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The Reaction between the Bromine Atom and the Water Trimer: High Level Theoretical Studies

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Abstract

Three different reaction pathways are found for the reaction of bromine atom (Br) with the lowest-energy structure of the water trimer [*uud*-(H_2O)$_3$], initially using the MPW1K-DFT method. The three bromine pathways have closely related geometries and energetics, analogous to those found for the fluorine and chlorine reactions. The lowest-energy pathway of the Br + *uud*-(H_2O)$_3$ reaction was further investigated using the “gold standard” CCSD(T) method and the correlation-consistent basis sets up to cc-pVQZ(-PP). Based on the CCSD(T)/cc-pVQZ(-PP)//CCSD(T)/cc-pVTZ(-PP) results, the Br + $(H_2O)_3$ reaction is endothermic by 33.3 kcal/mol. The classical barrier height is 29.0 kcal/mol between the reactants and the exit complex, and there is no barrier for the reverse reaction. The Br···$(H_2O)_3$ entrance complex is found to lie 4.7 kcal/mol below the separated reactants, and the HBr···$(H_2O)_2$OH exit complex is bound by 6.4 kcal/mol relative to the separated products. This potential energy profile is further corrected by the zero point energies and spin-orbit coupling effects. Structurally, the Br + $(H_2O)_3$ stationary points can be derived from those of the simpler Br + $(H_2O)_2$ reaction by judiciously appending a H_2O molecule. The Br + $(H_2O)_3$ potential energy profile is compared with the Br + $(H_2O)_2$ and Br + H_2O reactions, as well as to the valence isoelectronic Cl + $(H_2O)_3$ and F + $(H_2O)_3$ systems. It is reasonable to expect that the reactions between the bromine atom and larger water clusters would be similar to the Br + $(H_2O)_3$ reaction.

Key Words: Atom-molecule reaction, Bromine atom, Water trimer, Potential energy profile, CCSD(T) computations

1. Introduction

The bromine atom plus water monomer (Br + H_2O) reaction and its reverse reaction have been widely investigated,[1-12] since atomic bromine is an active ozone depletion catalyst,[13,14] and some brominated compounds play important roles in atmospheric and combustion chemistry.[15] The bromine atom plus water *polymer* reactions may be more important, for the water polymers detected in the atmosphere may lower the reaction barriers, as shown by our Br + $(H_2O)_2$ results.[16] To understand energy trends ranging from the water monomer to water polymers, we herein investigate the reaction between the bromine atom and the water trimer, Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$. This reaction was investigated using the "gold standard" CCSD(T) method with basis sets as large as cc-pVQZ(-PP). The Br + $(H_2O)_3$ potential energy profile was predicted and the stationary points therein were discussed. We also compare the Br + $(H_2O)_3$ reaction with the simpler bromine reactions Br + $H_2O/(H_2O)_2$ and with the valence isoelectronic water trimer reactions F/Cl + $(H_2O)_3$.[2,16-18]

2. Methodology

The computational methods used in present paper are similar to those successfully used for the reaction of bromine atom plus water dimer.[16] Briefly, the stationary points for the Br + $(H_2O)_3$ reaction were first investigated with MPW1K density functional theory (DFT), which was recommended by Truhlar et al.[19] and gave the best predictions for the F + H_2O reaction barrier among 49 DFT functionals.[20] The basis sets used here with the MPW1K method are the Dunning correlation-consistent polarized valence basis sets (cc-pVnZ). For the hydrogen and oxygen atoms, the cc-pVTZ basis sets[21,22] were used. For the bromine atom, a scalar relativistic pseudopotential (PP) and the corresponding cc-pVTZ-PP[23] were employed. With the pseudopotential, the 10 inner core electrons ($1s^22s^22p^6$) of Br were replaced by energy-consistent pseudopotentials, which were constructed from atomic multiconfigurational Dirac-Hartree-Fock results.[23]

All stationary points were characterized by harmonic vibrational frequency analyses, with the minima having all real frequencies and the transition states (TS) having only one imaginary frequency. The intrinsic reaction coordinate (IRC)[24-26] method at the same level was employed to confirm that each transition state connects the designated entrance complex and exit complex. All our DFT computations were carried out with the Gaussian 16 program suite.[27]

To obtain more reliable geometries, energies and vibrational frequencies, the geometry optimizations and frequency analyses were further performed with the higher level coupled-cluster single and double substitution method with perturbative treatment of triple excitations CCSD(T).[28-30] Restricted method was used for closed shell systems, while unrestricted approach was employed for open-shell species. In conjunction with the CCSD(T) method, the cc-pVnZ(-PP) basis sets[21-23] were used for geometry optimizations and frequency analyses up to cc-pVTZ(-PP), and for single-point energy computations up to cc-pVQZ(-PP). In all CCSD(T) computations, the 1s-like MO for oxygen and the 3s3p3d-like MOs for bromine are frozen. All the CCSD(T) computations were performed with the CFOUR program.[31]

