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Potential Energy Profile for the Cl + (H₂O)₃ → HCl + (H₂O)₂OH Reaction. A CCSD(T) Study

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Abstract

Four different reaction pathways are initially located for the reaction of Cl atom plus water trimer Cl + (H₂O)₃ → HCl + (H₂O)₂OH using a standard DFT method. As found for the analogous fluorine reaction, the geometrical and energetic results for the four chlorine pathways are closely related. However, the energetics for the Cl reaction are very different from those for fluorine. In the present paper, we investigate the lowest-energy chlorine pathway using the "gold standard" CCSD(T) method in conjunction with correlation-consistent basis sets up to cc-pVQZ. Structurally, the stationary points for the water trimer reaction Cl + (H₂O)₃ may be compared to those for the water monomer reaction Cl + H₂O and water dimer reaction Cl + (H₂O)₂. Based on the CCSD(T) energies, the title reaction is endothermic by 19.3 kcal/mol, with a classical barrier height of 16.7 kcal/mol between the reactants and the exit complex. There is no barrier for the reverse reaction. The Cl···(H₂O)₃ entrance complex lies 5.3 kcal/mol below the separated reactants. The HCl···(H₂O)₂OH exit complex is bound by 8.6 kcal/mol relative to the separated products. The Cl + (H₂O)₃ reaction is somewhat similar to the analogous Cl + (H₂O)₂ reaction, but qualitatively different from the Cl + H₂O reaction. It is reasonable to expect that the reactions between the chlorine atom and larger water clusters may be similar to the Cl + (H₂O)₃ reaction. The potential energy profile for the Cl + (H₂O)₃ reaction is radically different from that for the valence isoelectronic F + (H₂O)₃ system, which is related to the different bond energies between HCl and HF.

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

1. Introduction

Water is ubiquitous on earth and studies of water-containing reactions are very important to environmental chemistry, surface chemistry, catalytic reactions, and biological processes.[1-3]   The chlorine atom plus water reaction is of fundamental importance to atmospheric chemistry, because chlorine atoms produced by the ultraviolet photolysis of chlorine gas in the atmosphere readily react with a wide array of hydrogen-containing compounds, forming the relatively stable HCl molecule.[4,5] The water monomer reaction $Cl + H_2O$ has been the topic of various experimental[6-9] and theoretical studies.[10-18]   To understand trends in energetics ranging from the water monomer to water polymers, we also studied the water dimer reaction $Cl + (H_2O)_2 \rightarrow HCl + (H_2O)OH$.[19]   It was found that the second water molecule can lower all the other stationary points relative to separated $Cl + H_2O$.   What is the effect of more water molecules?   The purpose of this research is to address the reaction of the chlorine atom with the water trimer: $Cl + (H_2O)_3 \rightarrow HCl + (H_2O)_2OH$.

2. Methodology

The computational methods used in the present paper are similar to those successfully used for the reactions of chlorine atom plus water dimer[19] and fluorine atom plus water dimer/trimer/tetramer.[20-22]   Thus, the stationary points for the $Cl + (H_2O)_3 \rightarrow HCl + (H_2O)_2OH$ reaction were first investigated with a tested density functional theory (DFT) method using the Gaussian 16 program (Revision B.01).[23] The MPW1K functional developed by Truhlar et al.[24] was employed to begin, for it predicted the best barrier for the $F + H_2O$ reaction among a set of 49 DFT functionals.[25] In conjunction with the MPW1K method, the correlation-consistent polarized valence triple zeta basis set (cc-pVTZ) of Dunning, Kendall, Harrison, Woon, and Peterson

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was used.[26,27]   All the stationary points were fully optimized with the MPW1K/cc-pVTZ method and characterized by harmonic vibrational frequency analyses at the same level of theory.   The transition states were confirmed to connect designated entrance and exit complexes with intrinsic reaction coordinate (IRC) analyses.[28-30]

To derive more reliable geometries, energies and vibrational frequencies, the geometry optimizations and frequency analyses were further performed with higher level coupled-cluster single and double excitation method with perturbative treatment of triple excitations CCSD(T)[31-33] using the CFOUR program.[34]   In conjunction with the CCSD(T) method, the correlation-consistent polarized valence basis sets[26,27] were used for geometry optimizations and frequency analyses up to cc-pVTZ and for single-point energy computations up to cc-pVQZ.

