Computational Analysis of Tetrahedral Intermediate Formed in Acetylation of Phenol with Acetic Anhydride

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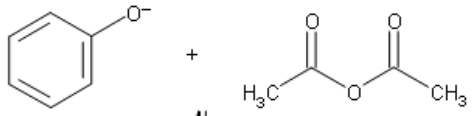
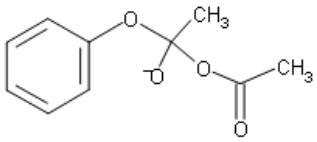
The rate –determining step of the reaction of the acetylation of phenol with acetic anhydride is either the formation or dissociation of the tetrahedral intermediate. As a result of this, the tetrahedral intermediate plays a large role in the overall kinetics of the reaction. However, the low activation energy for the dissociation of this compound makes the study of it and its properties quite challenging. A Monte Carlo conformational search was performed to generate possible conformers of the intermediate. Each structure was first optimized with Merck Molecular Force Field (MMFF), then the resulting structures were then optimized using MPW1K/6-31+G*level of theory. Difficulties arose during the second optimization. Namely, during optimization, many of the sixteen conformers dissociated to either reactants or products. In order to avoid these dissociations, partial and then stepwise optimizations were used. The activation energies for the dissociation of the intermediate to products and reactants were determined the quasi-Newton, synchronous transit-guided (QST3) method.

Reactants



Tetrahedral



Products