3. Results and Discussion

3.1 The potential energy profile of the Br + $(H_2O)_3$ reaction

It has been reported[32-38] that the lowest-energy isomer of the water trimer, *uud*-$(H_2O)_3$, has a six-membered ring structure. In *uud*-$(H_2O)_3$, the six-membered ring is formed by three OH bonds (from three water molecules) connecting with three hydrogen bonds, where each water molecule functions as both electron donor and acceptor. The three out-of-ring OH bonds of $(H_2O)_3$ are in the "up-up-down" (*uud*) orientation, relative to the pseudo-planar six-membered ring. When a Br atom reacts with the water trimer *uud*-$(H_2O)_3$, there are three different kinds of active sites, the three out-of-ring H atoms in *uud*-$(H_2O)_3$. Thus, there are three different kinds of Br + $(H_2O)_3$ reaction pathways, analogous to the F/Cl + $(H_2O)_3$ reactions.[17,18] As shown in Figure S1 in the supporting information, the three Br + $(H_2O)_3$ pathways predicted by the MPW1K/cc-pVTZ(-PP) method are closely related, both geometrically and energetically. Further, the lowest-energy Br + $(H_2O)_3$ reaction pathway was investigated using the more reliable CCSD(T) method along with basis sets as large as cc-pVQZ(-PP), with the results shown in Figure 1. In the following discussions, we will mainly consider the CCSD(T)/cc-pVTZ(-PP) geometries and the CCSD(T)/cc-pVQZ(-PP)//CCSD(T)/cc-pVTZ(-PP) energies, unless otherwise indicated.

As shown in Figure 1, in the entrance complex [Br···$(H_2O)_3$] of the Br + $(H_2O)_3$ reaction, the Br atom bound to one H_2O molecule with other two H_2O molecules loosely attached by hydrogen bonds. Compared with the separated Br + *uud*-$(H_2O)_3$ reactants, the Br···$(H_2O)_3$ complex lies 4.7 kcal/mol lower. In the TS, the distance between the Br atom and the H atoms being abstracted, i.e., that of Br-H7, is decreased to 1.542 Å, much shorter than 2.891 Å in the Br···$(H_2O)_3$ complex, forming an eight-membered ring structure.

The TS structure has been verified to be a first-order saddle point on the Br$(H_2O)_3$ potential energy surface (PES) for it has only one imaginary vibrational frequency (650*i* cm^{-1}). The energy of the TS is 29.0 kcal/mol above the separated Br + *uud*-$(H_2O)_3$ reactants. The exit complex [*ud*-HBr···$(H_2O)_2$OH] has its two out-of-plane OH moieties in "up-down" orientations, relative to the pseudo eight-membered ring plane. The chemically bound Br-H distance in the *ud*-HBr···$(H_2O)_2$OH complex is 1.451 Å,

