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Highly active Rh(I) complexes used for the catalytic oxidation of internal alkenes, terminal alkenes and alcohols

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ABSTRACT

Rh(I) complexes of azobenzene and anthranilic acid were found moderately efficient towards the catalytic oxidation of internal alkenes, terminal alkenes, and alcohol in C_2H_5OH-CH_2Cl_2 (1:1) mixed solvent system both under normal and high 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.

Key words: Rh(I) complexes; Catalytic oxidation; Internal alkene; Terminal alkene; Alcohol.

INTRODUCTION

The very efficient catalytic oxidation of various organic compounds lead to important products and find application in all areas of chemical industries[1-15]. Acetaldehyde, p-xylene, toluene, benzene are the parent compounds for the manufacture of million tonnes of valuable polymers and solvents and again these are mainly produced via the catalytic oxidation of the above substrates by molecular oxygen[2-7]. Transition metal having different oxidation states can readily interact with dioxygen, even to the extent of forming isolable oxygen adducts[16-28].

The metal centers (either in finely dispersed forms or in their salt or complex form) are commonly used for oxidation of different organic substrates[29-43]. Besides molecular oxygen, H_2O_2, iodosylbenzene, pyidine-N-oxide, t-BuOOH etc. have also been used as oxidant[44,45].

Catalytic potentiality of a good number of Rh (I) complexes of single and mixed ligand complexes have been studied both under normal and high pressure of molecular oxygen. t-BuOOH and hydrogen peroxide were also used as oxidant or as co-oxidant with molecular oxygen. The present paper reports the successful use of Rh(I) complexes of azobenzene and anthranilic acid for the catalytic oxidation of internal alkenes, terminal alkenes and alcohols.

EXPERIMENTAL

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 N_2, Ar and O_2 were always used. Solvents were preserved on molecular sieves (4A) under nitrogen / argon atmosphere. Carbon, Hydrogen, Nitrogen were estimated by semi-micro analytical methods. Halogen was estimated according to literature method[46]. Electronic, vibrational and NMR spectra were recorded on Pye-Unicam PU-8600, Pye-Unicam SP3-300, Bruker AC-300F 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.)**.** Commercially available anthranilic acid was used after recrystallising from benzene.

Preparation of catalysts

Preparation of Anthranilatodicarbonylrhodium(I) $[Rh(An)(CO)_2]$ was reported elsewhere[47]. Preparation of Rh(I) azobenzene complexes eg. dicarbonylchloro(2-phenylazobenzene-N$^{/}$)rhodium(I) $[Rh(AzH)Cl(CO)_2]$, dicarbonyl(2-phenylazophenyl-C^{1}N$^{/}$)rhodium(I) $[Rh(Az)(CO)_2]$ and carbonyl(2-phenylazophenyl-C^{1}N$^{/}$)(triphenylphosphine) rhodium(I) [Rh (Az) (CO) (PPh_3)] were reported in our previous paper[48].

Procedure for Oxidation

Normal pressure oxidations were carried out in 100 ml reaction flask fitted with septum-syringe arrangement and high-pressure oxidation was carried out in a non-magnetic stainless steel high pressure autoclave. Procedure for oxidation was mentioned in our previous paper[48].

RESULTS AND DISCUSSION

Rh(I) complexes were found active towards the catalytic oxidation of internal alkene, terminal alkene and alcohol at 1 atmospheric pressure of molecular oxygen and at 30°C. Reaction condition along with initial turn over number, nature and percentage yield of products for catalytic oxidation of different substrates at 1 atm. pressure and at 30°C are given in Table 1. Comparatively better catalytic activity was observed when tert-butyl hydroperoxide was used as oxidant. Reaction condition along with the amount of tert-butyl hydroperoxide used, initial turns over number, nature and percentage yield of products obtained are given in Table2. Substantial amount of catalytic activity was observed at high temperature and high pressure of molecular oxygen. High-pressure condition, initial turn over number; nature and percentage yield of products for different substrates are given in Table 3. In all cases at the end of reaction the percentage of conversion was always more than 92 %.

