Unravelling the Mechanism and Kinetics of Aerobic Baeyer-Villiger Oxidation of Cyclohexanone

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Abstract

This study explores the aerobic Baeyer-Villiger oxidation of cyclohexanone into ε-caprolactone using metalloporphyrin and benzaldehyde, a greener process to replace hazardous concentrated peroxyacid. The reaction mechanism involves a series of free radical reactions, identified through in-situ EPR. In this complex three-component reaction, we developed an intrinsic kinetic model based on the proposed mechanism. Utilizing a hyperbolic equation, the model well fits experimental data, describing biomimetic catalytic behavior of the aerobic Baeyer-Villiger oxidation. The reaction orders for the three reactants corroborate the kinetic model, with the activation energy of oxygen (130.27 kJ/mol) surpassing cyclohexanone (94.85 kJ/mol) and benzaldehyde (40.73 kJ/mol), implying slow initial oxygen activation while rapid subsequent benzaldehyde oxidation, making oxygen transfer and activation key steps. This unified approach to elementary reaction, mechanism, and intrinsic kinetics provides robust forecasts and lays the groundwork for additional studies, such as side reactions control and mass transfer enhancement and reactor design.

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