Trinuclear Manganese(II) Schiff Base Complexes as Epoxidation Catalysts: UHP Compared on H$_2$O$_2$ as Oxidant

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Controlled epoxidation of alkenes with stable and efficient catalysts using environmental friendly oxidants is an important goal. Since the first epoxidation of allylic alcohols by Sharpless [1], various manganese Schiff base catalysts has been developed using different oxygen sources such as iodosylbenzene, sodium hypochlorite, hydrogen peroxide [2], alkyl hydroperoxide [3,4], molecular oxygen [5] and more recently urea-hydrogen peroxide (UHP) [6,7].

The catalytic epoxidation of styrene using urea–hydrogen peroxide and heterotrinuclear Cu(II) complexes with general formula (MnL)$^n_2$Cu(acac)$_3$, where n = 1-3 is reported. Schiff base complexes ML$_n$ involving a 3,4-diaminopyrididine bridge with free coordination site were used as the ligand, where (L)$^2$ is [(5-x-Sal)$_2$Py]$^2$ and x = H, Br or NO$_2$. The complexes were characterized by physico-chemical and spectroscopic methods. The electrochemical properties of Mn were modified upon trinuclear complex formation. The trinuclear complexes show high catalytic activity, with up to 86% conversion and 93% selectivity, while no catalytic properties were observed for the monomeric complexes. The catalyst could be reused with some loss of activity.

In summary, while conversions using UHP and H$_2$O$_2$ as primary oxidant were similar, in the case of UHP the selectivity for styrene epoxide production was better. So, UHP as a water-free oxidant could be used as a stable, cheap, and environmentally friendly oxidant, capable of use in organic solvents and for water sensitive materials. The efficiency of these catalysts was strongly dependent on the structure of the dibasic Schiff-base ligands. These results could be due to several factors, such as the nature of the metals, their ability to coordinate the reactants, the solubility of the complexes, etc.