Notes

Catalytic Activities of Pt(II), Pd(II) and Ni(II)-diphosphine Complexes for Styrene Oxidation

Young-Je Cho†, Dong-Cheol Lee, Hwa-Jung Lee, Kyung-Chae Kim, and Yu-Chul Park*

†Central Research Institute, POSCO Chemical Co. Ltd., Sungnam 462-120, Korea
Department of Chemistry, Kyungpook National University, Taegu 702-701, Korea
Received June 11, 1996

Soluble transition metal complexes are used in the control of selective oxidation of olefins.[1] The direct oxidation of olefins with transition metal-phosphine complexes to obtain oxygenated intermediate is a particularly attractive synthetic pathway.[2] It is generally recognized that unsaturated ketones, aldehydes or other electronegatively substituted alkenes can be easily oxidized with H_2O_2 under basic conditions.[3] The nucleophilic addition of hydroperoxide anion to carbon-carbon double bond can be promoted by electron withdrawing substituents. From this point of view, transition metal ion is also capable of activating unsubstituted alkenes toward nucleophilic attack.[4] Our studies on styrene oxidation are focused on metal-diphosphine catalysts. The catalyst systems are designed to imploy metals and diphosphine ligands possessing appropriately selected electronic and steric properties. A discussion is also included concerning the origin of selectivity and yield based on mechanistic features.

When 35% H_2O_2 was added to a dichloroethane solution of metal-diphosphine complex containing an excess of styrene, direct oxidation of styrene took place. Identification of oxidation products was made with GC-Mass and GC by comparision with authentic samples. The overall product distribution and catalytic activities of metal-phosphine complexes are listed in Table 1. It is useful to consider the basic mechanistic features of this catalytic reaction. While a nucleophile does not add with ease to an unactivated double bond, it may readily react with an olefin coordinated to a transition metal. The diphosphine catalysts for styrene oxidation using H_2O_2 as terminal oxidant seems to play a bifunctional role in the system; i) they can exploit their basic behavior to enhance H_2O_2 reactivity through the formation of the hydroperoxide anion and Metal-OOH species ii) they activate unreactive styrene toward nucleophilic attack. A mechanistic basis for the oxidation process, the chemistry so far reported suggests for the active metal complexes the following set of equlibria.

$$M^+ + ol \rightleftarrows M(ol)^+ \quad (1)$$

$$M^+ + H_2O_2 \rightleftarrows MOOH + H^+ \quad (2)$$

$$MOH + H_2O_2 \rightleftarrows MOOH + H_2O \quad (3)$$

ol = styrene

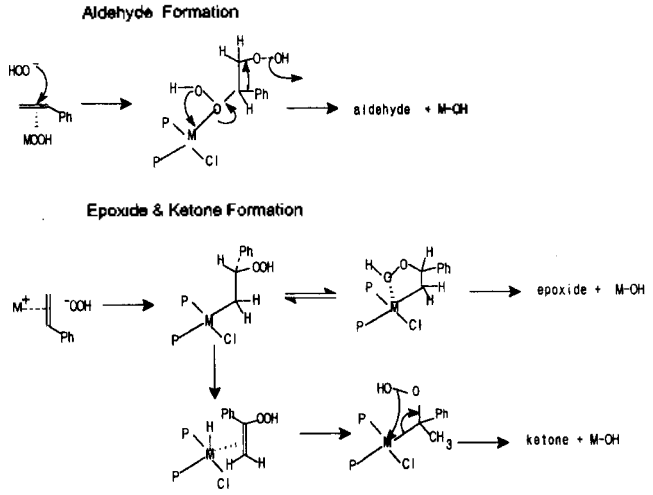
Based on product distribution and previously reported scheme,[5] a plausible mechanism for styrene oxidation is proposed in Scheme 1.

Pd-containing catalysts were found to show higher activities than Ni and Pt catalysts as shown in Table 1. This can be explained by metal size and electron density on the metal center which affect the formation of the activated metal-olefin complexes. The soft metal Pd(4d) can accept the electrophilic attack of styrene. The π-electron in carbon double bond readily transfers to Pd-phosphine complexes, and thus, nucleophilic attack on an olefin carbon in the activated Pd-olefin complex is much available. A relative hard metal, Ni can not effectively accept the electrophilic attack, making the olefin less activated for nucleophilic attack. On the other hand, the results obtained with Pt species must be carefully regarded. Turn over frequencies (TOF) of Pt systems are about 3 fold lower than those of Pd systems. The effective ionic radii of Pt(II) ion (74 pm) is slightly smaller than Pd(II) ion (78 pm), in addition, Pt(II) complexes have

