

CATALYTIC OXIDATION OF INTERNAL ALKENES, TERMINAL ALKENES AND ALCOHOLS BY Rh(I) COMPLEXES OF S-TRIAZENE DERIVATIVES

Varsha Sharma^{*a} and Priyanka Sagar^b

^{*a}Department of Chemistry, Arya Institute of Engineering and Technology, Kukas, Jaipur (Rajasthan) India

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

E-Mail: varsha2008@hotmail.com

ABSTRACT

Rh(I) complexes of S-triazene were found moderately efficient towards the catalytic oxidation of internal alkenes, terminal alkenes, and alcohol in C₂H₅OH-CH₂Cl₂ (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. On the basis of kinetics and other experimental observations, a reaction mechanism has also been proposed.

Keywords: Rh(I) complexes; Catalytic oxidation; Internal alkene; Terminal alkene; Alcohol

INTRODUCTION

Catalytic oxidation of organic compounds such as alkanes, alkenes, aromatic hydrocarbons, alcohols, aldehydes epoxides lead to important products and find application in all areas of chemical industries¹⁻¹⁵. Catalytic oxidation of cyclohexane to 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, 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 oxygen²⁻⁷. Transition metal having different oxidation states can readily interact with dioxygen, even to the extent of forming isolable oxygen adducts¹⁶⁻²⁸. The metal centers (either in finely dispersed forms or in their salt or complex form) are commonly used for oxidation of different organic substrates²⁹⁻⁴³. Besides molecular oxygen, H₂O₂, iodosylbenzene, pyridine-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 S-triazene 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 N₂, Ar and O₂ 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 method⁴⁶. 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.). S-triazenes (OR-TH, DEt-ATH, DEt-ATH) were prepared and purified as per literature methods^{47,48}.

Preparation of catalysts

Preparation of dicarbonyl(s-triazino)rhodium(I) [Rh(OR-T)(CO)₂] 1 (R=Me), 2 (R=Et) {where OR-TH = 2-o-hydroxyphenyl-4-amino-6-alkoxy-1,3,5-triazine}

RhCl₃.3H₂O (0.26 gm, 1.24mmol) in deoxygenated DMF (10 ml) was stirred with s-triazine (0.31g 1.35mmol) in nitrogen atmosphere for half an hour. The solution was then refluxed under nitrogen atmosphere for 2 h. During the first 10 min. the colour of the solution was changed from dark red to yellow. The solution was cooled to room temperature and diluted with deoxygenated water (35 ml). A yellow colored compound was observed. The reaction mixture was kept at 5°C for 1 h and then filtered in nitrogen atmosphere. The precipitate was washed with deoxygenated water and acetone successively and dried in vacuum. The other two rhodium-(s-triazine) complexes i.e., [Rh(DEt-ATH₂)(CO)₂] 3 and [Rh(DEt-AT)(CO)₂] 4, {where DEt-ATH₃ = 2-o-hydroxyphenyl-4-amino-6-diethylamino-1,2-dihydro-1,3,5-triazine, DEt-ATH = 2-o-hydroxyphenyl-4-amino-6-diethylamino-1,3,5-triazine} were synthesized following the same procedure.

Yield: 1- 68%, 2 -70%, 3 –68%, 4–65%

m.p.: 170°C. Anal.Data found: N,14.72 ; C,38.10 ; H,2.35, [Rh(OMe-T)(CO)₂] 1

Calcd: N,14.89; C,38.32 ; H,2.41. IR(KBr): νNH/NH₂ 3400-3300 cm⁻¹; ν-CO(phenol) 1540 cm⁻¹; νNH₂ 1610 cm⁻¹. UV/Vis(DMF) : 22475 cm⁻¹(d-d transition).

m.p.: 170°C. Anal.Data found: N,14.40 ; C,40.08 ; H,2.80 [Rh(OEt-T)(CO)₂] 2

Calcd: N,14.36 ; C,40.02 ; H,2.84. IR(KBr): νNH/NH₂ 3390-3300 cm⁻¹; ν-CO 2200-2000 cm⁻¹; ν-CO(phenol) 1545 cm⁻¹; νNH₂ 1615 cm⁻¹. UV/Vis(DMF) : 22472 cm⁻¹(d-d transition).

