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From Gas-Phase to Liquid-Water Chemical Reactions: The Fluorine Atom Plus Water Trimer System

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Abstract: *The potential energy profile for the $F+(H_2O)_3\rightarrow HF+(H_2O)_2OH$ reaction has been investigated using the "gold standard" CCSD(T) method with correlation-consistent basis sets up to cc-pVQZ. Four different reaction pathways have been found and these are related, both geometrically and energetically. The entrance complexes $F\cdots(H_2O)_3$ for all four reaction pathways are found lying ca. 7 kcal mol^{-1} below the separated reactants $F+(H_2O)_3$. The four reaction barriers on their respective reaction coordinates lie ca. 4 kcal mol^{-1} below the reactants. There are also corresponding exit complexes $HF\cdots(H_2O)_2OH$, lying about 13 kcal mol^{-1} below the separated products $HF+(H_2O)_2OH$. Compared with analogous $F+(H_2O)_2$ and $F+H_2O$ reactions, the $F+(H_2O)_3$ reaction is somewhat similar to the former but qualitatively different from the latter. It may be reasonable to predict that the reactions between atomic fluorine and water tetramer (or even larger water clusters) may be similar to the $F+(H_2O)_3$ reaction.*

For nearly 50 years the $F+H_2$ reaction has served as one of the pillars of modern chemical reaction dynamics. With the exception of the $H+H_2$ reaction, $F+H_2$ may reasonably be considered the best-understood of all chemical reactions.[1] There are indications that the $F+H_2O$ reaction may become a similar central feature of chemical kinetics.[2] Research toward the understanding of the $F+(H_2O)_2$ reaction[3] continues this quest.

An important theme of modern chemical physics is the progression from discrete gas-phase water species (monomer, dimer, trimer, etc.)[4] to water vapor to liquid water. In this context we present theoretical results for the reaction between the fluorine atom and the water trimer. As the water trimer possesses nine more degrees of freedom than the water dimer, the $F+(H_2O)_3$ potential energy surface (PES) is necessarily far more complicated. Important questions include the degree to which the $F+(H_2O)_3$ reaction may be anticipated from $F+H_2O$ and $F+(H_2O)_2$, and what this may tell us concerning the reactions involving $(H_2O)_4$ and larger water clusters.

In present research, all stationary points on the $F+(H_2O)_3$ reaction were fully optimized and characterized by harmonic vibrational frequency analyses using first the MPW1K method and then the CCSD(T) method. MPW1K is a density functional theory (DFT) method proposed by Truhlar et al.,[5] and it has been shown to give the best predictions among 49 DFT functionals used for the related $F+H_2O$ reaction barrier.[2b] CCSD(T) denotes the coupled-cluster single and double substitution method with a perturbative treatment of triple excitations.[6] Intrinsic reaction coordinate (IRC)[7] analyses were performed at the MPW1K level to confirm that the transition state connects the designated entrance and exit complexes. The basis sets used were Dunning's correlation-consistent polarized valence sets cc-pVnZ (n = D, T, Q).[8] All the MPW1K computations were carried out using the Gaussian 09 program suite,[9] and all the CCSD(T) computations were achieved with the CFOUR program.[10] The highest-level results, that is, the CCSD(T)/cc-pVTZ geometries and the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ energetics, for the $F+(H_2O)_3$ stationary points are reported in Figure 1 and discussed hereafter.

It is well known[11] that the water trimer $(H_2O)_3$ global minimum, denoted *uud*-$(H_2O)_3$, has a cyclic structure with each water molecule functioning as both electron donor and acceptor. The six-membered ring is formed with three OH bonds connected by three hydrogen bonds. The other three OH bonds are in the "up-up-down" (*uud*) orientations, with respect to the pseudoplanar six-membered ring (reactants in Figure 1 a, b, and c). A somewhat higher energy $(H_2O)_3$ local minimum *uuu*-$(H_2O)_3$ is a conformer of *uud*-$(H_2O)_3$ with the three out-of-plane OH bonds in "up-up-up" orientations (reactant in Figure 1 d). The energy difference between the two $(H_2O)_3$ conformers is predicted to be only 1.0 kcal mol^{-1}.

With a F atom approaching $(H_2O)_3$ from different positions, we find four $F\cdots(H_2O)_3$ complexes: three from $F+$ *uud*-$(H_2O)_3$ (entrance complexes in Figure 1 a, b, and c) and one from $F+$ *uuu*-$(H_2O)_3$ (entrance complex in Figure 1 d). The four $F\cdots(H_2O)_3$ complexes are related, each having the F atom bound to one water molecule with other two water molecules loosely attached. The four structures differ only by the orientations of the three out-of-plane OH moieties. These four $F\cdots(H_2O)_3$ complexes are predicted to lie 6.1–7.1 kcal mol^{-1} below the separated F and *uud*-$(H_2O)_3$ reactants.