3. Results and Discussion

It has been reported[35-41] that the water trimer $(H_2O)_3$ has two almost isoenergetic low-energy isomers, i.e. *uud*-$(H_2O)_3$ and *uuu*-$(H_2O)_3$, as shown in Figure 1.   Both the *uud*-$(H_2O)_3$ and *uuu*-$(H_2O)_3$ isomers have six-membered ring structures with the rings formed from three OH bonds connected by three hydrogen bonds and each water molecule functioning as both electron donor and acceptor.   The three out-of-ring OH
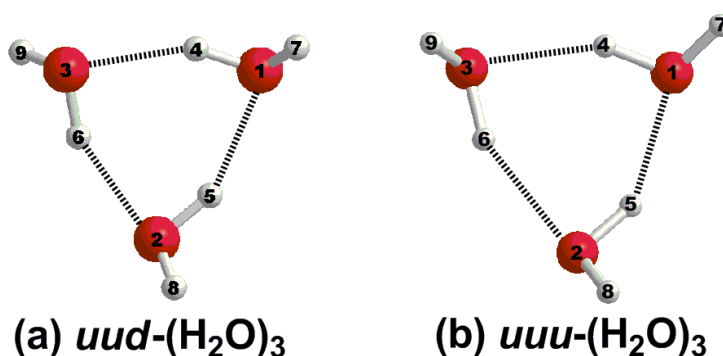

(a) *uud*-(H₂O)₃   **(b) *uuu*-(H₂O)₃**

Figure 1. Two dominant isomers of the $(H_2O)_3$ cluster.

bonds of $(H_2O)_3$ are in the "up-up-down" (*uud*) or "up-up-up" (*uuu*) orientations, respectively, relative to the pseudo-planar six-membered ring. CCSD(T)/cc-pVQZ computations predicted that the *uud*-$(H_2O)_3$ structure is the global minimum and the *uuu*-$(H_2O)_3$ structure lies higher by only 1.0 kcal/mol.

When an electron-withdrawing Cl atom reacts with each isomer of the water trimer $(H_2O)_3$, there are four different kinds of active sites. Three of these are from the three out-of-ring H atoms in *uud*-$(H_2O)_3$, and one from any of the equivalent out-of-ring H atoms in *uuu*-$(H_2O)_3$. This leads to four different kinds of Cl + $(H_2O)_3$ reaction pathways, analogous to the F + $(H_2O)_3$ reaction.[21] As shown in Figure S1 in the supporting information, the four Cl + $(H_2O)_3$ pathways predicted by the MPW1K/cc-pVTZ method are closely related, both geometrically and energetically. In the present research, with the more reliable CCSD(T) method along with basis sets as large as cc-pVQZ, the lowest-energy Cl + $(H_2O)_3$ reaction pathway is investigated. The latter results are reported in Figure 2. In the following discussions, the CCSD(T)/cc-pVTZ geometries and the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ energies are considered, unless otherwise indicated.

