

*News Item*

## Enzyme Mimics Made With Iron-Zeolites\*

A completely inorganic mimic of an enzyme has been developed by a research group at Du Pont. The mimic provides remarkable selectivity in partial oxidations of certain hydrocarbons under mild conditions.

Partial oxidation of hydrocarbons is a common industrial operation, but is usually carried out under extreme conditions with low selectivity. Chad A. Tolman, a researcher in Du Pont's central research and development department, pointed out at the national meeting of the American Chemical Society held recently in New Orleans that the most desirable products are usually bifunctional, with oxygenated carbon atoms at the ends of large, linear molecules. However, with current technology it is difficult to make bifunctional compounds from linear alkanes because of the nature of the reaction used and because the reaction preferentially occurs at the secondary C—H bonds in the middle of the chain rather than at the stronger terminal bonds.

There are enzymic reactions that, nevertheless, provide partial hydrocarbon oxidations at mild conditions and with high selectivity. Certain enzymes of cytochrome type P-450, for example, convert terminal methyl groups of linear hydrocarbons to  $-\text{CH}_2\text{OH}$  with high selectivity. It has been Tolman's hypothesis that this selectivity is the result of steric constraints to the approach of a substrate hydrocarbon to a reactive ferryl group ( $\text{FeO}$ ) inside the enzyme. He and his coworkers have constructed oxidation catalyst systems involving iron-zeolite structures in which the silicoaluminate framework of the zeolite replaces the protein of the enzyme.

The first of the new catalysts were made with iron phthalocyanine in X- or Y-type zeolites. These catalysts did exhibit a small catalytic effect. However, Tolman and coworkers were able to increase the selectivity for oxidation of *n*-octane in preference to cyclohexane from 1.2:1 to 10:1 by adding ammonium ions.

The latest catalysts contain iron ions without an organic ligand, in a narrow zeolite channel 5 Å in diameter. Molecular oxygen is the oxidizing agent, and molecular hydrogen is necessary as a reducing cofactor. The catalyst also contains Pd(0), which is necessary for it to function with oxygen. Tolman believes that the palladium catalyzes the reaction of molecular hydrogen and oxygen to form hydrogen peroxide, which reacts with the iron to form the reactive ferryl.

In the 5 Å system, the observed octane to cyclohexane selectivity is more than 150:1, with preferred hydroxylation of the terminal methyl group of the *n*-octane taking place at conditions of 25°C and about 50 psig. The enzyme mimic concept may not yet be commercially important, but it does demonstrate the possibility of applying an understanding of enzyme function to the design of a completely inorganic mimic.

Tolman is now in the process of exploring zeolites with channels large enough to allow oxidation products to escape while still giving good selectivity. The experiments with the very small channels, while demonstrating the desired selectivity, also resulted in entrapment of products in the zeolites.

Chicago

JOSEPH HAGGIN

\* Reprinted with permission from *Chem. Eng. News*, September 28, 1987, 85 (39), 27. © 1987 American Chemical Society.