

## Effects of the complexation energy on the thermochemistry and kinetics of oxidation reactions with oxidiperoxo complexes

Marcio Marcos da Silva<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>Departamento de Química Fundamental, Universidade Federal de Pernambuco

Keywords: Oxo-diperoxo complexes, DFT, ECPs, basis sets, activation energy.

### INTRODUCTION

Oxo-peroxo metal complexes,  $[MO(O_2)_2L_1L_2]$ ,  $M = Mo$  and  $W$ ,  $L_1 =$  pyrazol or N-oxo of pyridine,  $L_2 = H_2O$  or silica, oxidize unsaturated sulfides to the corresponding sulfoxides and these to sulfones, chemoselectively.<sup>1</sup> Despite their importance and studied, some aspects of the mechanistic reasons for this selectivity remain unknown. Electronic structure methods can be useful to understand this behavior and provide mechanistic information. Intrinsic Reaction coordinate (IRC) analyses are essential to assure that the transition state (TS) connects the proper reactants and products. In addition, the effects of complexation between the oxidant and the substrate should be taken into account in estimating the free energies profiles properly. However, these complexation effects are usually not considered and, in this work, we are investigating the complexation effects on these reactions.

### METHODS

The TS structures were characterized by their Hessian matrices for seven processes<sup>1</sup>. The IRC analysis from the TS structure provided the reaction path from the reactant to the product. We employed the B3LYP functional and the 6-311+G(2df,2p) basis sets for all atoms, except for Mo that the following basis sets were used LanL2DZ, Def2-SVP and dhf-SVP. All calculations were performed with Gaussian 09 program (Rev. D.01).

### RESULTS AND DISCUSSION

To illustrate, in Table 1, we present the values of activation ( $\Delta^\ddagger G$ ) and reaction ( $\Delta_r G$ ) free energies of processes I and II. Pathways I and II are the double bond and sulfur atom oxidations:  $[Mo(O_2)_2OPH_3] + CH_3-S-CH_2CH=CH_2$ .

**Table 1.** Free energies (kcal mol<sup>-1</sup>) of activation ( $\Delta^\ddagger G$ ) and reaction ( $\Delta_r G$ ). The complexation effects results are labeled with (\*).

Mo basis set	Process	$\Delta^\ddagger G$	$\Delta_r G$
dhf-SVP	I	27.3	-33.2
	II	19.3	-31.5
	I*	20.1	-38.4
	II*	11.8	-41.5
Sensato et al. <sup>1</sup>	I	26.4	-34.4
	II	19.0	-33.5

Process II has lower  $\Delta^\ddagger G$  than process I, thus the oxidation of the sulfur atom is kinetically favored compared to the oxidation of the double bond. Whereas, process II is more spontaneous than process I, namely,  $\Delta_r G(I) < \Delta_r G(II) < 0$ . However, when the complexation step is taken into consideration process II becomes kinetics and thermodynamically favored. This same trend is observed for LanL2DZ and Def2-SVP basis sets. Noteworthy the excellent results provided by the dhf-SVP compared to the more complete designed basis set for Mo by Sensato et al.<sup>1</sup>.

### CONCLUSIONS

Complexation effects decrease the activation energies and they make reactions more spontaneous. Additional calculations are in progress for other systems to corroborate this trend.

### ACKNOWLEDGMENTS

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

<sup>1</sup> F. R. Sensato, R. Custódio, E. Longo, V. S. Safont, J. Andrés, Eur. J. Org. Chem., 2406, (2005).