Evidence of O$_2$ Insertion in Palladium (II) Hydrides

Jason M. Keith, Jonas Oxgaard, William A. Goddard III

Materials Process and Simulation Center, Beckman Institute (139-74)
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125

Heterogeneous catalytic systems involving palladium(II) diamine complexes have been used to successfully oxidize alcohols with the use of molecular oxygen as a terminal oxidant. Recent attempts to determine the mechanism involved in these processes have varied. Our previous work has explained several aspects of the reaction mechanism including deprotonation of the alcohol, and the subsequent β-hydride elimination step resulting in the formation of a palladium(II)hydride (L$_2$PdH(X): X=OAc, Cl), but has heretofore ignored the role of O$_2$.

The current mechanisms believed to be active in this process can easily be divided into two classes, those which employ palladium(0) and those which do not. One class of mechanisms requires the direct insertion of O$_2$ in a palladium-hydride bond avoiding palladium zero altogether while the remaining proposals require the formation of palladium(0). Our current work has demonstrated the accessibility of a direct insertion pathway which recent experimental results have supported.