



Catalytic Oxidation of Internal and Terminal Alkenes by Using Pd (II) Complexes of Schiff Base Derivatives as Catalyst

Himanee Bisht^a, Priyanka Sagar^{a*}

^aDepartment of Chemistry, S.S.J. Campus, Kumaun University,
Almora, (Uttarakhand), India

Abstract: Pd (II) complexes of Schiff base derivatives were found highly efficient towards the catalytic oxidation of internal alkenes and terminal alkenes in DMF solvent under normal pressure of molecular oxygen. No diminished catalytic activity was observed even after 6-8 repeated catalytic runs. Effect of extra ligand on the rate of oxidation, nature and percentage yield of products was investigated. On the basis of kinetics and other experimental observations, a reaction mechanism has also been proposed.

Keywords: Pd (II) Complexes; Catalytic oxidation; Internal alkenes; Terminal alkenes

I. Introduction

Transition metal complexes or the metal centres either in finely dispersed forms or in their salt or complex form have long been used as catalyst towards the various catalytic reactions i.e., Oxidation, Hydrogenation of various organic substrates [1-26]. Catalytic oxidation of organic compounds such as alkanes, alkenes, aromatic hydrocarbons, alcohols, aldehydes and epoxides lead to important products and find applications in all areas of chemical industries [27-38]. Catalytic oxidation of cyclohexanol-cyclohexanone mixture is an important industrial process and these products are used largely in the manufacture of adipic acid and caprolactum. Acetaldehyde, p-xylene, toluene and benzene are the parent compounds for the manufacture of million tonnes of valuable polymers and solvents. These are mainly produced via the catalytic oxidation of the above substrates by molecular oxygen [39-44]. Besides molecular oxygen, H₂O₂, iodosylbenzene, pyridine-N-oxide and t-BuOOH etc. have also been used as oxidant [45-46].

The present paper reports the successful use of Pd (II) Schiff base complexes as catalysts for the catalytic oxidation of terminal and internal alkenes under normal pressure of molecular oxygen. t-BuOOH and hydrogen peroxide were also used as oxidant or as co-oxidant with molecular oxygen.

II. Experimental

A. Materials and Equipments

Aldrich, Fluka, E-Merck branded chemicals were used throughout the investigation. Analytical grade solvents were always used and the same were distilled under nitrogen / argon atmosphere prior to use. Ultra pure quality of N₂, Ar and O₂ were always used. Solvents were preserved on molecular sieves (4A) under nitrogen / argon atmosphere. Carbon, Hydrogen, Nitrogen was estimated by sending the sample to RSIC Chandigarh (on payment basis). Halogen was estimated according to literature method [47]. Vibrational and NMR spectra of complexes were recorded on Perkin Elmer 1800 (FT IR) and Bruker Avance II 400 NMR Spectrophotometer respectively. The product mixture were analysed by TLC using silica gel-coated plastic sheets (Merck silica gel F254) and by GLC (5700 Nucon gas chromatograph, using SE-30, Carbowax-20M or OV-17 column.). Schiff base and their palladium complexes were prepared, purified and characterized by using literature methods [48-49].

B. Preparation of Palladium Complex

Preparation of catalysts :

Preparation of di-μ-chloro-bis(benzylideneaniline-C¹N') palladium (II) [Pd₂(L1)₂Cl₂] 1 {where L1 = N-[(E)-phenylmethylidene]aniline}

Methanolic solution (15 ml) of Schiff base (4.88 mmol; 0.8844 g) in 15 ml of methanolic solution of Palladium chloride (2.44 mmol; 0.4330 g) was added dropwise with constant stirring at 30 °C. After complete addition of L1, the mixture was stirred for 1h more. The greenish yellow precipitate of the subject compound appeared slowly. Palladium complex was filtered and washed several time with methanol. Finally the compound was dried under vacuum. The other three palladium complexes [Pd₂(L2)₂Cl₂] 2, [Pd₂(L3)₂Cl₂] 3, [Pd₂(L4)₂Cl₂] 4 {where L2 = N-(diphenylmethylidene)aniline, L3 = 2-(phenylimino) methylphenol, L4 = N-(2-methoxyphenyl) methylidene aniline were prepared following the same procedure.