Among the different organic solvents, $C_2H_5OH\text{-}CH_2Cl_2$ (1:1) mixed solvent system was found best both in terms of higher rate of oxidation and as well as in terms of stability of the complexes which was established by their repeated use for the oxidation of a particular substrate. The catalytic activity of Rh(I) complexes were also investigated

Table 1: Catalytic oxidation of organic substrates in $CH_2Cl_2\text{-}C_2H_5OH$ (1:1) mixed solvent system using $[Rh(Az)(CO)_2]$ as catalyst at 1 atm. pressure of molecular oxygen and at 30^{O}C

Substrate	[cat.] (10^4mol/lit.)	[subs] (mol/lit.)	Initial turn over no. (min^{-1})	Nature of products	% yield*
Styrene	7.25	0.67	2.9	Acetophenone	39
				Benzaldehyde	1
Cyclohexene	6.64	0.94	2.4	2-cyclohexen-1-ol	37
				2-cyclohexen-1-one	2
				Cyclohexene oxide	1
1-pentene	8.82	0.91	2.1	2-pentanone	30
				3-penten-2-one	2
1-hexene	8.5	0.78	1.65	2-hexanone	43
1-heptene	8.5	0.70	1.5	2-heptanone	41
1-octene	8.07	0.63	1.25	2-octanone	40
1-dodecene	8.72	0.45	1.1	2-dodecanone	27
1-phenyl ethanol	8.08	0.82	2	Acetophenone	32

*yield at the end of 8 h.

in other solvents such as DMF, DMSO, acetonitrile, alcohol, benzene, toluene etc. In case of DMF, DMSO and acetonitrile, rate was found quite slow. This might be due to the moderate coordinating nature of solvent. In presence of these coordinating solvents both oxygen and substrate might be found difficulty to bind to metal center. As a consequence of this rate of oxidation was found slow. In case of pure alcohol (methanol and ethanol) the initial rate of oxidation was high but after an hour, due to decomposition of catalyst, rate of oxidation decreased rapidly. In non-polar solvents such as CH_2Cl_2 and benzene, catalytic oxidation was not observed; products were formed only in stoichiometry ratios.

The initial rate of oxidation, intial turn over number with percentage yield of product for the oxidation of 1-heptene and 1-octene with different Rh(I)-complexes under identical experimental condition are presented in Table-4. On the basis of the initial rate of oxidation and initial turn over number, the complexes may be arranged in the following order in accordance to their catalytic activity.

$[Rh(Az)(CO)_2] > [Rh(AzH)Cl(CO)_2]$ **>** $[Rh(Az)(CO)(PPh_3)]$ **>** $[Rh(An)(CO)_2]$

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. Styrene was oxidized to acetophenone and benzaldehyde. Acetophenone was the major product. The mol percentage of products formed with time is given in Fig.1. 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 accumulation of 60 mol percentage of 2-cyclohexen-1-ol in the product mixture. Mol percentage of product distribution with time for the catalytic oxidation of cyclohexene is given 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

Table 2: Catalytic oxidation of organic substrates in presence of tert-butyl hydroperoxide at 1 atm. pressure of argon and at 30^OC using $[Rh(Az)(CO)_2]$ as catalyst

Substrate	[cat.] (10^{-4} mol/lit.)	[subs] (mol/lit.)	Amount of t-BuOOH (mol/lit.)	Initial turn over no. (min^{-1})	Nature of products	% yield*
Styrene	7.25	0.67	5.22	6	Acetophenone	49
					Benzaldehyde	3
Cyclohexene	6.64	0.94	5.88	5	2-cyclohexen-1-ol	43
					2-cyclohexen-1-one	4
					Cyclohexene oxide	3
1-pentene	8.82	0.91	5.46	6.7	2-pentanone	33
					3-penten-2-one	35
1-hexene	8.5	0.78	4.74	6.5	2-hexanone	49
1-heptene	8.5	0.70	4.20	6	2-heptanone	43
1-octene	8.07	0.63	3.78	4.5	2-octanone	41
1-dodecene	8.92	0.45	2.70	3	2-dodecanone	45
Cyclohexane	8.72	0.92	5.52	4	Cyclohexanone	46
1-phenyl ethanol	8.07	0.82	4.92	6	Acetophenone	44

