XIX SBQT

Simpósio Brasileiro de Química Teórica 2017

Global and local reactivity descriptors based on quadratic and linear energy models in α, β-unsaturated systems

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Abstract: Global and local descriptors of chemical reactivity can be derived from conceptual density functional theory. Their explicit form, however, depends on how the energy is defined as a function of the number of electrons. Here, within the existing interpolation models the quadratic energy and the linear model were used to derive global descriptors as the electrophilicity (defined by Parr) and nucleophilicity (defined as the negative of the ionization potential), and local descriptors employing either the corresponding condensed fukui function in the linear model or the local response of the global descriptor in the quadratic model [1,2].

As test systems alpha, beta-unsaturated organic molecules have been studied, varying the heteroatom, resulting in alpha, beta-unsaturated thioesters, esters and amides. Specifically, the reduction of the neutral systems and following electrophilic attack by carbon dioxide reactions have been studied. These reactions represent the rate limiting steps in carboxylation reactions of thioesters under enzymatic environment studied experimentally by Erb et al. [3].

The respective descriptors for each molecule were calculated in the gas and solvent phase (water), using wB97X-D3 / 6-311G (d,p) level of theory. The calculation of the respective condensed fukui functions to derive the local descriptors was performed within the FMO (frontier molecular orbitals) approach using the Hirshfeld-I partitioning method [4].

Our results identify correctly the most reactive atom in each molecule for each reaction and show a correlation between the global descriptors and the local descriptors for the same energy model (quadratic, linear). The obtained descriptors agree with the reported experimental reactivity and present therefore a valuable tool to predict reactivity in heterogeneous environments.

Key-words: Conceptual DFT, condensed fukui function, global and local reactivity descriptors.

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