Yield: 1=80%, 2=80%, 3=82%, 4=81%

m.p.: 245 °C. Anal. Data found: M% 32.5; N, 3.22; C, 47.42; H, 2.88; Cl, 10.88; [Pd₂(L1)₂(Cl)₂] 1 Calcd: M % 33.0; N, 4.35; C, 48.48; H, 3.13; Cl, 11.01. IR(KBr): ν_{C=N} 1599 cm⁻¹, ν_{C=C} 1572 cm⁻¹, ν_{C-N} 1317 cm⁻¹, ν_{C-H} (benzene-out of plane) 692, 752, 760, 765, cm⁻¹, μ Pd-Cl 310-360 NMR: 7.2-7.5(m), 7.9(m), 8.4(s,1).

m.p.: 280 °C. Anal. Data found: M % 26.5; N, 2.45; C, 56.86; H, 2.24; Cl, 8.46; [Pd(L2)₂(Cl)₂] **2** Calcd: M % 26.7; N, 3.52; C, 57.31; H, 3.54; Cl, 8.90. IR (KBr): $\nu_{\text{C=N}}$ 1600 cm⁻¹, $\nu_{\text{C=C}}$ 1585 cm⁻¹, $\nu_{\text{C-N}}$ 1317 cm⁻¹, $\nu_{\text{C-H}}$ (benzene-out of plane) 759, 690, 630 cm⁻¹, μ Pd-Cl 310-360 cm⁻¹. NMR: 7.44-7.50(t), 7.55-7.61(t), 7.78-7.82(d). m.p.: 255 °C. Anal. Data found: M % 30.8; N, 3.56; C, 45.24; H, 1.86; Cl, 9.56. [Pd₂(L3)₂(Cl)₂] **3** Calcd: M % 31.5; N, 4.14; C, 46.18; H, 2.98; Cl, 10.49. IR(KBr) : $\nu_{\text{C=N}}$ 1597 cm⁻¹, $\nu_{\text{C=C}}$ 1572 cm⁻¹, $\nu_{\text{C-N}}$ 1274 cm⁻¹, $\nu_{\text{C-H}}$ (benzene-out of plane) 754, 687 cm⁻¹, $\nu_{\text{C-O}}$ 1274 cm⁻¹, $\nu_{\text{C-O}}$ 1026 cm⁻¹. NMR: 6.87-6.92(t), 6.98-7.02(d), 7.20-7.26(t), 7.30-7.40 (m), 8.5 (s, 1), 13.3 (s,1). m.p.: 250 °C. Anal. Data found: M% 29.4; N, 2.86; C, 46.35; H, 2.66; Cl, 9.12, Pd₂(L4)₂(Cl)₂] **4** Calcd: M % 30.2; N, 3.98; C, 47.75; H, 3.43; Cl, 10.07. IR (KBr): $\nu_{\text{C=N}}$ 1590 cm⁻¹, $\nu_{\text{C=C}}$ 1570 cm⁻¹, $\nu_{\text{C-N}}$ 1305 cm⁻¹, $\nu_{\text{C-H}}$ (benzene-out of plane) 775,769,722,794 cm⁻¹, $\nu_{\text{C-O}}$ 1252 cm⁻¹, $\nu_{\text{C-O}}$ 1073 cm⁻¹. NMR: 6.91-6.93(d), 7.15-7.19(t), 7.32-7.36(t), 7.79-7.829(d), 8.4 (s,1), 3.7(s, 3).

C. Procedure for Oxidation

Normal pressure oxidation reactions were carried out as per literature methods [48]. The components present in the reaction mixture were estimated by gas chromatograph without any significant delay. The effect of reaction parameters such as temperature, change of solvents, addition of extra ligand on the nature and yield of products were determined by keeping other reaction parameters constant.

