Acetylation of Phenols: Computational Determination of Activation Energies

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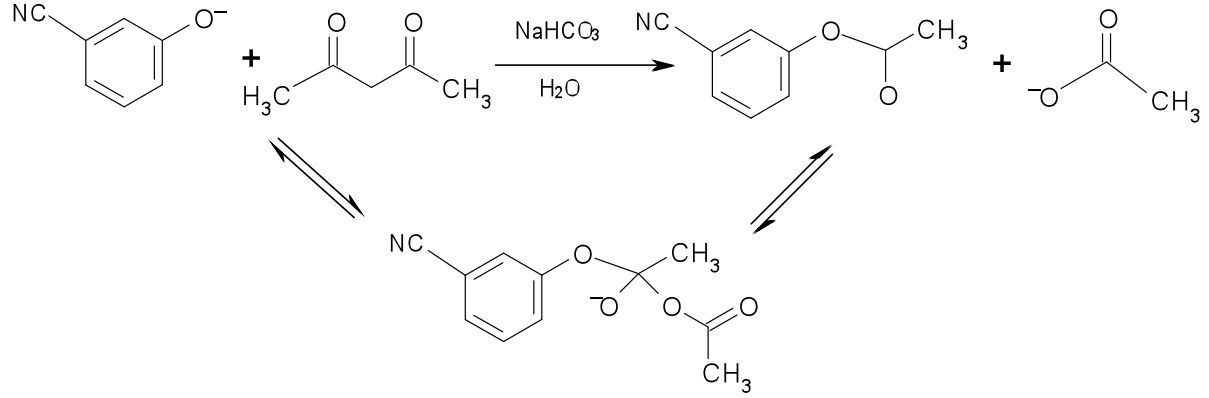
This research project's overall purpose is to examine the ability of available computational methods to reproduce experimental data. Specifically, my goal is to determine the activation energy of the reaction through calculating the activation energy for the acetylation of substituted phenols by acetic anhydride in aqueous sodium bicarbonate using two different computational methods; SM8/B3LYP/6-31+G** and PCM/MPW1K/6-31+G*. This data will then be compared to the experimental data. We will be determining the activation energies of various substituted phenols by acetic anhydride in aqueous sodium bicarbonate as shown in the reaction below. The reaction is a nucleophilic acyl substitution reaction.



tetrahedral intermediate

The research being done is important because in the past, little has been done to apply these methods to the calculation of transition state energies. The transition state energies are important and useful for understanding kinetically controlled processes. In this reaction, Monte Carlo and systematic searches were done to find a 44 conformer library of the *m*-cyanophenol. SM8/B3LYP/6-31+G** calculations provided 9 conformers within 10 kJ/mol of the lowest energy structure and PCM/MPW1K/6-31+G* provided 19 conformers within 10 kJ/mol of the lowest energy structure. Full optimizations were not possible for SM8/B3LYP/6-31+G** conformers due to dissociation, so partial optimizations with the tetrahedral carbon and acetate oxygen bond locked were performed. Full optimizations were obtained for PCM/MPW1K/6-31+G* conformers after multistep calculations. The transition states are being found using pseudo reactions coordinates from SM8/B3LYP/6-31+G** structures using Spartan '08 and by QST2/QST3 calculations using PCM/MPW1K/6-31+G* on the WARP and Glenn clusters.