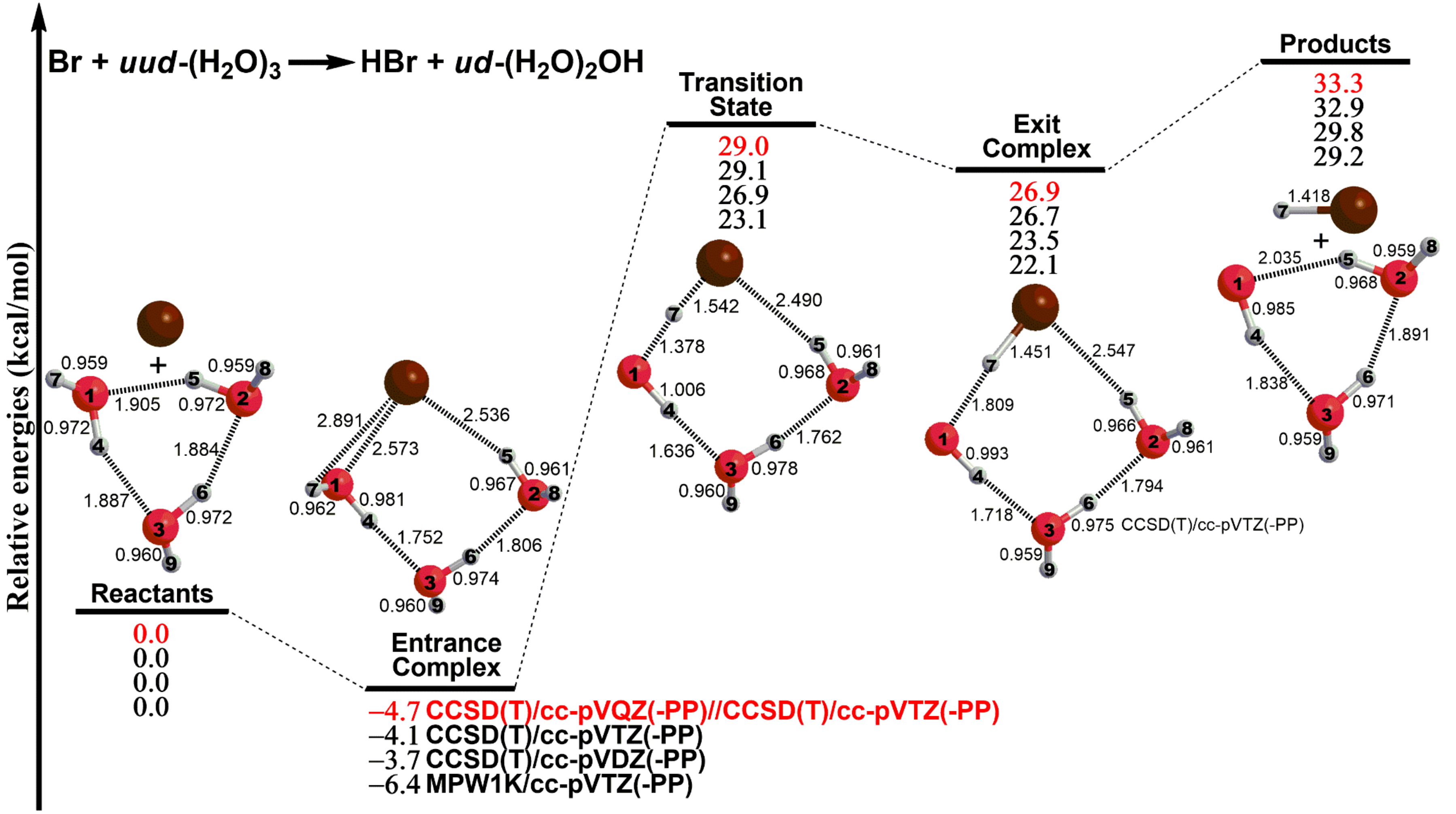


Figure 1. Stationary points along the Br + $(H_2O)_3$ potential energy profile. The bond distances and relative energies are given in angstroms and kcal/mol, respectively.

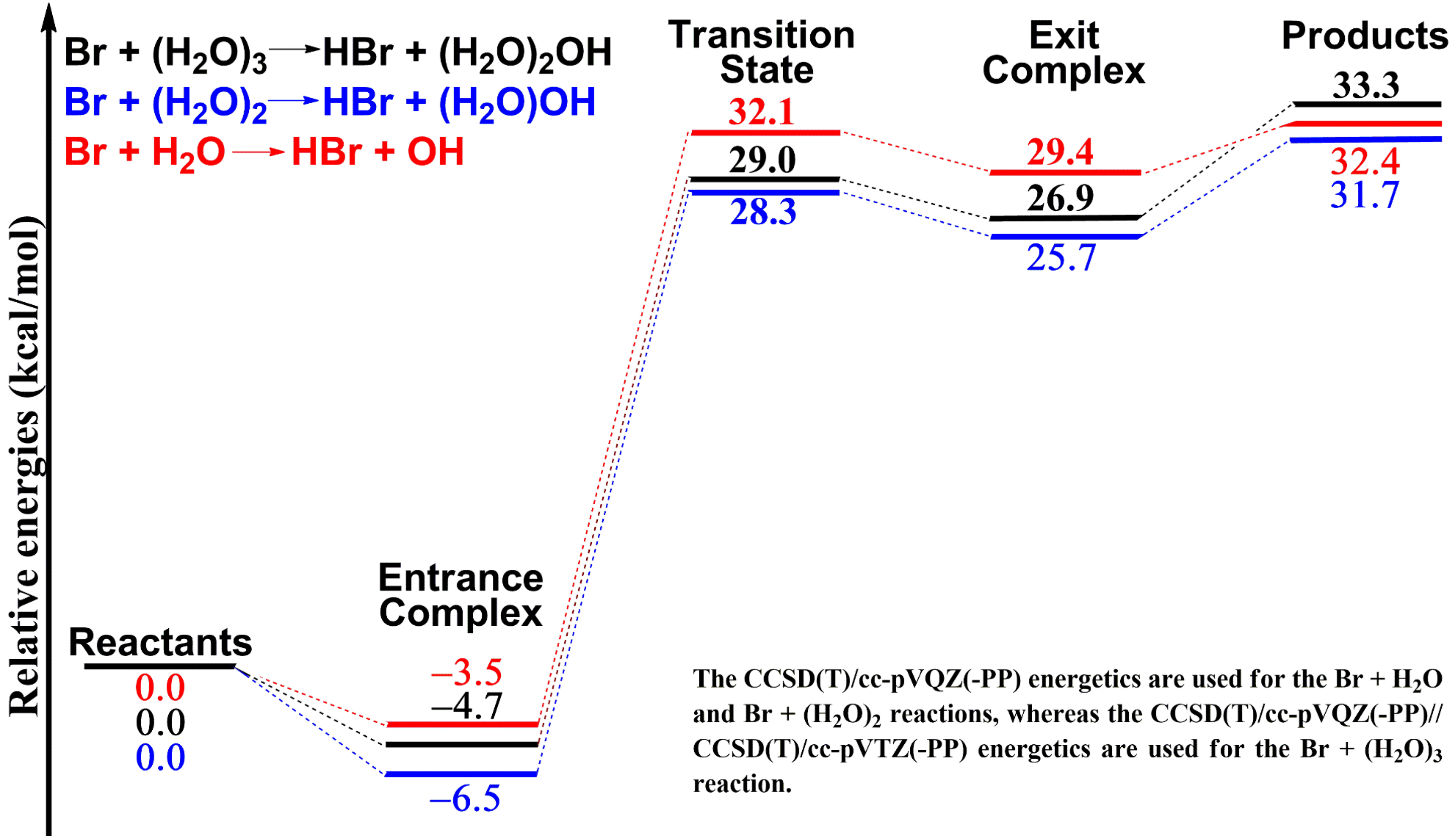
just a bit longer than the 1.418 Å for the free HBr molecule. The much longer Br···H distance in *ud*-HBr···$(H_2O)_2OH$ is 2.547 Å, which may be considered as a weaker Br···H hydrogen bond. The *ud*-HBr···$(H_2O)_2OH$ complex is 6.4 kcal/mol energetically lower than the separated HBr + $(H_2O)_2OH$ products, but 26.9 kcal/mol higher than the separated Br + *uud*-$(H_2O)_3$ reactants. Removing the HBr moiety from *ud*-HBr···$(H_2O)_2OH$ gives the radical reaction product *ud*-$(H_2O)_2OH$, with its two out-of-plane OH bonds in the "up-down" orientations relative to the six-membered ring. Energetically, the products HBr + *ud*-$(H_2O)_2OH$ lie 33.3 kcal/mol above the separated Br + *uud*-$(H_2O)_3$ reactants, indicating that the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction is significantly endothermic.

