

## Chemoselectivity of the molybdenum oxodiperoxo complexes in oxidation reactions

Lucelma Pereira de Carvalho<sup>a</sup> (IC), Marcus Vinicius Pereira dos Santos<sup>a</sup> (PQ), Juliana  
Angeiras Batista da Silva<sup>a</sup> (PQ), Ricardo Luiz Longo<sup>b</sup> (PQ)

<sup>a</sup>Centro Acadêmico do Agreste, Universidade Federal de Pernambuco

<sup>b</sup>dQF - Centro de Ciências Exatas e da Natureza, Universidade Federal de Pernambuco

Keywords: Oxo-diperoxo Complexes, DFT, Oxidation Reactions, Activation Energy

### INTRODUCTION

In recent years, many procedures were proposed for oxidations from sulfides to sulfoxides. Although, few of them are highly chemoselective to produce sulfoxide without to obtain the next level oxidation product, i. e., sulfone. Experimentally, it has been shown that the molybdenum oxodiperoxo complexes,  $[MO(O_2)_2L_1L_2]$ ,  $M = Mo$  and  $W$ ,  $L_1 =$  pyrazole or N-oxo of pyridine,  $L_2 = H_2O$  or silica, adsorbed onto silica gel are highly selective yielding only sulfoxide product.<sup>1</sup> However, the mechanistic reasons for this selectivity still remain unknown.

Quantum chemical (QC) methods can be useful to understand the behavior of oxygen transfer reactions, and proposing mechanisms to explain the observed chemoselectivity in sulfide oxidation reactions.<sup>2</sup> Thus, in this work, we investigated the chemoselectivity of these reactions by determining its activation energies ( $E_a$ ) in different substrates (alkenes, sulfur, and selenium, very susceptible to the oxidation process). The following substrates were chose:  $R_1-S-(CH_2)_nCH=CH-R_2$ ,  $R_1-Se-(CH_2)_nCH=CH-R_2$ , ( $n = 0$  ou  $1$ ), where the groups  $R_1$  e  $R_2$  can be electron donor and/or withdrawing can modify and control the chemoselectivity of the reaction.

### METHODS

Our group has performed earlier studies in order to obtain all molecular structures of the reagents and products considered in this work. Critical points in the PES have been characterized by Hessian matrix and the transition state by Intrinsic Reaction Coordinate (IRC) analysis. We have used B3LYP/6-311+G(2df,2p) method for all atoms, except for Mo, which were employed the following recipes: B3LYP/X, with X, basis set (BS) and effective core potential (ECP) = LanL2DZ, Def2-SVP, Def2-TZVP, Def2-QZVP, cc-pVDZ-PP and cc-pVTZ-PP. All calculations were performed with Gaussian 09 program (Rev. D.01).

### RESULTS AND DISCUSSION

In order to find out the appropriate QC method for these systems, we have obtained the free energy activation profile for the following reaction through two reactions pathways (oxidation of sulfur and oxidation of double bond):  $[Mo(O_2)_2OPH_3] + CH_3-S-CH_2CH=CH_2$ . These results were compared to Sensato *et al.* results (2005), and all scheme B3LYP/X produce values with great agreement to the literature results,<sup>2</sup> except for X = LanL2DZ option. Since Def2-SVP is the lower demand BS, this one was chose to proceed with studies. The free energy activation profiles for substrates showed that the transition state for the oxidation of the heteroatom (S and Se) has lower barrier height than the oxidation of alkene. The difference between these barriers is not affected when we increased the side chain of the substrates. Such results are in agreement with experimental results of oxidation reactions involving sulfides.

### CONCLUSIONS

Our results show that the chemoselectivity of the molybdenum oxodiperoxo complexes towards oxidation reactions of sulfides is less affected changing the functional groups  $R_1$  and  $R_2$ , in agreement with the experiments. However, for substrates with selenium, the oxidation of the selenium atom is still preferred than the alkenes functionality.

### ACKNOWLEDGMENTS

The authors would like to thank the FACEPE, CAPES and CNPq for the grant and scholarships.

<sup>1</sup>F. Batiglialha, M. Z. Hernades, A. G. Ferreira, I. Malvestiti and Q. B. Cass, *Tetrahedron*, 57, 9669, (2001).

<sup>2</sup>F. R. Sensato, R. Custódio, E. Longo, V. S. Safont and J. Andrés, *Eur. J. Org. Chem.*, 2406, (2005).