4.** Schematic energy diagrams of the DMS−BrO + H₂O reaction channel. Energies are in kcal mol⁻¹. The color coding is brown for bromine, yellow for sulfur, red for oxygen, gray for carbon, and white for hydrogen.

**Table 1.** Electronic Energies without and with ZPE Correction [ΔE and Δ(E + ZPE)], Enthalpies [ΔH (298 K)], and Gibbs Free Energies [ΔG(298 K)] of the Formation of All Intermediates in the DMS + BrO Reaction in the Absence of Water

| system         | ΔE   | Δ(E + ZPE) | ΔH (298 K) | ΔG (298 K) |
|----------------|------|------------|------------|------------|
| DMS + BrO      | 0    | 0          | 0          | 0          |
| IM1-trans      | −3.3 | −2.8       | −2.3       | 3.9        |
| TS1-t          | 3.4  | 3.9        | 3.6        | 12.6       |
| TS1a-t         | 0.4  | 1.0        | 0.6        | 10.5       |
| PC1-t          | −26.3| −24.4      | −24.6      | −16.0      |
| DMSO + Br      | −19.1| −17.6      | −17.9      | −14.9      |
| TS2-t          | 7.6  | 4.8        | 4.5        | 12.8       |
| PC2-t          | −8.2 | −8.5       | −8.0       | −1.8       |
| CH₃SCH₂ + HBrO | −1.8 | −3.8       | −3.2       | −5.9       |

"All energies (in kcal mol⁻¹) are relative to the energies of initial reactants.

**Table 2.** Electronic Energies without and with ZPE Correction [ΔE and Δ(E + ZPE)], Enthalpies and Gibbs Free Energies for the DMS + BrO Hydrated Reaction Occurring Through DMS−H₂O + BrO⁻

| system         | ΔE   | Δ(E + ZPE) | ΔH (298 K) | ΔG (298 K) |
|----------------|------|------------|------------|------------|
| DMS−H₂O       | −5.4 | −3.9       | −4.0       | 2.9        |
| IM1W1         | −8.7 | −6.9       | −6.3       | 5.2        |
| TS1W1         | −4.7 | −3.0       | −3.0       | 12.7       |
| PC1W1         | −32.4| −29.3      | −29.3      | −14.4      |
| TS1W1a        | 3.2  | 1.5        | 1.4        | 15.7       |
| PC1W1a        | −16.6| −15.0      | −14.8      | 0.1        |
| DMSO + Br + H₂O| −19.1| −17.6      | −17.9      | −14.9      |
| HOBr + CH₃SCH₂ + H₂O | −1.8 | −3.8      | −3.2        | −5.9        |

"All energies (in kcal mol⁻¹) are relative to the energies of initial reactants.

**Table 3.** Electronic Energies without and with ZPE Correction [ΔE and Δ(E + ZPE)], Enthalpies and Gibbs Free Energies for the Hydrated DMS + BrO Reaction Occurring Through BrO⁻H₂O + DMS⁻

| system         | ΔE   | Δ(E + ZPE) | ΔH (298 K) | ΔG (298 K) |
|----------------|------|------------|------------|------------|
| BrO−H₂O       | −4.0 | −2.9       | −2.9       | 2.0        |
| IM2W1         | −12.5| −9.7       | −9.8       | 6.7        |
| TS2W1         | −10.1| −7.6       | −8.3       | 9.9        |
| PC2W1         | −36.2| −32.5      | −32.9      | −16.6      |
| TS2W1a        | 0.4  | −0.6       | −1.0       | 14.6       |
| PC2W1a        | −14.5| −13.2      | −12.8      | 0.8        |
| TS2W1a"       | 13.0 | 11.5       | 10.0       | 29.8       |
| PC2W1a"       | −17.6| −15.7      | −15.6      | −0.9       |
| DMSO + Br + H₂O| −19.1| −17.6      | −17.9      | −14.9      |
| HOBr + CH₃SCH₂ + H₂O | −1.8 | −3.8      | −3.2        | −5.9        |

"All energies (in kcal mol⁻¹) are relative to the energies of initial reactants.

