Mechanistic Investigation of Molybdate-Catalysed Transfer Hydrodeoxygenation

The molybdate-catalysed transfer hydrodeoxygenation (HDO) of benzyl alcohol to toluene driven by oxidation of the solvent isopropyl alcohol to acetone has been investigated by using a combination of experimental and computational methods. A Hammett study that compared the relative rates for the transfer HDO of five para-substituted benzylic alcohols was carried out. Density-functional theory (DFT) calculations suggest a transition state with significant loss of aromaticity contributes to the lack of linearity observed in the Hammett study. The transfer HDO could also be carried out in neat PhCH$_2$OH at 175°C. Under these conditions, PhCH$_2$OH underwent disproportionation to yield benzaldehyde, toluene, and significant amounts of bibenzyl. Isotopic-labelling experiments (using PhCH$_2$OD and PhCD$_2$OH) showed that incorporation of deuterium into the resultant toluene originated from the $\alpha$position of benzyl alcohol, which is in line with the mechanism suggested by the DFT study.