Figure 1 also shows that the potential energy profile given by the DFT-MPW1K method is in reasonable agreement with that from the CCSD(T) method. The MPW1K/cc-pVTZ(-PP) barrier is 23.1 kcal/mol, 5.9 kcal/mol lower than the CCSD(T)/cc-pVQZ(-PP) prediction (29.0 kcal/mol). The MPW1K endothermicity of 29.2 kcal/mol is 4.1 kcal/mol less than the CCSD(T)/cc-pVQZ(-PP) prediction (33.3 kcal/mol). The MPW1K entrance complex is about 1.7 kcal/mol more strongly bound, and the MPW1K exit complex is about 0.7 [(29.2 – 22.1) – (33.3 – 26.9)] kcal/mol more strongly bound, compared with the CCSD(T)/cc-pVQZ(-PP) results. Thus, the DFT-MPW1K method may be a reasonable method for the initial study of larger water-containing systems.

It should be noted that the binding energy of H_2O to $Br(H_2O)_2$ is just under 8.0 kcal/mol at the CCSD(T)/aug-cc-pVDZ(-PP) level of theory by Shepler, Wright, Balabanov, and Peterson.[39] At the CCSD(T)/cc-pVQZ(-PP) level used in this paper, it is still only 9.9 kcal/mol, which is much lower than the classical barrier of 29 kcal/mol for the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction. Thus, another channel for the reaction of a bromine atom with the water trimer where the trimer just loses a water molecule, i.e., Br + $(H_2O)_3 \rightarrow Br(H_2O)_2 + H_2O$, may be more energetically favorable. However, we will not discuss it further, since our main concern in this paper is the hydrogen abstraction reaction.

3.2 Comparisons with Br + $(H_2O)_2$ and Br + H_2O

Next, we compare the water trimer reaction Br + $(H_2O)_3$ (Figure 1) with the water dimer reaction Br + $(H_2O)_2$ (the reverse reaction in Figure 1 of Ref. 16) and the water monomer reaction Br + H_2O (Figure 1 in Ref. 2). Structurally, the entrance complex, TS, and exit complex for the water trimer reaction Br + $(H_2O)_3$ can be derived from those of the water dimer reaction Br + $(H_2O)_2$ by inserting a third water molecule; or from the water monomer reaction Br + H_2O by appending a water dimer molecule. Thus, the stationary points for the water trimer reaction Br + $(H_2O)_3$ are closely related to those of the water dimer reaction Br + $(H_2O)_2$ and the water monomer reaction Br + H_2O. Energetically, the water trimer entrance complex $Br\cdots(H_2O)_3$ is bound by 4.7 kcal/mol (two new noncovalent interactions form but one is broken), 1.8 kcal/mol weaker than the binding energy of 6.5 kcal/mol (two new noncovalent interactions form) for the water dimer complex $Br\cdots(H_2O)_2$ but 1.2 kcal/mol stronger than that of 3.5 kcal/mol (one new noncovalent interaction forms) for the water monomer complex $Br\cdots H_2O$, as shown in Figure 2. For the TS, the relative energy of 29.0 kcal/mol for the water trimer reaction Br + $(H_2O)_3$ is very similar to that of 28.3 kcal/mol for the water dimer reaction Br + $(H_2O)_2$, but somewhat lower than that of 32.1 kcal/mol for the water monomer reaction Br + H_2O. This is also the case for the exit complex. So, the water trimer reaction Br + $(H_2O)_3$ looks in this case more similar to the water dimer reaction Br + $(H_2O)_2$ than to the water monomer reaction Br + H_2O.



The CCSD(T)/cc-pVQZ(-PP) energetics are used for the Br + H_2O and Br + $(H_2O)_2$ reactions, whereas the CCSD(T)/cc-pVQZ(-PP)//CCSD(T)/cc-pVTZ(-PP) energetics are used for the Br + $(H_2O)_3$ reaction.

Figure 2. Comparison of the potential energy profiles for the Br + $(H_2O)_3$, Br + $(H_2O)_2$ and Br + H_2O reactions.

3.3 Comparisons with Cl + $(H_2O)_3$ and F + $(H_2O)_3$

We also compare the bromine reaction Br + $(H_2O)_3$ PES with those for the chlorine reaction Cl + $(H_2O)_3$[18] and the fluorine reaction F + $(H_2O)_3$.[17] Structurally, all the stationary points on the PES of bromine reaction Br + $(H_2O)_3$ (Figure 1) can be compared to those for the chlorine reaction Cl + $(H_2O)_3$ (Figure 2 in Ref. 18) and the fluorine reaction F + $(H_2O)_3$ (Figure 1 in Ref. 17). However, the PES for Br + $(H_2O)_3$ is different from that for Cl + $(H_2O)_3$, and even more so from that for F + $(H_2O)_3$. As shown in Figure 3, the entrance well for Br···$(H_2O)_3$, lies below the reactants by 4.7 kcal/mol, slightly shallower than the analogous 5.3 kcal/mol for Cl···$(H_2O)_3$ and 7.1 kcal/mol for F···$(H_2O)_3$.