**Table 4.** Electronic Energies without and with ZPE Correction [ΔE and Δ(E + ZPE)], Enthalpies and Gibbs Free Energies for the DMS + BrO Reaction through DMS⁻ BrO + H₂O⁻

| system         | ΔE   | Δ(E + ZPE) | ΔH (298 K) | ΔG (298 K) |
|----------------|------|------------|------------|------------|
| IM1-W2         | −7.2 | −5.8       | −4.9       | 6.6        |
| TS1-W2         | −10.1| −7.6       | −8.3       | 9.9        |
| PC1-W2         | −36.6| −32.9      | −30.3      | −11.6      |
| TS1a-W2        | 2.3  | 0.6        | 0.5        | 15.9       |
| PC1a-W2        | −12.2| −11.5      | −10.7      | 2.0        |
| DMSO + Br + H₂O| −19.1| −17.6      | −17.9      | −14.9      |
| HOBr + CH₃SCH₂ + H₂O | −1.8 | −3.8      | −3.2        | −5.9        |

"The energies are in kcal mol⁻¹.

The rate coefficients for each reaction path within the temperature range 217−298 K are given in Tables S2 and S3. All transition states, pre-reactive, and postreactive complexes are denoted as TS, IM, and PC, respectively, followed by a number. The inclusion of "W" in these notations denotes the presence of a single water molecule.

2.1. CH₃SCH₂ + HBrO and DMSO + Br Formation. As can be seen in Figures 1 and S1, in the absence of water, there is formation of two different configurations of the pre-reactive
complex, trans and cis, henceforth denoted as IM1-t and IM1-c, respectively (shown in Figures 1 and S1, respectively). In these configurations, the oxygen atom of BrO interacts with the sulfur atom of DMS at a distance of 2.9 Å, in reasonable agreement with the 2.5 Å distance reported by Sayin and McKee using the B3LYP/6-311+G(d,p) method. As reported in their research, the weakly bonded DMS–BrO complex can be described by natural bond orbital analysis as a two-center one-electron interaction, where two α-spin electrons occupy lone pair orbitals (one localized on the oxygen atom and the other localized on the sulfur atom) and a β-spin electron occupies a σ bonding orbital (β-bond). As shown in Figure 1, the electronic energy change for the formation of the trans-pre-reactive complex (IM1-t) relative to the energy of the separated reactants (DMS + BrO) is −2.8 kcal mol\(^{-1}\). Starting from IM1-t, three reaction channels were identified, including two oxygen atom transfer paths that form dimethyl sulfoxide (DMSO) and Br (Paths 1 and 2) and the hydrogen abstraction reaction that forms CH\(_3\)SCH\(_2\) + HOBr (Path 3). As shown in Figure 1, the two oxygen atom transfer pathways proceeded through transition states with trans- and cis-configurations (denoted TS1-t and TS1a-t, respectively) to form the same post-reactive complex, PC1-t. The energy of the trans-transition state in the oxygen atom transfer channel (Path 1) is 3.9 kcal mol\(^{-1}\), while that of the cis-transition state (Path 2) is 1.0 kcal mol\(^{-1}\) above initial reactants, which indicates that Path 2 is kinetically more favorable than Path 1. In Path 3, one hydrogen atom on the –CH\(_3\) group of DMS is abstracted by the oxygen atom of BrO through the TS2-t transition state, forming the (PC2-t) hydrogen bonded complex at 8.5 kcal mol\(^{-1}\) below initial reactants and 4.7 kcal mol\(^{-1}\) below CH\(_3\)SCH\(_2\) + HOBr final products. The latter value is in reasonable agreement with the previously reported value of 5.2 kcal mol\(^{-1}\).21

