Unraveling the Wacker Oxidation Mechanisms

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The mechanism of aqueous PdCl₂ mediated olefin oxidation reaction (the Wacker process) has been studied with first-principles quantum mechanics with special emphasis on determining competitive pathways that explain the reaction’s dependence on reaction conditions. Our data, along with our interpretations of seminal experimental work was used in determining the nature of the rate laws for the reaction under high and low [Cl⁻] concentrations, shows that the rate-determining step under low [Cl⁻] conditions is not hydroxypalladation as generally believed, but intermolecular isomerization after equilibrium deprotonative water transfer. The pathway leading to anti-addition aldehyde products is only accessible when CuCl₂ is available in the reaction to specifically stabilize chloride dissociation. The controversial switch in mechanisms is caused by both the selective stabilization from CuCl₂ and the prerequisite dissociation of Cl⁻ prior to internal attack, which is inhibited by increased [Cl⁻]. Steady-state kinetics analysis from calculated results yield the experimentally known rate law for the reaction under low [Cl⁻] and high [Cl⁻] and predict the crossover point by an order of magnitude.