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Dioxygen Affinities and Catalytic Epoxidation Performance of Transition-Metal Hydroxamates

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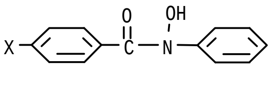
Abstract: The dioxygen affinities and catalytic epoxidation performance of transition-metal hydroxamates were investigated for the first time. The effects of substituents on these properties were also discussed in the paper.

keywords: Transition-metal hydroxamates; dioxygen affinities; catalytic epoxidation.

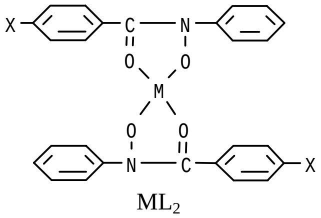
Hydroxamic acids and their derivatives are easily synthesized and have been extensively used as analytic reagents and medicines[1, 2]. Besides, palladium hydroxamates were employed to catalyze olefins preparing unsaturated esters by means of molecular oxygen[3]. Hydroxamic acid can form squaric tetradentate complex, which is possibly endowed with the properties of carrying oxygen and mimicking oxygenase like porphyrins, Schiff bases and macrocyclic ligands[4]. So the dioxygen affinities and catalytic epoxidation performance of transition-metal hydroxamates, which were unreported so far, were investigated in this paper. Oxygenation equilibrium constants of complexes were first measured in pyridine. The complexes as mimetic monooxygenase were also first employed to catalyze the epoxidation reaction of styrene.

Figure 1. Structures of ligands and complexes



LH

L^1H: X=H,
L^2H: X=Cl,
L^3H: X=NO_2,
L^4H: X=OCH_3,
L^5H: X=$OCOCH_3$,
L^6H: X=OCH_2CH_2OH,



ML_2
M=Co (II), Cu (II), Ni (II), Mn (III)

Except for ML_2^4, ML_2^6, the other complexes were prepared by the method of Majumdar[5]. ML_2^4, ML_2^6 were supplied by our laboratory. The structures of L^4H, L^6H and their complexes were characterized by IR, ^{1}HNMR, MS and elemental analysis.

Oxygen Uptake Measurements

The oxygenation equilibrium constants were determined by the method of Chen[6] in the presence of pyridine as solvent and axial ligand. The concentration of the complex is about 5×10^{-3} mol.dm^{-3} and the partial pressures of dioxygen is 97 KPa. The equilibrium constants (Ko_2) were calculated as following:

$$CoL_2 + B \rightleftharpoons CoL_2B \qquad CoL_2B + O_2 \rightleftharpoons CoL_2BO_2$$

$$Ko_2 = \frac{[CoL_2BO_2]}{[CoL_2B].Po_2}$$

B, Po_2 represent axial base and partial pressure of oxygen respectively. Thermodynamic parameters $\triangle H°$, $\triangle S°$ were determined from variation of Ko_2 and $K'o_2$ over a range of temperatures.

Catalytic Epoxidation of Styrene.

To a solution of bromobenzene (0.5 mmol), imidazole (0.1 mmol), styrene (0.5 mmol)and iodosobenzene (1 mmol) in acetonitrile (4 mL) was added MnL_2Cl (0.02 mmol). The resulting solution was vigorously stirred for 1h at 25℃ and were analyzed by GC (SE 30 column).