From an energetic standpoint, the TS2-t energy was predicted to be 7.6 kcal mol\(^{-1}\) above the energy of IM1-t, 0.9 kcal mol\(^{-1}\) higher than that of TS1-t, and 3.8 kcal mol\(^{-1}\) higher than that of TS1a-t. Thus, in the absence of water, Path 2 is the most favorable path in the DMS + BrO reaction. On the other hand, the Gibbs free energy of TS2-t is 5.6 kcal mol\(^{-1}\) higher than that of the pre-reactive complex IM1-t at 298 K, in reasonable agreement with the 6.0 kcal mol\(^{-1}\) value reported in a previous study using a different computational method.21 The product complex in this path, PC2-t (CH\(_3\)SCH\(_2\)···HOBr), is formed with an enthalpy change of −8.0 kcal mol\(^{-1}\) at 298 K, which is consistent with the value of −8.7 kcal mol\(^{-1}\) reported by Sayin and McKee.21 At 298 K, PC2-t is 14.2 kcal mol\(^{-1}\) less stable than the PC1-t (DMSO···Br) post-reactive complex with respect to the Gibbs free energy. PC1-t releases the final products, DMSO + Br, formed with −17.6 kcal mol\(^{-1}\) electronic energy and −14.9 kcal mol\(^{-1}\) Gibbs free energy changes relative to initial reactants. These energies are 13.8 and 9.0 kcal mol\(^{-1}\) higher than corresponding energy changes of the formation of the final products in the H-abstraction pathway (CH\(_3\)SCH\(_2\) + HOBr).

The relative electronic energy of formation of the cis-complex, IM1-c, is −1.6 kcal mol\(^{-1}\) below initial reactants, which is 1.2 kcal mol\(^{-1}\) lower than that of the trans isomer. The non-bonded Br···H distance in IM1-c is 3.2 Å, in good agreement with the 3.14 Å distance in Sayin’s study.21 This distance is close to the sum of van der Waals radii of Br (1.97 Å) and H (1.10 Å), which indicates that strong interactions might have taken place between BrO and DMS.33,44 Similar to the trans-isomer, IM1-c reacted through the oxygen atom transfer (Path 4) and the hydrogen abstraction (Path 5) mechanisms. In Path 4, the electronic energy barrier is 2.6 kcal mol\(^{-1}\), being 4.1 kcal mol\(^{-1}\) lower than in the corresponding path with the trans-isomer. In the TS1-c structure, the distance between the S atom and O atom is 1.9 Å, which is 1.0 Å shorter than in IM1-c and 0.034 Å longer than the corresponding bond in TS1-t. In the H-abstraction path (Path 5), the energy barrier is 6.4 kcal mol\(^{-1}\), which is 1.2 kcal mol\(^{-1}\) lower than the energy barrier in Path 2 and 3.8 kcal mol\(^{-1}\) higher than in the cis-oxygen atom transfer path (Path 4). The current results indicate that the paths proceeding through the cis-conformations to form DMSO + Br would proceed faster than the paths proceeding through the trans-conformations and much faster than the paths forming CH\(_3\)SCH\(_2\) + HOBr. This is in agreement with the result of an experimental study which indicated that the BrO + DMS reaction mainly follows the oxygen atom transfer pathway, forming DMSO as the single product at high yield.22,23 Hence, the hydrogen abstraction pathway does not appear to be important though it is the major pathway in the reaction of DMS with CI and NO.24,25

2.2. Mechanism of the Hydrated Reaction Proceeding through DMS−H\(_2\)O + BrO. In the presence of a single water molecule, both reactants are susceptible to form binary complexes with water via hydrogen bond or halogen bond interactions.38,45 Through one of its hydrogen atoms, water clustered to DMS in one direction, exclusively, via a 2.4 Å hydrogen bond with the S atom of DMS to form DMS−H\(_2\)O. It should be noted that this hydrogen bond with sulfur being longer than generally observed with oxygen is a result of a weaker interaction between the partial charge of the hydrogen atom and the dipole and quadrupole of the sulfur atom, as opposed to charge−charge interactions in hydrogen bonds with oxygen.46 Then, the BrO radical interacts with both DMS and H\(_2\)O moieties of the DMS−H\(_2\)O complex. As shown in Figure 2, BrO interacts with DMS−H\(_2\)O toward the S atom to form IM1W1, similar to the water-free case, except that the distance between DMS and BrO in IM1W1 is 0.3 Å longer than in IM1. Further, the IM1W1 reaction also followed the oxygen atom transfer (Path 1W1) and hydrogen abstraction (Path 1W2) mechanisms, forming hydrated DMSO−Br (denoted PC1W1) and CH\(_3\)SCH\(_2\)···HOBr (denoted PC1W1a), respectively, similar to the unhydrated reaction. Path 1W1 proceeds through the TS1W1 transition state, with an electronic energy of −3.0 kcal mol\(^{-1}\). This corresponds to an energy barrier of 3.9 kcal mol\(^{-1}\), which is 0.1 kcal mol\(^{-1}\) higher than that in the corresponding unhydrated reaction (Path 2). In addition, the Gibbs free energy barrier in Path 1W1 is 7.5 kcal mol\(^{-1}\), while it is 6.6 kcal mol\(^{-1}\) in the corresponding path in the absence of water. The post-reactive complex, PC1W1, in Path 1W1, is formed with −29.3 kcal mol\(^{-1}\) electronic energy relative to initial reactants, being 4.9 kcal mol\(^{-1}\) more stable than the unhydrated counterpart (PC1).

