Computational Methods to Determine Solvent Effects on the Reaction of Phenol and Bicarbonate

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Solvation has a large impact on equilibriums, rates of reactions, stabilities, polarities, and more. Biological reactions are conducted with water as the solvent, so it is important to understand how particular solvents, and in this case, water, affect the solutes. Computational methods have been developed to analyze these effects. However, the success of these methods have not been examined systematically, particularly their ability to model the effects of solvent upon reaction rates. This project was part of a larger effort aimed at examining the ability of PCM and SM6 methods to model the kinetics of the acetylation of phenol by acetic anhydride in aqueous bicarbonate. The purpose of this project was to determine which methods did the best in determining the change in Gibbs free energy of the first step, the deprotonation of phenol by bicarbonate. First, the gas phase acidities of phenol, and acetic acid were found through various computational methods and compared to experimental values from the NIST website. Then, the Gibbs free energy change for the acid-base reaction was calculated in the gas phase for the most promising methods. The best methods, those that gave the most accurate results without being overly computationally intensive, after this point were then used with explicit water molecules (either one or two) in the gas phase. After this, SM6 and PCM solvation methods were used, both with and without explicit water molecules. The most successful methods were density functional methods with basis sets without diffuse functions, specifically MPW1K/6-311G** and MPW1K/6-31G*.