

## **CHAPTER # 4**

# **KINETICS OF HYDROGENATION OF NITROBENZENE**

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#### 4.1 INTRODUCTION

Catalytic hydrogenation is one of the most powerful tool for the synthesis of organic compounds. Most of the functional groups can be reduced readily often under mild operating conditions. A number of heterogeneous catalysts has been used for hydrogenation reactions in chemical as well as in pharmaceutical industries (1-3). Homogeneous catalysts have however been found in some cases to be used for hydrogenation reaction viz. the wilkinson's catalyst  $[\text{Rh}(\text{PPh}_3)\text{Cl}]$  for olefin hydrogenation, synthesis of thermally unstable or otherwise sensitive products, the synthesis of the optically active compounds by asymmetric hydrogenation etc. (4-9). The recent development of homogeneous hydrogenation provides the model which is helpful in understanding the various factors in catalytic hydrogenation. In most of the cases, the transition metals of group (VIII) or their complexes were found suitable as hydrogenation catalysts (10-13). Effective combinations have resulted from  $d^8$  spin paired (low spin) configuration arising from strong ligand fields or electron delocalizing ligands. The mechanism by which these homogeneous catalysts activate molecular hydrogen and substrate molecules and transfer the activated hydrogen to the substrate often with considerable stereospecificity is well understood (14-16).

Transition metal ions/complexes have been widely used for catalyzing various reactions including homogeneous hydrogenation of olefins (17-24). The hydrogenation of maleic and fumaric acids to succinic acid has been studied in aqueous solution using  $\text{Ru(II)}$  chloride as catalyst (25). Rhodium complex of water soluble phosphine catalysed the hydrogenation of olefins dissolved in polar as well as in non-

polar solvents in a single step (26). The TPP complex of Ru(II) was found to be an efficient catalyst for the homogeneous hydrogenation of cyclohexene and benzaldehyde probably due to formation of the hydrido complex (15). An enhanced activity was also observed by Hallman et al (27) using Ru(II) complex of TPP due to formation of the hydrido complex in presence of trimethylamine. The complexes of Ru(II), Pt(II), Co(II), Rh(I) etc were found to activate molecular hydrogen and were able to catalyse the hydrogenation of olefins under homogeneous condition (28). Reduction of nitrobenzene was carried out using the metal complexes of Pd (29,30), Rh (31,32), Ru (33,34) and Co (35) and a considerable rate was observed. Investigations have also been made for the homogeneous hydrogenation of unsaturated organic compounds using various metal ions/complexes (36-40).

The main problem of the homogeneous catalyst is the separation of the expensive catalysts from the reaction system at the end of the reaction, handling of these sensitive organometallic compounds with metals in low oxidation states and the choice of the solvent, which invariably depends on the solubility of the catalyst. These catalysts are usually coordinatively unsaturated and have a tendency to aggregate thereby blocking the coordination sites necessary for catalysis. The catalytic activity of these metal complexes active in their monomeric form could be enhanced by anchoring them on to a rigid inorganic oxide.

A number of reactions has been carried out for olefin hydrogenation catalyzed by metal complexes supported on inorganic oxides (41-47). The hydrogenation of 1-hexene using

Pd / Zeolite (48) and aniline by Rh on alumina (49) has been carried out and the activity was found to be higher than their homogeneous counterparts. Gattania has used ruthenium clusters supported on alumina and silica for CO hydrogenation reaction (50). Other studies include the hydrogenation of toluene and xylene by Pd on  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  (51,52) and methyl ester by Pd, Pt, Rh and Ru on activated charcol (53). Studies have also been carried out for the hydrogenation of nitrobenzene using various metal ions supported on inorganic oxides and a considerable rate was observed (54-58).

The main difficulty with the anchored catalysts on inorganic oxides is the leaching of the metal ions from the surface which can deactivate the catalysts as also the susceptibility of poisoning the catalysts by adsorbed substances. This problem could be minimised by heterogenizing the homogeneous catalyst using polymer as a support (59-61). A number of studies have been carried out in the hydrogenation of olefins by metal ions/complexes supported on commercially available polymers (62-68).

Reduction of nitrobenzene to aniline has been studied by Drago et.al. using polystyrene-bipyridine dispersed palladium metal and it was found to be readily hydrogenated using this catalyst (69). Holy used palladium-anthranilic acid complex supported on chloromethylated polystyrene beads to investigate the hydrogenation of nitrobenzene and the catalyst was found to be active even at room temperature (70). Several other workers have also investigated the hydrogenation of nitrobenzene using various metal complexes supported on polymers (71-74). Yokerson et.al. (75) studied the hydrogenation of nitrobenzene using polymer supported  $\text{RhCl}_3$  catalyst

modified by methyl pyrazole, imidazole and benzimidazole. Nisibulin (76) has seen the influence of concentration of nitrobenzene on the rate of hydrogenation in aliphatic alcohol and an increase in the rate was observed. Recently, Yang Bin et al (77) have used poly-N-Vinyl-2-Pyrrolidone supported Pd - Pt bimetallic catalysts for the hydrogenation of nitroaromatics.

