DFT Study of the Molybdenum-Catalyzed Deoxydehydration of Vicinal Diols.

The mechanism of the molybdenum-catalyzed deoxydehydration (DODH) of vicinal diols has been investigated using density functional theory. The proposed catalytic cycle involves condensation of the diol with an MoVI oxo complex, oxidative cleavage of the diol resulting in an MoIV complex, and extrusion of the alkene. We have compared the proposed pathway with several alternatives, and the results have been corroborated by comparison with the molybdenum-catalyzed sulfoxide reduction recently published by Sanz et al. and with experimental observations for the DODH itself. Improved understanding of the mechanism should expedite future optimization of molybdenum-catalyzed biomass transformations.