Arene Hydroxylation and Styrene Epoxidation by Copper-Dioxygen Complexes

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Copper-dioxygen chemistry is of particular interest in dioxygen activation chemistry in biological and industrial processes. In this study, we report on endogenous arene hydroxylation of a supporting ligand and exogenous styrene epoxidation by μ-η^2:η^2-peroxo complexes.

A (μ-η^2:η^2-peroxo)dicopper(II) complex $[Cu_2(O_2)(Me_4\text{-pyxyl})]^{2+}$ (**1**) is capable of hydroxylation of benzene ring and epoxidation of styrene. To the best of our knowledge, this is the first example of the (μ-η^2:η^2-peroxo)dicopper(II) complex capable of epoxidation of styrene. Decay of **1** obeyed first-order kinetics and the activation parameters determined are $\Delta H^\ddagger$ = 65 kJ mol^{-1} and $\Delta S^\ddagger$ = -2 J mol^{-1} K^{-1}. The effects of *p*-substituents on the hydroxylation of benzene rings (R = OMe, *t*-Bu, H, and NO_2) were also studied. The Hammet plot of the first order rate constants vs. σ^+ gave $\rho = -2.0$. The epoxidation by **1** is first order in **1** and styrene, respectively, and the activation energy was determined as E_a = 41 kJ mol^{-1}. The effects of *p*-substituents on the epoxidation of styrenes (R = OMe, H, and Cl) were also studied. The Hammet plot of the second order rate constants vs. σ^+ gave $\rho = -1.9$, which is similar to that found for the arene hydroxylation performed by **1**, suggesting that the epoxidation and arene hydroxylation reactions proceed via similar mechanism involving electrophilic attack of the peroxo ligand.