The polymer bound nonchelated metal complexes have been studied extensively (78,79) but these transition metal complexes are occasionally so labile and they fail to act as a supported catalyst (80,81) or sometimes it results a significant metal leaching into the solution (82).

Metal ions attached to polymer bound chelating ligands were found to be more stable and showed high catalytic activity (83-86). Chelating resins employing phosphine ligands have been widely investigated in several catalytic studies during the past decade (87,88). Little work has been carried out using nitrogen and oxygen donor groups as a chelating ligand. Some of the most versatile chelating systems such as 2,2'-dipyridine has been attached to an insoluble polystyrene support and its potential as a polymer bound chelate has been demonstrated (89).

The present investigation deals with the synthesis of polymer bound chelating metal complexes of Ru(III) and Pd (II) using glycine and 2-amino butanol as ligands and to investigate the catalytic activity for the hydrogenation of nitrobenzene to aniline which has been widely used in manufacturing the chemical products and the intermediates in polymer, rubber, agricultural and dye industries (90). Application has also been made to manufacture the sulfa drugs, acetanilide, antipyretic

and sweetening agents (91). The kinetics of the above reaction has been studied. The influence of various parameters on the rate such as the catalyst and substrate concentration, temperature of the system and the variation of the solvents has been investigated. The life cycle of the catalysts has also been studied.

## 4.2 EXPERIMENTAL

### 4.2.1 MEASUREMENT OF CATALYTIC ACTIVITY FOR HYDROGENATION REACTIONS

The hydrogenation reaction was carried out in a magnetically stirred glass reactor in a controlled kinetic regime with a stirring speed of 650 rpm at 35°C using methanol as a solvent. The progress of the reaction was followed by measuring the uptake of hydrogen as a function of reaction time at a constant temperature and pressure using a glass manometric apparatus. The experimental setup and detailed procedures are described earlier (Chapter 2, Section 2.11)

## 4.3 ANALYSIS OF KINETIC DATA

The experiments were carried out at various temperatures, different concentrations of the catalysts and the substrates as well as by varying the nature of the solvents. The stoichiometry of the reaction was checked by carrying out a few experiments at constant temperature and atmospheric pressure of hydrogen at different concentration of nitrobenzene. The product was analysed by the use of gas chromatograph using carbowax column and no side product was

observed (the chromatograms are given in chapter 2 ). The plots of the variation of hydrogen uptake at various interval of time for different concentrations of the catalysts and the substrates are given in Figs. 4.1 and 4.2 respectively. The initial rate of the reaction was calculated from the slope of the above plots.

#### 4.4 RESULTS AND DISCUSSION

##### 4.4.1 EFFECT OF CONCENTRATION OF NITROBENZENE

Fig. 4.2 indicates that the  $H_2$  uptake is fast in the initial stages, slows down later and proceeds gradually toward saturation in ~30 minutes for all sets of experiments. The initial rate of hydrogenation calculated from the slope of the above plots was found to increase on increasing the concentration of nitrobenzene. The results are summarised in Tables 4.1 to 4.3. Thus in case of  $2P[Ru(L2AB)Cl_3]$  catalyst (Ru content:  $1.58 \times 10^{-5}$  mol lit<sup>-1</sup>) an enhanced rate was observed from  $8.0 \times 10^{-2}$  to  $12.6 \times 10^{-2}$  ml.min<sup>-1</sup> by varying the concentration of nitrobenzene from  $4.83 \times 10^{-3}$  to  $19.50 \times 10^{-3}$  mol.lit<sup>-1</sup> (Table 4.1) at 35°C and one atmospheric pressure; in the case of  $2P[Pd(L2AB)Cl_2]$  (Pd content:  $2.58 \times 10^{-5}$  mol.lit<sup>-1</sup>) the rate increased from  $10.0 \times 10^{-2}$  to  $14.4 \times 10^{-2}$  ml min<sup>-1</sup> by varying the concentration of nitrobenzene as above at 35°C and one atm pressure (Table 4.2).

The straight line plot of the reciprocal of the rate versus reciprocal of the concentration of nitrobenzene at a constant concentration of catalyst at 35°C indicates that the rate of hydrogenation of nitrobenzene  $R$  is related to  $[S]$  by relationship