*yield at the end of 8 h , medium = $C_2H_5Cl-C_2H_5OH(1:1)$ mixed solvent system

Table 3: Catalytic oxidation of organic substrates in CH_2Cl_2-C_2H_5OH (1:1) mixed solvent system using $[Rh(Az)(CO)_2]$ as catalyst at high pressure of molecular oxygen

Substrate	[cat.] (10^{-4}mol/lit.)	[subs] (mol/lit.)	Pressure (10^3KNm^{-2})	Temp (^{0}C)	Initial turn over no. (min^{-1})	Reaction time(min)	Nature of products	% yield
Styrene	4.63	0.86	4.14	50	26	125	Acetophenone	89
							Benzaldehyde	6
Cyclohexene	4.22	0.97	4.14	50	23	140	2-cyclohexen-1-ol	72
							2-cyclohexen-1-one	11
							Cyclohexene oxide	8
1-pentene	5.12	071	4.48	55	27	130	2-pentanone	50
							3-penten-2-one	15
1-hexene	4.75	0.79	4.48	55	24	125	2-hexanone	95
1-heptene	4.75	0.70	4.48	55	23	135	2-heptanone	86
1-octene	4.75	0.63	4.83	60	20	155	2-octanone	89
1-dodecene	5.11	0.45	4.99	60	17	170	2-dodecanone	82
1-phenyl ethanol	7.76	0.82	4.99	55	24	155	Acetophenone	84

Table 4: Relative activities of the Rh(I) complexes as oxidation catalysts in high pressure of molecular oxygen

Catalyst	[subs] (mol/lit.)	Pressure (10^3KNm^{-2})	Initial rate of oxidation (10^{-4}mol/min)	Initial turn over no.(min.$^{-1}$)	Nature of products	% yield
	1-heptene[a]					
[Rh(Az)(CO)$_2$]	0.70	4.48	1.6	22	2-heptanone	88
[Rh(AzH)Cl(CO)$_2$]	0.70	4.48	1.4	21	2-heptanone	88
[Rh (Az)(CO)(PPh$_3$)]	0.70	4.48	1.2	20	2-heptanone	88
[Rh(An)(CO) $_2$]	0.70	4.48	0.7	15	2-heptanone	86
	1-octene[b]					
[Rh(Az)(CO) $_2$]	0.63	4.83	1.7	20	2-octanone	89
[Rh(AzH)Cl(CO)$_2$]	0.63	4.83	1.5	18	2-octanone	89
[Rh (Az)(CO)(PPh$_3$)]	0.63	4.83	1.3	15	2-octanone	88
[Rh(An)(CO) $_2$]	0.63	4.83	0.6	11	2-octanone	86

Medium =CH_2Cl_2-C_2H_5OH(1:1) [cat] = 4.78 x 10^{-4}mol/lit.

Total volume =15 ml , [a]temp =55^{0}C [b]temp. = 60^{0}C 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. Catalytic oxidation of cyclohexene with molecular oxygen was not observed by any of the catalysts. But in presence of tert-butyl hydroperoxide cyclohexene was oxidized to cyclohexanone. The reaction condition, initial turn over number, nature and percentage yield of various products using $[Rh(Az)(CO)_2]$ are given in Table 2. 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