Despite the presence of water, the mechanism of the H atom abstraction path (Path 1W2) is similar to that of the unhydrated path with the H atom of DMS being abstracted by the O atom of BrO. One can see from the configuration of the pre-reactive three body IM1W1 complex that the plane containing the water molecule and BrO can divide DMS equitably in such a way that the oxygen atom of BrO is equidistant from two adjacent hydrogen atoms. Therefore, the
abstraction of either of the hydrogen atoms would yield the same results. In the transition state (TS1W1a) of this hydrogen abstraction pathway, the forming O=H bond is 1.3 Å and the breaking C−H bond is 1.2 Å, in agreement with previous reported values of 1.276 and 1.280 Å, respectively. The electronic and Gibbs free energies of this transition state are 8.4 and 10.5 kcal mol$^{-1}$, respectively, and 0.8 and 1.6 kcal mol$^{-1}$ higher than in the corresponding path in the absence of water. This indicates that water slightly destabilizes the transition state in this mechanism. The post-reactive complex in this path, PC1W1a (CH$_3$SCH$_2$−HOBr···H$_2$O), lies 15.0 kcal mol$^{-1}$ below the initial reactants and is 6.5 kcal mol$^{-1}$ more stable than PC2 (CH$_3$SCH$_2$−HOBr), with respect to the electronic energy. This stabilization can be attributed to the formation of a hydrogen bond between the water molecule and BrO. The energy barrier in the oxygen atom transfer pathway is 4.5 kcal mol$^{-1}$ lower than that in the hydrogen abstraction reaction, indicating that the former mechanism is more likely than the latter, regardless of the presence of water.

In addition to the IM1W1 pre-reactive intermediate discussed above, other pre-reactive complexes (IM1W2 and IM1W3) in Figures S2 and S3 in the Supporting Information were also formed with different water configurations around the DMS−BrO core. However, further reactions of these complexes followed similar mechanisms with those discussed above, with the main differences lying in the structures and energies of the reaction intermediate species. IM1W2 was formed with −9.4 kcal mol$^{-1}$ electronic energy relative to initial reactants, 2.5 kcal mol$^{-1}$ lower than the energy of IM1W1. This stability can be attributed to the formation of a halogen bond between the bromine atom of BrO and the oxygen atom of water. IM1W2 is rapidly converted through an oxygen atom transfer mechanism, by forming a transition state configuration located 1.8 kcal mol$^{-1}$ above it, into the PC1W2 product complex (Path 1W3, Figure S2). Further reaction of IM1W2 following the hydrogen abstraction reaction, depicted by Path 1W4 in Figure S2, is prevented by a 10 kcal mol$^{-1}$ energy barrier, higher than the barrier in the H abstraction path in the absence of water and much higher than that in the oxygen transfer path.

