CHAPTER # 5

KINETICS OF OXIDATION OF TOLUENE

5.1 KINETICS OF OXIDATION OF TOLUENE USING POLYMER SUPPORTED Ru(III) AND Pd(II) COMPLEXES AS CATALYSTS.

5.1.1 INTRODUCTION

Catalytic oxidation of hydrocarbons is an area of particular significance as it leads to the production of numerous industrially important products such as acetic acid, benzoic acid etc. (1,2). In the manufacture of bulk chemicals, catalytic oxidation has become very important for the conversion of alkenes, alkanes and aromatics into the more valueable oxygen containing materials Therefore, last few decades have wittnessed the termendous growth on this aspect both in terms of development of oxidation catalysts (homogeneous / heterogeneous) as well as oxidation processes. Among the developed catalysts/process an excessive use of transition metals has been found as homogeneous catalysts (3-5). However, the activity of transition metal ions was found to be less as such, while an enhanced activity was observed when the metal ions were either supported on a solid or in the complex form (6).

These complexes were found suitable as homogeneous catalysts for the oxidation of hydrocarbons. The schiff base complexes of transition metal ions in solution were found to be effective catalysts for oxidation of phenols (7,8) and primary amines (9,10). Pyridineamide complexes of chromium (III) and Manganese (III) were used for olefin epoxidation in presence of iodosobenzene and oxidation of alkenes in presence of benzene (11). Yamada et al (12-14) have studied Nickel (II) complexes catalysed oxidation of aldehydes to corresponding acids with molecular oxygen using acetone as a solvent and enantioselective oxidation of olefins with molecular oxygen and aldehyde catalysed by optically active Manganese(II) complexes. The cobalt catalyzed cleavage of 1,2 glycols by molecular oxygen in aprotic polar solvent at 100°C has been reported by Vries et. al. (15) and it was found that the resulting aldehydes or carboxylic acids can be isolated as the major product depending on the reaction time. The selective oxidation of hydrocarbons using transition metal complexes in homogeneous system under mild operating conditions have been reported by several other workers (16-18).

The complexes of platinum group metals have received much attention in recent years because of the structural variety and their role in catalytic oxidation reaction (19,20). Recently several ruthenium (III) complexes have been used as effective catalysts for the oxidation of a variety of chlorinated hydrocarbons in the liquid phase and a faster rate was observed when the reaction was carried out in polar medium (21). The oxidation of hydrocarbons has been studied in the presence of variety of synthetic metalloporphyrins (22-24). Selective oxidation of olefins, alcohols, aldehydes and sulphides with molecular oxygen has been carried out using ruthenium (III) and rhodium (III) complexes (25). Metal complexes of this group have been shown to be reactive towards a variety of organic and inorganic substrate (26-29). Taquikhan et al have studied oxygenation reactions of saturated and unsaturated substrates by molecular oxygen using ruthenium-EDTA complex in homogeneous system (30). Kinetics of ruthenium (III) catalysed oxidation reactions in homogeneous systems was carried out by Kandpal et al (31). Palladium (II) in liquid phase was used for oxidation of hydrogen peroxide by Zubovich and coworkers(32). Oxo ruthenium complexes were used for selective oxidation of hydrocarbons like cyclohexane, toluene and cyclohexanol (33).

However, the homogeneous catalysts have the disadvantages as mentioned earlier, the heterogenised homogeneous catalysts for oxidation process were tried out to overcome such problems.

Efforts have been made to anchor the metal ions either on inorganic oxides or organic polymers for their potential use as a catalyst (34-37). Buyevskaya et al (38) have studied partial oxidation of methane to CO and CO_2 using rhodium anchored on alumina catalyst. The oxidation of glucose using Pd/Al_2O_3 was studied by Nikov et al (39). Selective catalytic epoxidation of ethylene and vinylacetate as well as oxidation of methanol and carbonmonoxide using heterogeneous transition metal catalysts has been reported by Van Santen (40). Yeping et. al. (41) studied catalytic oxidation of CO using platinum, rhodium and platinum-rhodium bimetallic catalysts supported on γ-Al_2O_3 however platinum catalyst was found to be more active. Several other workers have also studied the oxidation of toluene using various metal ions/complexes supported on inorganic oxides under various conditions and a considerable conversion of toluene to benzaldehyde was observed (42-45).

A number of studies has been carried out in the oxidation reactions using metal ions/complexes supported on commercially available polymers (46-49). Drago et al (50) have studied oxidation of 2,6 dimethylphenol using Co(II) complexes as catalyst. Oxidation of cyclohexane using polymer supported schiff base cobaltous palmitate complex has been studied by Kumar et. al (51) and the catalyst was found to be selective for cyclohexanone. Sherrington et al (52) have studied oxidation of alkene using cynomethylated polybenzimidazole supported Pd(II) Wacker type catalysts in alcoholic medium. Recently selective epoxidation of olefins using polymer bound Mn(II) complexes in the presence of iodosylbenzene as the terminal oxidant has been investigated by Sivram et. al. (53) and a considerable rate was observed. An aerobic wacker oxidation of 1-octene in tert-butyl alcohol using polymer supported palladium (II) complexes was performed by Jianbiao et al (54). As mentioned earlier, attempts have been made to carryout the catalytic oxidation of alkylbenzene to industrially important fine chemicals such as benzaldehyde which is a prime constituent used to manufacture dyes, drugs, food products and agrochemicals. One of the routes to obtain this industrially important fine chemical is the oxidation of toluene. However studies using polymer supported chelated metal complexes as catalyst are found to be sparse on this aspect. The polymer bound metalloporphyrins of Fe(III) and Mn(II) have been used as catalysts for epoxidation of olefins and oxidation of alkenes using H_2O_2 as an oxidant and a higher catalytic activity was observed as compared to homogeneous system (55). The cationic latex bound Co(II) complex of schiff base showed high catalytic activity in the autooxidation of 2,6 dibutyl phenol in water (56) Ruthenium catalysts supported on polyquinolins designed to chelate ruthenium has been utilised for the selective oxidation of alcohols to aldehydes (57). Ziqiang et al (58,59) have carried out the vapour phase oxidation of alkylbenzene to the corresponding ketones and alcohols using ruthenium-polymer bound 2,2′ bipyridine complexes.

Here we have made an attempt to investigate the catalytic oxidation of toluene to benzaldehyde as a model reaction with polymer bound chelated metal complexes using glycine and L-2 amino butanol as chelating agents. The brief description of the present work is as follows.