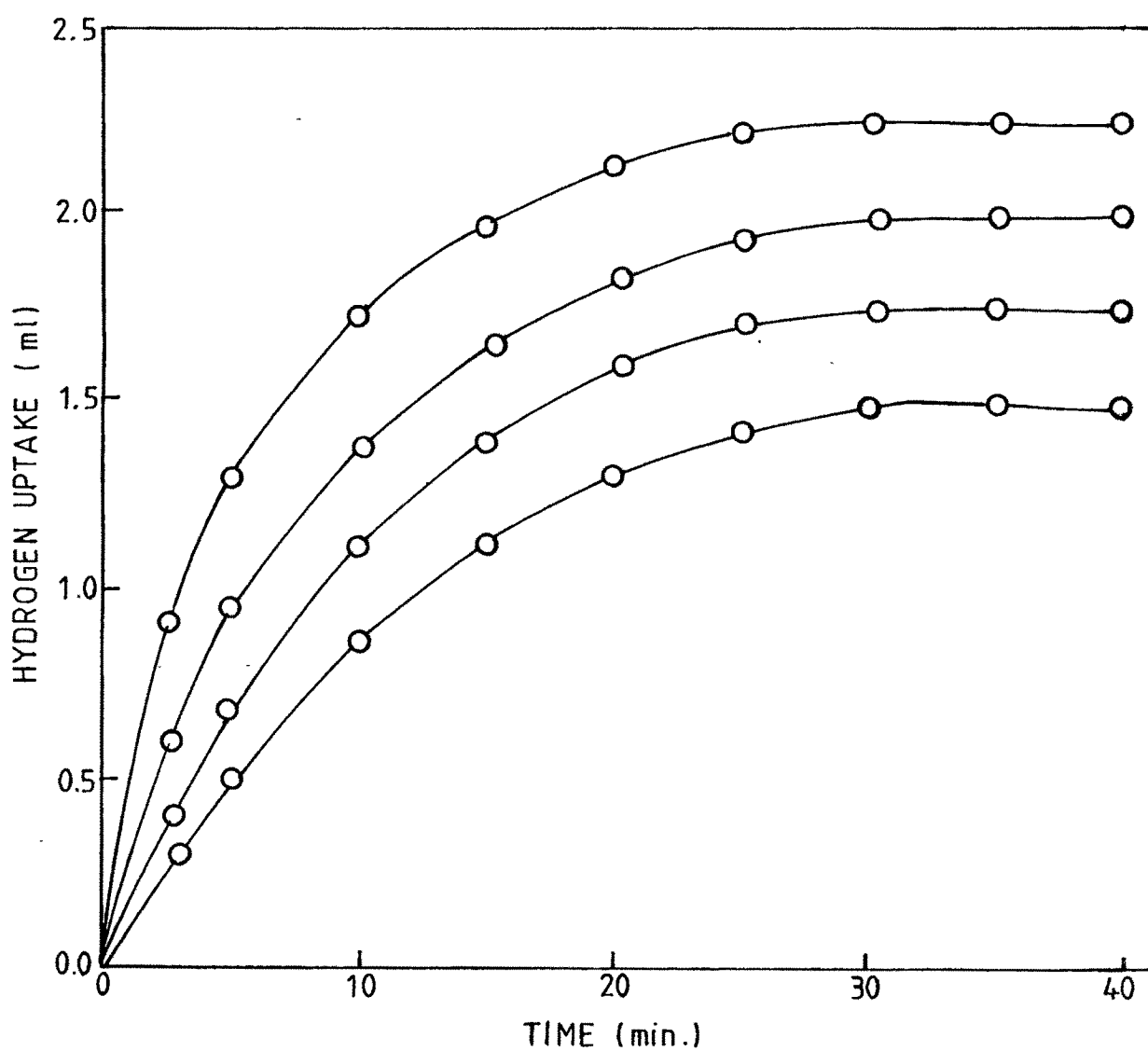


Fig. 4.1 Plot of hydrogen uptake against time for different concentration of catalyst.