Table 1. Catalytic activities of metal-diphosphine complexes for styrene oxidation

Run	Complexes		Product selectivity (%)				TOF
			A	B	C	D	
1	[$PtCl_2$(dppm)]	4.5	61.7	20.5	4.4	13.2	3.4
2	[$PtCl_2$(dppe)]	2.3	61.0	18.5	4.0	16.5	1.7
3	[$PtCl_2$(dppp)]	4.3	59.1	21.6	1.1	18.2	3.2
4	[$PtCl_2$(dppety)]	1.1	71.0	11.8		17.2	0.8
5	[$PtCl_2$(chirapos)]	3.6	54.8	30.4	3.7	11.1	2.7
6	[$PtCl_2$(dmpe)]	0.8	58.4			41.6	0.6
7	[$PdCl_2$(dppm)]	15.6	21.7	0.4	0.4	77.4	11.7
8	[$PdCl_2$(dppe)]	7.1	35.5	4.7		59.8	5.4
9	[$PdCl_2$(dppp)]	9.8	27.9	14.3	3.4	54.4	7.4
10	[$PdCl_2$(dppety)]	2.6	62.5	22.5		15.0	2.0
11	[$PdCl_2$(dppe)]	0.5				90	0.4
12	[$PdCl_2$(dppm)]	8.7	49.6	44.2		3.8	6.6
13	[$NiCl_2$(dppe)]	2.6	76.9	23.1			2.0
14	[$NiCl_2$(dppp)]	4.7	60.6	31.0	5.6	2.8	3.6
15	[$NiCl_2$(dppety)]	2.0	86.6	13.4			1.5

Experimental conditions: complex, 0.1 mmol; styrene, 15 mmol; H_2O_2, 5 mmol; solvent; dichloroethane 10 mL, temperature; 83 °C, reaction time; 2 hr product A; benzaldehyde, B; styreneoxide, C; phenylacetaldehyde, D; acetophenone, conversion(%)=100× [oxdation product]/[initial styrene] TOF(turn over frequency)= prouct mmol/Pb mmol/hr.



Scheme 1.

6d orbital. This induces a higher electron density on the metal, which therefore is much available for back donation(M → olefin) in metal olefin complex formation.

The effects of varying ring size of diphosphine complexes are illustrated in Figure 1. The reaction rates(TOF) showed a dependence on the chelating patterns. [MCl_2(dppe)] complexes(M=Pt, Pd and Ni) forming 5-membered chelate ring gave rise to worse catalysts. The chelating patterns are important to olefin activation. The optimum ring size for metal having natural bond angle is five in forming chelate complexes. It has long been known that the dppe is an excellent chelate ligand. The dppm chelates a four membered ring complex, and thus, the ring is strained. The chelating tendency also decreases as the chain length increases, so that, for the ligands $Ph_2P(CH_2)_nPPh_2$, the tendency to chelation is greatest for n=2.[3] The five membered ring complexes showed lower activities due to a higher electron density on the metal center. Exceptionally, chiral diphosphine complex, [$PtCl_2$(chiraphos)] forming 5-membered ring, accelerated the rate comparing to the other complexes. Sinigaria and co-workers[4] have reported chiral diphosphine complex, [$Pt(CF_3)X$(chirapos)], efficiently catalyzes the epoxidation of olefin. This catalytic feature is also observed in [$PtCl_2$(chirapos)] complex. All Pt(II) catalysts in Table 1 performed an aldehyde selective oxidation. However, styrene were considerably converted to epoxide in a case of [$PtCl_2$(chirapos)] catalyst(run 5, selectivity 30.4%).

Based on π-electron accepting property of phosphorus atom in phosphine ligands, One can deduce the catalytic activities for olefin oxidation. The substituents(phenyl or methyl group) of phosphorus atom and ligand type (saturated or unsaturated) can change the π-electron accepting property of phosphorus atom. The back donation of π-electron (Metal → Phosphine) is interrupted by electron donating methyl group(dmpe; run 6 and 11) and -electron of unsaturated ligand(dppety; run 4, 10 and 15), when activated species, metal-olefin compexes, are formed.

The screening of the active complexes for styrene oxidation suggests viability of obtaining the acetophenone selective Pd-diphosphine catalyst. The studies to improve activity and selectivity of diphosphine complexes are in progress.