The other stationary points (TS, exit complex and products) for the Br + $(H_2O)_3$ reaction have their relative energies higher than those for the Cl + $(H_2O)_3$ reaction by 12 – 15 kcal/mol, and those for the F + $(H_2O)_3$ reaction by 33 – 55 kcal/mol. Despite the different energy profiles among the three reactions, we noticed that all transition states, exit complexes, and products for the Br + $(H_2O)_3$ reaction and for the Cl + $(H_2O)_3$ reaction lie *above* the reactants. In contrast, for the F + $(H_2O)_3$ reaction, the TS, exit complex, and products all lie *below* the reactants. Thus, the Br + $(H_2O)_3$ and Cl + $(H_2O)_3$ reactions are endothermic with no barriers for the reverse direction, while the F + $(H_2O)_3$ reaction is an exothermic reaction with no barrier from the reactants. These substantial energy differences may be attributed to the very strong H-F bond.

3.4 Vibrational frequencies and zero-point energy corrections

The harmonic vibrational frequencies for all the stationary points of the Br + $(H_2O)_3$ reaction predicted by the CCSD(T)/cc-pVTZ(-PP) method were shown in Table S1 in the supplemental material. Our H-bonded OH stretching frequencies of 3613 ~

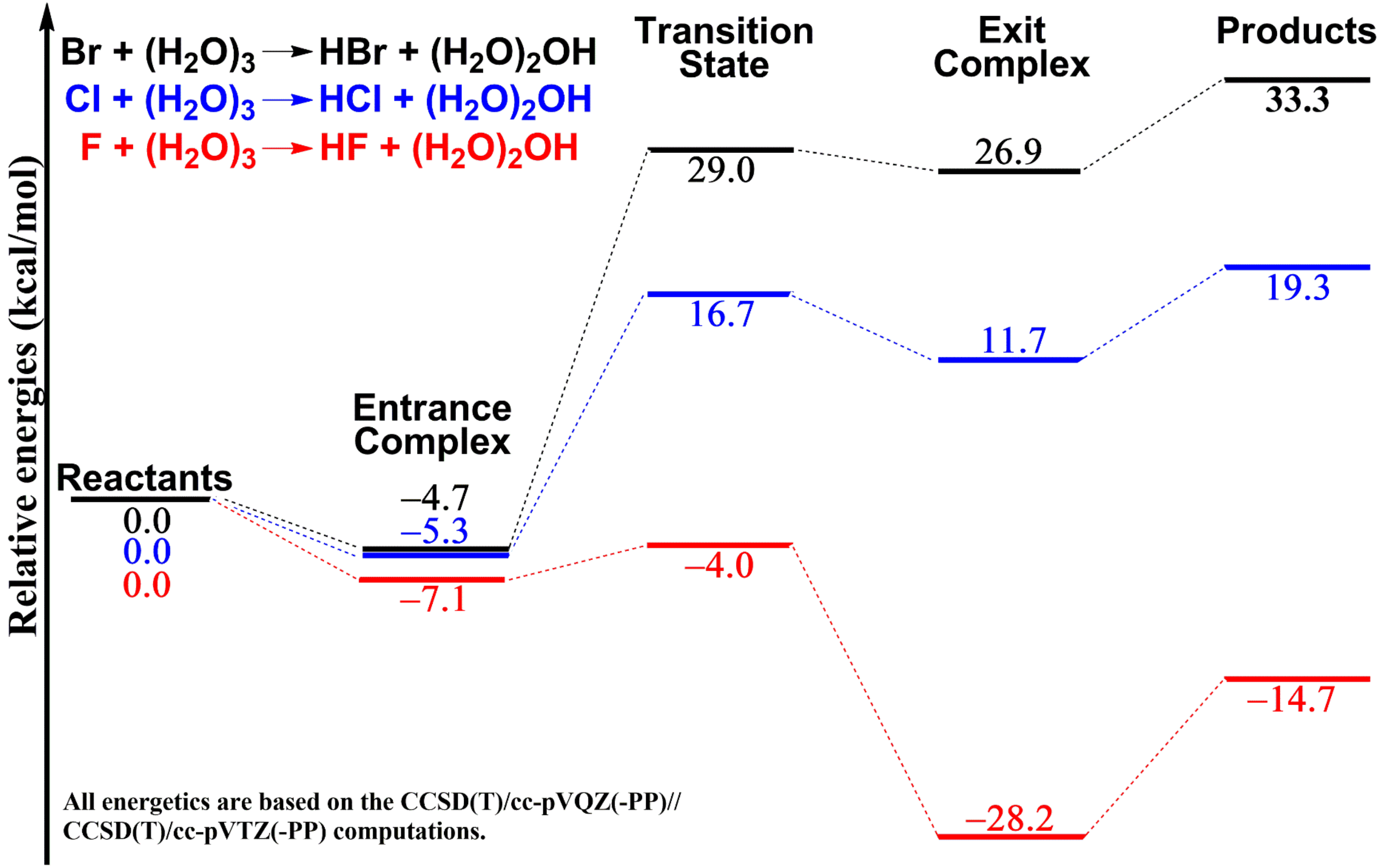


Figure 3. Comparison of the potential energy profiles for the Br + $(H_2O)_3$ (black), Cl + $(H_2O)_3$ (blue) and F + $(H_2O)_3$ (red) reactions.

