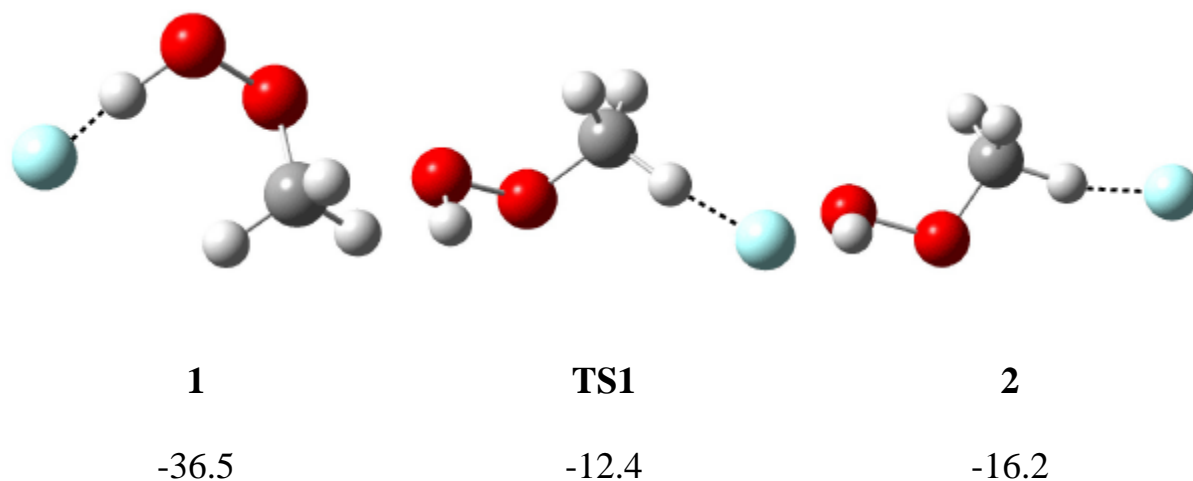
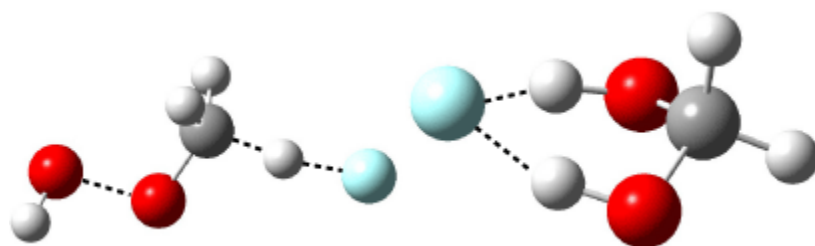


DYNAMIC EFFECTS IN THE REACTION OF FLUORIDE AND CH₃OOH

Dynamic and non-statistical behavior is the subject of Chapter 7 in my book. Hase and co-workers have uncovered another interesting case of dynamic behavior.¹ The reaction of interest here is $F^- + CH_3OOH$. A number of different critical points and reactions exist on this surface. The complex $CH_3OOH \cdots F^-$ (**1**) lies $36.5 \text{ kcal mol}^{-1}$ below separated reactants. **1** can rearrange through **TS1** (with a barrier of $24.1 \text{ kcal mol}^{-1}$) to give $F^- \cdots CH_3OOH$ (**2**). **2** can then cross a second transition state (**TS2**) with a barrier of $4.7 \text{ kcal mol}^{-1}$) to give $CH_2(OH)_2 \cdots F^-$ (**3**), which lies in a very deep well. The B3LYP/6-311+G(d,p) geometries of these critical points are shown in Figure 1.





TS2

-11.5

3

-104.8

Figure 1. B3LYP/6-311+G(d,p) optimized geometries of the critical points on the PES for the reaction of F^- with CH_3OOH .¹ Energies in $kcal\ mol^{-1}$ relative to separated reactants

What drew Hase to this problem were the interesting experimental results of Blanksby, Ellison, Bierbaum and Kato.² The gas phase reaction produced $HF + CH_2O + OH^-$, not **3** or $HF + CH_2(OH)O^-$. Hase and coworkers ran a number of trajectories simulating reaction at 300 K, the experimental condition. Reactions were started at three points: (1) F^- separated by 15 Å from CH_3OOH , (2) at **TS2** or (3) at a point along the intrinsic reaction coordinate (IRC) of the form $HOCH_2O^- \cdots HF$.

76 of the 80 trajectories that start from **TS2** result in the formation of $HF + CH_2O + OH^-$. The majority of the trajectories that start with separated reactants produce

the complex **1** (97 out of 200), reflecting its low energy and high exit barriers. 55 of these 200 trajectories remain as isolated reactants. However, 45 trajectories give $\text{HF} + \text{CH}_2\text{O} + \text{OH}^-$, as do all 5 trajectories that start with $\text{HOCH}_2\text{O} \cdots \text{HF}$. No trajectories give **3**, the product expected from following the IRC. The computations are in complete agreement with the experimental results; the unusual decomposition products result from following a non-IRC pathway!

Since motion along the imaginary frequency of **TS2** initially is to cleave the O-O bond and the C-H bond, momentum in that direction carries the reaction over to the decomposition product rather than making a tight turn on the PES necessary to make **3**. These computations show once again that reactions can follow pathways that lie far from steepest descent or IRC pathways.

Source: <http://comporgchem.com/blog/?p=35>