III. Results and Discussion

Pd (II) complexes were found catalytically active towards the oxidation of internal alkenes and terminal alkenes at 1 atmospheric pressure of molecular oxygen and at 30⁰ C. The initial rate of oxidation and initial turn over number of 1-hexene and cyclohexene with different Pd (II) complexes under identical experimental conditions are presented in Table-1. The nature of products for a particular substrate using different complexes, as catalysts were found almost same but the yield of different products were depended on the nature of catalyst.

Table-1: Relative activities of the Pd (II) complexes as homogeneous oxidation catalyst

Catalyst	[Subs](Mol L ⁻¹)	Initial turnover no (min ⁻¹)	Nature of product with % yield	
1-Hexene				
[Pd ₂ (L1) ₂ Cl ₂]	0.79	3.50	2-Hexanone	52
[Pd ₂ (L4) ₂ Cl ₂]	0.79	3.25	2-Hexanone	52
[Pd ₂ (L2) ₂ Cl ₂]	0.79	3.00	2-Hexanone	52
[Pd ₂ (L3) ₂ Cl ₂]	0.79	2.95	2-Hexanone	51
Cyclohexene				
[Pd ₂ (L1) ₂ Cl ₂]	0.98	2.75	2-Cyclohexen-1-ol	48
			2-Cyclohexen-1-one	4
			Cyclohexene oxide	2
[Pd ₂ (L4) ₂ Cl ₂]	0.98	2.50	2-Cyclohexen-1-ol	48
			2-Cyclohexen-1-one	4
			Cyclohexene oxide	2
[Pd ₂ (L2) ₂ Cl ₂]	0.98	2.25	2-Cyclohexen-1-ol	48
			2-Cyclohexen-1-one	4
			Cyclohexene oxide	2
[Pd ₂ (L3) ₂ Cl ₂]	0.98	2.10	2-Cyclohexen-1-ol	46
			2-Cyclohexen-1-one	3
			Cyclohexene oxide	1

[Cat] = 2.6 x 10⁻⁴ Mol L⁻¹, Medium = DMF

On the basis of both initial rate of oxidation and initial turn over number. The complexes may arrange in the following order of their catalytic activity. [Pd₂(L1)₂Cl₂] > [Pd₂(L4)₂Cl₂] > [Pd₂(L2)₂Cl₂] > [Pd₂(L3)₂Cl₂]

In the present paper the detail study has been proposed by using the catalyst [Pd₂(L_A)₂Cl₂]. Reaction condition, initial turn over number, nature and percentage yield of product for catalytic oxidation of different substrates using [Pd₂(L1)₂Cl₂] at 1 atm. pressure and at 30⁰C are given in **Table-2**.

Comparatively better catalytic activity was observed when tert-butyl hydroperoxide was used as co-oxidant. Reaction condition along with the tert-butyl hydroperoxide, initial turns over number, nature and percentage yield of products obtained are given in **Table-3**.

Table-2: Catalytic oxidation of organic substrates in DMF using [Pd₂(L1)₂Cl₂] as catalyst at 1atm. pressure of molecular oxygen and at 30⁰C, Yield at the end of 8 h., Medium = DMF

Substrate	[Cat]x10 ⁻⁴ (Mol L ⁻¹)	[Subs] (Mol L ⁻¹)	Initial turn over no.(min ⁻¹)	Nature of products with % yield	
Styrene	2.6	0.87	3.90	Acetophenone	50
				Benzaldehyde	2
1-Pentene	2.6	0.91	3.75	2-Pentanone	39
				3-Penten-2-one	38
1-Hexene	2.6	0.79	3.5	2-Hexanone	52
1-Heptene	2.6	0.70	2.8	2-Heptanone	51
1-Octene	2.6	0.63	2.4	2-Octanone	50
1-Dodecene	2.6	0.45	2.1	2-Dodecanone	38
Cyclohexene	2.6	0.98	2.75	2-Cyclohexen-1-ol	48
				2-Cyclohexen-1-one	4
				Cyclohexene oxide	2