In the present investigation, the synthesised polymer bound chelated metal complexes of ruthenium (III) and palladium (II) have been used to study the kinetics of oxidation reaction in the presence of molecular oxygen under mild operating conditions. The influence of various parameters such as concentration of the catalyst and the substrate, temperature of the system and of various solvents on the rate of oxidation has been investigated. Furthermore, stability of the catalysts has also been seen by studying life cycle efficiency of the catalysts.

5.2 EXPERIMENTAL

5.2.1 MEASUREMENT OF CATALYTIC ACTIVITY FOR OXIDATION REACTIONS

The oxidation reactions were carried out in a magnetically stirred glass reactor using an alcoholic medium for heterogenised homogeneous systems. However, methanol was found to be a suitable solvent for above reactions because of its better swelling characteristics (chapter-3). The progress of the reaction was followed by measuring the uptake of oxygen as a function of time at a constant pressure using a glass manometric apparatus. The experimental setup and detailed procedures are described earlier (chapter-2).

5.2.2 ANALYSIS OF KINETIC DATA

The kinetic data for the oxidation reaction were obtained in a kinetic regime for a stirring speed of 650 rpm at 35°C. The stoichiometry of the reaction was checked by carrying out a few experiments at constant temperature and oxygen pressure at different concentration of toluene. The product analysis was confirmed by Gas Chromatograph using carbowax column and no side product was formed except benzaldehyde under the reaction conditions. (Chromatograms are given in chapter-2). In each kinetic run, the uptake of oxygen was measured as a function of time. The initial rate of oxidation was calculated from the tangent of the slope of the plots of volume of oxygen consumed against time. The influence of various parameters on the rate of reaction such as concentration of catalyst and the substrate, nature of various solvents and the temperature of the system was investigated.

5.3 RESULTS AND DISCUSSION

5.3.1 EFFECT OF THE CONCENTRATION OF TOLUENE

From Fig. 5.0 it is seen that the variation of oxygen uptake with time increases initially and after sometime it reaches towards saturation gradually. The rate of the oxidation was calculated from the tangent of the slope of the above plot and was found to increase on increasing the concentration of the toluene using a fixed quantity of polymer anchored ruthenium and palladium complexes The results are summarised in Tables 5.1 and 5.2. Thus an enhanced rate was observed from $7.6x10^{-2}$ ml min^{-1} as the concentration of toluene varies from $4.70x10^{-3}$ to 18 $80x10^{-3}$ $mol.lit^{-1}$ at 35°C

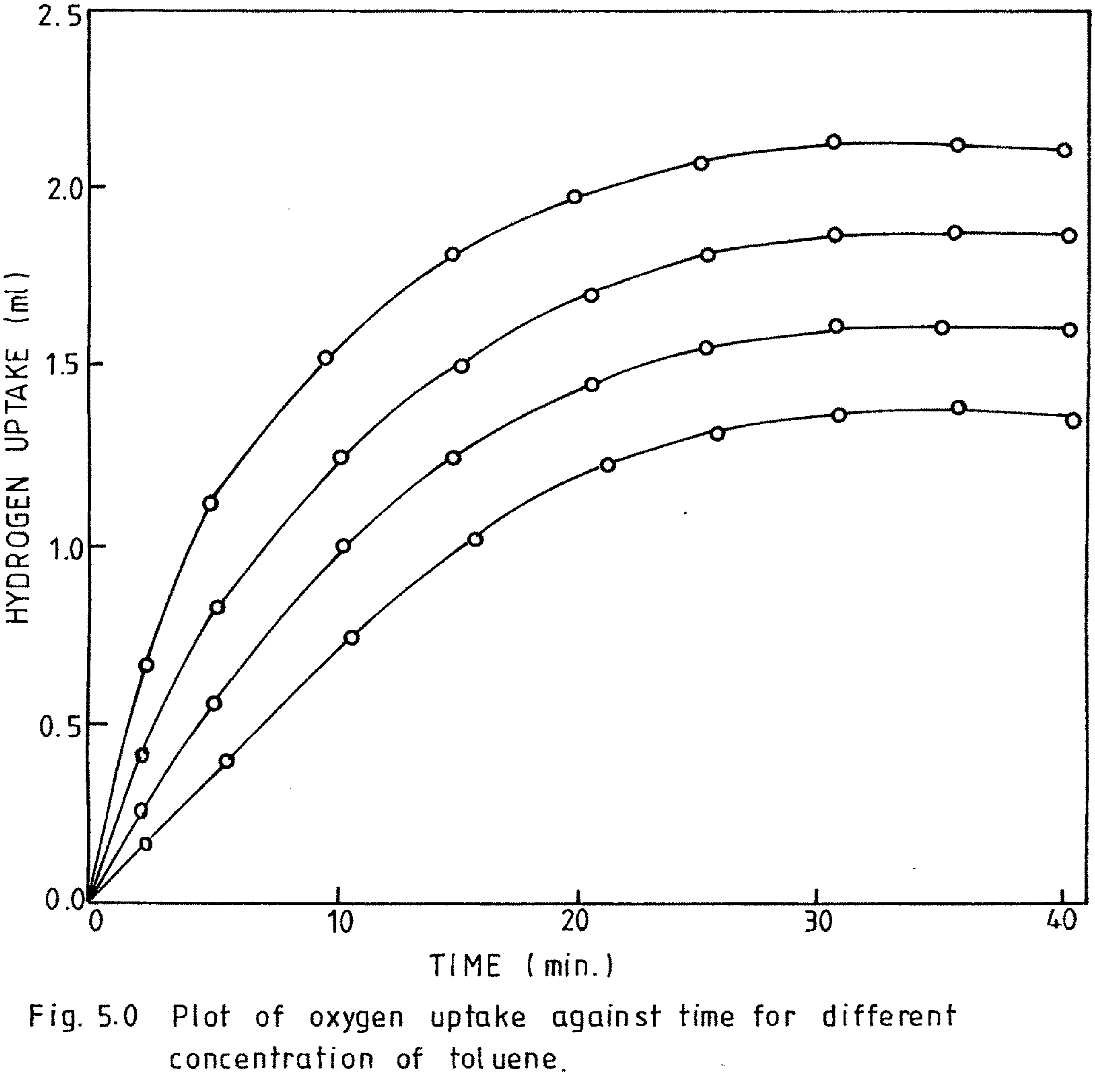


Fig. 5.0 Plot of oxygen uptake against time for different concentration of toluene.

