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

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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 1 and frustration 2 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.