As shown in Figure 2, the entrance complex Cl$\cdots$$(H_2O)_3$ of the Cl + $(H_2O)_3$ reaction has the Cl atom bound to one water molecule with other two water molecules loosely attached. Compared with the separated Cl and *uud*-$(H_2O)_3$ reactants, the Cl$\cdots$$(H_2O)_3$ entrance complex lies 5.3 kcal/mol below. In the transition state (TS), the distance between the Cl atom and one of the H atoms being abstracted, i.e., that of Cl-H7, is decreased to 1.469 Å, much shorter than 2.667 Å in the Cl$\cdots$$(H_2O)_3$ entrance complex, forming an eight-membered ring structure. The TS structure has been verified to be the first-order saddle point on the $Cl(H_2O)_3$ potential energy surface (PES) for it has only one imaginary vibrational frequency ($1217i$ cm^{-1}). The energy

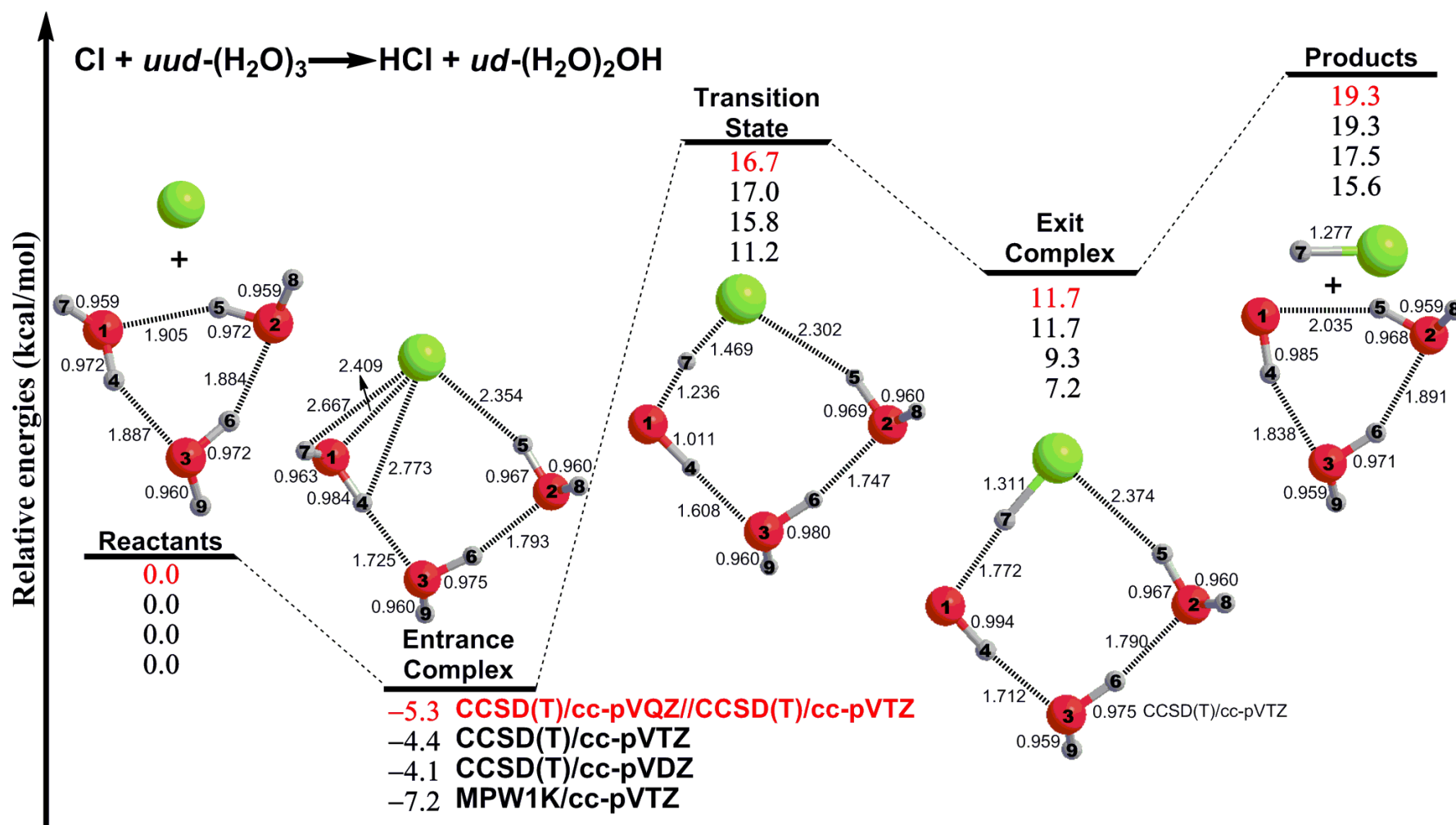**Figure 2.** Stationary points along the Cl + (H₂O)₃ potential energy profile. The bond distances and relative energies are given in angstroms and kcal/mol, respectively.