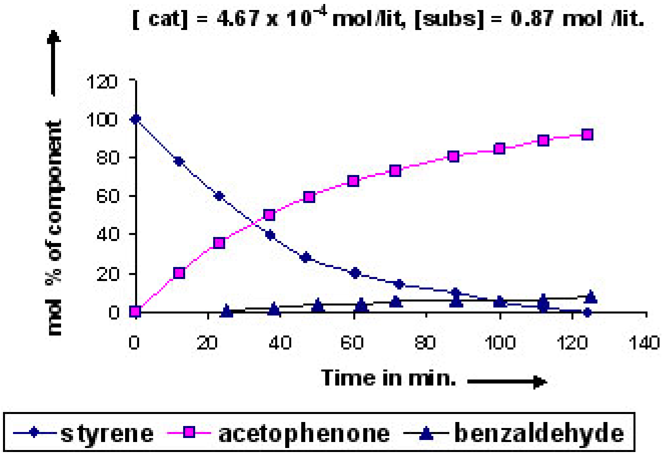

Fig. 1: Catalytic oxidation of styrene with catalyst $[Rh(Az)(CO)_2]$ in CH_2Cl_2-C_2H_5OH (1:1) mixed solvent at 50^0 C and 4.14×10^3 KNm^{-2} pressure of oxygen

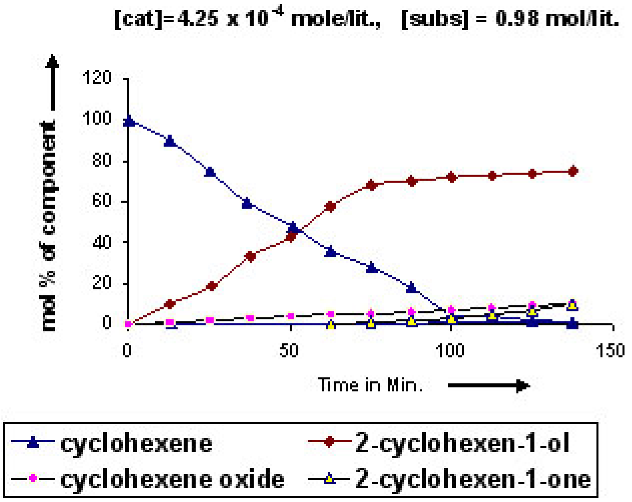

Fig. 2: Catalytic oxidation of cyclohexene with catalyst $[Rh(Az)(CO)_2]$ in CH_2Cl_2-C_2H_5OH (1: 1) mixed solvent at 50^0 C and 4.14×10^3 KNm^{-2} pressure of oxygen

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.

Effect of temperature

The catalytic solution of Rh(I) complexes in CH_2Cl_2-C_2H_5OH were found stable upto 60°c. The decreased rate of oxidation above 60°c might be due to the formation of some other stable

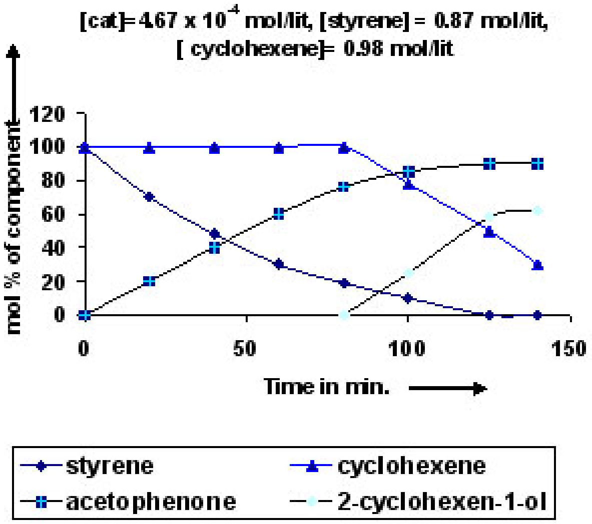

Fig. 3: Preferential oxidation of styrene over cyclohexene using catalyst $[Rh(Az)(CO)_2]$ in CH_2Cl_2-C_2H_5OH (1:1) mixed solvent at 50^0 C and 4.14 x 10^3 KNm^{-2} pressure of oxygen