In case of cyclohexene, the oxidation products were 2-cyclohexen-1-ol, 2-cyclohexen-1-one and cyclohexene oxide. 2-cyclohexen-1-one was formed only after the 60 percent conversion of cyclohexene to 2-cyclohexen-1-ol **Fig.1**. Styrene was oxidized to acetophenone and benzaldehyde. Acetophenone was the major product as shown in **Fig.2**. 2-pentanone and 3-penten-2-one were the oxidation products of 1-pentene. Though at the end of catalytic run, the conversion was more than 90 percent but the sum of the mol percentage of 2-pentanone and 3-penten-2-one was only 65 percent. Rest was obtained in the form of unidentified polymeric tarry materials. In case of 1-hexene, 1-heptene, 1-octene and 1-dodecene corresponding 2-one were the products. Hexanal, heptanal, octanal and dodecanal were identified in trace amount whereas the formation of formaldehyde was not detected in any of the above cases. Cyclohexene was oxidized to cyclohexanone at much higher rate in presence of tert-butyl hydroperoxide as co-oxidant with molecular oxygen.

On the basis of this experimental data the substrates may be arranged in the following order-

Styrene > 1-pentene > 1-hexene > 1-heptene > cyclohexene > 1-dodecene

From the rate of oxidation of substrates, it appeared that the double bond, as the part of a delocalized system, was oxidized more quickly than the localized one. Styrene was found to oxidize more quickly than 1-hexene and cyclohexene. Internal double bond was found to oxidize at slower rate than that of terminal olefins. In case of cyclohexene the initial turn over number was lower than that of 1-hexene. In case of terminal olefins, the rate of oxidation was decreased with the increase of molecular weight of the alkenes. In case of the oxidation of 2-hexene and 2-heptene the rate of oxidation was found 40-50 percent slower than that of respective 1-alkenes. Steric factor might be responsible for this type of observation.

Table-3: Catalytic oxidation of organic substrates in presence of tert-butyl hydroperoxide at 1 atm. pressure of molecular oxygen and at 30°C using $[Pd_2(L1)_2Cl_2]$ as catalyst Yield at the end of 8 h., Medium = DMF

Substrate	[Cat.] $\times 10^{-4}$ (Mol L ⁻¹)	[Subs](Mol L ⁻¹)	Amount of t-BuOOH (Mol L ⁻¹)	Initial turn over no.	Nature of products with % yield	
Styrene	2.6	0.87	5.22	11.0	Acetophenone	60
1-Pentene	2.6	0.91	5.46	9.98	Benzaldehyde	4
					2-Pentanone	45
1-Hexene	2.6	0.79	4.74	10.75	3-Penten-2-one	46
					2-Hexanone	58
1-Heptene	2.6	0.70	4.20	10.25	2-Heptanone	54
1-Octene	2.6	0.63	3.78	8.25	2-Octanone	51
1-Dodecene	2.6	0.45	2.70	6.7	2-Dodecanone	48
Cyclohexene	2.6	0.98	5.88	7.00	2-Cyclohexen-1-ol	54
					2-Cyclohexen-1-one	8
					Cyclohexene oxide	6

III.1 Effect of temperature

The rate of oxidation of different substrates was found to increase with increasing temperature up to 60°C. The decreased rate of oxidation above 60°C might be due to the formation of some other stable species of catalytic solution of Pd (II) complexes. Decomposition of Pd (II) complexes either to metallic palladium or in the form of any insoluble palladium compound was not observed.

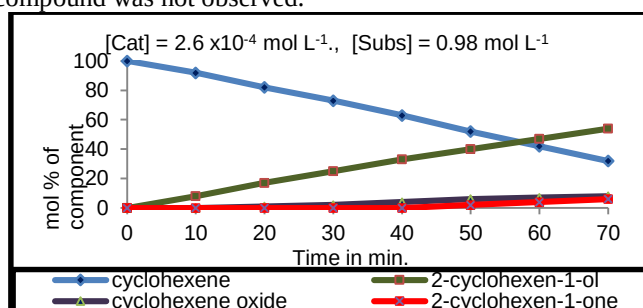


Fig-1: Catalytic oxidation of cyclohexene with $[Pd_2(L1)_2Cl_2]$ in DMF solvent at 30°C and 1 atm pressure of oxygen