of the TS is 16.7 kcal/mol above the separated Cl + uud-$(H_2O)_3$ reactants, giving a barrier of 22.0 [16.7 − (-5.3)] kcal/mol, based on the energy difference between the entrance complex and the TS.   The exit complex ud-HCl···$(H_2O)_2$OH has its two out-of-plane OH moieties in "up-down" orientations, relative to the pseudo eight-membered ring plane.   The covalently bound Cl-H distance in the ud-HCl···$(H_2O)_2$OH complex is 1.311 Å, just a bit longer than the 1.277 Å for the free HCl molecule.   The longer Cl···H distance in ud-HCl···$(H_2O)_2$OH is 2.374 Å, which may be considered as a weaker Cl···H hydrogen bond.   The ud-HCl···$(H_2O)_2$OH complex is 7.6 kcal/mol energetically lower than the separated HCl + $(H_2O)_2$OH products, but 11.7 kcal/mol higher than the separated Cl + uud-$(H_2O)_3$ reactants. Removing the HCl moiety from ud-HCl···$(H_2O)_2$OH gives the radical reaction product ud-$(H_2O)_2$OH, with its two out-of-plane OH bonds in the "up-down" orientations relative to the six-membered ring.   Energetically, the products HCl + ud-$(H_2O)_2$OH lie 19.3 kcal/mol above the separated Cl + uud-$(H_2O)_3$ reactants, indicating that the Cl + $(H_2O)_3 \rightarrow$ HCl + $(H_2O)_2$OH reaction is significantly endothermic.

Table 1 shows the harmonic vibrational frequencies and zero-point vibrational energies (ZPVEs) for all the stationary points of the Cl + $(H_2O)_3$ reaction at the CCSD(T)/cc-pVTZ level of theory.   For the water trimer, our H-bonded OH stretching frequencies of 3613~3689 cm^{-1} are in reasonable agreement with available experimental results of 3533 (in gas phase), 3544/3529 (in liquid He),[42] 3528 (in solid Ne),[43] 3531.8±1.2, and 3516.7±2.3 cm^{-1}.[44]   Our free OH stretching frequencies of 3903~3909 cm^{-1} may be compared with the experimental values of 3726 (in gas phase) and 3717 cm^{-1} (in liquid He).[42]   Our OH radical stretching frequency of 3498 cm^{-1} for $(H_2O)_2$OH is in reasonable agreement with available experimental value of 3365.2 cm^{-1} in a solid Ne matrix.[43]   Remarkable agreement occurs between our theoretical

H-Cl stretching frequency of 3000 cm^{-1} and the experimental harmonic value of 2990.9 cm^{-1}.[45,46]   The transition state is predicted to have an imaginary vibrational frequency of 1217i cm^{-1}, while its normal mode reveals simultaneous Cl-H7 bond formation and O2-H7 bond breaking proceeding toward the Cl + $(H_2O)_3$ → HCl + $(H_2O)_2OH$ reaction.   With the ZPVE shown in Table 1, the relative energies of the entrance complex, TS, exit complex and products for the forward Cl + $(H_2O)_3$ → HCl + $(H_2O)_2OH$ reaction are further corrected to be -4.8, 12.6, 8.9, and 15.0 kcal/mol, respectively.

Table 1. Harmonic vibrational frequencies (in cm^{-1}) and zero-point vibrational energies (ZPVE, in kcal/mol) for the stationary points of the Cl + $(H_2O)_3$ → HCl + $OH_2 \cdot (H_2O)$ reaction obtained at the CCSD(T)/cc-pVTZ level of theory.   Experimental results are also noted for comparison.