3689 cm^{-1} for $(H_2O)_3$ agree with the experimental values of 3533,[40] 3544/3529,[40] 3528,[41] 3531.8±1.2,[42] and 3516.7±2.3 cm^{-1}.[42] Our free OH stretching frequencies of 3903~3909 cm^{-1} for $(H_2O)_3$ can be compared with the experimental values of 3726 and 3717 cm^{-1}.[40] Our OH radical stretching frequency of 3498 cm^{-1} for $(H_2O)_2OH$ well agrees with the experimental result of 3365.2 cm^{-1}.[41] Especially, our theoretical H-Br stretching frequency of 2649 cm^{-1} for free HBr molecule reproduces the experimental harmonic frequency of 2649 cm^{-1}.[43] The TS is predicted to have an imaginary vibrational frequency of 650i cm^{-1}, with the corresponding normal mode revealing simultaneous Br-H7 bond formation and O1-H7 bond breaking as the reaction proceeds toward $Br + (H_2O)_3 \rightarrow HBr + (H_2O)_2OH$.

Table S1 also shows the zero-point energies (ZPEs) for all the stationary points of the $Br + (H_2O)_3$ reaction at the CCSD(T)/cc-pVTZ(-PP) level of theory. The ZPE corrections increase the relative energy of the entrance complex by 0.2 kcal/mol and decrease those of the TS, exit complex, and products by 4.6, 3.6, and 4.8 kcal/mol, respectively. Thus, with the ZPE corrections, the relative energies of the entrance complex, TS, exit complex, and products are predicted to be -4.5, 24.4, 23.3, and 28.5 kcal/mol, respectively, at the CCSD(T)/cc-pVQZ(-PP)//CCSD(T)/cc-pVTZ(-PP) level of theory.

3.5 Spin-orbit coupling corrections

The relativistic effects emerging for atomic Br may be important, and these should be considered in the present study. The quasirelativistic effects for the Br core electrons have been included with the scalar relativistic pseudopotentials.[23,44] The spin-orbit (SO) coupling effects arising from the Br valence electrons were treated here in two ways. In the most simplified way, we considered the SO coupling effects only for the reactants $Br + (H_2O)_3$, assuming that they are quenched for the entrance complex, TS, exit complex, and products. It is known from experiment[45] that the SO splitting between the ground $^2P_{3/2}$ state (fourfold) and the excited $^2P_{1/2}$ states (twofold) of the Br atom is 3685 cm^{-1}, which causes the SO ground state of the Br atom to lie below the spin-averaged (non-SO) energy by 3685/3 = 1228 cm^{-1} (3.5 kcal/mol). With this value, the relative energies of the entrance complex, TS, exit complex, and products for the forward $Br + (H_2O)_3 \rightarrow HBr + (H_2O)_2OH$ reaction all rise by 3.5 kcal/mol, respectively.

In a more rigorous approach, we predict SO coupling corrections using the Breit-Pauli operator, employing the complete active space self-consistent field (CASSCF) method and the cc-pVQZ(-PP) basis sets. In the state-averaged CASSCF calculations, three states were included. For bromine atom, the active space includes 4 full-valence orbitals and 7 electrons (7e, 4o). For the $(H_2O)_2OH$ product, the (23e, 12o) active space is chosen, while for entrance complex, transition state, and exit complex the (31e, 16o) active space is used. The MOLPRO program package[46] is used for this purpose. Our theoretical CASSCF SO corrections for the reactant (Br atom), the entrance complex, the TS, the exit complex, and the product [$(H_2O)_2OH$] are predicted to be 1132; 306; 1; 3; and 4 cm^{-1} (that is, 3.2, 0.9, 0.0, 0.0, and 0.0 kcal/mol), respectively. Thus, we see that the Br atom *does* have much more SO coupling than the other stationary points. The SO correction for Br(^{2}P) of 1132 cm^{-1} obtained here is in good agreement with experiment (1228 cm^{-1}).[45] The near-zero values of the SO corrections for the entrance complex, TS, exit complex, and $(H_2O)_2OH$ indicate that the simplified treatment above is reasonable. A similar situation has also be noted by Czakó for the reaction $Br + CH_4 \rightarrow HBr + CH_3$.[47] After our theoretical ZPE and SO coupling corrections, the relative energies of the entrance complex, TS, exit complex, and products become -2.2, 27.6, 26.5, and 31.7 kcal/mol, respectively, at the CCSD(T)/cc-pVQZ(-PP)//CCSD(T)/cc-pVTZ(-PP) level of theory.

