

Predictive Catalysis Based on the Activation Strain Model

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Reactivity is one of the central issues, if not the core business, of chemistry. Yet, our understanding of chemical reactivity, in particular, the height of reaction barriers, still lags behind the minute understanding that we have today of molecular structure and stability. What is missing is a general model that provides physical insight into why a particular reaction has a higher or lower barrier than another (competing) reaction.

Here, we present the Activation Strain model which aims at providing such insight into chemical reactivity, *in terms of the reactants*. In the Activation Strain model, the potential energy surface $\Delta E(\xi)$ along the reaction coordinate ξ is decomposed into the strain energy $\Delta E_{\text{strain}}(\xi)$ associated with the geometrical deformation that the reactants undergo, plus the interaction energy $\Delta E_{\text{int}}(\xi)$ between the deformed reactants: $\Delta E(\xi) = \Delta E_{\text{strain}}(\xi) + \Delta E_{\text{int}}(\xi)$.

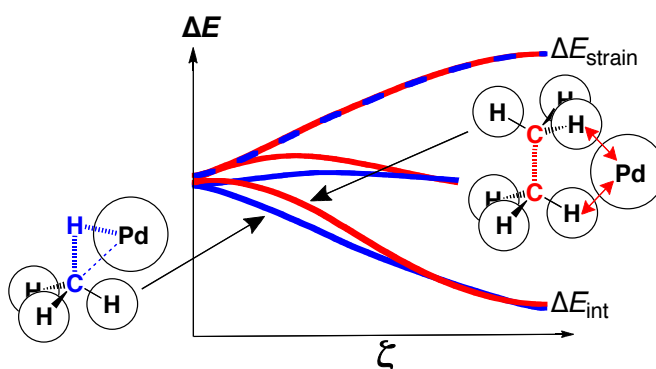


Figure 1. Activation-Strain analysis of palladium-catalyzed C–H *versus* C–C bond activation.

Various phenomena and tuning parameters in catalytic bond activation are discussed. What determines the course of oxidative addition via direct insertion or an S_N2 pathway? Why is activation of the weaker C–C bond more difficult than that of the stronger C–H bond? (The clue is contained in Figure 1). But also archetypal organic reactions are addressed. The main focus of this talk will however be on the nature of the bite angle in catalysts with bridged biphosphine ligands. It will be shown that, at variance with common text book knowledge, the mechanism behind bite angle tuning is primarily steric (i.e., steric hindrance between ligands and substrate) and not so much electronic (i.e., d orbital energies tuned by ligand orbitals).

Literature

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