	ZPVE	Vibrational Frequencies
$(H_2O)_3$	46.46	188, 194, 202, 209, 228, 253, 360, 372, 471, 614, 689, 926, 1685, 1690, 1707, 3613, 3683, 3689, 3903, 3907, 3909
Entrance Complex	46.93	30, 72, 137, 205, 214, 250, 266, 274, 288, 403, 432, 480, 545, 791, 967, 1675, 1683, 1703, 3407, 3601, 3750, 3855, 3898, 3902
Transition State	42.34	1217i, 36, 91, 149, 224, 239, 298, 309, 329, 459, 492, 568, 757, 840, 941, 1138, 1340, 1674, 1702, 3002, 3517, 3717, 3896, 3900
Exit Complex	43.69	32, 63, 132, 177, 194, 234, 267, 281, 292, 412, 494, 508, 619, 651, 793, 974, 1675, 1699, 2554, 3347, 3596, 3762, 3902, 3905
$(H_2O)_2OH$	37.85	163, 196, 211, 230, 252, 291, 375, 534, 557, 668, 916, 1667, 1687, 3498, 3675, 3737, 3908, 3911
HCl	4.29	3000
Experiment		
Bonded OH in $(H_2O)_3$		3533,[a] 3544/3529,[a] 3528,[b] 3531.8±1.2,[c] 3516.7±2.3[c]
Free OH in $(H_2O)_3$		3726,[a] 3717[a]
OH radical in $(H_2O)_2OH$		3365.2[b]
HCl	4.28	2990.9[d]

[a] In gas phase and liquid He from Ref. 42.   [b] In solid Ne from Ref. 43.   [c] From Ref. 44.
[d] From Ref. 45 and 46.

The spin-orbit (SO) effect emerging for atomic Cl was also considered.   The experimental spin-orbit (SO) splitting between the ground $^2P_{3/2}$ state (fourfold) and the excited $^2P_{1/2}$ states (twofold) of the Cl atom is known as 882 cm^{-1}.[47]   Thus, the

SO ground state lies below the spin-averaged (non-SO) energy by 882/3 = 294 cm^{-1} (0.8 kcal/mol). For the Cl + (H$_2$O)$_3$ potential energy surface, the SO coupling can be simplified only for the reactants Cl + (H$_2$O)$_3$, by assuming that SO coupling is quenched for the entrance complex, transition state, exit complex, and products. With this consideration, the relative energies of the entrance complex, TS, exit complex and products for the forward Cl + (H$_2$O)$_3$ → HCl + (H$_2$O)$_2$OH reaction all raise by 0.8 kcal/mol, respectively. We also adopt a more rigorous theoretical treatment using the Breit-Pauli operator to provide SO coupling corrections,[48] with the CASSCF/cc-pVQZ method. Our theoretical SO corrections for the reactant (Cl atom), the entrance complex, the transition state, the exit complex, and the product [(H$_2$O)$_2$OH] are predicted to be 265, 16, 1, 2, and 4 cm^{-1} (i.e., 0.8, 0.0, 0.0, 0.0, and 0.1 kcal/mol), respectively. Our SO coupling correction for Cl(^{2}P) of 265 cm^{-1} is in reasonable agreement with experiment (294 cm^{-1}). The SO corrections with this theoretical treatment are same as those with simple treatment above.