Table 5.1

Effect of [Toluene] on the rate of oxidation using polymer supported catalysts at atmospheric pressure

Reaction temperature : 35°C
Volume of methanol : 20 ml

Catalyst	[Catalyst] (mol.lit^{-1})x10^{5}	[Toluene] (mol.lit^{-1})x10^{3}	Initial rate of reaction (ml.min^{-1})x10^{2}	Order of rea^{n}. w.r.t. [Toluene]
8P[Pd(L2AB)Cl$_2$]	2.58	4.70	8.5	0.30
		9.40	9.1	
		14.10	11.7	
		18.80	12.5	
8P[Ru(L2AB)Cl$_3$]	1.60	4.70	8.6	0.34
		9.40	9.0	
		14.10	10.9	
		18.80	12.3	
8P[Ru(Gly)Cl$_3$]	3.34	4.70	7.6	0.44
		9.40	9.4	
		14.10	12.5	
		18.80	15.9	
8P[Pd(Gly)Cl$_2$]	2.93	4.70	7.1	0.36
		9.40	8.5	
		14.10	10.6	
		18.80	15.1	

Table 5.2

Effect of [Toluene] on the rate of oxidation using homogeneous catalysts at atmospheric pressure

Reaction temperature : 35°C

Volume of methanol : 20 ml

Catalyst	[Catalyst] (mol.lit^{-1})x10^{4}	[Toluene] (mol.lit^{-1})x10^{3}	Initial rate of reaction (ml.min^{-1})x10^{2}	Order of rea^{n}. w.r.t. [Toluene]
[Ru(L2AB)Cl$_3$]	7.50	4.70	6.1	
		9.40	6.9	0.24
		14.10	7.9	
		18.80	8.5	
[Pd(L2AB)Cl$_2$]	7.50	4.70	6.0	
		9.40	7.2	0.28
		14.10	8.0	
		18.80	9.1	

using 8P[Ru(Gly)Cl_3] (Ru content is $3.34x10^{-5}$ $mol.lit^{-1}$) catalyst. Similar results were obtained using 8P[Pd(L2AB)Cl_2] catalyst; the rate was found to increase from $8.5x10^{-2}$ $ml.min^{-1}$ (Pd content is $2.58x10^{-5}$ $mol.lit^{-1}$) under similar conditions.

An attempt has been made in a separate experiment to synthesise the glycine complex of ruthenium and palladium ions in homogeneous system but no indication was found for the formation of the metal complex using UV-Vis spectral studies. However the study was made with L-2 aminobutanol complex of ruthenium and palladium ions in order to check the catalytic oxidation in homogeneous system. A considerable rate of oxidation was observed using a higher concentration of the metal complex catalyst. Thus in case of [Ru (L2AB)Cl_3] (metal content: $7.50x10^{-4}$ $mol.lit^{-1}$) the rate was found to vary from $6.1x10^{-2}$ to $8.5x10^{-2}$ ml. min^{-1} as the concentration of toluene varies from $4.70x10^{-3}$ to $18.80x10^{-3}$ $mol.lit^{-1}$ at 35°C. The other results are summarised in Table 5.2. The plot of log (initial rate) against log [toluene] was found to be straight line for homogeneous and heterogenised systems. (Figs. 5.1 and 5 2(a)). The order of reaction calculated from the slope of the above plots was found to be fractional.

5.3 2 INFLUENCE OF THE CATALYST CONCENTRATION

The influence of the concentration of catalyst on the rate of oxidation of toluene for all the supported catalysts was investigated and an enhanced rate was observed on increasing the amount of the catalyst The results are summarised in Table 5.3. In case of 8P[Ru(Gly)Cl_3], the rate was found to increase from $9.4x10^{-2}$ to $16.0x10^{-2}$ $ml.min^{-1}$ as the concentration of the catalyst varies from $3.34x10^{-5}$ to $5.84x10^{-5}$

Table 5.3

Influence of [Catalyst] on the rate of oxidation using polymer supported catalysts at atmospheric pressure

Reaction temperature : 35°C

Volume of methanol : 20 ml

Catalyst	[Toluene] (mol.lit^{-1})x10^{3}	[Catalyst] (mol.lit^{-1})x10^{5}	Initial rate of reaction (ml.min^{-1})x10^{2}	Order of rea^{n}. w.r.t. [Catalyst]
8P[Pd(L2AB)Cl$_2$]	9.40	2.58	8.8	
		3.23	9.1	0.71
		3.87	10.2	
		4.52	12.0	
8P[Ru(L2AB)Cl$_3$]	9.40	1.60	9.0	
		2.01	10.7	0.68
		2.41	12.0	
		2.81	13.4	
8P[Ru(Gly)Cl$_3$]	9.40	3.34	9.4	
		4.17	13.6	0.88
		5.01	14.5	
		5.84	16.0	
8P[Pd(Gly)Cl$_2$]	9.40	2.93	8.5	
		3.67	12.5	0.86
		4.40	13.8	
		5.13	15.0	

