

Spin-Polarized Conceptual Density Functional Theory

Freija De Vleeschouwer

Free radical chemistry constitutes a substantial part of important large-scale industrial chemical processes. Some examples are radical chain polymerization (resulting in a whole variety of industrial plastics like for instance polyethylene, polypropylene, poly(vinyl chloride) and polystyrene), combustion of fuels, pyrolysis and steam cracking. Radicals are also essential in atmospheric chemistry through the oxidation of other molecules in the air and in biochemistry through cell damage. The main obstacle in understanding radical reactions is the high reactivity and short lifetime of radicals. Quantum chemistry and more specifically Conceptual DFT allows us to address these issues theoretically and computationally. In this work various chemical concepts, essential to explain the reactivity of radical systems, are being studied and in some cases even quantified, resulting in easily accessible scales. The first investigated concepts are electrophilicity and nucleophilicity. It is stated that radicals can be regarded as electrophilic or nucleophilic and that the nature of radicals is certainly of relevance in a variety of radical reactions, as is illustrated in this work. The definition of the electrophilicity index, as introduced by Parr, was used to construct an electrophilicity scale of 47 radicals, important in organic chemistry. This scale is independent of the reaction partner and free from experimental or theoretical reaction data. Next, the somewhat vague concept of stability was studied. The intrinsic stability of a radical is intuitively defined as the reactivity of that radical with respect to a range of different chemical environments, so irrespective of the reaction partner, the presence of a solvent, and so on. A model is presented that breaks down Bond Dissociation Enthalpies into parts that only incorporate properties of the individual radical fragments, that is radical electrophilicity, radical stability and Pauling electronegativity of the radical center. The resulting scale reproduces several acknowledged stability sequences from literature, such as the effect of increasing alkylation and delocalization. In addition, the BDE model is suitable to compute intrinsic stabilities for other (uncharged) intermediates like biradical and divalent systems. A third and last studied concept in this work is kinetic (ir)reversibility in intramolecular radical reactions. This concept is very important when considering side reaction in radical polymerization. Through the analysis of the spin-polarized Fukui function and dual descriptor along the reaction path of 4 intramolecular side reactions in the polymerization of PVC and within the framework of the reaction force concept, the irreversibility of the 1,2-Cl shift, the 1,5- and the 1,6-backbiting reactions as well as the reversibility of the 2,3-Cl shift could be explained. Finally, the last Chapter focuses on intramolecular cyclization reactions, for which the regioselectivity is rationalized through a special form of the spin-polarized dual descriptor via the positive orbital overlap between the radical center and one of the carbon atoms of the radical's double bond, agreeing with the experimental findings.