

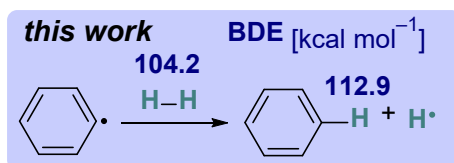
Phenyl Radical Activates Molecular Hydrogen Through Protium and Deuterium Tunneling

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Activating dihydrogen (H₂) poses a significant challenge, typically tackled by transition metal centers.¹ Although rare, there have been discoveries of pure main group molecules with the ability to split the strong and non-polar dihydrogen bond in recent decades.²⁻⁵ These systems rely on cooperative interactions of donor and acceptor orbitals with the antibonding σ^* and bonding σ orbitals of dihydrogen, respectively. An alternative method could involve the utilization of (hydrocarbon) radicals, yet the strength of the dihydrogen bond (104.2 kcal mol⁻¹) typically exceeds that of most C–H bonds.⁶ This study explores the potential of the phenyl radical to address this challenge by interacting with H₂ to yield benzene featuring a high C–H bond energy (112.9 kcal mol⁻¹) and thus providing a favorable thermodynamic driving force. The hydrogen atom abstraction primarily involves the transfer of a single hydrogen atom, increasing the likelihood of quantum mechanical tunneling to occur.⁷ Consequently, upon photolysis of iodobenzene in an H₂-doped neon matrix at 4.4 K, the formation of a benzene–HI complex is observed. Using the heavier D₂ isotopologue leads to the production of phenyl radical, indicating a notable primary kinetic isotope effect. Furthermore, with the diffusion of D₂ molecules to the reaction centers, mono-deuterated benzene gradually forms over hours, despite encountering a reaction barrier of 7.7 kcal mol⁻¹.



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