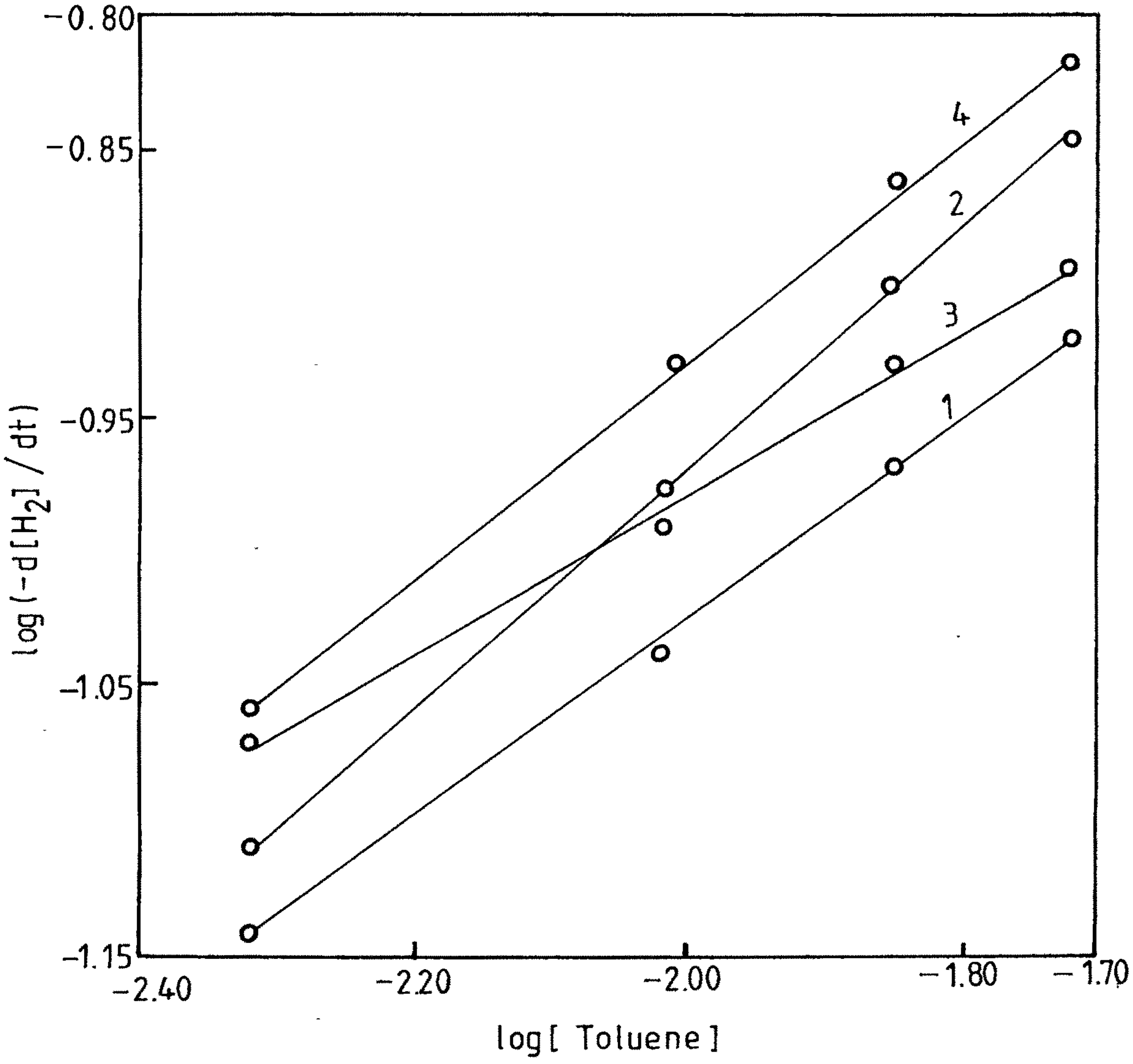


Fig. 5.1 log-log plot of initial rate vs.[Toluene] for

(1) 8P[Pd(Gly)Cl$_2$] (2) 8P[Ru(Gly)Cl$_3$]

(3) 8P[Pd(L2AB)Cl$_2$] (4) 8P[Ru(L2AB) Cl$_3$]

mol.lit^{-1} at a constant concentration of toluene (i e. 9.40x10^{-3} mol.lit^{-1}). Similar results were obtained while using 8P[Ru(L2AB)Cl$_3$] catalyst, the rate was found to increase from 9.0x10^{-2} to 13.4x10^{-2} ml.min^{-1} as the concentration of the catalyst varies from 1.60x10^{-5} to 2.81x10^{-5} mol.lit^{-1} under similar condition.

The study was made at various concentration of the catalysts in homogeneous system and the rate was found to increase by varying the concentration of the catalyst. Thus in case of [Ru(L2AB)Cl$_3$] an enhanced rate was observed from 5.1x10^{-2} to 9.2x10^{-2} ml.min^{-1} as the concentration varies from 5.0x10^{-5} to 12.5x10^{-5} mol.lit^{-1} at 35°C. The results for other catalysts are reported in Table 5 4. The order of reaction calculated from the linear plot of log (initial rate) against log [Catalyst] for homogeneous as well as heterogenised systems was found to be fractional (Figs. 5.2(b) and 5.3). The results are given in Tables 5.3 and 5.4. The fractional order of reaction is indicative of the fact that all the active sites especially in heterogenised systems may not be available on the surface to catalyse the reaction because of the swellability of the polymers. The steric hindrance of the complex molecules present on the surface can also be taken into consideration as has already been discussed in chapter-4

5.3.3 EFFECT OF TEMPERATURE

The effect of temperature on the rate of oxidation of toluene was studied in the range of 30-45°C and the results are summarised in Tables 5 5 and 5.6. The rate of oxidation was found to increase with an increase in temperature for all the catalysts An enhanced rate was observed from 7.3x10^{-2} to

Table 5 4

Influence of [Catalyst] on the rate of oxidation using homogeneous catalysts at atmospheric pressure

Reaction temperature . 35°C

Volume of methanol . 20 ml

Catalyst	[Toluene] (mol lit^{-1})x10^{3}	[Catalyst] (mol.lit^{-1})x10^{4}	Initial rate of reaction (ml min^{-1})x10^{2}	Order of rea^{n}. w.r.t [Catalyst]
[Ru(L2AB)Cl$_3$]	9 40	5.00	5.1	
		7.50	6.9	0.68
		10.00	8.7	
		12.50	9 2	
[Pd(L2AB)Cl$_2$]	9 40	5.00	5.7	
		7.50	7.2	0.58
		10.00	8.5	
		12.50	9.7	