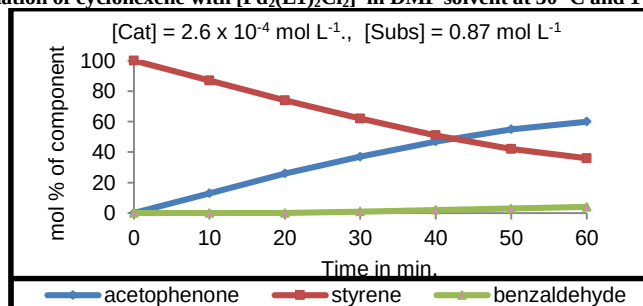


Fig-2: Catalytic oxidation of styrene with $[Pd_2(L1)_2Cl_2]$ in DMF solvent at 30°C and 1 atm. pressure of oxygen

III.2. Effect of acid and alkali

The rate of oxidation was increased significantly in presence of small amount of acid (0.01 Mol L^{-1}). In presence of acid greater than (0.01 Mol L^{-1}) the recycling activity of catalyst was found to decrease. Alkali with concentration greater than (0.005 Mol L^{-1}) had an adverse effect on rate of oxidation. No catalytic oxidation was observed at alkali concentration greater than (0.01 Mol L^{-1}).

III.3 Preferential oxidation

Preferential oxidation of styrene over cyclohexene was observed. Oxidation of cyclohexene was started only after approximately 80 percent conversion of styrene to its product. The preferential oxidation of styrene in presence of cyclohexene is shown in **Fig.3**. Preferential oxidation was also observed when 1-alkene was oxidized in presence of 2-alkene. The oxidation of 2-alkene was observed only after approximately 50 percent conversion of 1-alkene.

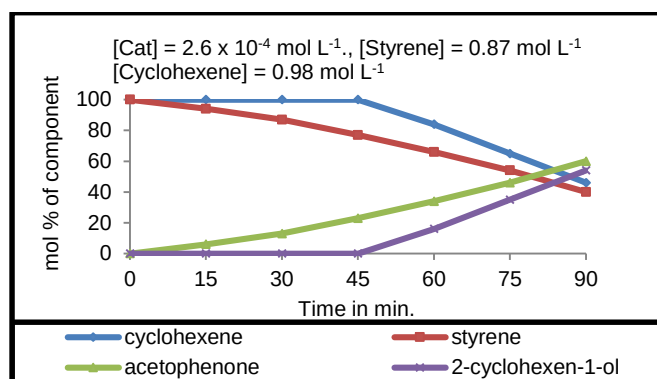


Fig-3: Preferential oxidation of styrene over cyclohexene using $[\text{Pd}_2(\text{L1})_2\text{Cl}_2]$ in DMF solvent at 30°C and 1 atm. pressure of oxygen

III.4. Recycle of the catalyst

In the case of oxidation of terminal alkenes, the addition of fresh substrate to the reaction mixture at the end of catalytic run resumed catalytic oxidation with almost initial rate. In case of other substrates, the products and the unreacted substrate were removed by fractional distillation under reduced pressure of nitrogen. The catalytic activity of the residual solution was found almost same to that of original one. The catalyst could be repeatedly used 6-7 times without any diminished catalytic activity.

III.5. Kinetics and mechanism

Kinetic studies were carried out mainly with 1-hexene and 1-heptene using $[\text{Pd}_2(\text{L1})_2\text{Cl}_2]$ as catalyst. The total volume of the reacting solution was always kept to 15 ml. The initial rate were determined from graphical extrapolation of rate curve to $t = 0$.

III.5.a. Variation of catalyst concentration

During the variation of catalyst concentration, the substrate concentration and oxygen pressure were kept constant. The effect of variation of catalyst concentration on the rate of oxidation was carried out under normal pressure of molecular oxygen (**Fig.-4**). Kinetic studies revealed that the initial rate of oxidation of both 1-hexene and 1-heptene were first order dependent on catalyst concentration.

