

甲烷单加氧酶的化学模拟: 酚氧双羧酸根桥联Fe~2(III)和 Mn~2(III)配合物合成、表征及催化性能
魏俊发,何地平,俞贤达,金道森

陕西师范大学化学系,西安(710062);中国科学院兰州化学物理研究所,兰州 (730000)

收稿日期 修回日期 网络版发布日期 接受日期

摘要 合成表征了酚氧、双羧基桥联双组氨酸的手性双铁核配合物和双锰核配合物,研究了它们催化亚碘酰苯对烯烃的环氧化反应和对环烷烃的羟化反应。结果表明这种Fe~2(III)和Mn~2(III)配合物均是有效的甲烷单加氧酶(MMO)模型化合物,其中Fe~2配合物能较好地再现MMO的某些性质,如电子光谱等。Fe~2配合物催化苯乙烯环氧化反应生成环氧苯乙烯的产率为840%(以催化剂计),且R-(+)-构型对映体过量(e.e.)达45.4%。相庆的Mn~2配合物则以7080%产率给出环氧苯乙烯,R-(+)-构型对映体过量51.6%。Mn~2配合物还能够催化环己烯和环己烷的氧化反应,产物及其分布分别为环氧环己烷3880%、环乙烯醇603%、环己烯酮189%和环己醇1053%、环己酮639%(以催化剂计)。EPR研究表明MM=O是反应的活性中间体。

关键词 [甲烷单加氧酶](#) [铁络合物](#) [锰络合物](#) [催化性能](#) [苯P](#) [烯烃](#) [环氧化反应](#)

分类号 [0611.662](#)

Model systems for methane monooxygenase: Synthesis, characterization and catalytic property of (μ -phenoxo)bis(μ -carboxylato) dimetal [Fe(III), Mn(III)] complexes

Wei Junfa, He Diping, Yu Xianda, Jin Daosen

Shanxi Normal Univ, Dept Chem, Xian(710062); Lanzhou Inst Chem Phys, CAS, Lanzhou(730000)

Abstract A methane monooxygenase (MMO)-like dinuclear metal (iron/manganese) complex which consists of a [μ -phenoxo]bis(μ -carboxylato)dimetal core and a chiral phenolic ligand bearing two chelating arms of L-histidine has been synthesized and characterized. Its catalytic properties in olefin epoxidations and in alkane hydroxylations were investigated with iodosylbenzene as a terminal oxidant. It has been found that the Fe~2 complex nicely reproduces some qualitative characteristics of electronic spectrum of MMO. It is able to catalyze the epoxidation of styrene giving styrene oxide in a 840% yield (based on the catalyst) and a 45.4% e.e. for the R-(+)-enantiomer. Similarly, using the Mn~2 analogue complex, styrene gave corresponding epoxide in a 7080% yield and a 51.6% e.e. for the R-enantiomer and cyclohexene gave epoxy cyclohexane (3880%) as a major product together with cyclohexenol (603%) and cyclohexenone (189%). In addition, the Mn~2 complex catalyzed the hydroxylation of cyclohexane giving cyclohexanol (1053%) and cyclohexanone (639%). EPR evidence suggested the presence of a high valent metal-oxo intermediate in the reactions.

Key words [IRON COMPLEX](#) [MANGANESE COMPLEX](#) [CATALYTIC BEHAVIOUR](#) [BENZENE P](#) [ALKENE EPOXIDATION REACTION](#)

DOI:

通讯作者

扩展功能

本文信息

▶ [Supporting info](#)

▶ [PDF\(585KB\)](#)

▶ [\[HTML全文\]\(0KB\)](#)

▶ [参考文献](#)

服务与反馈

▶ [把本文推荐给朋友](#)

▶ [加入我的书架](#)

▶ [加入引用管理器](#)

▶ [复制索引](#)

▶ [Email Alert](#)

▶ [文章反馈](#)

▶ [浏览反馈信息](#)

相关信息

▶ [本刊中 包含“甲烷单加氧酶” 的相关文章](#)

▶ [本文作者相关文章](#)

- [魏俊发](#)
- [何地平](#)
- [俞贤达](#)
- [金道森](#)