m.p.: 175°C. Anal.Data found: N,16.55; C,42.95 ; H,4.30 [Rh(DEt-ATH₂)(CO)₂] 3

Calcd: N,18.70 ; C,42.97 ; H,4.33. IR(KBr) : νNH/NH₂ 3455-3220 cm⁻¹; ν-CO 2085-2010 cm⁻¹; ν-CO(phenol) 1535 cm⁻¹; νNH₂ 1615 cm⁻¹. UV/Vis(DMF) : 21978cm⁻¹(d-d transition).

m.p. :180°C. Anal.Data found: N,16.75; C,43.00 ; H,3.85 [Rh(DEt-AT)(CO)₂] 4

Calcd: N,16.78 ; C,43.18 ; H,3.86. IR(KBr): νNH/NH₂ 3395-3230 cm⁻¹; ν-CO 2080-2019 cm⁻¹; ν-CO(phenol) 1545 cm⁻¹; νNH₂ 1615 cm⁻¹. UV/Vis(DMF) : 22358cm⁻¹(d-d transition).

Procedure for Oxidation

Normal pressure oxidations were carried out in 100 ml reaction flask fitted with septum-syringe arrangement. Reaction set up was first evacuated and purged several times with pure and dry nitrogen. The reaction mixture containing the catalyst (10.24 x 10⁻⁶ to 13.38 x 10⁻⁶ mol) and deoxygenated solvent in requisite amount were introduced in the reaction flask with the help of septum-syringe arrangement. The temperature of reacting solution was kept constant by immersing the flask in a constant temperature silicone oil bath and stirring the solution vigorously with help of magnetic stirrer. The oxygen was introduced into the flask. During the first 10 min, the original yellow colour of the catalyst {[Rh(OMe-T)(CO)₂] [Rh(OEt-T)(CO)₂], [Rh(DEt-ATH₂)(CO)₂], and [Rh(DEt-AT)(CO)₂]} solution changed to reddish brown. The total volume of the catalytic solution was always maintained to (15-n) ml. Addition of n ml of substrate (6.75 x 10⁻³ to 14.8 x 10⁻³ mol) to the reddish brown solution slightly faded the colour of the solution and started oxygen absorption in all cases. The oxygen pressure was noted by mercury manometer. Oxygen absorption was noted with the help of accurately calibrated gas burette. Small amount of reacting solution (10⁻³ ml) was taken out from the reaction flask at regular intervals of time with the help of a syringe under oxygen without altering the reaction pressure. The components present in this solution 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.

High-pressure oxidation was carried out in a non-magnetic stainless steel high pressure autoclave. Desired quantity of catalyst (6.37×10^{-6} to 11.6×10^{-6} mol) in minimum amount of DMF was taken in a glass liner and was kept in the autoclave. Autoclave was then evacuated and purged several times with pure, dry oxygen. Substrate (6.75×10^{-3} to 14.8×10^{-3} mol) in appropriate solvent was then added. The total volume of the solution was always kept to 15 ml. The reaction mixture was then subjected to the desired pressure of the oxygen in the reactor. The autoclave was then immersed in a constant temperature silicone oil bath. Pressure as indicated by pressure gauge attached to the reactor was taken as reaction pressure. The solution was continuously stirred with the help of a magnetic stirrer during the whole reaction period. At regular intervals of time the product mixture was taken out by product release assembly and the components present in the mixture were separated and estimated without any significant delay.

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 Table-2. 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 %.

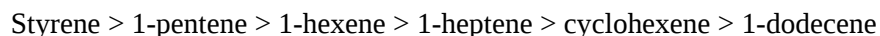
Among the different organic solvents, $C_2H_5OH-CH_2Cl_2$ (1:1) mixed solvent system was found best both in terms of higher rate of oxidation and as well as in terms of stability of the complexes which was established by their repeated use for the oxidation of a particular substrate. The catalytic activity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



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 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 $[\text{Rh}(\text{OEt-T})(\text{CO})_2]$ are given in Table-2. On the basis of this experimental data the substrates may be arranged in the following order-



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.