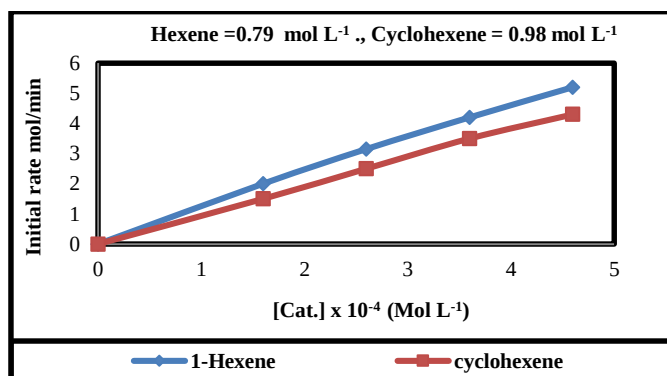


Fig-4: on catalyst concentration using catalyst $[\text{Pd}_2(\text{L1})_2\text{Cl}_2]$ in DMF solvent at 30°C and 1 atm. pressure of oxygen

III.5.b. Variation of substrate concentration

Initial rate of oxidation was found first order dependent on substrate concentration at constant catalyst concentration and oxygen pressure (**Fig.-5**).

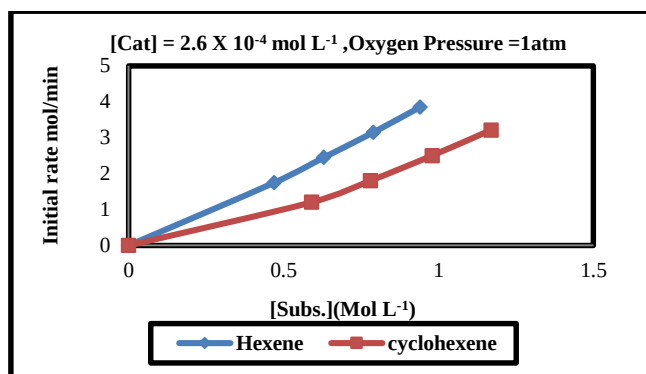


Fig.-5: Rate dependence on substrate concentration using $[Pd_2(L1)_2Cl_2]$ in DMF solvent at 30° C and 1 atm. pressure of oxygen III.5.c. **Variation of oxygen concentration:**

It was assumed that at constant temperature the concentration of oxygen in solution was directly proportional to the oxygen pressure. During the variation of oxygen pressure, the substrate concentration and catalyst concentration was kept constant. Pressure of oxygen was varied from 250-900 mm of Hg. The initial rate of oxidation was found independent of oxygen pressure in this range. On the basis of kinetics and other experimental observations, the following mechanism has been proposed for the oxidation of 1-alkene in the presence of molecular oxygen as oxidant Scheme 1.

IV. Conclusion

Pd (II) complexes of Schiff base derivative were used as efficient homogeneous catalyst for oxidation of a number of organic substrates. Among all the four palladium complexes $[Pd_2(L1)_2Cl_2]$ was found most efficient catalyst. DMF was found best solvent for these catalytic reactions at normal pressure of oxygen and at 30°C.

