# MECHANISTIC MODEL OF HYDROCARBON EPOXIDATION

The researchers are using kinetics and quantum mechanical calculations to elucidate the catalytic reaction mechanism of hydrocarbon epoxidation.

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Objective: Synthetic metalloporphyrins are capable of catalyzing epoxidation of hydrocarbons at mild conditions, but their utility is limited by the ease of deactivation via the formation of μ-oxo dimers. Encapsulation of synthetic metalloporphyrins into "molecular squares" – self-assembling metal-containing systems with nano-sized pores – is designed to increase their stability, selectivity and specificity in the same way a protein framework does it for naturally occurring metalloporphyrins. Kinetic studies supported by quantum mechanical calculations should provide new clues about the reaction mechanisms that involve encapsulated synthetic metalloporphyrins and help to improve their performance as catalysts.

Approach: Kinetic studies of hydrocarbon epoxidation are conducted in batch reactors at constant temperature, and the rates of the reaction and catalyst deactivation are quantified by the disappearance of the reaction components. A microkinetic model, in which elementary steps are explicitly considered, is then developed. Rate constants required for the microkinetic model are guided by the reaction energetics, which are calculated using both Density Functional Theory (DFT) and a quantum/classical ONIOM model. For the DFT calculations and for the high-level part of ONIOM, PW91 exchange-correlation functional is used, and the LANL2DZ basis set is employed. For the low-level part of the ONIOM calculations of epoxidation, the UFF force field is utilized.

Results: The Broadbelt and Snurr groups have performed a kinetic study of epoxidation of styrene with iodosylbenzene catalyzed by non-encapsulated Mn tetraphenyl porphyrin (MnTPP). Results indicate that the orders of this reaction, assuming power law kinetics, are dependent on the concentration of the reactants. For example, the order of the reaction for styrene increases from 0.4 to 1 as the concentration of the catalyst decreases, and the order of the reaction for MnTPP decreases from 3 to 1.5 as the concentration of styrene increases. However, at high catalyst concentrations, the order of the reaction for MnTPP remains nearly constant at 0.8. The DFT and ONIOM calculations of MnTPP show that it exists in a saddle conformation with bond lengths in very good agreement with its crystal structure. Analyses of different spin states of MnTPP and the reaction intermediates with both levels of theory indicate that the concerted intermediate has the lowest energy. Studies of encapsulated MnTPP will be conducted in the near future.
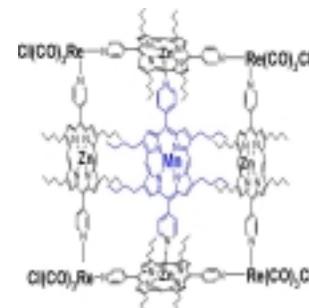
MnTPP encapsulated within a "molecular square."

metallaoxetane

↑ ΔE = 154.5 kJ/mol

radical

↑ ΔE = 12.6 kJ/mol

concerted
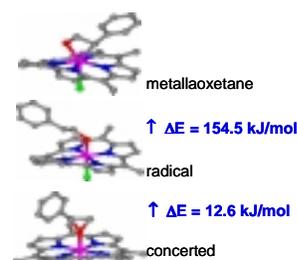
Calculated energy differences for MnTPP-styrene intermediates.
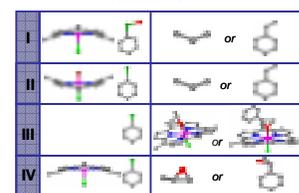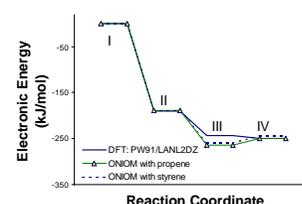
Electronic energies for reaction pathways.