It is interesting that the DFT-MPW1K method, though much more restricted theoretically, predicts a plausible potential energy profile compared to the CCSD(T)/cc-pVQZ method, as shown in Figure 2. The DFT-MPW1K/cc-pVTZ barrier is 11.2 kcal/mol, 5.5 kcal/mol lower than the CCSD(T)/cc-pVQZ prediction (16.7 kcal/mol). The DFT-MPW1K endothermicity of 15.6 kcal/mol is about 3.7 kcal/mol below the CCSD(T)/cc-pVQZ prediction (19.3 kcal/mol). The DFT-MPW1K entrance complex is about 1.9 kcal/mol more strongly bound, and the exit complex is about 0.8 kcal/mol more strongly bound, compared with the CCSD(T)/cc-pVQZ results. Thus, the DFT-MPW1K method may be a reasonable method for the initial study of larger water-containing systems. Various DFT optimizations followed by CCSD(T)/cc-pVQZ single point energy computations for the Cl + (H$_2$O)$_n$ (n=1-3)

reactions have been reported by Sugiura, Tachikawa and Udagawa. [49]

Next, it is helpful to further compare the water trimer reaction $Cl + (H_2O)_3$ (Figure 2) with the water dimer reaction $Cl + (H_2O)_2$ (the reverse reaction in Figure 1 of Ref. 19) and the water monomer reaction $Cl + H_2O$ (Figure 1 in Ref. 16). Structurally, the entrance complex for the water trimer geometry $Cl\cdots(H_2O)_3$ is closely related to the water dimer complex $Cl\cdots(H_2O)_2$ and the water monomer complex $Cl\cdots H_2O$. The former can be derived from the water dimer complex by appending a third water molecule or from the water monomer complex by attaching two more water molecules. Similarly, the transition state and exit complex for the water trimer reaction $Cl + (H_2O)_3$ also have something in common with those for the water dimer reaction $Cl + (H_2O)_2$ and the water monomer reaction $Cl + H_2O$. The third water molecule in the water trimer TS/exit complex is loosely connected to the water dimer TS/exit complex, just as the second water molecule in the dimer TS/exit complex (the reverse reaction in Figure 1 of Ref. 19) is loosely connected to the monomer TS/exit complex. Energetically, the water trimer complex $Cl\cdots(H_2O)_3$ is bound by 5.3 kcal/mol, somewhat weaker than the binding energy of 6.8 kcal/mol for the water dimer complex $Cl\cdots(H_2O)_2$ but stronger than that of 3.5 kcal/mol for the water monomer complex $Cl\cdots H_2O$, as shown in Figure 3. As for the transition state, the relative energy of 16.7 kcal/mol for the water trimer reaction $Cl + (H_2O)_3$ is very similar to that of 16.5 kcal/mol for the water dimer reaction $Cl + (H_2O)_2$ but much lower than that of 20.8 kcal/mol for the water monomer reaction $Cl + H_2O$. A similar situation occurs for the exit complexes. Thus, the water trimer reaction $Cl + (H_2O)_3$ looks more similar to the water dimer reaction $Cl + (H_2O)_2$ than to the water monomer reaction $Cl + H_2O$.
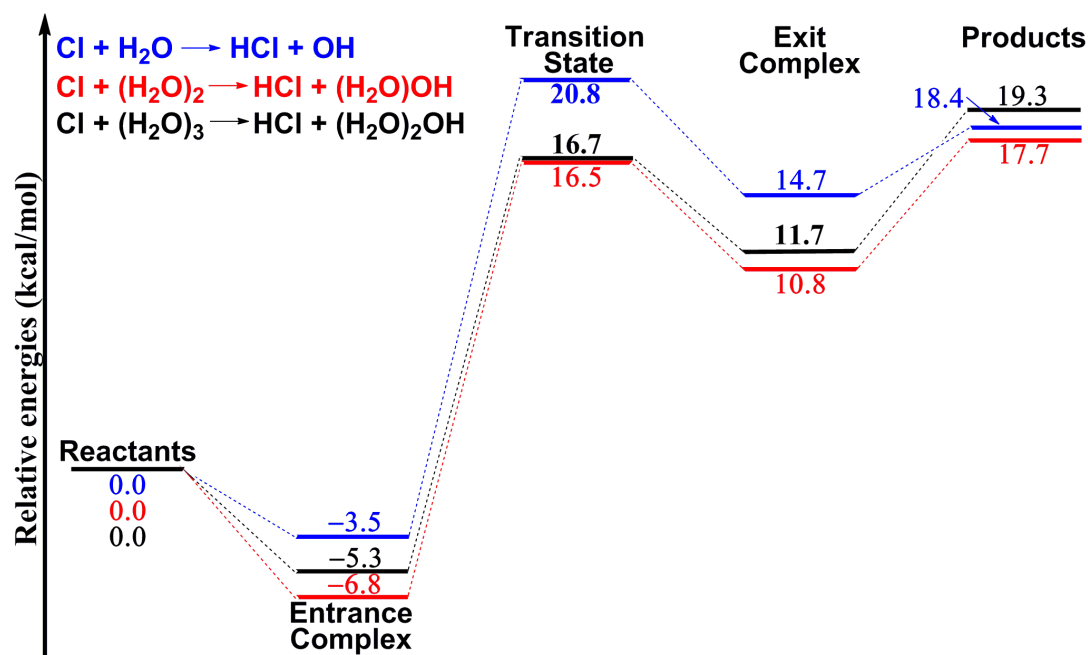
Figure 3. Comparison of the potential energy profiles for the $Cl + (H_2O)_3$, $Cl + (H_2O)_2$ and $Cl + H_2O$ reactions. All relative energies (in kcal/mol) are based on CCSD(T)/cc-pVQZ computations.