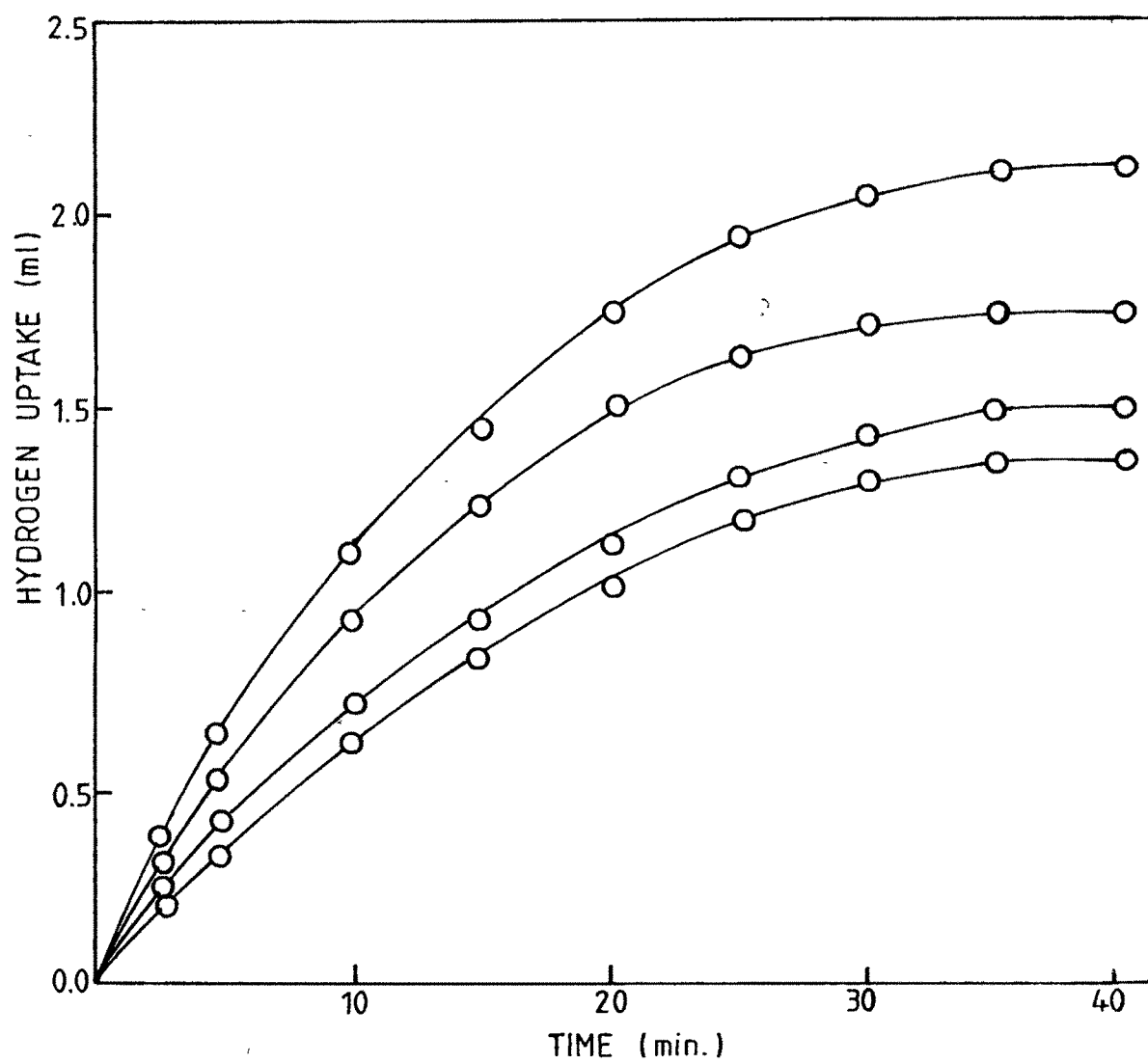


Fig. 4.2 Plot of hydrogen uptake against time for different concentration of nitrobenzene.

Table 4.1

Effect of [nitrobenzene] on rate of hydrogenation for polymer supported ruthenium catalysts in methanol at atmospheric pressure.

Reaction temperature : 35°C

Volume of methanol : 20 ml

Catalyst	[Catalyst] (mol.lit <sup>-1</sup> )x10 <sup>5</sup>	[Nitrobenzene] (mol.lit <sup>-1</sup> )x10 <sup>3</sup>	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Order of reac. <sup>n</sup> w.r.t [Nitrobenzene]
2P[Ru(L2AB)Cl <sub>3</sub> ]	1.58	4.83	8.0	
		9.72	8.8	0.35
		14.50	11.5	
		19.40	12.6	
8P[Ru(L2AB)Cl <sub>3</sub> ]	1.60	4.83	9.7	
		9.72	11.2	0.30
		14.50	12.6	
		19.40	13.8	
2P[Ru(Gly)Cl <sub>3</sub> ]	2.22	4.83	8.1	
		9.72	11.0	0.36
		14.50	12.3	
		19.40	13.6	
8P[Ru(Gly)Cl <sub>3</sub> ]	3.34	4.83	11.5	
		9.72	12.1	0.30
		14.50	13.0	
		19.40	14.8	

Table 4.2

Effect of [nitrobenzene] on rate of hydrogenation for polymer supported palladium catalysts in methanol at atmospheric pressure.

Reaction temperature : 35°C

Volume of methanol : 20 ml

Catalyst	[Catalyst] (mol.lit <sup>-1</sup> )x10 <sup>5</sup>	[Nitrobenzene] (mol.lit <sup>-1</sup> )x10 <sup>3</sup>	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Order of rea. <sup>n</sup> w.r.t. [Nitrobenzene]
2P[Pd(L2AB)Cl <sub>2</sub> ]	2.58	4.83	10.0	0.31
		9.72	13.6	
		14.50	14.1	
		19.40	14.4	
8P[Pd(L2AB)Cl <sub>2</sub> ]	2.58	4.83	14.1	0.33
		9.72	15.3	
		14.50	17.2	
		19.40	19.4	
8P[Pd(Gly)Cl <sub>2</sub> ]	2.93	4.83	9.2	0.20
		9.72	10.1	
		14.50	11.4	
		19.40	12.6	
14P[Pd(Gly)Cl <sub>2</sub> ]	2.90	4.83	9.9	0.30
		9.72	10.7	
		14.50	12.0	
		19.40	13.8	
14P[Pd(L2AB)Cl <sub>2</sub> ]	2.55	4.83	14.7	0.23
		9.72	15.8	
		14.50	18.7	
		19.40	20.0	

Table 4.3

Effect of [nitrobenzene] on the rate of hydrogenation for homogeneous catalysts in methanol at atmospheric pressure.

