Investigations into the effect of SMD solvent on Nucleophilic Substitution Reactions and with M06-2X

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Acetic anhydride reacts with *m*-nitro or *m*-methylphenolates through either a concerted or step-wise nucleophilic acyl substitution reaction. One of the main goals of this investigation is to model the reaction mechanism in both gas and aqueous phase by studying tetrahedral intermediate and transition state geometries and energies, as well as studying charge distribution changes as the reactions progress. The project uses the M06-2X hybrid density functional method, the SMD solvation model and the 6-31+G** basis set, which will most accurately describe these reactions according to previous work on this topic. The Merz-Kollman electrostatic mapping model was used to study charge distribution across the different states of the reaction. Results obtained from several conformers so far indicate that the general reaction profiles vary significantly between conformers across both types of phenolates, and both step-wise and concerted mechanisms have been observed within each phenolate group. Several transition state search attempts have failed due to the acetate methyl group being pulled towards the aromatic ring. For both *m*-methyl and *m*-nitro addition of solvent seems to destabilize the first transition states and stabilize the second transition states relative to the tetrahedral intermediate. By comparing these results with those produced previously using the MP2 method in both gas and solution phase, we hope to shed more light on the mechanistic properties of these NAS reactions.

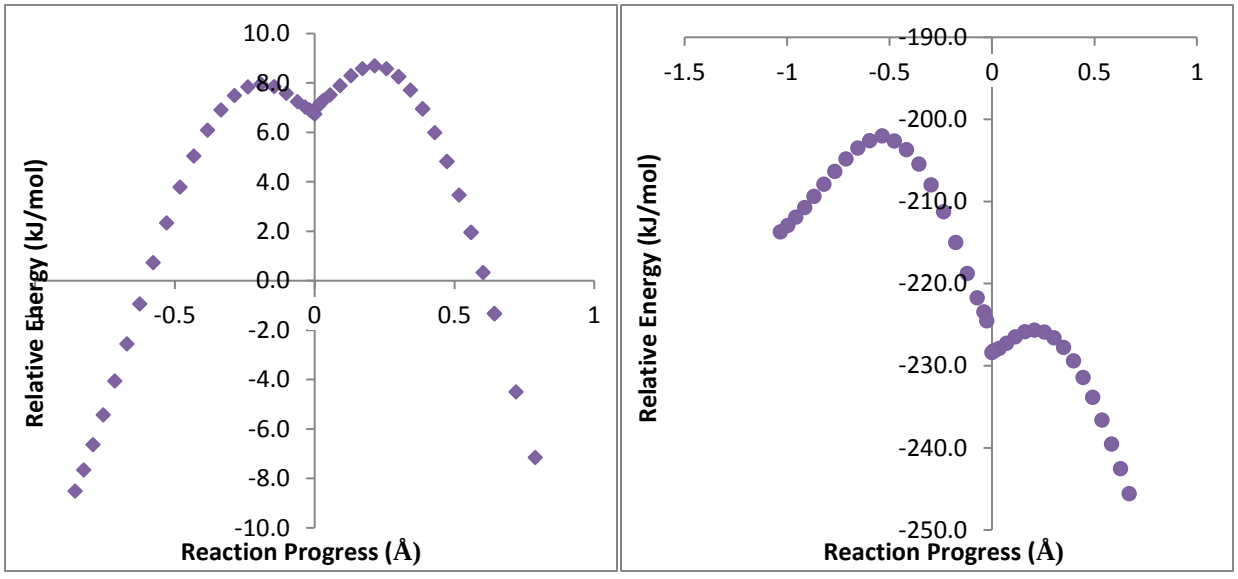

Figure 1. The reaction profiles for the lowest energy conformers of *m*-nitrophenolate conformers in gas phase (left) and SMD solution phase (right), generated with the M06-2X method and 6-31+G** basis set.