It is also instructive to compare the chlorine reaction $Cl + (H_2O)_3$ potential energy surface with that for the fluorine reaction $F + (H_2O)_3$.[21] Structurally, all the stationary points for the chlorine reaction $Cl + (H_2O)_3$ (Figure 2) can be compared to those for the fluorine reaction $F + (H_2O)_3$ (see Figure 1 in Ref. 21). However, the two potential energy surfaces are much different. As shown in Figure 4, although the entrance well for chlorine complex $Cl\cdots(H_2O)_3$, lying below the reactants by 5.3 kcal/mol, is somewhat similar to the analogous 7.1 kcal/mol for the fluorine complex $F\cdots(H_2O)_3$, the relative energies of the other stationary points for the chlorine reaction $Cl + (H_2O)_3$ and the fluorine reaction $F + (H_2O)_3$ are fundamentally different. For the $Cl + (H_2O)_3$ reaction, the transition state, exit complex, and products all lie *above* the reactants by more than 11 kcal/mol. In contrast, for the $F + (H_2O)_3$ reaction, the transition state, exit complex, and products all lie *below* the reactants by at least 4 kcal/mol. These substantial energy differences may be attributed at least in part to the fact that the bond energy of HCl is much less than that for HF.

For both Cl + (H$_2$O)$_3$ and F + (H$_2$O)$_3$ reactions, the transition states geometrically resemble their exit complexes (see Figure 2 in this work and Figure 1 in Ref. 21). For the Cl + (H$_2$O)$_3$ reaction, the transition state is also energetically similar to the exit complex (Figure 4), which can be explained by Hammond's postulate.[50] However, exceptions of Hammond's postulate are known.[51]   For the F + (H$_2$O)$_3$ reaction, the transition state is energetically similar to the entrance complex, which may also be attributed to the large bond energy of HF.
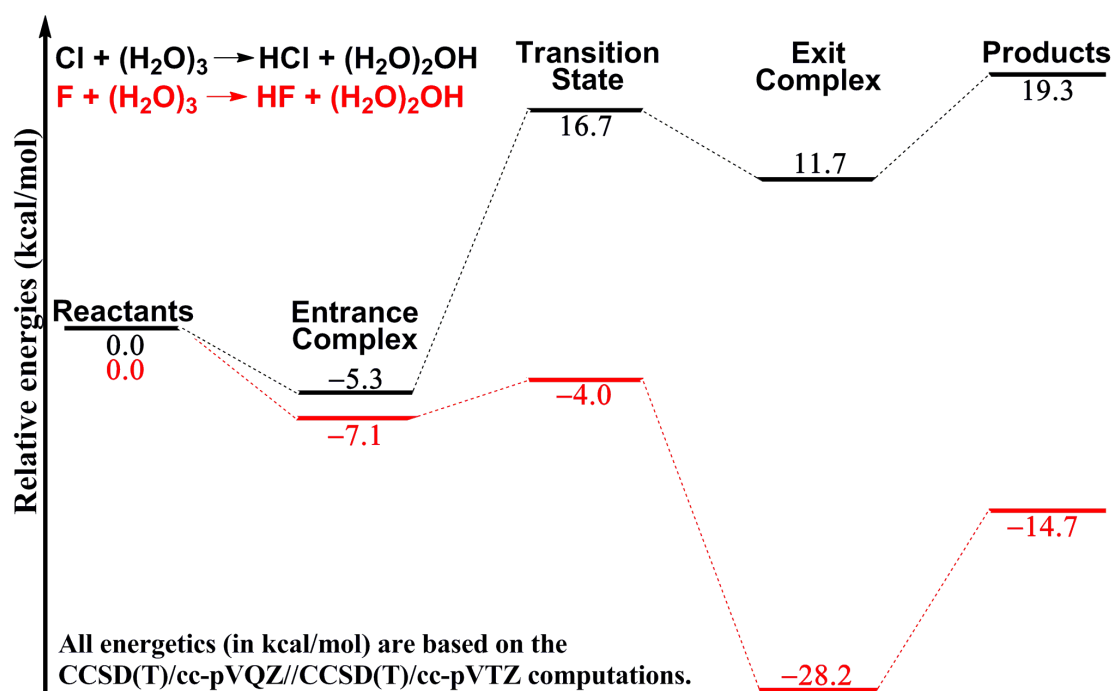

Figure 4. Comparison of the potential energy profiles for the Cl + (H$_2$O)$_3$ (black) and F + (H$_2$O)$_3$ (red) reactions.

4. Conclusions