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

Catalyst	[Catalyst] (mol.lit <sup>-1</sup> )x10 <sup>4</sup>	[Nitrobenzene] (mol.lit <sup>-1</sup> )x10 <sup>3</sup>	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Order of rea. <sup>n</sup> w.r.t. [ Nitrobenzene]
[Ru(L2AB)Cl <sub>3</sub> ]	7.5	4.83	6.0	0.33
		9.72	6.6	
		14.50	8.8	
		19.40	9.7	
[Pd(L2AB)Cl <sub>2</sub> ]	7.5	4.83	6.3	0.38
		9.72	7.7	
		14.50	9.4	
		19.40	10.8	

$$\frac{1}{R} = a \frac{1}{[S]} + b$$

Where [S] is the concentration of the substrate and 'a' and 'b' are the slope and the intercept of the above plot respectively (Fig. 4.2a). Similar results have been given by Taquikhan et al (92) in the homogeneous hydrogenation of 1-heptene catalysed by Rh(I) complex.

The order of reaction calculated from the slope of the straight line plot of log (initial rate) against log [nitrobenzene] at a fixed concentration of catalyst, hydrogen pressure and temperature and was found to be fractional. The plots are shown in Figs. 4.3, 4.4 and 4.8(b) and the values for the fractional orders are given in Tables 4.1 to 4.3.

The hydrogenation reaction was also carried out in homogeneous system using Ru(III) and Pd(II) complexes of L2AB under similar condition and the rate was found to be slow as compared to the heterogenised homogeneous catalysts. In order to compare the results, the experiments were carried out keeping same concentration of the catalyst in homogeneous system as was present on polymer support a measurable hydrogen uptake was not observed. On the basis of few trial experiments higher concentration of the catalyst was thus chosen and a considerable rate of consumption of hydrogen obtained in homogeneous system. The results are summarized in Table 4.3. Thus in case of homogeneous and heterogenised homogeneous systems the values for the rate of reactions were found to be  $6.0 \times 10^{-2} \text{ ml.min}^{-1}$  and  $8.0 \times 10^{-2} \text{ ml.min}^{-1}$  as Ru concentration present in the system are  $7.5 \times 10^{-4} \text{ mol.lit}^{-1}$  and