The IM1W3 that also involves the formation of a halogen bond is slightly more stable than IM1W2, formed with 10.0 kcal mol$^{-1}$ electronic energy beneath initial reactants. In both oxygen atom transfer (Path 1W5) and hydrogen abstraction (Path 1W6) mechanisms that IM1W3 undergoes, the energy barriers are, respectively, 1.8 and 1.4 kcal mol$^{-1}$ higher than in corresponding mechanisms starting with IM1W2. These energy differences are even higher than in corresponding mechanisms in the absence of water discussed above. In view of all mechanisms where DMS starts by forming a hydrate prior to reaction with BrO, it is obvious that water has a mixed effect on the energy barrier in the oxygen atom transfer mechanism while slightly increasing it in the H abstraction reaction. Overall, it can also be noted that the barrier height in the oxygen atom transfer reaction (formation of DMSO + Br) is lower than in the hydrogen abstraction reaction (formation of CH$_3$SCH$_2$ + HOBr), regardless of the presence of water. These results demonstrate that despite the role of a single water molecule, the DMS + BrO reaction would weakly impede the formation of the Br reservoir species (HOBr), whereas DMSO remains the dominant product. Exploration of the paths in Figures 2, S2, and S3 indicate that the path starting from the halogen-bonded pre-reactive complex IM1W2 (Path 1W3) is most likely to form DMSO in regard to its low energy barrier of 1.8 kcal mol$^{-1}$.

2.3. Mechanism for Hydrated Reactions through BrO···H$_2$O + DMS and H$_2$O···BrO + DMS. In our previous studies, we found that reactive halogen radicals (ClO and BrO) could form hydrogen-bonded and halogen-bonded hydrates with different water configurations. Similar BrO hydrates (BrO···H$_2$O and H$_2$O···BrO) were considered to be formed in this study.

The DMS interaction with BrO···H$_2$O leads to immediate formation of three ternary complexes, IM2W1, IM2W2, and IM2W3, among which IM2W1 and IM2W3 are cyclic as can be seen in Figures 3, S4, and S5. Although these complexes slightly differ in their formation energies and structures, their further reactions follow similar mechanisms and form the same final products. Hence, only the mechanism of the path involving IM2W1 will be discussed here, while the paths involving other intermediates are given in the Supporting Information. IM2W1 is formed with an electronic energy of −9.7 kcal mol$^{-1}$ and almost keeps the configuration of BrO···H$_2$O unchanged upon its clustering with DMS. IM2W1 subsequently reacts following three channels, including one oxygen atom transfer (Path 2W1) and two hydrogen abstraction (Paths 2W2 and 2W3). The mechanisms of these reactions differ from those described above only by the structures and energies of reaction intermediate species. In the oxygen atom transfer mechanism of Path 2W1, the transition state TS2W1 to form the product complex (PC2W1) is 2.1 kcal mol$^{-1}$ above that of IM2W1. The Gibbs free energy barrier for this path is 3.2 kcal mol$^{-1}$, which is obviously lower than in the corresponding water-free path (Path 2), which has an energy barrier height of 6.6 kcal mol$^{-1}$. The structure of the post-reactive complex PC2W1 formed with −32.5 kcal mol$^{-1}$ electronic energy is similar to that of the transition state in which the hydrogen bond is formed between the hydrogen atom of water and the oxygen atom of DMSO. Similar mechanisms starting with the IM2W2 and IM2W3 complexes form respective PC2W2 and PC2W3 product complexes through corresponding TS2W2 and TS2W3 transition states (see Paths 2W2 and 2W6, Figures S4 and S5 in the Supporting Information) with electronic energies within 1 kcal mol$^{-1}$ of the energies in Path 2W1.

The two hydrogen abstraction paths that involve the IM2W1 pre-reactive intermediate possess different reaction mechanisms: Path 2W2 and Path 2W3. In Path 2W2, the hydrogen atom is directly abstracted by BrO through a transition state formed with 9.1 kcal mol$^{-1}$ electronic energy above IM2W1, 7.0 kcal mol$^{-1}$ higher than in the oxygen transfer path (see Figure 3). In Path 2W3, however, there is a double hydrogen transfer in which water acts as a bridge between DMS and BrO, giving rise to the formation of a transition state with very high electronic energy, 21.2 kcal mol$^{-1}$ above IM2W1, which indicates that this path is unlikely. A similar process is also observed in the transformation of the IM2W2 to the products (Path 2W5, Figure S4). This double proton transfer mechanism has already been observed in some hydrated reactions. Another direct hydrogen abstraction happening in the presence of water involves the IM2W3 reactant intermediate (Path 2W7, Figure S5). This is seemingly the most favorable pathway in this mechanism, having 3.2 kcal mol$^{-1}$ electronic energy barrier and 6.0 kcal mol$^{-1}$ Gibbs free energy barrier, respectively, 4.4 and 2.7 kcal mol$^{-1}$ lower than in the water-free reaction. This is the only hydrogen
abstraction path for which water decreases the energy barrier. The product complexes in above hydrogen abstraction paths (CH$_3$SCH$_2$−···HOBr−···H$_2$O) are 16.8−19.3 kcal mol$^{-1}$ less stable than the product complexes in the oxygen transfer mechanisms. In comparison with the water-free path, the barrier height of the oxygen transfer path starting from IM2W1 is 1.7 kcal mol$^{-1}$ lower, whereas the energy barrier in the most favorable hydrogen abstraction path starting from the same reactant intermediate is 1.5 kcal mol$^{-1}$ higher than in the path without water.

