

## On the role of asynchronicity and frustration in C-H bond activation by metal-oxo complexes

M. Srnec,<sup>a\*</sup> M., Maldonado-Domínguez,<sup>a</sup> D. Bím<sup>a</sup>

<sup>a</sup> J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Prague, Czech Republic

*martin.srnec@jh-inst.cas.cz*

We formulated an original and unique theoretical framework aiming at the prediction of C-H bond activation reactivity. In its current form, it features two thermodynamic factors that we named asynchronicity<sup>1</sup> and frustration<sup>2</sup> that together modulate coupled proton-electron transfer reactivity. Only after addition of these two factors to the classical well-documented effect known as linear free energy relationship (LFER capturing the effect of reaction energy on the barrier) a complete thermodynamic basis for the control of reactivity/selectivity is formed. Asynchronicity lowers the reaction barrier (increasing the reaction rate) so that a more asynchronous reaction gets faster, whereas frustration acts on the barrier in the opposite way so that a more frustrated reaction gets slower. In principle, each of the two factors and their combination enable changing the preference of which C-H-bond is likely to be activated that would be otherwise driven by LFER, which favors the weakest C-H bonds in molecules. To demonstrate the power of the approach, we will show and discuss H-atom abstraction reactivity of several transition-metal complexes and organic radicals.

---

<sup>1</sup> M. Bím, M. Maldonado-Domínguez, L. Rulišek, M. Srnec *Proc.Nat. Sci. Acad. U.S.A.*, **2018**, *115*, E10287-E10294.

<sup>2</sup> M. Maldonado-Domínguez, M. Srnec *ChemRxiv*, **2022**, 10.26434/chemrxiv-2022-k6l4p.