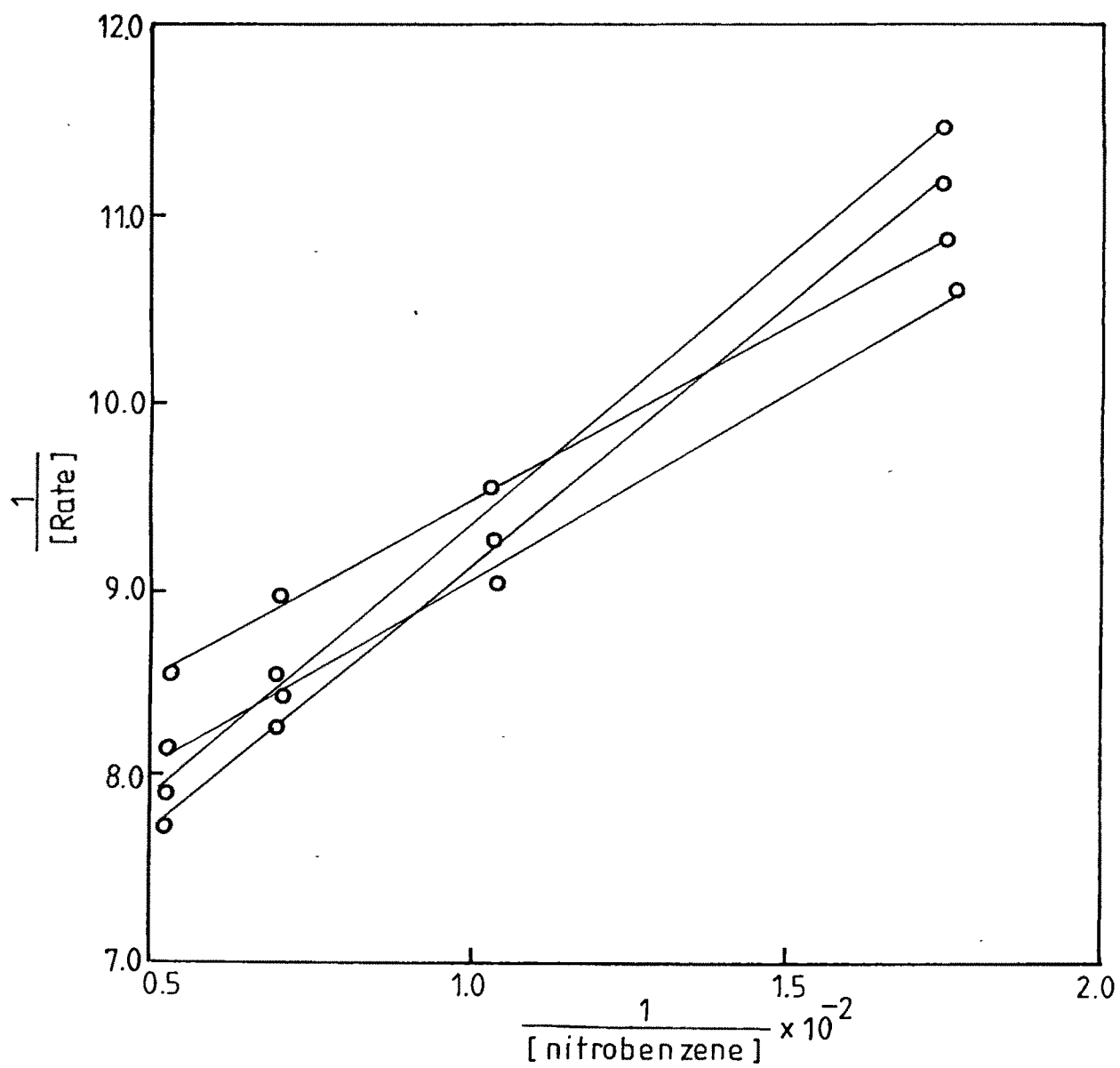


Fig. 4.2(a) Plot of  $\frac{1}{[\text{nitrobenzene}]}$  vs.  $\frac{1}{\text{Rate}}$  for polymer supported ruthenium catalysts.

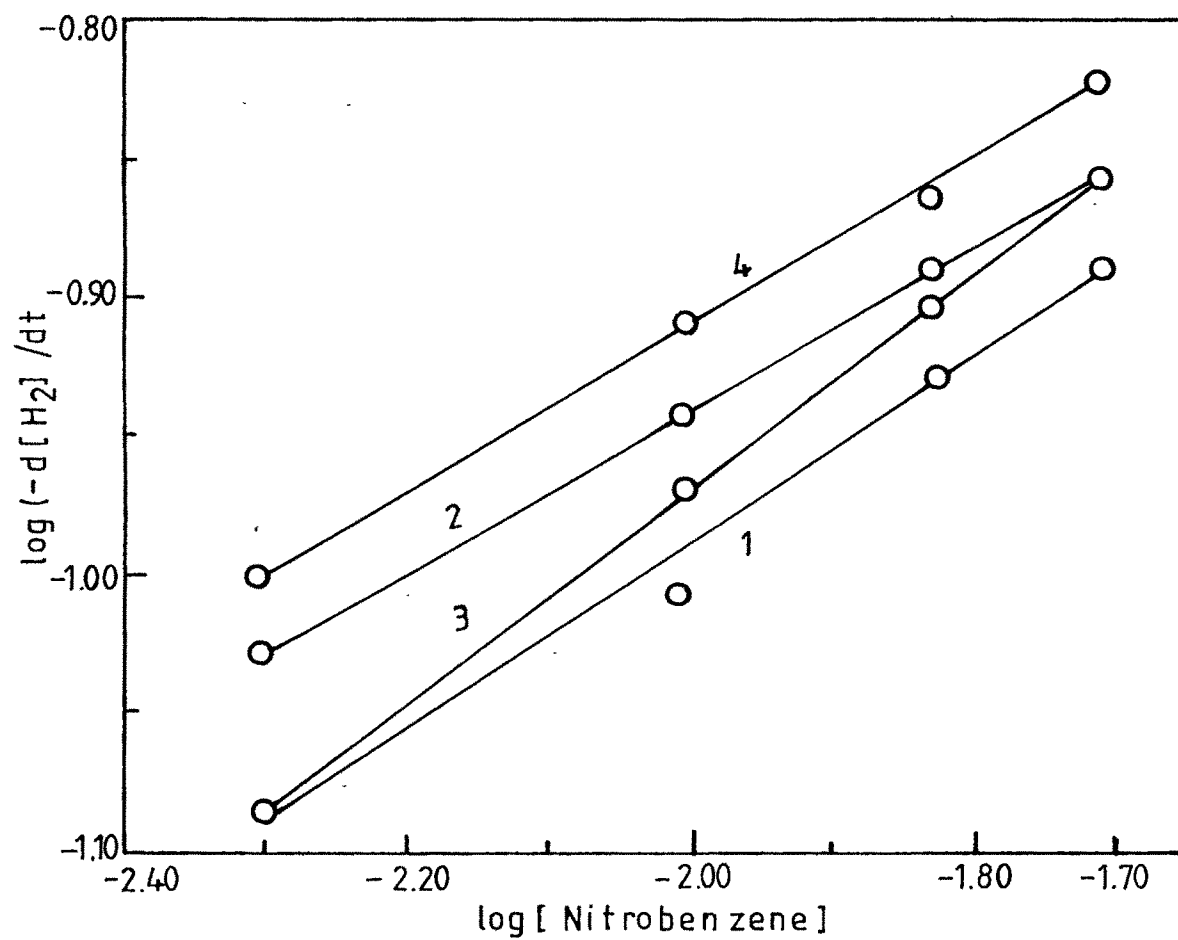


FIG. 4.3  $\log - \log$  plot of the initial rate Vs [ Nitrobenzene ] for  
 [1]  $2P[Ru(L2AB)Cl_3]$  [2]  $8P[Ru(L2AB)Cl_3]$   
 [3]  $2P[Ru(Gly)Cl_3]$  [4]  $8P[Ru(Gly)Cl_3]$