2.4. Mechanism for the Hydrated DMS + BrO Reaction through DMS···BrO + H$_2$O. DMS emitted to the atmosphere from ocean can interact with BrO to form the DMS−BrO binary complex, which in turn can interact with water to form a hydrogen-bonded or a halogen-bonded complex. As shown in Figures 4, S7, and S8, three hydrated complexes were found, IM1-W1, IM1-W2, and IM1-W3. This is equivalent to the hydration process of IM1 discussed in Section 2.1. These interactions led to ternary complexes similar to those formed from the interactions between hydrated DMS/BrO and the third species. For example, the IM1-W1 and IM1-W3 pre-reactive complexes are identical to IM1W3 and IM1W1 complexes, respectively, which form from DMS···H$_2$O. Therefore, the reaction channels in Figures S7 and S8 will not be discussed in detail here. However, it is worth noting that a single water molecule could interact and cluster to the Br atom of BrO through a halogen bond. The formed halogen-bonded complex IM1-W2 is less stable than the two other ternary complexes formed from the DMS−BrO cluster, with a relative energy of −5.8 kcal mol$^{-1}$. The subsequent reaction beginning with IM1-W2 follows a similar reaction mechanism of oxygen atom transfer/H-abstraction and leads to the same products as the other reactions discussed above (Figure 4). For the H abstraction path beginning with IM1-W2 (Path 3W4) and going through the TS1a-W2 transition state, the barrier height is 6.4 kcal mol$^{-1}$. Compared to Path 2, the hydrogen abstraction path without the participation of water, the energy barrier is reduced by 1.8 kcal mol$^{-1}$. The post-reactive complex (CH$_3$SCH$_2$−···HOBr−···H$_2$O) is also a halogen-bonded compound, which is 3.5 kcal mol$^{-1}$ less stable than the corresponding hydrogen-bonded product PC1a-W1. Different from other oxygen atom transfer channels, water keeps interacting with the IM1 complex via a halogen bond in the whole reaction process and does not engage in the atom transfer, while slightly facilitating the reaction. However, for the oxygen atom transfer path starting from IM1-W2, the electronic energy of the TS1-W2 transition state (−7.6 kcal mol$^{-1}$) is lower than the energy of the IM1-W2 complex (−5.8 kcal mol$^{-1}$). Nakano et al. have also suggested in their study that the oxygen atom transfer reaction path could have negative activation energy. It should be noted that the Gibbs free energy of the oxygen atom transfer transition state TS1-W2 is 9.9, 3.3 kcal mol$^{-1}$ higher than the Gibbs free energy of IM1-W2 and 6.0 kcal mol$^{-1}$ lower than the Gibbs free energy barrier in the H-abstraction path (Path 3W4). Thus, the oxygen atom transfer mechanism of DMS + BrO is more favorable than H-transfer in any cases investigated, whether a single water molecule is involved or not.

2.5. Reaction Kinetics. From the reaction mechanisms discussed above, it is easy to draw a conclusion that a single water molecule can slightly decrease the barrier of the DMS + BrO reaction to form DMSO + Br if the BrO···H$_2$O hydrate is formed first, whereas it increases the energy barrier in the formation of CH$_3$SCH$_2$ + HOBr. We also found that regardless of the presence of water, oxygen atom transfer paths are more favorable than hydrogen abstraction paths. To assess the role of water in the kinetics of the DMS + BrO reaction, we determined the reaction rate coefficients using eq 8. Table S2 lists the rate coefficients for relevant paths calculated at different altitudes both in the absence and in the presence of water.

