

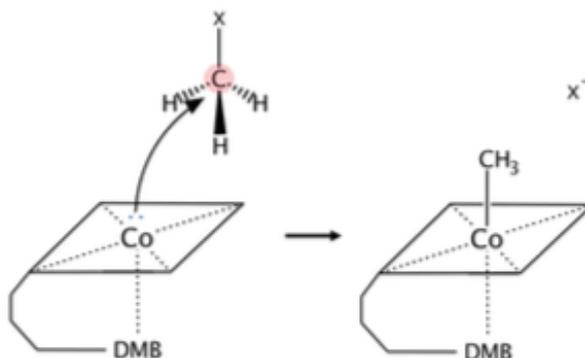
## Computational Study of the C—X (X = F, Cl, Br, and I) Bond Cleavage Mediated by Cob[N]alamin

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**Abstract:** Cob[N]alamin, Cbl, is a macrocyclic complex ( $\sim 200$  atoms/molecule) composed of a cobalt atom of variable oxidation state (*i.e.*,  $\text{Co}^{1+}$ ,  $\text{Co}^{2+}$ , or  $\text{Co}^{3+}$ ) located at the center of an almost- flat deprotonated corrin ring [1, 2]. This macromolecule is well-known for its relevance in different metabolic processes occurring at the cellular level. However, recent experimental evidence has demonstrated that, beyond its biological importance, Cbl plays a fundamental role in the reductive dehalogenation of halocarbon compounds [3, 4]. In the present work, the C—X (X = F, Cl, Br, and I) bond cleavage process mediated by Cbl is thoroughly studied by the computational description of the a SN2 model reaction:



A DFT/SemiEmpirical ONIOM scheme was adopted, where different functional and basis-set combinations were tested together with the PM6 method. The results of the first stage of the study showed that the employed ONIOM approach is well-suited for describing the different forms of Cbls, being the computed geometric and electronic properties comparable with results obtained from a full DFT description by adopting state-of-the-art dispersion-corrected methods [5]. Regarding the Cbl potential to cleave the different C—X bonds, various methodologies for the analysis of chemical reactions such as: the reaction force concept, the natural bond orders and charges, the reaction synchronicity, among others, suggested that both the oxidation state and the coordination number of the Co atom are determinant factors in the efficiency of reaction.



# XIX SBQT

Simpósio Brasileiro de Química Teórica 2017

12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

**Key-words:** DFT, Cob[N]alamin, Reductive Dehalogenation, Halocarbons

**Support:** This work has been performed by employing the resources of the USFQ's High Performance Computing System (HPC-USFQ). Authors would like to thank USFQ's POLI-GRANTS program for financial support.

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