Following the four $F\cdots(H_2O)_3$ entrance complexes, four transition states (TS) were found (Figure 1). In these transition states, the distances between the F atom and the H atom being abstracted, i.e., F–H7 in path (a), F–H8 in path (b), F–

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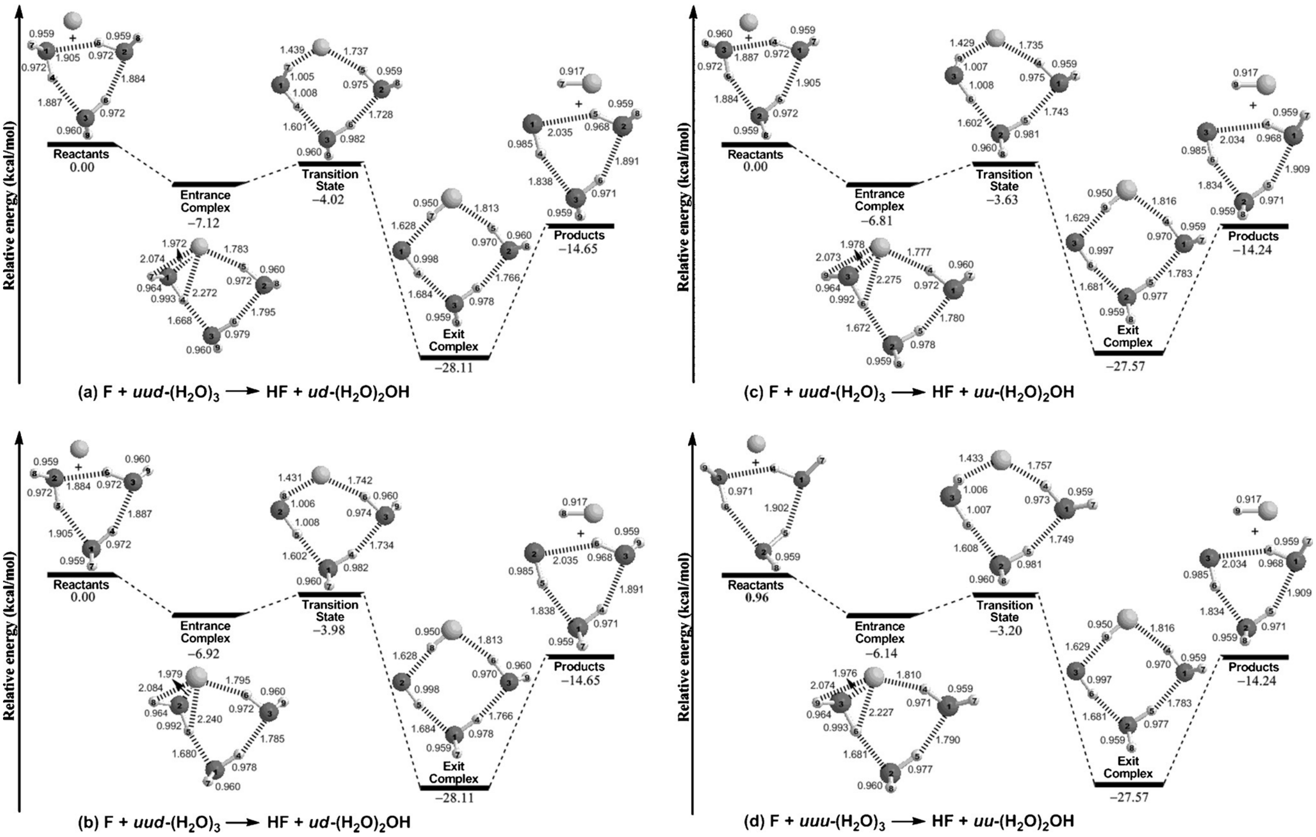

Figure 1. Four pathways of the water trimer reaction $F + (H_2O)_3 \rightarrow HF + (H_2O)_2OH$. The geometries of all stationary points were fully optimized at the CCSD(T)/cc-pVTZ level of theory whereas the energies are obtained by the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ method. Internuclear separations were given in Ångstroms. All energies are relative to separated F + *uud*-$(H_2O)_3$.