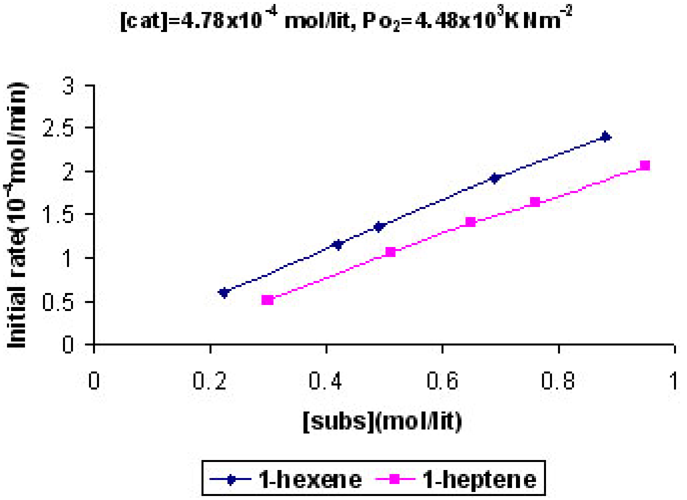

Fig. 4: Rate dependence on substrate concentration using catalyst $[Rh(Az)\ (CO)_2]$ in CH_2Cl_2-C_2H_5OH(1:1)mixed solvent at 55^0C and at 4.48 x $10^3$$KNm^{-2}$ pressure of oxygen

species. Decomposition of Rh(I) complexes either to metallic rhodium or in the form of any insoluble rhodium com pound was not observed. At normal pressure up to 50°C the rate was not increased very significantly. At normal pressure, catalytic oxidations were carried out mainly at 30°C and it was considered as suitable operating temperature.

Effect of acid and alkali

The rate of oxidation was increased significantly in presence of small amount of acid (0.01 mol/lit.). Methyl sulphonic acid was used to investigate the effect of acid on the rate of oxidation. In presence and absence of acid no significant changes in the nature of products was observed. In presence of acid greater than 0.01 mol/lit., the recycling activity of catalyst was found to decrease. Alkali with concentration greater than 0.005 mol/lit had an adverse effect on rate of oxidation. No catalytic oxidation was observed at concentration greater than 0.01 mol/litre.

Effect of foreign ligand

Initial addition of the extra ligand (~10^{-4} mol/lit) such as triphenyl phosphine, pyridine, quinoline etc., decreased the rate of oxidation greatly without affecting the nature and yield of products both under normal and high pressure of molecular oxygen. No catalytic oxidation was observed when the concentration of triphenyl phosphine was made greater than 10^{-2} mol/lit. In presence of extra CO and coordinating ligand such as PPh_3, pyridine, quinoline etc., the dissociation of CO inhibited and thereby the decrease in rate of oxidation was observed.

Preferential oxidation

Preferential oxidation of styrene over cyclohexene was observed when the catalyst solution was stirred simultaneously with styrene and cyclohexene in presence of molecular oxygen at high pressure. Oxidation of cyclohexene was started only after the 80 percent conversion of styrene to its product. Preferential oxidation was also observed when 1-alkene was oxidized in presence of 2-alkene. The oxidation of 2-alkene was observed only after the 80 percent conversion of 1-alkene. The preferential oxidation of styrene in presence of cyclohexene is shown if Fig.3.

Recycle of the catalyst

In the case of oxidation of 1-hexene and 1-heptene, the addition of the fresh substrate to the reaction mixture at the end of catalytic run resumed catalytic oxidation with almost initial rate. In case of other substrate 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 used several times without any diminished catalytic activity.

CONCLUSION

Rh(I) complexes of azobenzene and anthranilic acid derivatives were used as active catalyst for oxidation of a number of organic coumpounds. Among all the four Rh(I) complexes, $[Rh(Az)(CO)_2]$ was found most efficient. C_2H_5OH-CH_2Cl_2 (1:1) mixed solvent system was found best solvent for these catalytic systems.

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