Effect of temperature

The catalytic solution of Rh(I) complexes in CH_2Cl_2 - $\text{C}_2\text{H}_5\text{OH}$ were found stable upto 60°C . The decreased rate of oxidation above 60°C might be due to the formation of some other stable species. Decomposition of Rh(I) complexes either to metallic rhodium or in the form of any insoluble rhodium compound 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/lit.

Effect of foreign ligand

Initial addition of the extra ligand ($\sim 10^{-4}$ 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 in 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.

Kinetics and mechanism

Kinetic studies were carried out mainly with 1-hexene and 1-heptene using $[\text{Rh}(\text{OEt-T})(\text{CO})_2]$ 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 $t = 0$. The rate was determined by estimating the reaction mixture at regular intervals of time with the help of Nucon-5700 gas chromatograph.

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 (1.70×10^{-4} mol/lit to 9.70×10^{-4} mol/lit) on the rate of oxidation was carried out both under normal and high pressure of molecular oxygen. Kinetic studies revealed that the initial rate of oxidation of both 1-hexene and 1-heptene were first order dependent on catalyst concentration.

Variation of substrate concentration

Initial rate of oxidation was found first order dependent on substrate concentration at constant catalyst concentration and oxygen pressure. The effect of variation of substrate concentration (0.25 to 0.98 mol/lit.) on the rate of oxidation were studied both under normal and high-pressure. Rate was found first order dependent on substrate concentration same as catalyst concentration. The variation of substrate concentration and the corresponding rate of oxidation at high pressure of oxygen are given in Fig 4.

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 were kept constant. Pressure of oxygen was varied from 250-900mm 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].

In order to investigate the possibility that a free radical mechanism might be occurring in this oxidation, analogous reactions were also conducted in presence of 4-

methyl-2,6-di-*t*-butylphenol (3.1×10^{-2} mol/lit.). No significant changes were observed in the profiles of mol % of conversion and the product formation. Thus the possibility of the oxidation process being associated with the radical chain reaction may judiciously be ruled out and the involvement of metal oxygen and metal olefin mediated reaction may be proposed as reported elsewhere^{49,50}.

It was further observed that in presence of molecular oxygen the yellow colour of the catalyst $[\text{Rh}(\text{OEt-T})(\text{CO})_2]$ solution was slowly changed to reddish brown within 10 min. The IR spectra of the compound obtained after vacuum evaporation of solvent showed peak at 850 cm^{-1} . The appearance of peak at 850 cm^{-1} indicated the formation of metal peroxide group in the oxidation process. This further substantiated the involvement of metal oxygen coordination in the present catalytic process. $[\text{Rh}(\text{OEt-T})(\text{CO})_2]$ was reported as an olefin isomerization catalyst in ethanol. Isomerisation proceeded by an addition elimination mechanism. This again substantiated the involvement of metal olefin coordinated mechanism. Similar type of metal olefin and metal oxygen coordinated mechanism are also reported elsewhere^{49,50}. Catalytic oxidation of 1-alkene by $[\text{Rh}(\text{OEt-T})(\text{CO})_2]$ in presence of *t*-BuOOH may tentatively be proposed as same as scheme-1 but here the source of oxidation is *t*-BuOOH instead of oxygen.