4. Conclusions

Using the “gold standard” CCSD(T) method, the lowest-energy pathway of the Br + $(H_2O)_3$ reaction has been fully investigated with Dunning correlation consistent basis sets up to cc-pVTZ(-PP) for geometry optimization and cc-pVQZ(-PP) for the energetics. At the CCSD(T)/cc-pVQZ(-PP)//CCSD(T)/cc-pVTZ(-PP) level of theory, the reaction is endothermic by 33.3 kcal/mol (Figure 1). The reaction barrier is predicted to be 29.0 kcal/mol, implying that there is no barrier for the reverse reaction. The relative energies for the entrance complex and the exit complex are predicted to be -4.7 and 26.9 kcal/mol, respectively. After the zero-point vibrational energy and spin-orbit coupling effect corrections, the final relative energies for entrance complex, TS, exit complex, and products become -2.2, 27.6, 26.5, and 31.7 kcal/mol, respectively.

Compared to the water dimer reaction Br + $(H_2O)_2$ and water monomer reaction Br + H_2O, the entrance complex, transition state and exit complex for the water trimer Br + $(H_2O)_3$ reaction are closely related. The trimer reaction structures may be derived by inserting a water molecule to the dimer reaction or appending a water dimer molecule to the monomer reaction.

The relative energies of the entrance complex, the transition state and the exit complex for the water trimer relation Br + $(H_2O)_3$ are all lower than those for the water monomer reaction Br + H_2O, but somewhat higher than those of the water dimer reaction Br + $(H_2O)_2$. Considering the reaction barrier, the second water molecule lowers the barrier by 3.8 kcal/mol with respect to the water monomer reaction, while the third water molecule changes the barrier by only 0.7 kcal/mol with respect to the water dimer reaction (Figure 2). Thus, it is expected that larger water cluster or even liquid water reactions may behave somewhat like that for the water trimer when they react with atomic bromine. Of course, much more research needs be done to confirm these expectations.

Compared to the analogous chlorine reaction Cl + $(H_2O)_3$ and fluorine reaction F + $(H_2O)_3$, the bromine reaction Br + $(H_2O)_3$ is qualitatively similar to the former, but much different from the latter, as the latter reaction is exothermic and has no barrier from the F + $(H_2O)_3$ side (Figure 3).

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Supporting Information

Three pathways of the water trimer reaction Br + *uud*-$(H_2O)_3$ → HBr + *ud*-$(H_2O)_2OH$ with the MPW1K/cc-pVTZ(-PP) method. Harmonic vibrational frequencies and zero-point energies for the stationary points of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction obtained at the CCSD(T)/cc-pVTZ(-PP) level of theory. Cartesian coordinates for optimized stationary points in different pathways of the Br + $(H_2O)_3$ → HBr + $(H_2O)_2OH$ reaction at various levels of theory. Complete Gaussian 16 reference.

References

1. A. G. S. de Oliveira-Filho, F. R. Ornellas and J. M. Bowman, *J. Phys. Chem. Lett.*, 2014, **5**, 706-712.
2. M. Zhang, Y. Guo, Y. Xie and H. F. Schaefer, *Theor. Chem. Acc.*, 2014, **133**, 1513.
3. I. R. Sims, I. W. M. Smith, D. C. Clary, P. Bocherel and B. R. Rowe, *J. Chem. Phys.*, 1994, **101**, 1748-1751.
4. D. C. Clary, G. Nyman and R. Hernandez, *J. Chem. Phys.*, 1994, **101**, 3704-3714.
5. B. Nizamov, D. W. Setser, H. Wang, G. H. Peslherbe and W. L. Hase, *J. Chem. Phys.*, 1996, **105**, 9897-9911.
6. D. B. Atkinson, V. I. Jaramillo and M. A. Smith, *J. Phys. Chem. A*, 1997, **101**, 3356-3359.
7. Y. Bedjianian, V. Riffault, G. Le Bras and G. Poulet, *J. Photochem. Photobiol. A: Chem.*, 1999, **128**, 15-25.
8. N. Rougeau, G. Nyman and C. Kubach, *Phys. Chem. Chem. Phys.*, 1999, **1**, 1191-1196.
9. J. Y. Liu, Z. S. Li, Z. W. Dai, X. R. Huang and C. C. Sun, *J. Phys. Chem. A*, 2001, **105**, 7707-7712.
10. V. I. Jaramillo, S. Gougeon, S. D. Le Picard, A. Canosa, M. A. Smith and B. R. Rowe, *Int. J. Chem. Kinet.*, 2002, **34**, 339-344.
11. D. C. Che, T. Matsuo, Y. Yano, L. Bonnet and T. Kasai, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1419-1423.
12. P. Y. Tsai, D. C. Che, M. Nakamura, K. C. Lin and T. Kasai, *Phys. Chem. Chem. Phys.*, 2011, **13**, 1419-1423.
13. S. P. Sander, R. R. Friedl, J. Abbatt, J. R. Barker, J. B. Burkholder, D. M. Golden, C. E. Kolb, M. J. Kurylo, G. K. Moortgat, P. H. Wine, R. E. Huie and V. L. Orkin, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Studies Evaluation Number 16* (NASA, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, 2009).
14. A. M. Holloway and R. P. Wayne, *Atmospheric Chemistry* (RSC Publishing, Cambridge, 2010).
15. D. R. Clark, R. F. Simmons and D. A. Smith, *Trans. Faraday Soc.*, 1970, **66,** 1423-1435.
16 G. Li, H. Wang, Q.-S. Li, Y. Xie and H. F. Schaefer, *J. Comput. Chem.*, 2016, **37**, 177-182.
17. G. Li, Q.-S. Li, Y. Xie and H. F. Schaefer, *Angew. Chem. Int. Ed.*, 2015, **54**, 11223-11226.
18. G. Li, Y. Yao, S. Lü, Y. Xie, G. E. Douberly and H. F. Schaefer, *Phys. Chem. Chem. Phys.*, 2021, **23**, 26837-26842.
19. B. J. Lynch, P. L. Fast, M. Harris and D. G. Truhlar, *J. Phys. Chem. A*, 2000, **104**, 4811-4815.
20. G. Li, L. Zhou, Q.-S. Li, Y. Xie and H. F. Schaefer, *Phys. Chem. Chem. Phys.*, 2012, **14**, 10891-10895.
21. T. H. Dunning, *J. Chem. Phys.*, 1989, **90**, 1007-1023.
22. R. A. Kendall, T. H. Dunning and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796-6806.
23. K. A. Peterson, D. Figgen, E. Goll, H. Stoll and M. Dolg, *J. Chem. Phys.*, 2003, **119**, 11113-11123.
24. H. P. Hratchian and H. B. Schlegel, *J. Chem. Phys.*, 2004, **120**, 9918-9924.
25. H. P. Hratchian and H. B. Schlegel, in *Theory and Applications of Computational Chemistry:*