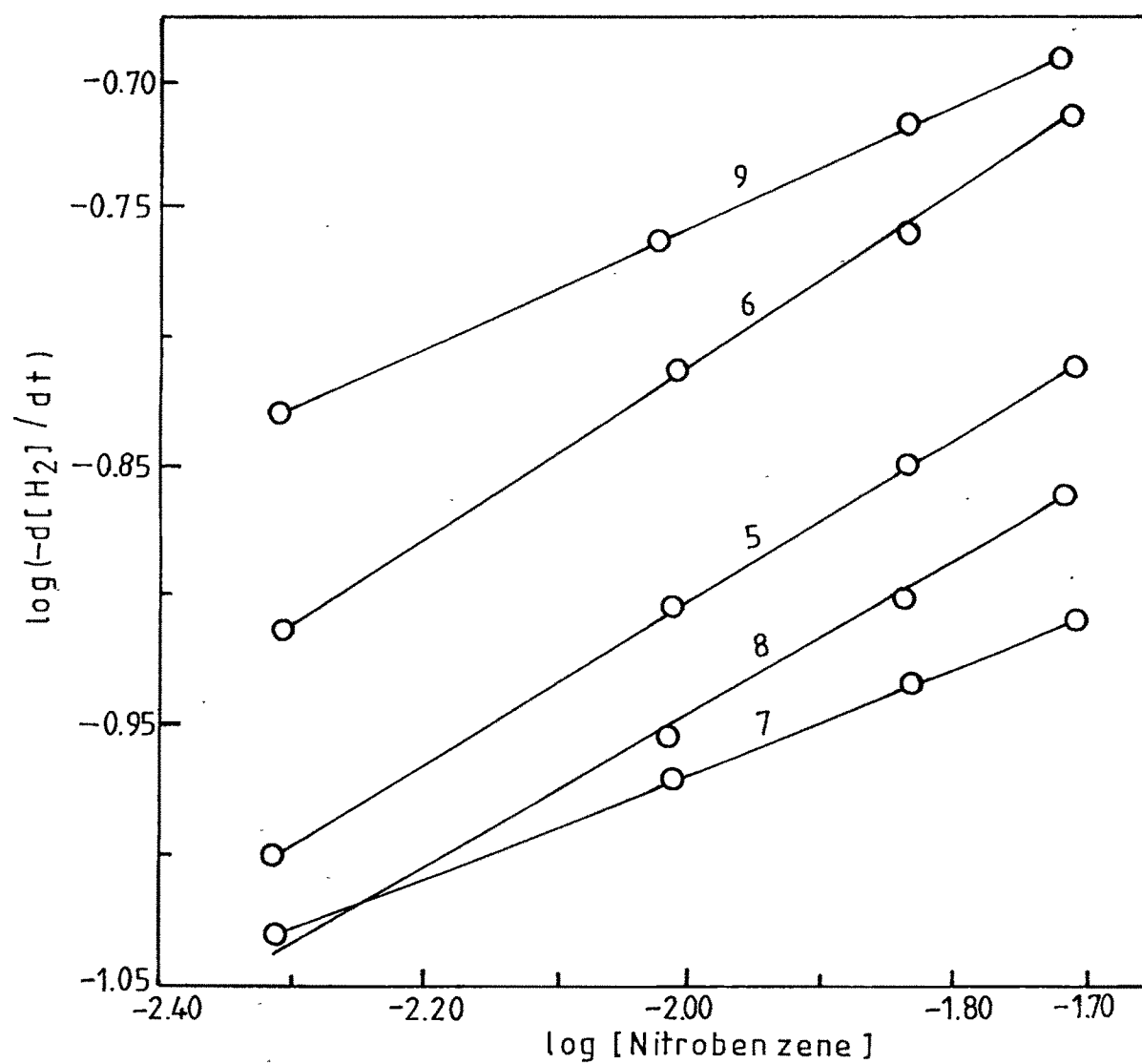


FIG. 4.4 log - log plot of the initial rate Vs [ Nitrobenzene ] for  
 [5]  $2P[Pd(L2AB)Cl_2]$  [6]  $8P[Pd(L2AB)Cl_2]$   
 [7]  $8P[Pd(Gly)Cl_2]$  [8]  $14P[Pd(Gly)Cl_2]$   
 [9]  $14P[Pd(L2AB)Cl_2]$

$1.58 \times 10^{-5} \text{ mol.lit}^{-1}$  respectively. Similar results were also observed using palladium complexes as catalysts ( Tables 4.2 and 4.3 )