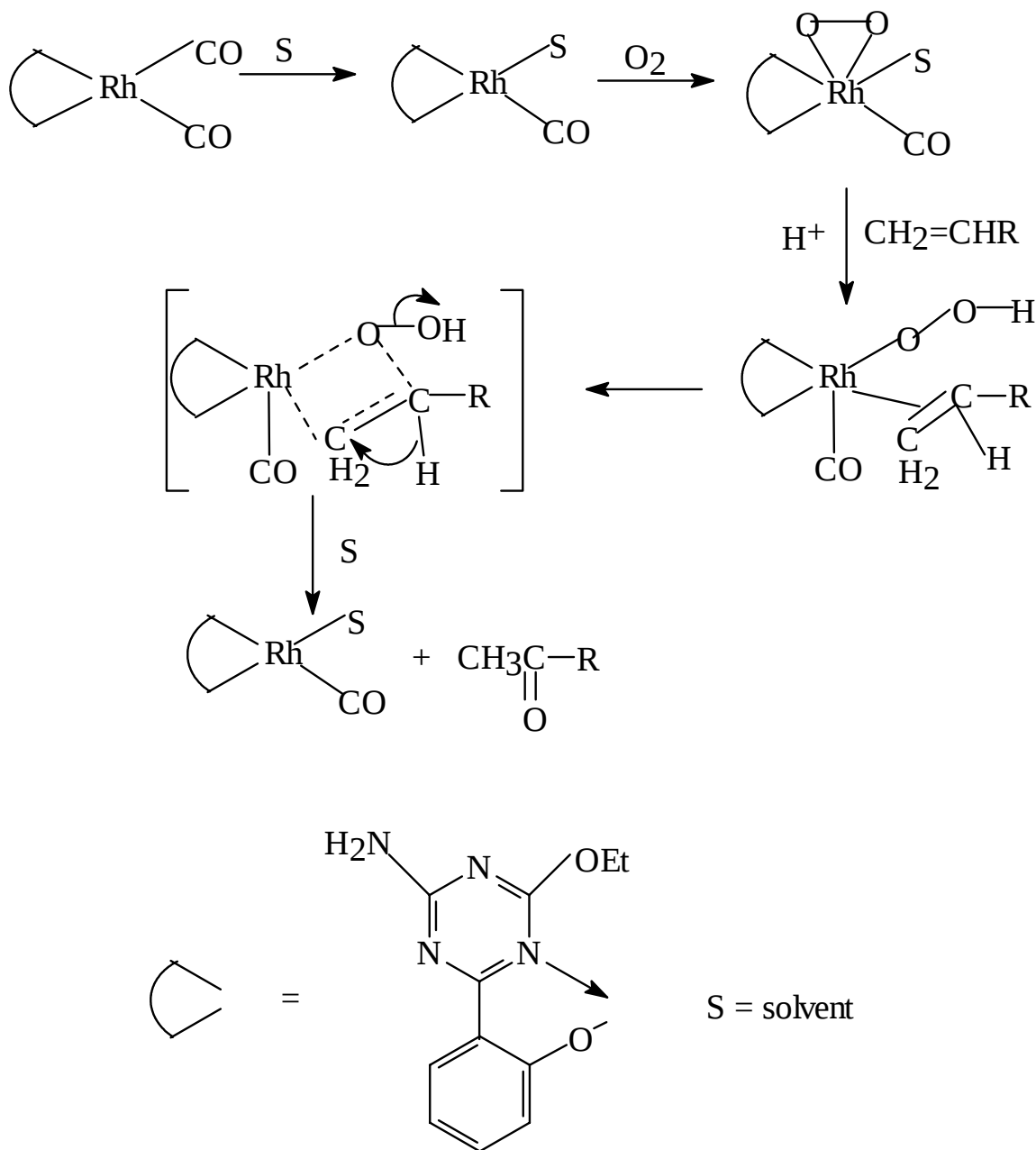
CONCLUSION

Rh(I) complexes of S-triazene derivatives were used as active catalyst for oxidation of a number of organic compounds. Among all the four Rh(I) complexes, $[\text{Rh}(\text{OEt-T})(\text{CO})_2]$ was found most efficient. $\text{C}_2\text{H}_5\text{OH}-\text{CH}_2\text{Cl}_2$ (1:1) mixed solvent system was found best solvent for these catalytic systems.