H9 in path (c), and F–H9 in path (d), are decreased to about 1.43 Å, which is much shorter than the 2.08 Å found for the entrance complexes, forming eight-membered ring structures. These TS structures were verified to be the first-order saddle points on the PES, as they all have one imaginary vibrational frequency. The relative energies of the transition states are 3.2–4.0 kcal mol^{-1} below the separated F and *uud*-$(H_2O)_3$ reactants. Based on the energy difference between the entrance complexes and the TSs, the reaction-potential barrier heights predicted are ca. 3 kcal mol^{-1} (Figure 1).

When the F atoms more closely approach the abstracting H atoms, the exit complexes $HF\cdots(H_2O)_2OH$ are formed (Figure 1). Generally speaking, there are two kinds of $HF\cdots(H_2O)_2OH$ complexes: a) the *ud*-$HF\cdots(H_2O)_2OH$ structure (Figure 1 a and b) with its two out-of-plane OH moieties in the "up-down" orientations, relative to the pseudo eight-membered ring plane; b) the *uu*-$HF\cdots(H_2O)_2OH$ structure (Figure 1 c and d) with its two out-of-plane OH moieties in the "up-up" orientations. The chemically bound F–H distances in these $HF\cdots(H_2O)_2OH$ exit complexes are ca. 0.950 Å, which is a bit more than the 0.917 Å for the free HF molecule, whereas the F···H distances are ca. 1.815 Å, close to the typical F···H hydrogen bonding distance. The $HF\cdots(H_2O)_2OH$ exit complexes are about 13 kcal mol^{-1} energetically lower than the products $HF + (H_2O)_2OH$, and about 28 kcal mol^{-1} lower than the separated F and *uud*-$(H_2O)_3$ reactants.

The departure of the HF moiety from the $HF\cdots(H_2O)_2OH$ complex leads to the formation of the reaction products HF and $(H_2O)_2OH$. Analogous to $(H_2O)_3$, there are two types of $(H_2O)_2OH$ radical conformers. The *ud*-$(H_2O)_2OH$ structure (Figure 1 a and b) has its two out-of-plane OH bonds in the "up-down" orientation relative to the six-membered ring, whereas the *uu*-$(H_2O)_2OH$ structure (Figure 1 c and d) has its two out-of-plane OH bonds in the "up-up" orientation. The energy difference between these two $(H_2O)_2OH$ conformers is only 0.4 kcal mol^{-1}, with the *ud*-$(H_2O)_2OH$ structure lower in energy. The products HF + *ud*-$(H_2O)_2OH$ and HF + *uu*-$(H_2O)_2OH$ are predicted to lie 14.7 and 14.2 kcal mol^{-1}, respectively, below the separated F + *uud*-$(H_2O)_3$ reactants. Therefore, the reaction $F + (H_2O)_3 \rightarrow HF + (H_2O)_2OH$ is significantly exothermic, due to the large dissociation energy of diatomic HF.

The comparison of the water trimer reaction $F + (H_2O)_3$ (Figure 1) with the water dimer reaction $F + (H_2O)_2$ (Ref. [3]) and the water monomer reaction $F + H_2O$ (Ref. [2b,3]) is particularly instructive. The entrance complexes for the water monomer $F\cdots H_2O$, dimer $F\cdots(H_2O)_2$, and trimer $F\cdots(H_2O)_3$ are structurally related. In fact the water trimer complexes look very much like the water dimer complex attached to a third water molecule, or the water monomer complex interacting with two water molecules. The trimer complex $F\cdots(H_2O)_3$ is predicted to be bound by ca. 7 kcal mol^{-1}, very similar to the

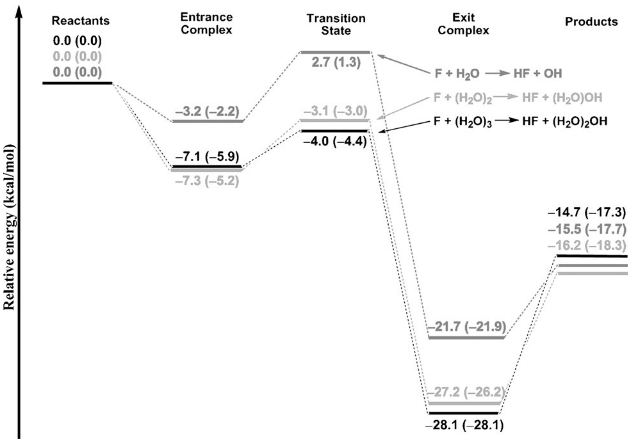

Figure 2. Comparison of the potential energy profiles for the $F + H_2O$, $F + (H_2O)_2$, and $F + (H_2O)_3$ reactions. Only the lowest (of four) energy channel of the $F + (H_2O)_3$ reaction is presented here. The CCSD(T)/cc-pVQZ energetics are used for the $F + H_2O$ and $F + (H_2O)_2$ reactions, whereas the CCSD(T)/cc-pVQZ//CCSD(T)/cc-pVTZ energetics are used for the $F + (H_2O)_3$ reaction. The energies with zero-point vibrational energy corrections are given in parentheses.