Results and Disussion

Oxygenation of transition-metal hydroxamates

The oxygenation constants and thermodynamic constants of these complexes are presented in **Table 1**. The data in **Table 1** indicate the oxygenation constants were significantly influenced by the electronic properties of substituents on aromatic rings. The bigger oxygenation constant is, the higher dioxygen affinity is. The dioxygen affinities of complexes decrease in the order $CoL_2^5 > Co\ L_2^6 > Co\ L_2^4 > Co\ L_2^1 > Co\ L_2^2 > Co\ L_2^3$. The species which are substituted by electron-releasing groups on the aromatic rings show high dioxygen affinities. The electron-releasing group on aromatic ring *via* π-conjugation system can increase electron density of central metal ion so that the Co (II)-dioxygen bond was stabilized[6]. In contrast, the affinities of complexes were decreased by electron-withdrawing groups. So the dioxygen affinities of CoL_2^3 containing strong electron-withdrawing group (NO_2） is the least. The affinities of ML_2^1 based on various metal ions decrease in the order Cu (II)～Co (II)＞Ni (II) at 15℃. The species with high dioxygen affinities have small values of entropy and enthalpy. This suggests the data of entropy and enthalpy also can be applied to predict the dioxygen affinities of complexes.

Table 1. Equilibrium Constants and Thermodynamic Constants for Oxygenation of Complexes.

Complexe	t (℃)	LnKo$_2$ (mm^{-1})	ΔH^o (KJ.mol^{-1})	ΔS^o (J.K^{-1}.mol^{-1})
CoL^1_2	-5	-4.86	-35.37±0.07	-172.33±0.03
	15	-5.96		
	25	-6.47		
CuL^1_2	15	-5.51		
NiL^1_2	15	-7.32		
CoL^2_2	-5	-5.68	-26.34±0.03	-145.84±0.07
	15	-6.50		
	25	-6.91		
CoL^3_2	-5	-5.76	-31.02±0.01	-163.63±0.04
	15	-6.73		
	25	-7.15		
CoL^4_2	-5	-3.54	-43.81±0.03	-192.91±0.09
	15	-4.91		
	25	-5.49		
CoL^5_2	-5	-2.44	-47.79±0.02	-199.03±0.07
	15	-3.93		
	25	-4.57		
CoL^6_2	-5	-3.07	-43.17±0.01	-186.61±0.04
	15	-4.42		
	25	-5.01		

Catalytic Epoxidation of Styrene

In order to investigate the properties of complexes as mimetic monooxygenase, these complexes were employed to catalyze the epoxidation of styene. The experimental results are listed in **Table 2**. As illustrated in **Table 2**, a very obvious relationship exists between of catalytic activities of complexes and the electronic properties of substituents on the aromatic rings. The catalytic activities of complexes with various substituents decrease in the order $Cl > H > OCH_2CH_2OH > NO_2 > OCOCH_3 > OCH_3$. Those complexes substituted by electron-releasing groups show poor catalytic activities. However, the species with mild electron-withdrawing group (Cl) is the most efficient catalyst for this reaction. It is due to that the complexes are activated toward electron-seeking oxidation attack and the catalytic activities are decreased in the presence of electron-releasing groups. On the contrary, The aromatic ring is deactivated by halogen atom (Cl), which can prevent the catalyst from oxidation degradation. On the other hand, the π - awarding is increased through p-πconjugation between halogen atom and aromatic ring,

Table 2. epoxidation of styrene catalyzed by MnL_2Cl

Cat.	Conv. (%)	Epoxide yield (%)	Selectivity (%)
MnL^1_2Cl	43.90	41.12	93.66
MnL^2_2Cl	53.62	53.62	100
MnL^3_2Cl	34.00	34.00	100
MnL^4_2Cl	22.67	22.67	100
MnL^5_2Cl	31.06	31.06	100
MnL^6_2Cl	39.55	37.23	94.13

which is favorable for the formation and stability of active Mn (V)=O complex[7]. So the activity of MnL^2_2Cl is the best. The catalytic activity of MnL^6_2Cl is superior to that of MnL^4_2 Cl. This is attributable to the ability of terminal hydroxyl group to stabilize the active Mn (V)=O complex[8]. The effects of other factors on the epoxidation yield of styrene will be discussed in the near future.

As expected, the transition-metal hydroxamates show satisfactory properties of mimetic oxygen carriers and monooxygenase, which are comparable with the extensively investigated Schiff bases complexes.

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