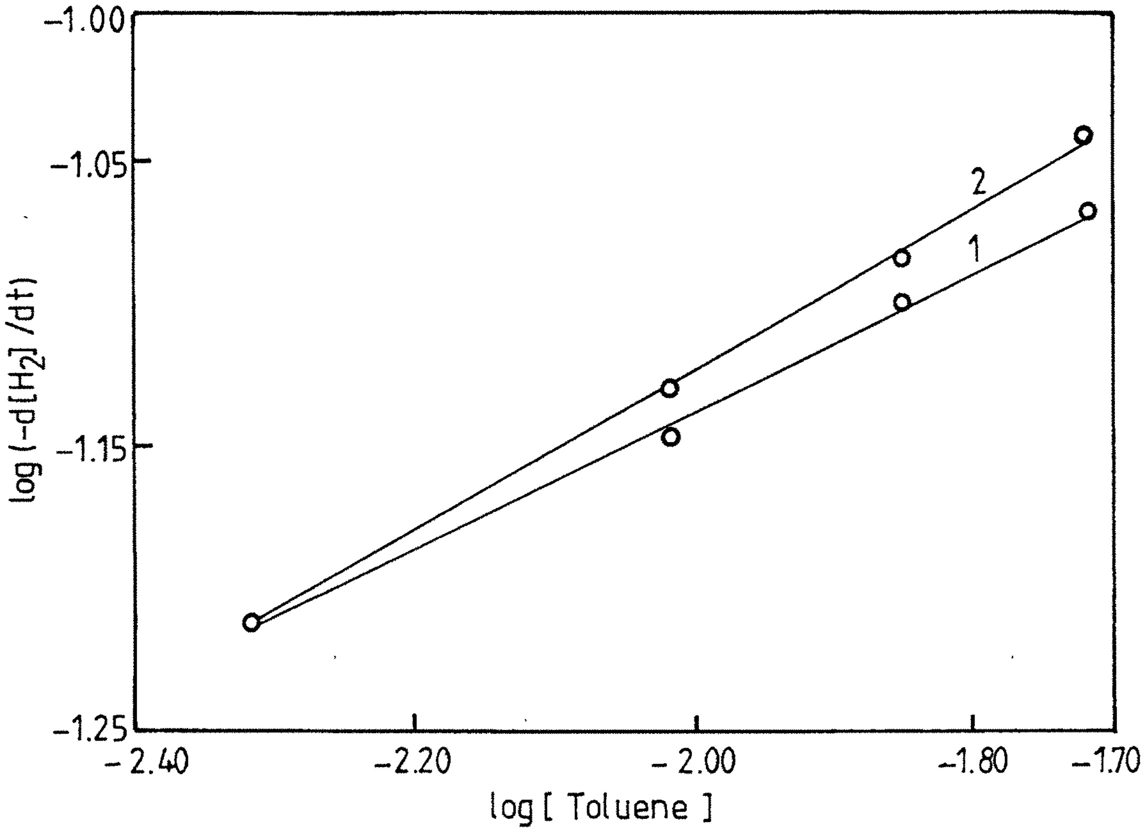


Fig. 5.2(a) log-log Plot of initial rate vs. [Toluene] for (1) [Ru(L2AB)Cl$_3$] (2)[Pd (L2AB) Cl$_2$]

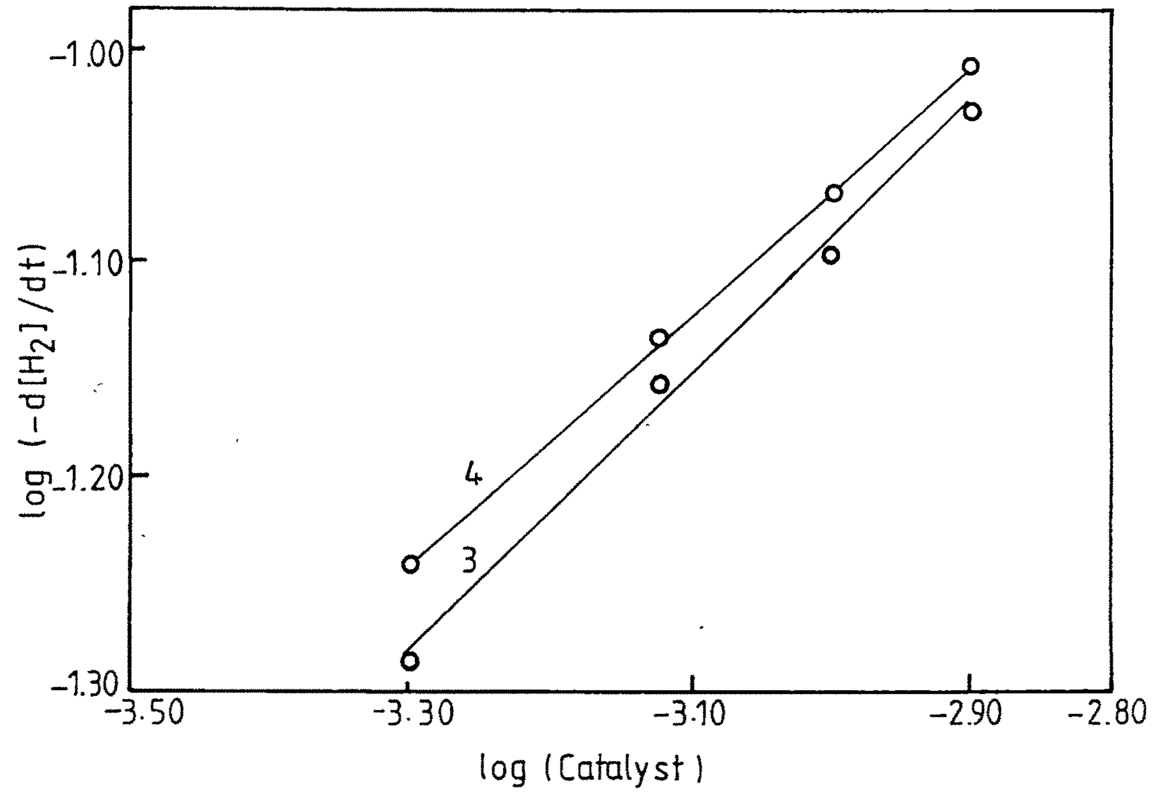


Fig. 5.2 (b) log-log plot of initial rate vs. [catalyst]
(3) [Ru(L2AB)Cl$_3$) (4) [Pd(L2AB)Cl$_2$]

