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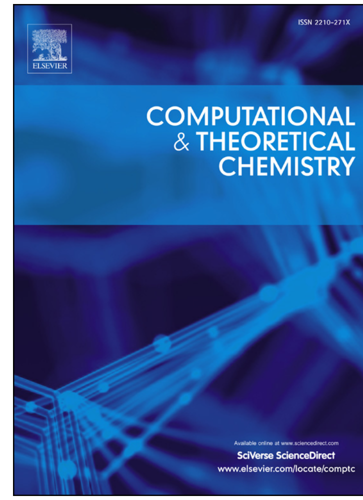

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Formation of reactive oxygen species by vanadium complexes

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Abstract

The role of the ligand in vanadium IV and V complexes to produce reactive oxygen species ($OH\cdot$ and $O_2^-\cdot$) by Fenton and Haber-Weiss reactions is analyzed theoretically, in gas phase and considering solvated ions. By using reactivity indexes, we found that the presence of the oxo group induces the electron donating process over complexes that in first instance does not present it. Also, we show that the vanadyl ion promotes the production of $OH\cdot$ radicals, which is a contrary behavior presented by others vanadium complexes that may act as $O_2^-\cdot$ producers or scavengers. For Haber-Weiss reactions, the analysis of the Gibbs free energy predict the following ordering: $H_2O > NH_3 > Cl^- > OH^- > C_2O_4^{2-}, Cl^- > C_2O_4^{2-}, NH_3 > oxo, H_2O > oxo, NH_3 > oxo, Cl^-$, for ligands with vanadium V and IV in the formation of reactive oxygen species (ROS); which allow for the first time a criteria to predict ROS activity in vanadium complexes. All the results were obtained by using the Density Functional Theory, in its Kohn-Sham version, with four different exchange-correlation functionals (PBE, PBE0, B3LYP and M06-2X) coupled with the aug-cc-pVDZ basis set. It is well-known that transition metals sometimes exhibit a multireference character, for that reason several tests were considered over the vanadium complexes reported here. In particular, T1 test, multiconfiguration self-consistent field and coupled-clusters calculations were performed in order to test the feasibility of our results. In general, we can say that the M06-2X exchange-correlation functional exhibits the best performance to study theoretically vanadium complexes.

Keywords: Vanadium complexes, antioxidant agents, fenton reactions, exchange-correlation functionals, coupled-clusters, multireference character. 31.15.A-, 31.10.+z, 33.15.-e, 31.15.xr, 33.15.Fm

1. Introduction

The chemistry of vanadium is recognized as complex and sometimes unpredictable. However, it is well-known that even though this element exhibits many oxidation states, compounds with vanadium IV and V predominate in biological systems, in particular, for treatments of some chronic diseases.[1] The coordination chemistry of vanadium(IV) and vanadium(V) is singularly flexible, presenting several coordination numbers and different oxidative processes.[2] These features give to vanadium an important role in biological systems. This transition element is known to influence a wide range of enzymatic systems, namely, phosphatases, peroxidases, ATPases, ribonucleases, oxidoreductases and protein kinases.[3] Over the past

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