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 \( \mu^{2}\eta^{2}:\eta^{2}\)-peroxo complexes.

A \( \mu^{2}\eta^{2}:\eta^{2}\)-peroxo)dicopper(II) complex \([\text{Cu}_{2}(\text{O}_2)(\text{Me}_4\text{-pyxyl})]^{2+}\) (I) is capable of hydroxylation of benzene ring and epoxidation of styrene. To the best of our knowledge, this is the first example of the \( \mu^{2}:\eta^{2}\)-peroxo)dicopper(II) complex capable of epoxidation of styrene. Decay of I obeyed first-order kinetics and the activation parameters determined are \( \Delta H^\ddagger = 65 \text{ kJ mol}^{-1} \) and \( \Delta S^\ddagger = -2 \text{ J mol}^{-1} \text{ K}^{-1} \). The effects of \( p \)-substituents on the hydroxylation of benzene rings (\( R = \text{OMe}, \text{t-Bu}, \text{H}, \text{and NO}_2 \)) were also studied. The Hammet plot of the first order rate constants vs. \( \sigma^+ \) gave \( \rho = -2.0 \). The epoxidation by I is first order in I and styrene, respectively, and the activation energy was determined as \( E_a = 41 \text{ kJ mol}^{-1} \). The effects of \( p \)-substituents on the epoxidation of styrenes (\( R = \text{OMe}, \text{H}, \text{and Cl} \)) were also studied. The Hammet plot of the second order rate constants vs. \( \sigma^+ \) gave \( \rho = -1.9 \), which is similar to that found for the arene hydroxylation performed by I, suggesting that the epoxidation and arene hydroxylation reactions proceed via similar mechanism involving electrophilic attack of the peroxo ligand.