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Relevance between the chemical structure modifications and physicochemical descriptors of chemical reactivity for series of nitroxide radicals

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Abstract

This work presents an experimental and theoretical study to address the chemical reactivity of series of nitroxide radicals. For that purpose two physicochemical properties: the half-wave potential and the hyperfine coupling constants of the nitrogen nuclei, were analyzed. Experimental values are compared with electronic structure calculations at the BHandHLYP/6-311++G(2d,2p) level. $E_{1/2}$ values were in good agreement with the adiabatic ionization potential when including the solvent effects by the Cramer and Truhlar Solvation Model. Preliminary experimental electron spin delocalization studies suggest that structural hindrance plays an important role in their delocalization mechanism.

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1. Introduction

Secondary batteries are electrochemical devices for energy storage and conversion, in which released electrons by electrochemical reactions, can be transported from one electrode to other one in a charge/discharge cycle.¹ This type of devices usually employ as electrode materials compounds derived from lithium-type spinels, layer oxides, polyanions or other structures composed of Ni, Co, Mn, Fe;¹ however, technical shortcomings arise from their

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instable structures, thus restricting their specific capacities for scale-up applications. For example, lithium ions, in spite of exhibiting good characteristics as conductivity and reducing agents, often tend to form dendritic deposits during the charging step, diminishing the coulombic efficiency in the device and limiting the lifecycle of the secondary battery.²

As an alternative, electroactive organic units like nitroxide radicals can be used to design a new generation of polymer materials called organic radical polymers for organic-based functional batteries;^{3,4} nitroxide radicals are useful molecular carrier systems due to their chemical stability and electrochemical reversibility of their electron transfer processes. The constructed organic-based battery is known as organic radical battery (ORB)⁴⁻⁶. The electrochemical properties are the sum of the ET process of each radical monomer in the polymer material.^{3,4,7}

There are few reported systematic studies on the effect that molecular modifications could have in the electrochemical behavior of the monomeric units. Nakahara and coworkers analyzed the energies of SOMO orbitals respect to semiempirical calculations for a series of nitroxide radicals⁸ with the aim of predicting increases in potential in batteries where nitroxide radicals could be used as electrode materials. Nevertheless, these results showed a limited description of the experimental values. On the other hand, Coote and coworkers^{9,10} made a correlation between experimental $E_{1/2}$ values and the ionization process using the thermodynamic cycle of Born-Haber, followed by calculations considering the solvent effect over the optimized structures in the gas phase. They obtained a good agreement between the experimental $E_{1/2}$ values and the calculated ionization energies, providing a general description of the reactive trend.¹¹

From a chemical point of view, it would be suitable to obtain a detailed description of the specific role that chemical structures and their modifications play in the oxidation potential values. This is important for non-aromatic nitroxide radicals (for example, derivatives from PROXYL and TEMPO compounds), as the lack of a π system suggests that alternative pathways for communicating the electronic properties of the substituent into the nitroxide ring are used. Furthermore, this analysis should provide information on how does the substituent also affects the spin density of the system, due to the presence of unpaired electrons. The main suitable approaches are done by considering local and global descriptors of the chemical reactivity, in the framework of the Density Functional Theory.^{12,13} These approaches stand that reactivity can be described and studied by changes in the energy of a system as a response of changes in its electron number (N), at a given external potential, $v(\mathbf{r})$ within this approximation the reactivity can be evaluated by means of the first and second derivative of the energy respect to the number of electrons at constant electrostatic potential, described as follows

$$\mu^{\pm} = \left(\frac{\partial E}{\partial N} \right)_{v(r)}^{\pm} \quad (1)$$

$$\eta^{\pm} = \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)}^{\pm} = \left(\frac{\partial \mu}{\partial N} \right)_{v(r)}^{\pm} \quad (2)$$

Where μ and η describe the chemical potential and the chemical hardness, respectively.¹⁴ The positive and negative signs (+ or -), point out that the right and left derivatives are different when evaluated at a given integer value of N and are correspondingly associated to the process of increasing and decreasing the number of electrons, respectively. On a local scale, site reactivity can be analyzed considering the Fukui function, or

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)} \quad (3)$$

Equations (1), (2) and (3) have been successfully used for describing the reactivity behavior of different chemical species.^{15,16} Therefore, in this work the electrochemical reactivity of a series of nitroxide radicals will be addressed by analyzing the role of the presence of the substituent groups in the molecular structure and their spin density changes.

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