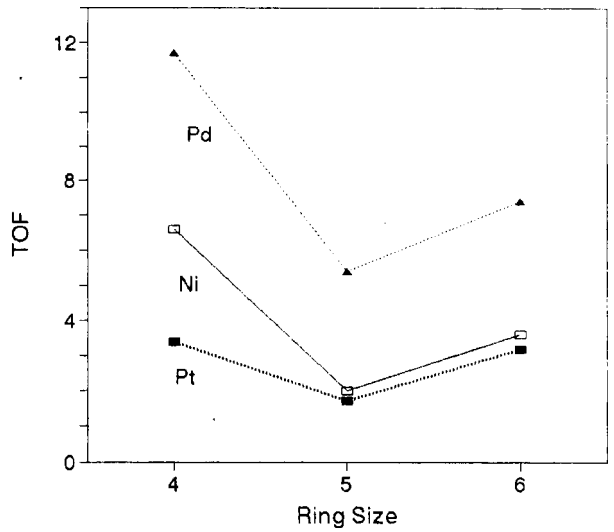


Figure 1. Effects of varying ring size of metal-diphosphine complexes for the rates of styrene oxidation (4-membered ring; [MCl_2(dppm)], 5-membered ring; [MCl_2(dppe)] and 6-membered ring; [MCl_2(dppp)]).

Experimental

Preparation of Compounds

[MCl_2(P^P)] (M=Pt,[6~7]Pd,[7]Ni[8]) Complexes. K_2MCl_4(M=Pt or Pd, 0.72 mmol) was dissolved in 1 mL hot water and 0.5 mL conc. HCl. n-Propanol (60 mL) was added and stirred for 15 min. The equimolar diphosphine ligand (0.72 mmol) was added and stirred for 30 min. and then the solution was refluxed for 2 hr. The pale yellow solid, [MCl_2(P^P)](M=Pt or Pd), was cooled and collected by vacuum filteration. The solid was washed with an ice-water and an ether and dried in vacuo for 12 hr. [$NiCl_2$(P^P)] complexes were prepared by similar procedures. [MCl_2(P^P)] complexes (M=Pt, Pd, Ni) were air stable in the solid state. The prepared complexes have been characterized by ^1H nmr, ^{31}P nmr, UV-visible spectroscopies and in most cases elemental analyses.[7,8]

here, P^P=diphosphine ligands
P^P=Ph_2P-(CH_2)n-PPh_2
n=1, bis(diphenylphosphino)methane(dppm)
n=2, 1,2-bis(diphenylphosphino)ethane(dppe)
n=3, 1,3-bis(diphenylphosphino)propane(dppp)
P^P=$(CH_3)_2P$-CH_2CH_2-$P(CH_3)_2$
1,2-bis(dimethylphosphino)ethane(dmpe)
P^P=Ph_2P-CH=CH-PPh_2
1,2-bis(diphenylphosphino)ethylene(dppety)

$$P\text{^}P=Ph_2P\text{-}\underset{CH_3}{CH}\text{-}CH\text{-}PPh_2$$

2S,3S-bis(diphenylphosphino)butane(chirapos)

Materials and Instruments

Styrene (Aldrich) was purified by passing it through neutral alumina and distilled and stored under N_2 in the dark. Diphosphine ligands such as dppm, dppe, dppp, dppety, dmpe and chirapos (all from Aldrich) were commercial pro-

ducts and used without purification. Hydrogen peroxide (Junsei) was commercial product. GC measurements were taken on a Hewlett-Packard 5890 gas chromatograph equipped with a Hewlett-Packard 3390A integrator. Identification of products was made with Hewlett-Packard 5970 GC-MASS. UV-visible spectra were recorded on a Shimadzu Model 2100 spectrophotometer. Elemental analyses were taken on a Hewlett-Packard Model 185B elemental analyzer.

Catalytic Reactions

Catalytic oxidations were carried out in a 25 mL round bottom flask equipped with side arm fitted with a screw capped silicon septum. In a typical experiment, [$PdCl_2$(dppm)] (56 mg, 0.1 mmol) was put into a flask. Solvent (10 mL) was added and followed by a styrene (15 mmol). After stirring for a few minutes, 35% H_2O_2 solution (0.5 mL, 5 mmol) was injected and the temperature was controlled and the time was started. The reaction was monitored with GC by periodic sampling. Relative oxidation rates were calculated from the concentration of product formation and were expressed in TOF (Turn Over Frequency=[oxidation product]/[catalyst]/hr).