The First 40 Years; C. E. Dykstra, G. Frenking, K. S. Kim, G. Scuseria, Elsevier: Amsterdam, The Netherlands, 2005.

26. H. P. Hratchian and H.B. Schlegel, *J. Chem. Theory Comput.*, 2005, **1**, 61-69.
27. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian 16, Revision B.01, Gaussian, Inc., Wallingford CT, **2016** (see Supporting Information for details).
28. G. D. Purvis and R. J. Bartlett, *J. Chem. Phys.*, 1982, **76,** 1910-1918.
29. G. E. Scuseria, C. L. Janssen and H. F. Schaefer, *J. Chem. Phys.*, 1988, **89**, 7382-7387.
30. K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys. Lett.*, 1989, **157**, 479-483.
31. CFOUR, a quantum chemical program package written by J. F. Stanton, J. Gauss, M. E. Harding and P. G. Szalay, with contributions from A. A. Auer, R. J. Bartlett, U. Benedikt, C. Berger, D. E. Bernholdt, Y. J. Bomble, L. Cheng, O. Christiansen, M. Heckert, O. Heun, C. Huber, T.-C. Jagau, D. Jonsson, J. Jusélius, K. Klein, W. J. Lauderdale, D. A. Matthews, T. Metzroth, D. P. O'Neill, D. R. Price, E. Prochnow, K. Ruud, F. Schiffmann, W. Schwalbach, S. Stopkowicz, A. Tajti, J. Vázquez, F. Wang and J. D. Watts; with the integral packages MOLECULE (J. Almlöf and P. R. Taylor), PROPS (P. R. Taylor), ABACUS (T. Helgaker, H. J. Aa. Jensen, P. Jorgensen and J. Olsen) and ECP routines by A. V. Mitin and C. van Wullen, 2010.
32. J. C. Howard and G. S. Tschumper, *WIREs Comput. Mol. Sci.*, 2014, **4**, 199-224.
33. E. Miliordos, E. Aprà and S. S. Xantheas, *J. Chem. Phys.*, 2013, **139**, 114302.
34. L. C. Ch'ng, A. K. Samanta, Y. Wang, J. M. Bowman and H. Reisler, *J. Phys. Chem. A*, 2013 **117**, 7207-7216.
35. Y. Wang, B. C. Shepler, B. J. Braams and J. M. Bowman, *J. Chem. Phys.*, 2009, **131**, 054511.
36. F. N. Keutsch, J. D. Cruzan and R. J. Saykally, *Chem. Rev.*, 2003, **103**, 2533-2578.
37 J. E. Fowler and H. F. Schaefer, *J. Am. Chem. Soc.*, 1995, **177**, 446-452.
38. N. Pugliano and R. J. Saykally, *Science*, 1992, **257**, 1937-1940.
39. B. C. Shepler, A. D. Wright, N. B. Balabanov and K. A. Peterson, *J. Phys. Chem. A*, 2007, **111**, 11342-11349.
40. C. J. Burnham, S. S. Xantheas, M. A. Miller, B. E. Applegate and R. E. Miller, *J. Chem. Phys.*, 2002, **117**, 1109-1122.
41. K. Tsuji and K. Shibuya, *J. Phys. Chem. A*, 2009, **113**, 9945-9951.
42. A. Moudens, R. Georges, M. Goubet, J. Makarewicz, S. E. Lokshtanov and A. A. Vigasin, *J. Chem. Phys.*, 2009, **131**, 204312.
43. K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold Company, New York, 1979).
44. B. Metz, H. Stoll and M. Dolg, *J. Chem. Phys.*, 2000, **113**, 2563-2569.
45. C.E. Moore, *Atomic energy levels, Volume II* (NSRDS-NBS 35, Washington, DC, 1971).
46. H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby and M. Schütz *et al.*, MOLPRO, version 2010.1, a package of *ab initio* programs, see http://www.molpro.net.
47. G. Czakó, *J. Chem. Phys.*, 2013, **138**, 134301-134305.