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Scheme-1

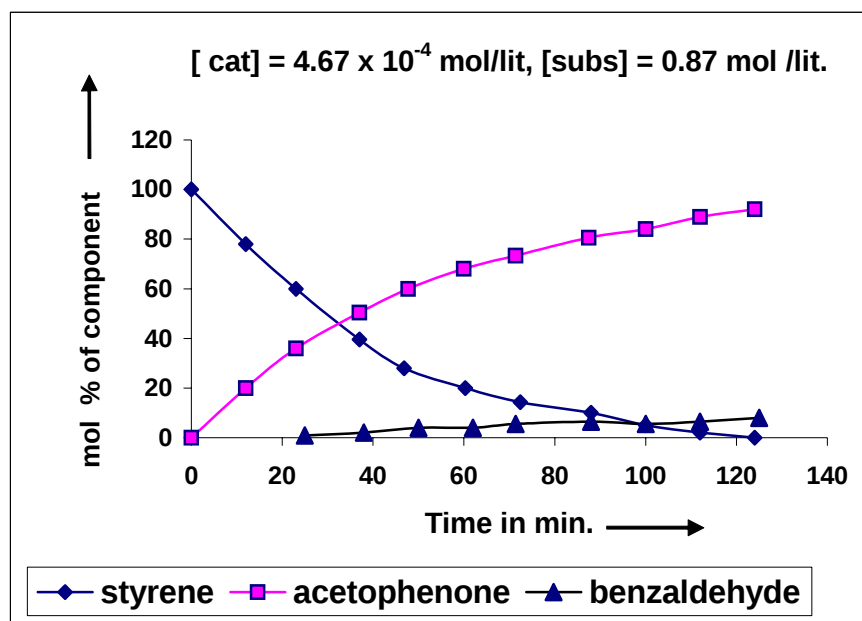


Fig.-1: Catalytic oxidation of styrene with catalyst $[\text{Rh}(\text{OEt-T})(\text{CO})_2]$ in CH_2Cl_2 - $\text{C}_2\text{H}_5\text{OH}$ (1:1) mixed solvent at 50°C and $4.14 \times 10^3 \text{ KNm}^{-2}$ pressure of oxygen

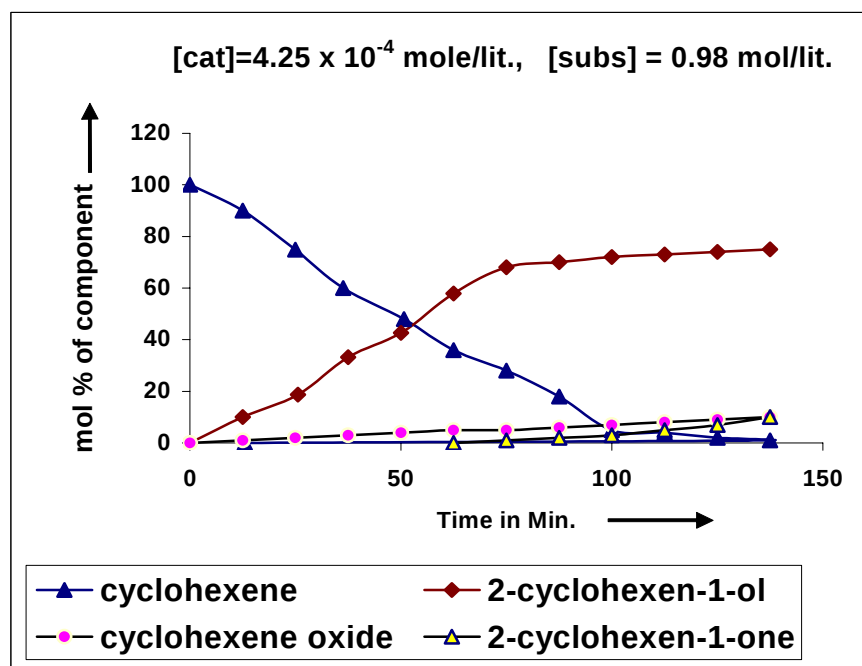


Fig.-2: Catalytic oxidation of cyclohexene with catalyst $[\text{Rh}(\text{OEt-T})(\text{CO})_2]$ in CH_2Cl_2 - $\text{C}_2\text{H}_5\text{OH}$ (1:1) mixed solvent at 50°C and $4.14 \times 10^3 \text{ KNm}^{-2}$ pressure of oxygen

