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杯[6]芳烃－双金属卟啉仿P450酶模型的研究 2: 轴向配体对环己烯 环氧化反应的影响及反应动力学考察

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摘要 研究了轴向配体对杯[6]芳烃－双金属卟啉仿P450酶模型催化环己烯环氧化反应的影响,并考察了反应的动力学规律,结合UV-vis监测反应的结果,提出了一种可能的反应机制。

关键词 杯芳烃 卟啉 环己烯 环氧化反应 反应动力学 反应机理

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Calix[6]arene-bismetalloporphyrins as enzyme models for cytochrome P450 2: Influence of axail ligand on the epoxidation of cyclohexene and kinetic law of the reaction

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Abstract The influence of axial ligand on the epoxidation of cyclohexene under the catalysis of manganito-calix[6]arene-bisporphyrin P450 enzyme model compound was investigated. It was found that the stronger the electron donating ability of the axial ligand the more effective is the auxocatalysis. The result also shows that the larger the cavity, the higher the catalytic activity. The OH on the calixarene also plays a certain role.Such findings strongly suggest that there are two parameters that enhance the catalysis,namely electronic factor and the steric interaction of the axial ligand. Kinetic study indicated that with the concentration of catalyst varying within the range of 5. 0*10^-^5～2.5*10^-^4mol.L^-^1,the rate of epoxidation increased first, then approached a constant value as the concentration reached 2.0*10^- ^4mol. L^-^1,indicating of a less reactvie μ-OXOMn(IV) dimer which lower the effective concentration while the reaction order varies from 1 to zero.The optimum concentration is 2.0*10^-^4mol.L^-^1. Variation of the concentration of the cyclohexene causes the order of epoxidation changing from 1 to zero, indicating that cyclohexene is involved in the rate determining step of the catalytic reaction only at low concentration. It was found that the epoxidation under the catalysis of Mn(Ⅲ)Por.(Cl) abides Michaelis-Menten behavior withv~m~a~x=2.58*10^-^2.mol.L^-^1.min^-^1,Michaelis- Menten constant=0.0279 and K~c~a~t=206.4min^-^1.On the basis of all the experimantal results,a mechanism was proposed.

Key words CALIXARENE PORPHYRIN CYCLOHEXENE EPOXIDATION REACTION REACTION KINETICS REACTION MECHANISM

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