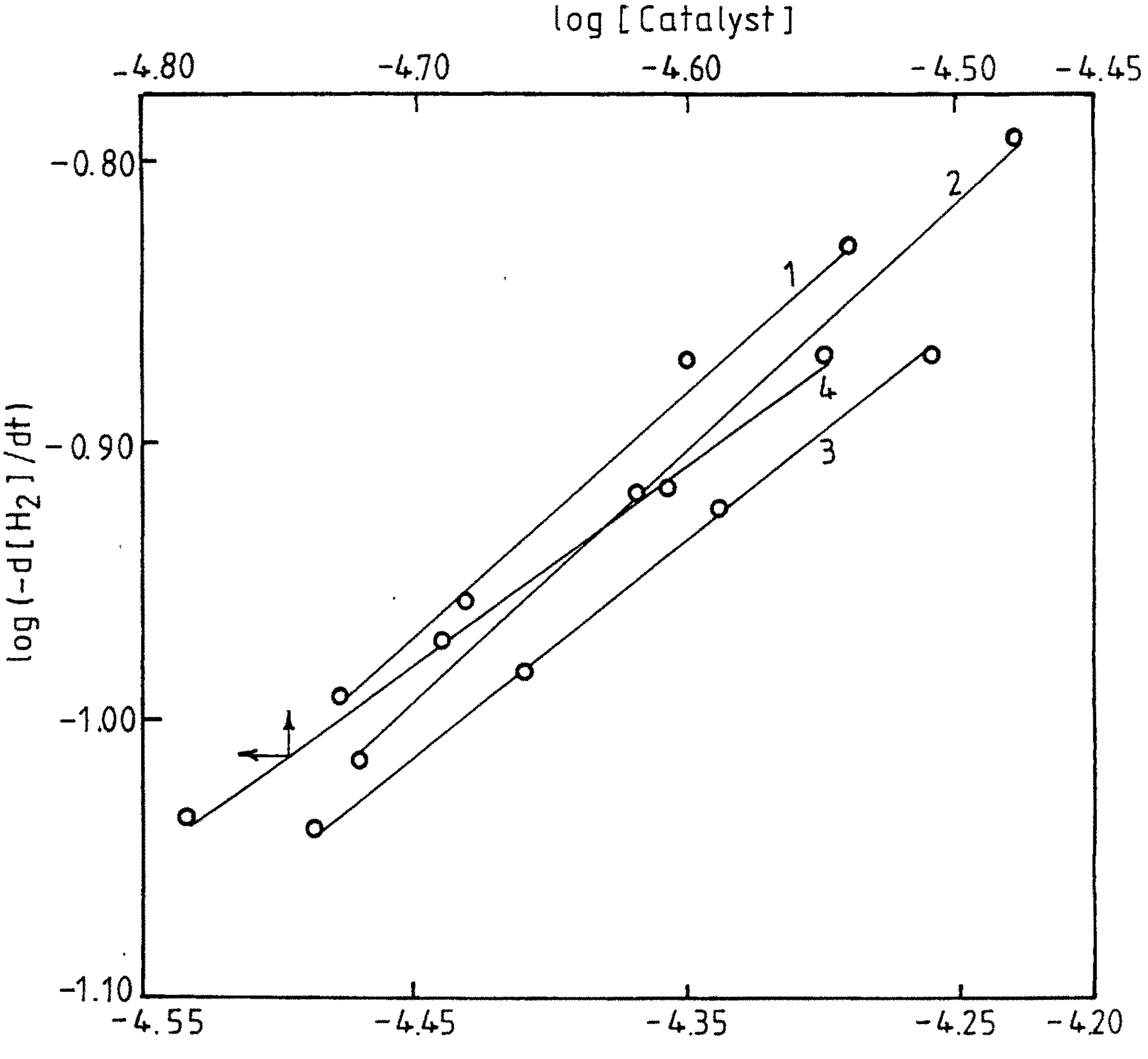


Fig. 5.3 log-log plot of initial rate vs. [catalyst] for
(1) 8P[Pd(Gly)Cl_2] (2) 8P[Ru(Gly)Cl_3]
(3) 8P[Pd(L2AB) Cl_2] (4) 8P[Ru(L2AB)Cl_3]

Table 5.5

Effect of temperature on oxidation of toluene using polymer supported catalysts at atmospheric pressure

[Toluene] (mol.lit^{-1}) 9.40x10^{-3}

Volume of methanol : 20 ml

Catalyst	[Catalyst] (mol.lit^{-1})x10^{5}	Temp. (°C)	Initial rate of reaction (ml.min^{-1})x10^{2}	Energy of activation (kcal.mol^{-1})	Entropy of activation (eu)
8P[Pd(L2AB)Cl$_2$]	2.58	30	7.4	8.7	-45.4
		35	9.1		
		40	11.4		
		45	13.1		
8P[Ru(L2AB)Cl$_3$]	1.60	30	7.2	7.6	-49 6
		35	9.0		
		40	10.9		
		45	13.1		
8P[Ru(Gly)Cl$_3$]	3.34	30	7.3	9.0	-43.7
		35	9.4		
		40	13.0		
		45	15.2		
8P[Pd(Gly)Cl$_2$]	2.93	30	6.9	8.0	-47 6
		35	8.5		
		40	10.4		
		45	13.1		

Table 5.6

Effect of temperature on oxidation of toluene using homogeneous catalysts at atmospheric pressure

[Toluene] (mol.lit^{-1}) : 9.40x10^{-3}

Volume of methanol · 20 ml

Catalyst	[Catalyst] (mol.lit^{-1})x10^4	Temp. (°C)	Initial rate of reaction (ml.min^{-1})x10^2	Energy of activation (kcal.mol^{-1})	Entropy of activation (eu)
[Ru(L2AB)Cl$_3$]	7.50	30	5.7		
		35	6.9	6.2	-53.9
		40	8.2		
		45	9.3		
[Pd(L2AB)Cl$_2$]	7.50	30	6.5		
		35	7.2	4.2	-60.3
		40	8.3		
		45	9.1		

15.2×10^{-2} ml.min^{-1} for 8P[Ru(Gly)Cl$_3$] (metal content : 3.34×10^{-5} mol.lit^{-1}) catalyst as the temperature is raised from 30 to 45°C keeping constant concentration of toluene as 9.40×10^{-3} mol.lit^{-1}.Similar results were observed for 8P[Ru(L2AB)Cl$_3$] catalyst; the rate was found to increase from 7.2×10^{-2} to 13.1×10^{-2} ml.min^{-1} as the temperature raised from 30 to 45°C under similar condition (Table 5.5).

The values for the energy of activation calculated from the Arrhenius plot were found to be low and dependent on the nature of the catalyst for homogeneous as well as heterogenised systems. Thus in case of 8P[Ru(Gly)Cl$_3$] and 8P[Pd(L2AB)Cl$_2$] the values obtained for energy of activation were found to be 9.0 and 8.7 kcal.mol^{-1} respectively. The other results are tabulated in Tables 5.5 and 5.6. In all cases low energy of activation was observed which is indicative of the fast process. The quick attainment of the equilibrium found in the present study is in agreement with the above result.(Figs 5.4,5.5)

The entropy of activation calculated by the use of the rate values and the energy of activation (wide supra) was found to be negative i.e. in the range of -43.7 to -60.3 eu (Tables 5.5, 5.6). A decrease in entropy of activation is indicative of a decrease in the randomness of the system. This is associated with a loss of freedom of motion due to fixation of the catalyst molecules on the surface of the polymer matrix.

The study was also made in homogeneous system using two different catalysts keeping a higher concentration of the metal ions (wide supra) at various temperature in order to get a considerable rate of the reacting system and the corresponding energy of activation was also calculated using Arrhenius