References

- [1] O. Hayaish, "Oxygenases" Molecular Mechanisms of oxygen Activation, Hayaishi(ed), Academic Press, New York, 1. 1976.
- [2] L.Vaska, Dioxygen-metal complexes: toward a unified view Acc. Chem. Res. 9, 1976; 175-183.
- [3] J.S.Valentine, Dioxygen ligand in mononuclear Group VIII transition metal complexes, Chem. Rev. 73, 1973; 235-245.
- [4] E. Bayer, P. Stretzman, Struct. Bonding (Berlin), 2, 1967; 181.
- [5] J.A. McGinetti, MTP, Int. Rev. Sci, Inorg. Chem. 5, 1972; 229.
- [6] V.Y. Chay, C.J. O'Connov, chelating dioxygen compounds of the platinum metal Coord. Chem. Rev. 9, 1972; 145-170.
- [7] G. Henrici Olive, S. Angew, Chem. Int. Ed. Engl. 13, 1974; 29.
- [8] A.V. Satviski, Nelyobin, V.L., Activation of molecular oxygen on interaction with transition metal complexes. Russ. Chem., Rev. [Eng. Trans.] 44, 1975; 110.
- [9] R.W. Erskine, B.O. Field, Struct. Bonding(Berlin). 28, 1976; 1.
- [10] R.D.Jones, et.al., Synthetic oxygen carriers related to biological systems. 1979 Chem. Rev. 79, 1979; 139-179.
- [11] R. Boca, Dioxygen activation in transition metal complexes in the light of molecular orbital calculations. Coord. Chem. Rev. 50, 1983; 1-72.
- [12] H. Mimoun, "Chemical and Physical Aspects of Catalytic Oxidation", ed. CNRS, Paris. 19. 1980.
- [13] C.V. Hiremath, et al., Ruthenium (III) catalysed oxidation of gabapentin (neurontin) by diperoxidatonickelate(IV) in aqueous alkaline medium: A kinetic and mechanistic study. J. Mol. Catal. A: Chem. 269, 2007; 246-253.
- [14] B.P. Buffin, et al., Pd (II)-biquinoline catalyzed aerobic oxidation of alcohols in water, J. Mol. Catal. A: Chemi. 225, 2005; 111-116.
- [15] V.B. Valodkar, et al., Catalytic oxidation of alkanes and alkenes by polymer anchored amino acid ruthenium complexes. J. Mol. Catal. A: Chem. 223, 2004; 38.
- [16] Z. Li, C.G. Xia., Oxidation of hydrocarbons with iodobenzene diacetate catalyzed by manganese (III) porphyrins in a room temperature ionic liquid. J.Mol. Catal. A: Chem. 214, 2004; 95-101.
- [17] J.E. Remias, A. Sen, Palladium-mediated aerobic oxidation of organic substrates: role of metal versus hydrogen peroxide J. Mol. Catal. A: Chem. 189, 2002 33-38.
- [18] Z.W.Yang, et al., Oxidation of cyclohexene by dendritic PAMAMSA-Mn (II) complexes J. Mol. Catal. A: Chem. 213, 2004; 169-176.
- [19] A. Hussian, et al., Ru (III) analogue of model methane monooxygenase in the effective catalytic oxidation of cyclohexane by molecular oxygen. J. Mol. Catal. A: Chem. 193, 2003; 1.
- [20] B.A. Allal, et al., Catalytic oxidation of α -pinene by transition metal using t-butyl hydroperoxide and hydrogen peroxide, J. Mol. Catal. A: Chem. 200, 2003; 177-184.]
- [21] V. Sharma, P. Sagar, Catalytic oxidation of internal alkenes, terminal alkenes and alcohols by Rh (I) complexes of s-triazene derivatives. Rasayan J.Mol. Catal. 3, 2010; 16-26.
- [22] P. Sagar, V. Sharma, R. Kumar Rh (I) -S triazene complexes as effective homogeneous recyclable catalyst for catalytic hydrogenation of organic substrates , Orien. J. of Chem. 26, 2010; 629-636.
- [23] J.D. Grunwaldt, A. Baiker, Axial Variation of the oxidation state of Pt- Rh/ Al₂ during partial methane oxidation in a fixed-bed reactor: an in situ X-ray absorption spectroscopy study. A.,Catal. Lett. 99, 2005; 5-12.
- [24] L.G. Cuervo, et al., Oxidation of saturated hydrocarbons with peroxyacetic catalyzed by vanadium complexes. J. Mol. Catal. A: Chem. 218, 2004; 171-177.
- [25] M.D. Khokhar, et. al., Selectivity oxidation of methane by molecular oxygen catalyzed by a bridged binuclear ruthenium complex at moderate pressures and ambient temperature. J. Mol. Catal. A: Chem. 299, 2009; 108-116.
- [26] C.F. Chang, S.T. Liu, Catalytic oxidation of anilines into azoxybenzenes on mesoporous silicas containing cobalt oxide. J. Mol. Catal. A: Chem. 299, 2009. 121-126.
- [27] Verlag., Chemie, Weinhein, 1972, Ulmanns Encyclopedia der Technischen Chemie, 1983.
- [28] G.T. Austin, Chem. Eng., (NY), 81 (1) 127; (2) 125; (3) 87; (4) 86. 1974.