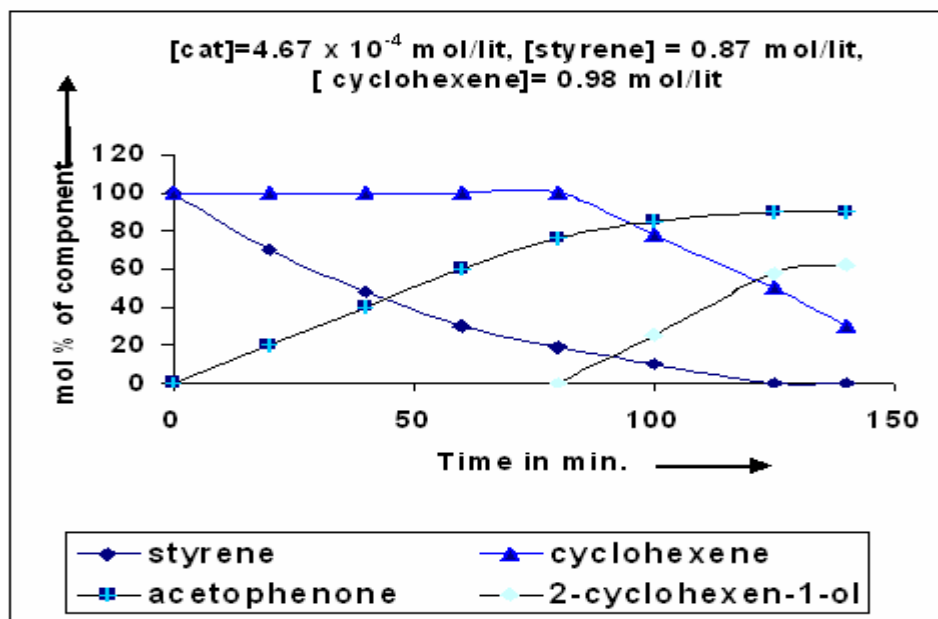


Fig.-3: Preferential oxidation of styrene over cyclohexene using catalyst $[Rh(OEt-T)(CO)_2]$ in $CH_2Cl_2-C_2H_5OH$ (1:1) mixed solvent at $50^\circ C$ and $4.14 \times 10^3 \text{ KNm}^{-2}$ pressure of oxygen

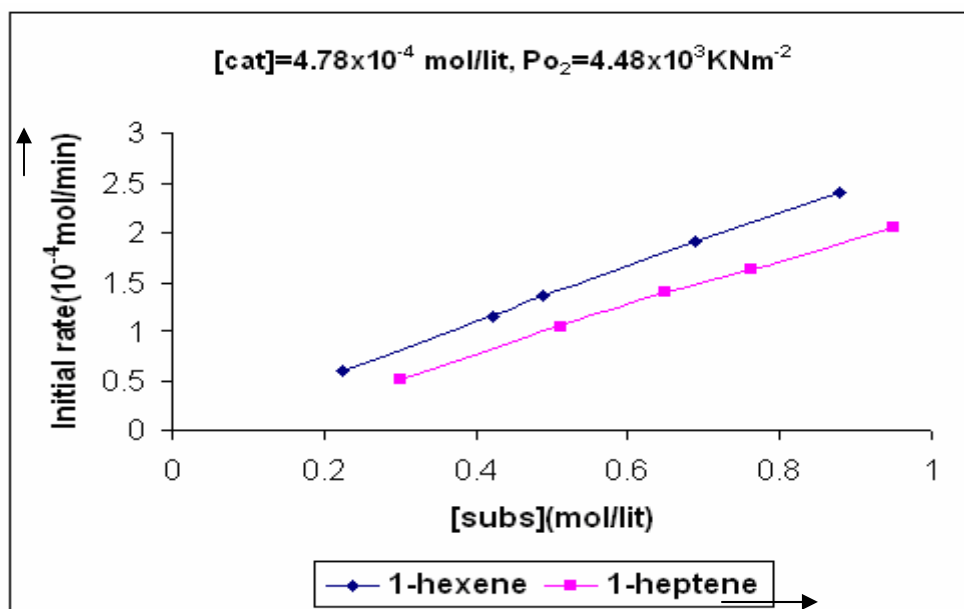


Fig.-4: Rate dependence on substrate concentration using catalyst $[Rh(OEt-T)(CO)_2]$ in $CH_2Cl_2-C_2H_5OH$ (1:1) mixed solvent at $55^\circ C$ and at $4.48 \times 10^3 \text{ KNm}^{-2}$ pressure of oxygen

Table-1: Catalytic oxidation of organic substrates in CH₂Cl₂-C₂H₅OH (1:1) mixed solvent system using [Rh(OEt-T)(CO)₂] as catalyst at 1 atm. pressure of molecular oxygen and at 30°C

Substrate	[cat.] (10 ⁻⁴ mol/lit.)	[subs] (mol/lit.)	Initial turn over no. (min ⁻¹)	Nature of products with % yield *
Styrene	7.65	0.87	3	Acetophenone 40 Benzaldehyde 1
Cyclohexene	6.84	0.98	2.5	2-cyclohexen-1-ol 38 2-cyclohexen-1-one 2 Cyclohexene oxide 1
1-pentene	8.92	0.91	2	2-pentanone 29 3-penten-2-one 2
1-hexene	8.5	0.79	1.75	2-hexanone 42
1-heptene	8.5	0.70	1.5	2-heptanone 41
1-octene	8.07	0.63	1.25	2-octanone 40
1-dodecene	8.92	0.45	1	2-dodecanone 28
1-phenyl ethanol	8.07	0.82	2	Acetophenone 33

* yield at the end of 8 h.