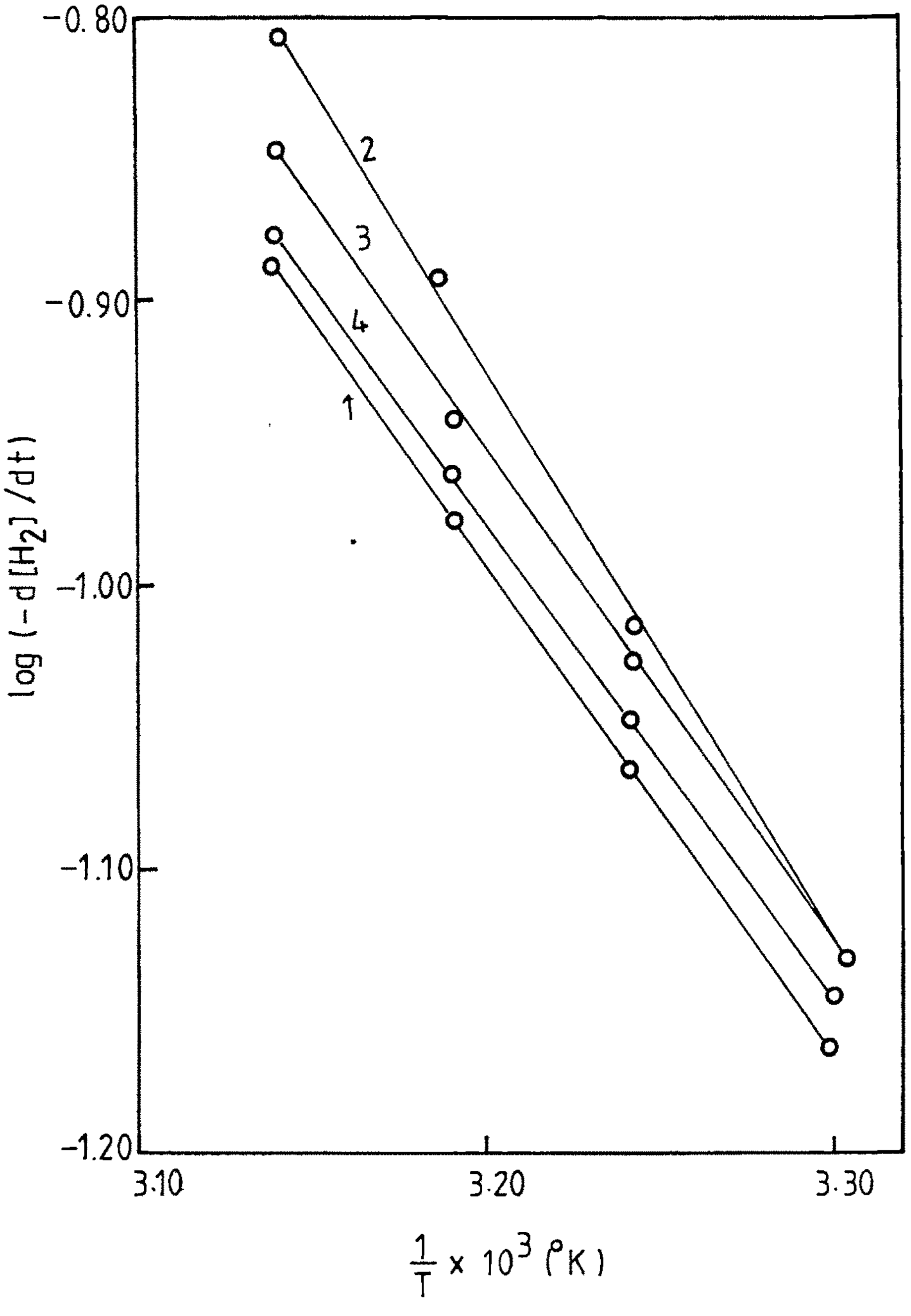


Fig. 5.4 Arrhenius plot for catalysts

(1) 8P [Pd(Gly) Cl_2] (2) 8P [Ru(Gly) Cl_3]

(3) 8P [Pd(L2AB) Cl_2] (4) 8P [Ru(L2AB) Cl_3]

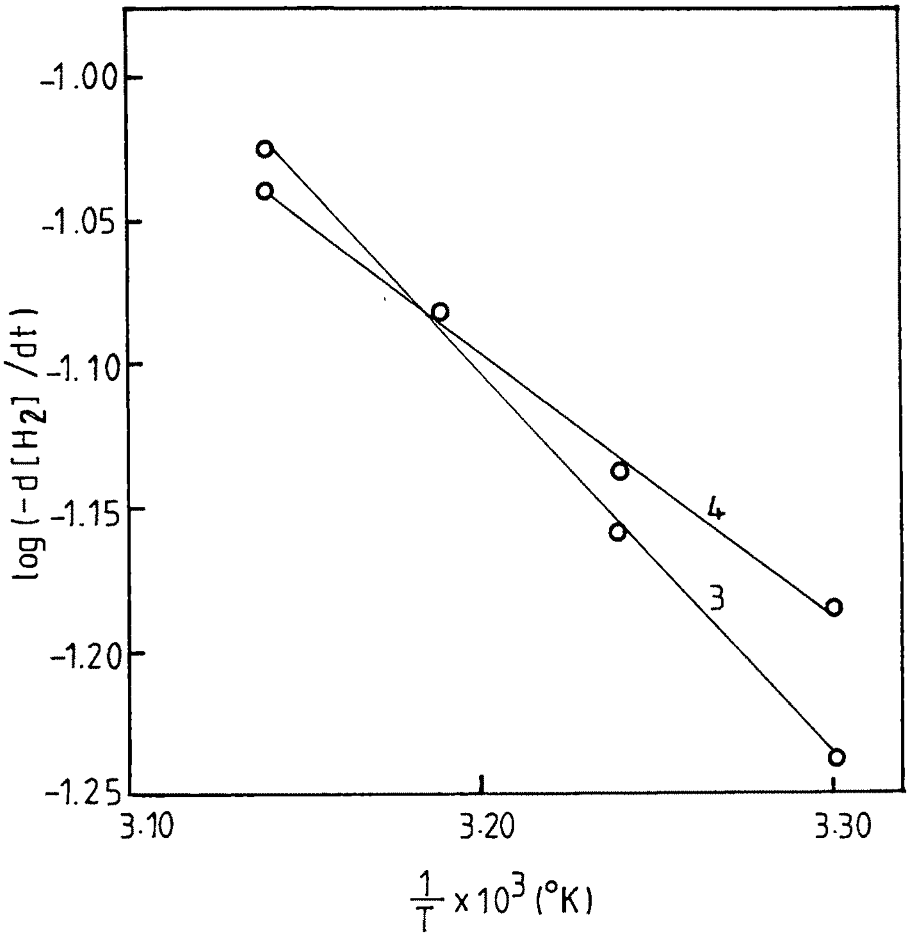


Fig. 5.5 Arrhenius plot for catalysts
(3) $[Ru(L2AB)Cl_3]$ (4) $[Pd(L2AB)Cl_2]$

equation. Thus the rate observed for the oxidation of toluene using [Ru(L2AB)Cl_3] as a homogeneous catalyst was found to increase from 5.7x10^{-2} to 7.3x10^{-2} ml.min^{-1} on increasing the temperature from 30 to 45°C; the energy of activation was found to be 6.2 kcal.mol^{-1}. The values for entropy of activation calculated were found to be -53.9 eu and -60.3 eu for [Ru(L2AB)Cl_3] and [Pd(L2AB)Cl_2] respectively.