The stationary points for the lowest-energy pathway of the Cl + (H$_2$O)$_3$ reaction have been fully optimized with the "Gold Standard" CCSD(T) method with Dunning correlation consistent basis sets up to cc-pVTZ.   Single point energies were determined with the CCSD(T)/cc-pVQZ method.   The energy barrier for this reaction is predicted to be 16.7 kcal/mol at the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ level of

theory, while the products lie above the reactants by 19.3 kcal/mol. The relative energies for the entrance complex and the exit complex are predicted to be -5.3 and 11.7 kcal/mol, respectively.

The Cl + $(H_2O)_3$ reaction has been compared with the Cl + $(H_2O)_2$ and the Cl + H_2O reactions. The entrance complex, transition state and exit complex for the Cl + $(H_2O)_3$ reaction are closely related to their corresponding dimer and monomer counterparts. The trimer structures can be derived by attaching one or two more water molecules to the dimer and monomer ones. The relative energies of the entrance complex, transition state and exit complex for the Cl + $(H_2O)_3$ reaction are all lower than those for the Cl + H_2O reaction, but slightly higher than those of the Cl + $(H_2O)_2$ reaction. That is, from the water monomer to dimer, the second water molecule lower the energy barrier by 4.1 kcal/mol. From the water dimer to trimer, the third water molecule changes the energy barrier by only 0.2 kcal/mol. Thus, we suggest that when liquid water reacts with atomic chlorine, its behavior may be somewhat like that for the water trimer. However, more research should be done to confirm this suggestion.

The chlorine reaction Cl + $(H_2O)_3$ has also been compared with the analogous fluorine reaction F + $(H_2O)_3$, and significant energetic differences are discussed.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Supporting Information

Four pathways of the water trimer reaction $Cl + (H_2O)_3 \rightarrow HCl + (H_2O)_2OH$ with the MPW1K/cc-pVTZ method.   Complete Gaussian 16 reference.

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