Table-2: Catalytic oxidation of organic substrates in presence of tert-butyl hydroperoxide at 1 atm. pressure of argon and at 30°C using [Rh(OEt-T)(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 with % yield*
Styrene	7.65	0.87	5.22	6	Acetophenone 50 Benzaldehyde 3
Cyclohexene	6.84	0.98	5.88	5	2-cyclohexen-1-ol 44 2-cyclohexen-1-one 4 Cyclohexene oxide 3
1-pentene	8.92	0.91	5.46	6.7	2-pentanone 35 3-penten-2-one 36
1-hexene	8.5	0.79	4.74	6.5	2-hexanone 48
1-heptene	8.5	0.70	4.20	6	2-heptanone 44
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	8.92	0.92	5.52	4	Cyclohexanone 48
1-phenyl ethanol	8.07	0.82	4.92	6	Acetophenone 46

* yield at the end of 8 h , medium = C₂H₅Cl-C₂H₅OH(1:1) mixed solvent system

Table-3: Catalytic oxidation of organic substrates in CH₂Cl₂-C₂H₅OH (1:1) mixed solvent system using [Rh(OEt-T)(CO)₂] as catalyst at high pressure of molecular oxygen

Substrate	[cat.] (10 ⁻⁴ mol/lit.)	[subs] (mol/lit.)	Pressure (10 ³ KNm ⁻²)	Temp (°C)	Initial turn over no. (min ⁻¹)	Reaction time (min)	Nature of products with % yield
Styrene	4.67	0.87	4.14	50	27	125	Acetophenone 90 Benzaldehyde 7
Cyclohexene	4.25	0.98	4.14	50	22	140	2-cyclohexen-1-ol 74 2-cyclohexen-1-one 10 Cyclohexene oxide 8
1-pentene	5.12	0.91	4.48	55	28	130	2-pentanone 50 3-penten-2-one 15
1-hexene	4.78	0.79	4.48	55	26	125	2-hexanone 95
1-heptene	4.78	0.70	4.48	55	23	135	2-heptanone 88
1-octene	4.78	0.63	4.83	60	20	155	2-octanone 89
1-dodecene	5.12	0.45	4.99	60	18	170	2-dodecanone 82
1-phenyl ethanol	7.78	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 ³ KNm ⁻²)	Initial rate of oxidation (10 ⁻⁴ mol/min)	Initial turn over no. (min. ⁻¹)	Product with %yield
	1-heptene ^a				
[Rh(OEt-T)(CO) ₂]	0.70	4.48	1.6	23	2-heptanone 88
[Rh(OMe-T)(CO) ₂]	0.70	4.48	1.4	20	2-heptanone 88
[Rh(DEt-AT)(CO) ₂]	0.70	4.48	1.2	19	2-heptanone 88
[Rh(DEt-ATH ₂)(CO) ₂]	0.70	4.48	0.7	15	2-heptanone 86
	1-octene ^b				
[Rh(OEt-T)(CO) ₂]	0.63	4.83	1.7	20	2-octanone 89
[Rh(OMe-T)(CO) ₂]	0.63	4.83	1.5	18	2-octanone 89
[Rh(DEt-AT)(CO) ₂]	0.63	4.83	1.3	15	2-octanone 88
[Rh(DEt-ATH ₂)(CO) ₂]	0.63	4.83	0.6	11	2-octanone 86

Medium =CH₂Cl₂-C₂H₅OH(1:1)
Total volume =15 ml ,
(Received: 6 March 2010

[cat] = 4.78 x 10⁻⁴mol/lit.
^atemp =55⁰C ^btemp. = 60⁰C
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