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Nota di contenuto	From the Contents: Hydrocarbon Oxygenation by Heme-Thiolate Enzymes Efficient and Selective Alkane Hydroxylation Reactions Catalyzed by the Fungal Peroxygenase AaeAPO Hydrocarbon Hydroxylations Catalyzed by AaeAPO: Evidence of Radical Intermediates and Kinetic Isotope Effects.
Sommario/riassunto	In this thesis, Xiaoshi Wang investigates the function and mechanism of a newly discovered heme-thiolate peroxygenase, AaeAPO. This enzyme class comes from Agrocybe aegerita and is used in the conversion of inert hydrocarbons to alcohols. Xiaoshi's work focuses on an extracellular P450 enzyme which is not limited in its stability and lack of solubility and therefore is relevant for widespread industrial use. The author demonstrates that the peroxygenase catalyzes a wide range of reactions. In some cases the author even describes very difficult transformations in molecules that are highly inert. Her detailed investigations provide a mechanistic framework for how the peroxygenase catalyzes such a large number of reactions. A major highlight of this thesis is the identification of key short-lived intermediates in the catalytic cycle of the peroxygenase, using rapid kinetic and spectroscopic methods, as well as the elucidation of the

1.

thermodynamic properties of these high-energy intermediates. This work adds new insight into an important class of enzymes.