

A comparison of DFT calculations and experiments for the rate of a Menshutkin reaction in several solvents.

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Most industrial liquid-phase reactions take place in solution. It is known that the solvent can play a determining role to the outcome of the reaction, and that selecting an optimal solvent for a given reaction is crucial. Most of the time, however, the choice of solvent is based on experience, insight and limited heuristics. A desirable goal would be to predict how solvents behave with respect to selected reaction indicators, such as rate of reaction, yield and selectivity. With a view to develop new computational methods to determine the effect of solvents on reactions, we present a study comparing theoretical rate constants with experimental data for a Menshutkin reaction involving pyridine and phenacyl bromide as the reactants (Barnard and Smith 1981).

The computed rate constants are obtained from quantum mechanical transition-state calculations, using density functional theory to compute the free energy barrier associated with the formation of the activated complex. We use the continuum solvation model IEF-PCM (Tomasi et al. 1999) at the B3LYP/6-31+G* level of theory. The range of solvents chosen is based on their dielectric constant values. Specifically, we investigate: toluene, ethyl acetate, chlorobenzene, aniline, tetrahydrofuran, dichloromethane, methanol, nitromethane and DMSO. These theoretical data are contrasted with measured reaction rate constants obtained from solution calorimetry experiments. The reactants are added in different excesses and the heat of reaction measured and subsequently subtracted from the calorimetry measurements to identify the rate of reaction constant. Nitromethane is identified as the best solvent.

References

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