Accurate and Efficient Calculations of the Gas Phase Acidity of Phenols and Carboxylic Acids

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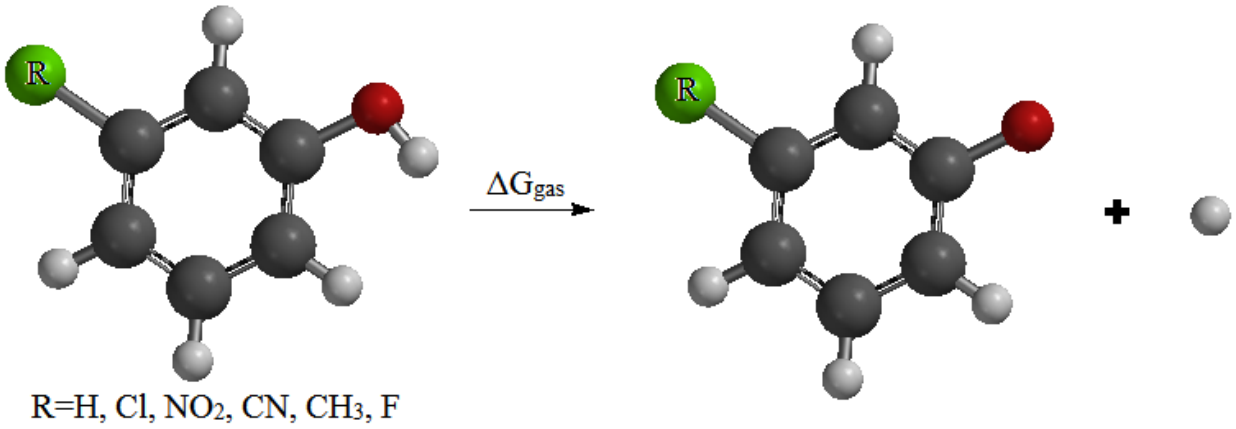
Recipe methods such as CBS-QB3, G2, and G3 have enabled computational chemists to perform highly accurate calculations due to their ability to account for electron correlation and the incorporation of several basis sets. These methods allow for a better estimation of the Schrödinger wave equation, but as a consequence to accuracy, they are often costly in terms of time and CPU memory usage. The purpose of this research is to explore other, less complex, computational methods, while also looking at a range of basis sets, and to gauge their accuracies. In doing so, it will be possible to find methods that are both accurate and less time-intensive. The long-term goal is to accurately perform kinetics studies on phenolate esterification, which require the optimization of many structures with fourteen or more heavy atoms, unsuitable for recipe methods due to time constraints. This information also lays the foundation for calculation of solution phase acidities (pK_a). The gas phase acidities of phenol, five *m*-substituted phenols, and three carboxylic acids were calculated at the HF, B3LYP, MPW1K, MP2, MP3, CBS-QB3, G2, and G3 levels of theory with a range of basis sets. Gas phase acidity values were used to gauge accuracy and were compared to experimental values (Fujio, McIver, et al., 1981). Results have been promising so far as the basis set 6-31+G** seems to produce a significant drop in mean unsigned error in comparison to 6-31+G*. B3LYP, MPW1K, and MP2 in particular have shown improvement between these two basis sets. B3LYP/6-31+G** and MPW1K/6-31+G** are of interest because their CPU times are anywhere from one half to one third of the CPU times for CBS-QB3 calculations.



R=H, Cl, NO_2, CN, CH_3, F