As evidenced in Table S3, for the oxygen atom transfer paths in the absence of water, the calculated rate coefficients for the reaction proceeding via the trans-conformer path ($k_{trans}$) range between 6.7 × 10$^{-18}$ and 4.0 × 10$^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in the 217−298 K temperature range, whereas those of the reaction proceeding through the cis-conformer path ($k_{cis}$) range between 7.5 × 10$^{-16}$ and 2.4 × 10$^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in the same temperature range. The rate coefficient of the DMS + BrO → DMSO + Br reaction at 298 K and 760 Torr, 2.4 × 10$^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, is in good agreement with experimental results ranging between (2.7 ± 0.5) × 10$^{-13}$ and (4.4 ± 0.6) × 10$^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and the theoretical result of 8.7 × 10$^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. 25 Given the 2 orders of magnitude difference between the rate coefficients of the paths proceeding through cis and tran reactant intermediates, it is concluded that the rate of DMSO + Br formation is controlled by the rate of the cis conformer path. As can be seen from the results, the reaction rate coefficients exhibit positive temperature dependence.

In the presence of water, the rate coefficients for the formation of DMSO + Br from DMS−H$_2$O + BrO ($k_{H2OW2}$, Path 1W3), BrO···H$_2$O + DMS ($k_{IM1W2}$, Path 2W4), and H$_2$O···BrO + DMS ($k_{IM2W2}$, Path 2W10) interactions form reactant intermediates with trans configurations are ~2−4 times higher than the rate coefficient of Path 2 ($k_{1c-O}$). However, for the paths starting from BrO···H$_2$O + DMS that proceed through formation of the reactant intermediate with a cis conformation ($k_{IM2W2}$, Path 2W8), the rate coefficients range from 1.3 × 10$^{-15}$ to 3.5 × 10$^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ in the temperature range considered, and they are about 1−2 times higher than the rate coefficient of corresponding water-free reaction ($k_{1c-O}$, Path 4).

The rate coefficients of the CH$_3$SCH$_2$ + HOBr formation in the absence of water (Table S5) are 1−2 orders of magnitude lower than those of the DMSO + Br formation in the 217−298 K temperature range. As expected from the energetics of these two paths, the kinetics indicates that the DMSO + Br formation is more favorable than the CH$_3$SCH$_2$ + HOBr formation under investigated conditions. At 298 K and 760 Torr, the rate coefficient of the hydrogen abstraction reaction proceeding through the cis DMS−BrO conformer ($k_{1c}$) is calculated to be 7.9 × 10$^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, which is consistent with a previously calculated result of 8.9 × 10$^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.

In the presence of water, the H-abstraction path beginning with the pre-reactive IM2W2 ternary complex that undergoes a double hydrogen transfer mechanism with a very high energy barrier of 21.6 kcal mol$^{-1}$ has a rate coefficient of 9.1 × 10$^{-31}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K. This specific path is highly unlikely under relevant atmospheric temperatures. Other hydrogen abstraction paths in the presence of water, namely, BrO···H$_2$O + DMS ($k_{IM2W1a}$, Path 2W2), DMS···H$_2$O + BrO ($k_{IM2W2a}$, Path 1W4), and H$_2$O···Br + DMS ($k_{IM2W1a}$, Path 2W11) listed in Table S2, among which Path 2 is the fastest, have rate coefficients ranging between 1.3 × 10$^{-17}$ and 9.5 ×
shown in Table S4 in the Supporting Information, while the fractions of DMS/BrO that are complexed with water are given in Table S5. The absence and in the presence of water, respectively. The values of e

Taking the BrO concentrations determined in order to evaluate the effect of atmospheric water on the DMS + BrO reaction, and the values are provided in Table 5. We found that the fraction of reactants that are complexed with water are so small that the majority of these species remain dry at the investigated atmospheric temperatures. The results showed that only 0.026% of DMS and 0.17% of BrO are complexed with water at 298 K, while most of the species remain unhydrated. Hence, the overall effect of a single water molecule on the kinetics of the DMSO + Br is negligible.

