Exploration of Density Functional Methods for One-Electron Reduction Potential of Energetic Compounds

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Performance of the set of density functional approaches for calculation of one-electron reduction potentials of nitroaromatic compounds was investigated. In order to select the most precise and affordable method, we selected a set of model molecules and investigated effects of basis set, density functional and solvation model on the calculation of reduction potentials. It was found that the mPWB1K/TZVP method provides the most accurate gas phase electron affinity values (RMS error is 0.1 eV). This method in conjunction with the PCM(Bondi) method yields also the most accurate difference in solvation energies of neutral oxidized form and anion-radical reduced form. The final E^0 values were calculated with RMS error of 0.10 V, compared to experimental values.

The described above computational protocol has been used to predict one electron reduction potentials for number of energetic materials that include nitroaromatics (dinitrobenzenes, dinitroanisoles), nitroamines (RDX, HMX, CL-20), and nitrogen reach (triazoles, tetrazoles) compounds.