Commun. Comput. Chem.
doi: 10.4208/cicc.2016.v4.n1.3

Vol.4, No.1, pp.24-35
June 2016

REGULAR ARTICLE

Theoretical study of the reactivity between RuIV(O) complexes and their inverted-isomers

Peng Zhang[1], Zhe Tang[2], Yi Wang [2*]

[1]*School of Mechanical Engineering and Automation, Dalian Polytechnic University, Dalian 116034, P. R.China;*

[2]*School of Biological Engineering, Dalian Polytechnic University, Dalian 116034, P. R.China*

Received 13 May 2016; Accepted (in revised version) 23 June 2016

Abstract: Density functional theory calculations were carried out to investigate geometric and electronic structures and mechanisms for hydrogen abstraction from cyclohexane for six non-heme ruthenium-oxo complexes [RuIV(O)(TMC)(X)]+ (1-Ru-X) and their inverted isomers [RuIV(X)(TMC)(O)]+ (2-Ru-X; Scheme 1; where TMC is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; X = TF-, N3- and SR-). The calculations offer a mechanistic view and reveal the following features: (a) all six ruthenium (IV)-oxo complexes possess a triplet ground spin state, and the quintet spin state is too high to participate in the reaction. (b) The six complexes react with cyclohexane via a single-state reactivity pattern only on the triplet spin surface. (c) A more negative ΔqCT results in a greater tunneling contribution effect. (d) At the B2//B1+ZPE level, the relative reactivity of the hydrogen abstraction follows the trend: 1-Ru-SR > 1-Ru-N3 > 1-Ru-TF and 2-Ru-SR > 2-Ru-N3 > 2-Ru-TF. The relative reactivity of 2-Ru-X is greater than that of 1-Ru-X. (e) The effect of the tunneling contribution is higher for 1-Ru-X than for 2-Ru-X; with the tunneling correction, the relative reactivities between 1-Ru-X and 2-Ru-X change and the trend becomes: 2-Ru-TF > 1-Ru-TF, 2-Ru-N3 > 1-Ru-N3 and 2-Ru-SR < 1-Ru-SR.

AMS subject classifications: 74E40, 74F45

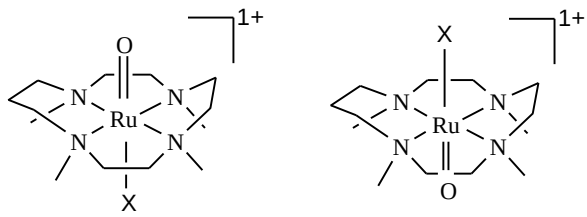
Key Words: Non-heme; Ruthenium-oxo; Steric Hindrance; H-abstraction; Density functional theory

Introduction

* Corresponding author. *Email address:* wangyi@dlpu.edu.cn, Fax: +86 0411-86323646

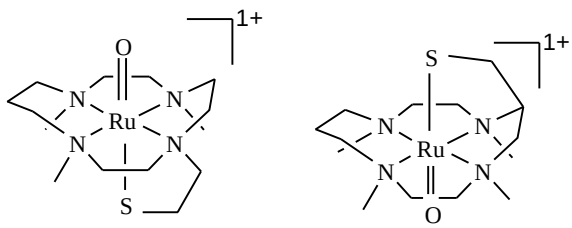
Oxygen-activating enzymes with mononuclear non-heme iron active sites participate in many metabolically important reactions that have environmental, pharmaceutical, and medical significance [1]. These enzymes activate dioxygen, with the aid of a two-electron sacrificial reductant, to generate a highly reactive oxoiron (IV) species, which is proposed to be the active intermediate in the oxidation of a number of important biomolecules [2]. To data, many mononuclear non-heme iron complexes have been synthesized as chemical models of the non-heme iron enzymes [3]. In the non-heme systems, the axial and equatorial ligands to the metal-oxo moiety on the reactivities of the non-heme iron(IV)-oxo complexes have attracted much attention in the electron-transfer and oxidation reactions[4-6].

In 2003, the first structurally characterized synthetic oxoiron (IV) complex, [FeIV(O)(TMC)(NCMe)]2+ has been reported (where TMC is 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) [7]. In 2005, the effect of a thiolate ligand on the catalytic properties of non-heme oxoiron complexes was studied [8, 9]. Since then, many studies of the analogous complexes have been carried out [4,10-12]. An inverted-isomers, [FeIV(NCMe)(TMC)(O)]2+, of [FeIV(O)(TMC)(NCMe)]2+ , in which the oxo group binds to the site syn to the four N-methyl groups, was synthesized by Ray et al [13]. The different reactivities between the [FeIV(O)(TMC)(X)]n+ and their inverted-isomers, and the factors, which can influence the reactivity of C-H hydroxylation and C=C epoxidation by [FeIV(X)(TMC)(O)]n+ have been calculated [14].



1-Ru-X 2-Ru-X

X=TF, N3



1-Ru-SR 2-Ru-SR

1-Ru-SR: SR is appended to an N-atom through an ethyl linker
2-Ru-SR: SR is attached to a methylene linker in the TMC backbone

Scheme 1 Structures of 1-Ru-X and 2-Ru-X.