

MECHANISTIC INSIGHTS IN THE PSEUDOPERICYCLIC OXIDATION OF 5-MEMBER CYCLIC HYDROXYLAMINES WITH RUTHENIUM TETROXIDE

Jose Manuel Pedrón^a, Pedro Merino^a, Tomas Tejero^b

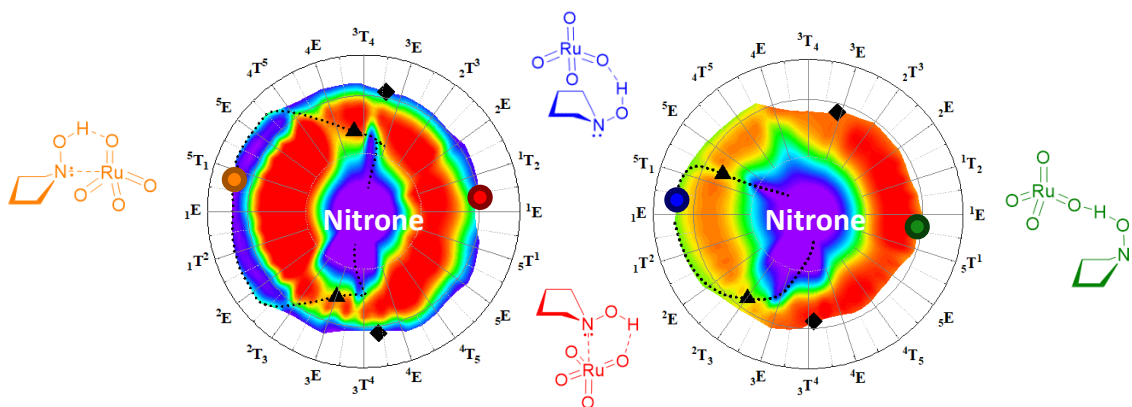
^a*Instituto de Biocomputación y Física de Sistemas Complejos (BIFI). Universidad de Zaragoza. 50009 Zaragoza. Spain.*

^b*Instituto de Síntesis Química y Catálisis Homogénea (ISQCH). Universidad de Zaragoza-CSIC. 50009 Zaragoza. Spain.*

e-mail: manolo@unizar.es

Keywords: DFT, Mechanism, ELF, PES analysis, Transition Structure, Oxidation, Transition Metal, pseudopericyclic.

The mechanism of the hitherto unknown oxidation of cyclic hydroxylamines with ruthenium tetroxide has been studied in detail. Several plausible mechanisms are suggested including stepwise and more or less asynchronous concerted processes.^[1] Among these possibilities, an asynchronous concerted mechanism in which transfer of both hydrogen atoms from the hydroxylamine to the oxidant take place in an almost concomitant way results the most favorable.^[2,3] The topological analysis of the variation of the electron localization function (ELF) along the reaction coordinate allowed determining the concertedness of the reaction and the different events happening. 3-Substituted-*N*-hydroxypyrrolidines have been also calculated to predict the regioselectivity in the formation of the corresponding nitron. Since there are no precedents in the literature on this reaction, several oxidation reactions have been carried out experimentally to assess the quality of the predictions.



References

- [1] The ruthenium tetroxide oxidation of cyclic saturated hydrocarbons. Formation of alcohols. Bakke, J. M.; Lundquist, M. *Acta Chem. Scand., Ser. B* **1986**, *B40*, 430-433.
- [2] Ruthenium tetroxide as an oxidant for alcohols. Beynon, P. J.; Collins, P. M.; Gardner, D.; Overend, W. G. *Carbohydr. Res.* **1968**, *6*, 431-435.
- [3] Rzepa, H. R. <https://www.ch.imperial.ac.uk/rzepa/blog/?p=8776>.