Quantum Mechanical Investigation of Fundamental Concepts in Hydrocarbon C-H Bond Activation

Daniel H. Ess, Department of Chemistry & Biochemistry, Brigham Young University

Thermodynamics

DFT analysis of late-transition-metal M-C and M-X bonds (M = Pt, Ru, Rh, and Ir) shows:

1) Orbital charge transfer stabilization determines bonding trends along CH_3 , NH_2 , OH, F series.

2) Pauli repulsion and d_{π} - p_{π} repulsion does not determine relative bond energies.



Kinetics (Transition States)

 H_2 provides a model for C-H σ -type bonds without complication by a tetrahedral sp³ carbon center or effects from π -type interactions. Energy decomposition calculations on dihydrogen activation transition states with d⁰, d⁶, d⁸, and d¹⁰ metal centers and a range of metal ligands revealed:

1) Transition states, similar to dihydrogen σ complexes, have a continuum of activated H–H bond lengths.

2) The transition-structure geometry depends on back-bonding orbital interactions and not forward-bonding orbital interactions no matter the mechanism or whether the metal ligand complex acts as an electrophile, ambiphile, or nucleophile towards dihydrogen.