It is evident from the above results that in case of oxidation reaction also, the rate was found to be lower even after using a higher concentration of the metal ions in homogeneous system. Thus the rate was found to be 5.7x10^{-2} ml.min^{-1} in homogeneous system (Ru content : 7.50x10^{-4} mol.lit^{-1}) while in case of heterogenised homogeneous system it was observed to be 7.2x10^{-2} ml.min^{-1} (Ru content : 1.60x10^{-5} mol.lit^{-1}) at 30°C (Tables 5.5 and 5.6)

5.3.4 EFFECT OF SOLVENT

As already mentioned in previous chapter that the solvent plays very important role to control the activity and the selectivity of the polymer anchored catalysts, the study was made by varying the solvents in order to investigate the oxidation of toluene and the rate was found to increase in this case also with the polarity of the solvents. The results are summarised in Table 5.7. Thus with 8P[Ru(Gly)Cl_3] (catalyst content:3.34x10^{-5} mol.lit^{-1}), the rate was found to be 5.7x10^{-2} ml.min^{-1} using benzene as a solvent while with methanol, it was found to be 9.4x10^{-2} ml.min^{-1} at a constant concentration of toluene i.e. 9.40x10^{-3} mol.lit^{-1}. Ford et al have also reported that the rate of the reaction increases with the swelling power of the solvent in the reaction of 1-bromooctane

Table 5.7

Kinetics of oxidation of toluene by polymer supported catalysts at atmospheric pressure using various solvents

Reaction temperature : 35°C

Volume of methanol : 20 ml

[Toluene] (mol.lit^{-1}) : 9.40x10^{-3}

Catalyst	[Catalyst] (mol.lit^{-1})x10^{5}	Solvent	Initial rate of reaction (ml.min^{-1})x10^{2}
8P[Ru(Gly)Cl$_3$]	3.34	Methanol	9.4
		Ethanol	8.5
		THF	6.6
		Benzene	5.7
8P[Pd(Gly)Cl$_2$]	2.93	Methanol	8.5
		Ethanol	7.5
		THF	5.5
		Benzene	5.0

with aqueous sodium cynide catalysed by polystyrene bound butyl phosphonium ion (60). The more swollen the catalyst, the faster intraparticle diffusion and the faster reaction, hence selection of good swelling agent is essential to achieve maximum efficiency with polymer bound catalysts.

5.3.5 STABILITY STUDY OF CATALYSTS

The stability test of both the polymer anchored catalysts was carried out at 35°C for 10 hours. The detailed procedure is given in the preceding chapter. 20.0µl of the substrate was injected in each cycle. After completion of the reaction, 30 minutes were allowed to lapse before the next injection was made. The rate of oxidation of toluene was measured as a function of time for both fresh as well as used catalysts. The results are given in Table 5.8. It was found that the rate is unaltered till four hours after which it decreases slowly. The estimation of metal content at the end of the reaction showed a loss of about 50% of the metal from the polymer support This indicates that these catalysts can be used at least for four cycles without much alteration of the rate.

5.3.6 RATE EQUATION

In the present study the partial pressure of oxygen and the amount of catalyst were kept constant in all the experiments, the solvent along with the catalyst was initially saturated with oxygen followed by the injection of toluene and hence actual uptake of oxygen was measured. A slight colour change in the beads was observed in case of ruthenium complex catalysts during the reaction while no change was observed in case of polymer supported palladium complex catalyst

Table 5.8

Life cycle study for the polymer supported catalysts

Total time on stream : 10h

Reaction temperature : 35°C

Volume of methanol : 20 ml

[Toluene] $(mol.lit^{-1})$. $9.40x10^{-3}$

		Fresh catalyst	Used catalyst
	Time (min)	Initial rate of reaction $(ml.min^{-1})x10^2$	Initial rate of reaction $(ml.min^{-1})x10^2$
$8P[Ru(Gly)Cl_3]$[a]	60	9.4	9.3
	120	9.3	9.2
	180	9.1	9.0
	240	9.0	8.8
	300	8.6	8.3
$8P[Pd(Gly)Cl_2]$[b]	60	6.1	6.1
	120	6.1	6.1
	180	6.1	6.1
	240	5.6	5.4
	300	5.1	5.0

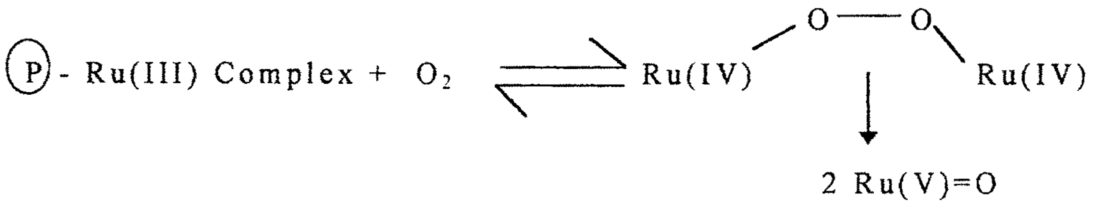
a . Amount of catalyst : $3.34x10^{-5}$ $mol.lit^{-1}$ Ru present on the surface.

b : Amount of catalyst . $2.93x10^{-5}$ $mol.lit^{-1}$ Pd present on the surface.

In order to investigate the mechanism of the reaction, ruthenium chloride was mixed with L2AB (1:1) in homogeneous medium and oxygen was bubbled through it. A change in colour was observed from greyish to violet which after adding toluene as a substrate disappeared slowly. However no peak was observed in UV-Vis spectrophotometric studies probebly due to the unstable nature of the complex formed at intermediate stage. This is an indicative of the fact that on addition of the substrate, there is a transfer of oxygen from the complex to the substrate thereby disappearing in colour is observed.

The reaction mechanism for the oxidation of olefins by the use of metal ions/complexes in the homogeneous system has been studied widely (19-22,30) and the formation of peroxo and oxo complexes was suggested to be responsible for the transfer of oxygen to the substrate. Vaska et al have reported the formation of peroxo and superoxo complexes when dioxygen is covalently bound to the metal centre(61). The formation of the oxo complex and the transfer of oxygen via this route has been suggested by Taquikhan et al in the ruthenium (III) complex catalysed oxidation of olefins(62).

On the basis of the experimental evidences and literature data a probable reaction mechanism is proposed.



$$\text{(P)-Ru(III) Complex} + O_2 \rightleftharpoons \text{Ru(IV)}-O-O-\text{Ru(IV)} \longrightarrow 2\ \text{Ru(V)=O}$$

$$\text{Ru(V)=O} + \text{Toluene} \longrightarrow \text{Benzaldehyde} + \text{Ru(III) Complex}$$

Keeping the amount of O_2 constant, the rate law may be written as

$$R = k^{1}\ [\text{ Catalyst}]\ [\text{ Toluene }]$$

Thus on increasing the amount of the catalyst as well as the concentration of toluene, an increase in rate was observed which is in agreement with the above rate equation.

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