binding energy of 7.3 kcal mol^{-1} for the analogous dimer entrance complex F···(H$_2$O)$_2$ but much stronger than that of 3.2 kcal mol^{-1} for the monomer complex F···H$_2$O (Figure 2). Thus it is seen that the second water increases the F···H$_2$O binding energy by ca. 4 kcal mol^{-1} whereas the third water adds little to the F···(H$_2$O)$_2$ dissociation energy. Clearly, the interaction energy for the F···(H$_2$O)$_3$ complex differs from the sum of those of F···H$_2$O and F···(H$_2$O)$_2$. Consistent with the energetics, the F···H and F···O distances in the trimer entrance complex are similar to those for the dimer complex but clearly shorter than those for the monomer complex. For example, with the CCSD(T)/cc-pVTZ method, the F···H distance for the monomer complex is 2.330 Å, whereas the analogous F···H4 and F···H5 distances for the dimer complex are 2.170 Å and 2.176 Å, respectively, and those for the trimer complex are about 2.08 and 2.25 Å. Similarly, the F···O distance for the monomer entrance complex (2.214 Å) is much longer than that for the dimer complex (2.030 Å) and that for the trimer complex (≈1.97 Å). Thus, we have a consistent picture of the F atom being more strongly bound to the water trimer or water dimer than to the water monomer, although the interaction energy between F and (H$_2$O)$_3$ is similar to that between F and (H$_2$O)$_2$.

For the $F + (H_2O)_n$ transition states, the most interesting conclusion is that the second water molecule removes the barrier, like a catalyst, from the monomer $F + H_2O \rightarrow HF + OH$ reaction, lowering the barrier by 5.8 kcal mol^{-1}, whereas the third water molecule further lowers the barrier by only approximately 1 kcal mol^{-1} (Figure 2). Structurally, the transition states for the trimer reactions and those for the dimer and monomer reactions have something in common. As in the dimer TS (Ref. [3]) the second water molecule is loosely connected to the monomer TS, whereas in the trimer TS the third water molecule is loosely connected to the dimer TS. However, unlike the entrance complexes, the distances between the F atom and the H atom being abstracted (≈1.43 Å, Figure 1) in the trimer transition states are larger than that for the dimer TS (1.372 Å) and that for the monomer TS (1.280 Å). These distance differences could be interpreted to imply that hydrogen bonding in the trimer transition states is diverted by another F···H interaction (≈1.74 Å). This second hydrogen bond is absent in the monomer TS and much weaker (≈2.0 Å) in the dimer TS.

The water trimer exit complexes HF···(H$_2$O)$_2$OH, lie about 28 kcal mol^{-1} below separated $F + (H_2O)_3$, or about 13 kcal mol^{-1} with respect to products $HF + (H_2O)_2OH$. These exit complexes are more strongly bound than the analogous water dimer complex (11.0 kcal mol^{-1} with respect to products $F + H_3O_2$) and water monomer complex (only 6.2 kcal mol^{-1} with respect to separated $HF + OH$). Also, consistent with the energetics, the separations between the abstracting H atoms and its connecting O atoms for the trimer exit complexes are ca. 1.63 Å, shorter than that for the analogous dimer distance 1.736 Å and even shorter than the monomer distance 1.823 Å.

In summary, the "gold standard" CCSD(T) method with Dunning correlation-consistent basis sets up to cc-pVQZ predicts that the potential energy profile of the water trimer reaction $F + (H_2O)_3 \rightarrow HF + (H_2O)_2OH$ is similar to that of the water dimer reaction $F + (H_2O)_2 \rightarrow HF + (H_2O)OH$, but it is very different from that of the water monomer reaction $F + H_2O \rightarrow HF + OH$. The second water molecule, like a catalyst, removes the barrier of the water monomer reaction, and the third water molecule makes the barrier even lower, though by a much smaller difference. That is, we predict no barrier for both the water trimer reaction $F + (H_2O)_3$ and the water dimer reaction $F + (H_2O)_2$, although the water monomer reaction $F + H_2O$ has a barrier comparable to that for the prototypical $F + H_2$. Perhaps the behavior of water trimer is somewhat like the behavior of liquid water when it reacts with atomic fluorine. Of course, much further research is needed to prove this hypothesis.

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