

The Computational Determination of Barriers of Decomposition:

Acetylation of *m*-Methylphenol

Kevin Bond, Justin B. Houseknecht*

Wittenberg University

The reaction of acetic anhydride with substituted phenolate ions, nucleophilic acyl substitution, is taught in organic chemistry as a step-wise, addition-elimination process. However, there is evidence that suggests that nucleophilic acyl substitution reactions are not always step-wise, meaning this family of reactions could be concerted, depending on the substituent attached to the phenolate ion. Computational chemistry has been used in order to better determine the energies, geometries, and reaction profile for this process. The reaction of *m*-methylphenolate with acetic anhydride was studied using the 6-31+G** basis set with the MP2, B3LYP, and MPW1K methods. Transition states leading to and away from the two lowest-energy tetrahedral intermediates were found using the QST3 method. All structures were confirmed as minima or maxima using frequency calculations and transition states were additionally confirmed with IRC calculations. Results have shown for the reaction *m*-methylphenol and acetic anhydride the process is a step-wise process. For the B3LYP method, the barriers of decomposition of reactants is 0.7 kJ/mol and products is 5.0 kJ/mol. For MPW1K, the barriers of decomposition are 9.9 kJ/mol and 13.0 kJ/mol, respectively. Other students working on this project using substituents other than methyl have had results consistent with a concerted process.

