The mechanism for the rhodium-catalyzed decarbonylation of aldehydes: A combined experimental and theoretical study

The mechanism for the rhodium-catalyzed decarbonylation of aldehydes was investigated by experimental techniques (Hammett studies and kinetic isotope effects) and extended by a computational study (DFT calculations). For both benzaldehyde and phenyl acetaldehyde derivatives, linear Hammett plots were obtained with positive slopes of +0.79 and +0.43, respectively, which indicate a buildup of negative charge in the selectivity-determining step. The kinetic isotope effects were similar for these substrates (1.73 and 1.77 for benzaldehyde and phenyl acetaldehyde, respectively), indicating that similar mechanisms are operating. A DFT (B3LYP) study of the catalytic cycle indicated a rapid oxidative addition into the C(O)-H bond followed by a rate-limiting extrusion of CO and reductive elimination. The theoretical kinetic isotope effects based on this mechanism were in excellent agreement with the experimental values for both substrates, but only when migratory extrusion of 00 was selected as the rate-determining step.

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