3. CONCLUSIONS
The effect of one water molecule on the mechanism and kinetics of the reaction between BrO and DMS has been examined theoretically using quantum chemical calculations. Regardless of the presence of water, this reaction follows two main mechanisms: the oxygen atom transfer and the hydrogen abstraction, forming DMSO + Br and CH2CH3S + HOBr, respectively. In the absence of water, the DMS + BrO reaction first forms trans and cis pre-reactive complexes that react thereafter to form the final products. In each case, the hydrogen abstraction pathway is less favorable than the oxygen atom transfer both in terms of energetics and kinetics, and the main expected product of this reaction is DMSO + Br, formed with a rate coefficient of 2.4 × 10−13 cm3 molecule−1 s−1 at 298 K. This rate coefficient is 2 orders of magnitude higher than that of the hydrogen abstraction pathway.

In the presence of water, the oxygen atom transfer is still the dominant mechanism, with rate coefficients 2–4 orders of magnitude higher than those of the hydrogen abstraction path within the 217–298 K temperature range. Moreover, the effective rate coefficients of oxygen atom transfer reactions in the presence of water are 3–7 orders of magnitude lower than those of the reaction in the absence of water. However, considering the negligible concentration of hydrated reactants that decrease the reaction rates and hinder the DMSO + Br formation, the overall rates of the DMS + BrO reaction that takes humidity into account are not shifted. This means that the effect of humidity may not significantly impact ozone depletion through the formation of HOBr from the DMS + BrO reaction.

4. COMPUTATIONAL METHODS
Geometry optimizations and vibrational frequency calculations of all the stationary points were carried out at the BH&HLYP/ aug-cc-pVTZ level of theory. The density functional BH&HLYP has been shown to provide energy barrier heights with good agreement with experiments.48 For the transition
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corresponding product complexes along the reaction coordinate (IRC) calculations were performed to con 
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frequency analysis could also provide the zero-point vibrational 
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reactive coordinate, whereas other stationary points were 
exhibited one imaginary frequency corresponding to the
pre-reactive intermediate from reactants
reactive intermediate and transition state, 
k
products through a transition-state con 
back into initial reactants or further react and form new
reactants. The pre-reactive intermediates could either revert
intermediates depending on the collision orientation of

R1 could be expressed as

\[ k_1 = \frac{k_{eq}k_2}{k_{-1}} \]

(8) where \( k_2 \) is the unimolecular rate coefficient 
of the reactant and \( k_{-1} \) is the rate constant of the pre-reactive
intermediate to form the products.

Applying the steady-state approximation on the pre-reactive
intermediate, the rate coefficient, \( k \), of reaction R1 is
determined to be

\[ k = \frac{k_1}{k_{-1} + k_2} \]

(9) where \( k_{eq} \) is the equilibrium constant for the formation of the
pre-reactive intermediate from reactants

\[ k_{eq} = \frac{1}{\rho \exp \left( -\frac{\Delta G}{RT} \right)} \]

(10) where \( \rho \) denotes the standard density, \( \Delta G \) is the Gibbs free
energy change for the formation of the pre-reactive intermediate, \( R \) is the molar gas constant, and \( T \) is the absolute temperature.

\[ k_2(T) = \Gamma \frac{k_BT}{h} \exp \left( -\frac{\Delta G^r}{RT} \right) \]

(11) where \( \Delta G^r \) is the Gibbs free energy barrier between the pre-
reactive intermediate and transition state, \( k_B \) is Boltzmann’s
constant, and \( h \) denotes the Planck constant. \( \Gamma \) is the quantum
mechanical tunneling coefficient calculated by the Winger
correction

\[ \Gamma = 1 + \frac{1}{24} \left( \frac{h\nu^r}{k_B T} \right) \]

(12) where \( \nu^r \) is the imaginary frequency of the transition states.
The values for \( \Gamma \) are listed in Table S1 in the Supporting
Information.

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https://dx.doi.org/10.1021/acsomega.0c05945

ACS Omega 2021, 6, 2410–2419

2419