Acknowledgment. This work has been supported by Korea Science & Engineering Foundation (93-0500-08-01-3) and Basic Science Research Institute Program (96-3403), Ministry of Education, Korea.

References

1. (a) Dargo, R. S.; *Coord. Chem. Rev.* **1992**, *117*, 185. (b) Akhrem, I. S.; Volpin, M. E. *Russ. Chem. Rev.* **1990**, *59*, 1906. (c) Pignolet, L. H.; *Homogenous Catalysis with Metal Phosphine Complexes*; Plenum Press : New York, 1983. (d) Drent, E.; *Pure & Appl. Chem.* **1990**, 62, 661. (e) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic: New York, 1981.
2. (a) Cusumano, J. A.; *Chemtech*, **1992**, *22(8)*, 482. (b) Gore, A. *Chemtech* **1995**, *25(3)*, 6.
3. Puddephatt, R. J.; *J. Chem. Soc. Rev.* **1983**, *12*, 99.
4. Sinigalia, R.; Michelin, R. A.; Pinna, F.; Strukul, G. *Organometallics* **1987**, *6*, 728.
5. Strukul, G.; Smigalia, R.; Zanardo, A.; Pinna, F.; Michelin, R. A. *Inorg. Chem.* **1989**, *28*, 554.
6. (a) Appleton, T. G.; Bennet, M. A.; Tomkins, I. B. *J. Chem. Soc. Dalton.* **1976**, 439. (b) Stern, E. W.; Maple, P. K. *J. Catal.* **1972**, *27*, 134.
7. (a) Muir, L. M.; Grossel, M. C.; Brown, M. P. *J. Chem. Soc. Dalton.* **1986**, 1955. (b) Park, Y. C.; Cho, Y. *J. Bull. Kor. Chem. Soc.* **1889**, *10*, 220. (c) Park, Y. C.; Kim, K. C.; Cho, Y. J. *J. Kor. Chem. Soc.* **1992**, *36*, 5, 685.
8. (a) Cooper, S. J.; Brown, M. P.; Puddephatt, R. J. *Inorg. Chem.* **1981**, *20*, 1374. (b) Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 2267.

Liquid Chromatographic Resolution of Racemic Cyclic Amines

Myung Ho Hyun*, Jong Sung Jin, and Wonjae Lee*†

Department of Chemistry, Pusan National University, Pusan 609-735, Korea
†LG Chemical Ltd., Science Town, Taejon 305-380, Korea
Received October 31, 1996

Optically active cyclic amines are abundant in nature and often show significant biological activity.[1] In addition, optically active cyclic amines have been widely employed as important intermediates or chiral building blocks in synthesizing biologically active natural products.[2] Consequently, optically active cyclic amines have been subjected to asymmetric synthesis.[3] In this context, the methods which allow a simple and accurate assessment of the enantiomeric purity of chiral cyclic amines synthesized asymmetrically or obtained from nature are required. Among various techniques, liquid chromatographic separation of enantiomers on chiral stationary phases (CSPs) has been known to be one of the most accurate and convenient means in determining the enantiomeric purity of optically active chemicals.[4]

Previously, several CSPs have been employed in resolving the enantiomers of chiral cyclic amines without much real understanding how CSPs distinguish between enantiomers.[5] However, CSP **1**, recently designed by Pirkle specifically for the resolution of α-arylpropionic acids, commercialized [(S,S)-Whelk-O 1] by Regis Chemical Company (Morton Grove, Illinois, U.S.A.) and found to be applicable in resolving broad spectrum of racemates,[6] has not been utilized in resolving racemic cyclic amines.

In this study, we wish to report that CSP **1** can be successfully utilized in resolving the enantiomers of racemic cyclic amines **2-4** as their *N*-α- and/or *N*-β-naphthoyl derivatives and wish to propose a possible chiral recognition mechanism based on the chromatographic resolution results and from the study of CPK molecular models. In addition, the resolution of the corresponding derivatives of cyclic amino esters **5**, which are structurally similar to cyclic amines, is reported.

CSP **1** possesses a strong π-acidic 3,5-dinitrobenzamide group. To utilize the strong π-acidic group of CSP **1** for the enantioselective π-π donor acceptor interaction with analytes,[7] racemic cyclic amines **2-4** available from prior study[5c] and cyclic amino esters **5** were derivatized by treating with α-naphthoyl and/or β-naphthoyl chloride. The strong π-basic na-