#### 4.4.2 INFLUENCE OF THE CATALYST CONCENTRATION

The influence of the catalyst concentration on the rate of hydrogenation of nitrobenzene for different catalysts was investigated. The results are shown in Tables 4.4 to 4.6. An enhanced rate of hydrogenation was observed on increasing the concentration of the catalysts keeping the substrate concentration constant at a constant temperature. Thus in case of  $8\text{P}[\text{Ru}(\text{L2AB})\text{Cl}_3]$  rate of reaction was found to increase from  $11.2 \times 10^{-2}$  to  $14.0 \times 10^{-2} \text{ ml min}^{-1}$  when the concentration of catalyst varies from  $1.60 \times 10^{-5}$  to  $2.81 \times 10^{-5} \text{ mol.lit}^{-1}$  keeping nitrobenzene concentration constant as  $9.72 \times 10^{-3} \text{ mol.lit}^{-1}$  (Table 4.4); in case of  $8\text{P}[\text{Pd}(\text{L2AB})\text{Cl}_2]$ , the rate increased from  $15.3 \times 10^{-2}$  to  $22.0 \times 10^{-2} \text{ ml.min}^{-1}$  by varying the concentration of palladium from  $2.58 \times 10^{-5}$  to  $4.52 \times 10^{-5} \text{ mol.lit}^{-1}$  (Table 4.5). The rate of hydrogen consumption was found to be linear with the catalyst concentration (Fig. 4.5) which is an indicative of the avoiding the mass transfer under the reaction condition studied (93).

The order of reaction with respect to the concentration of catalyst calculated from the plots of  $\log (\text{initial rate})$  versus  $\log [\text{catalyst}]$  at a fixed concentration of substrate at  $35^\circ\text{C}$  was found to be fractional in all cases. The plots are given in Figs. 4.6 to 4.8(a) and the values for fractional order are given in Tables 4.4 to 4.6. The fractional order of the reaction may be due to non-accessibility of some of the catalytic sites and steric hindrance due to the ligand molecules.

Table 4.4

Influence of [Catalyst] on the rate of hydrogenation for the polymer supported ruthenium catalysts in methanol at atmospheric pressure.

Reaction temperature : 35°C			
Volume of methanol : 20 ml			
[Nitrobenzene](mol.lit <sup>-1</sup> ) : 9.72 x 10 <sup>-3</sup>			
Catalyst	[Catalyst] (mol.lit <sup>-1</sup> )x10 <sup>5</sup>	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Order of reaction w.r.t. [ Catalyst ]
2P[Ru(L2AB)Cl <sub>3</sub> ]	1.58	8.8	
	1.98	10.0	0.60
	2.38	11.0	
	2.77	12.9	
8P[Ru(L2AB)Cl <sub>3</sub> ]	1.60	11.2	
	2.01	12.2	0.41
	2.41	13.3	
	2.81	14.0	
2P[Ru(Gly)Cl <sub>3</sub> ]	2.22	11.0	
	2.78	11.5	0.16
	3.34	11.8	
	3.89	12.3	
8P[Ru(Gly)Cl <sub>3</sub> ]	3.34	12.1	
	4.17	13.3	0.38
	5.01	13.9	
	5.84	15.0	

Table 4.5

Influence of [Catalyst] on the rate of hydrogenation for the polymer supported palladium catalysts in methanol at atmospheric pressure.

Reaction temperature : 35°C

Volume of methanol : 20 ml

[Nitrobenzene](mol.lit<sup>-1</sup>) : 9.72 x 10<sup>-3</sup>

Catalyst	[Catalyst] (mol.lit <sup>-1</sup> )x10 <sup>5</sup>	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Order of reaction w.r.t. [ catalyst ]
2P[Pd(L2AB)Cl <sub>2</sub> ]	2.58	13.6	0.45
	3.23	14.2	
	3.87	17.0	
	4.52	17.5	
8P[Pd(L2AB)Cl <sub>2</sub> ]	2.58	15.3	0.66
	3.23	17.7	
	3.87	20.0	
	4.52	22.0	
8P[Pd(Gly)Cl <sub>2</sub> ]	2.93	10.1	0.41
	3.67	10.9	
	4.40	11.8	
	5.13	12.2	
14P[Pd(Gly)Cl <sub>2</sub> ]	2.90	10.7	0.53
	3.63	12.2	
	4.36	13.3	
	5.08	14.5	
14P[Pd(L2AB)Cl <sub>2</sub> ]	2.55	15.8	0.68
	3.19	18.3	
	3.83	20.8	
	4.47	23.1	

Table 4.6

Influence of [catalyst] on the rate of hydrogenation for the homogeneous catalysts in methanol at atmospheric pressure.

Reaction temperature : 35°C			
Volume of methanol : 20 ml			
[Nitrobenzene] (mol lit <sup>-1</sup> ) : 9.72 x 10 <sup>-3</sup>			
Catalyst	[Catalyst] (mol.lit <sup>-1</sup> )x10 <sup>4</sup>	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Order of reaction w.r.t. [Catalyst]
[Ru(L2AB)Cl <sub>3</sub> ]	5.00	5.4	0.64
	7.50	6.6	
	10.00	9.0	
	12.50	10.0	
[Pd(L2AB)Cl <sub>2</sub> ]	5.00	6.1	0.57
	7.50	7.7	
	10.00	9.3	
	12.50	10.4	

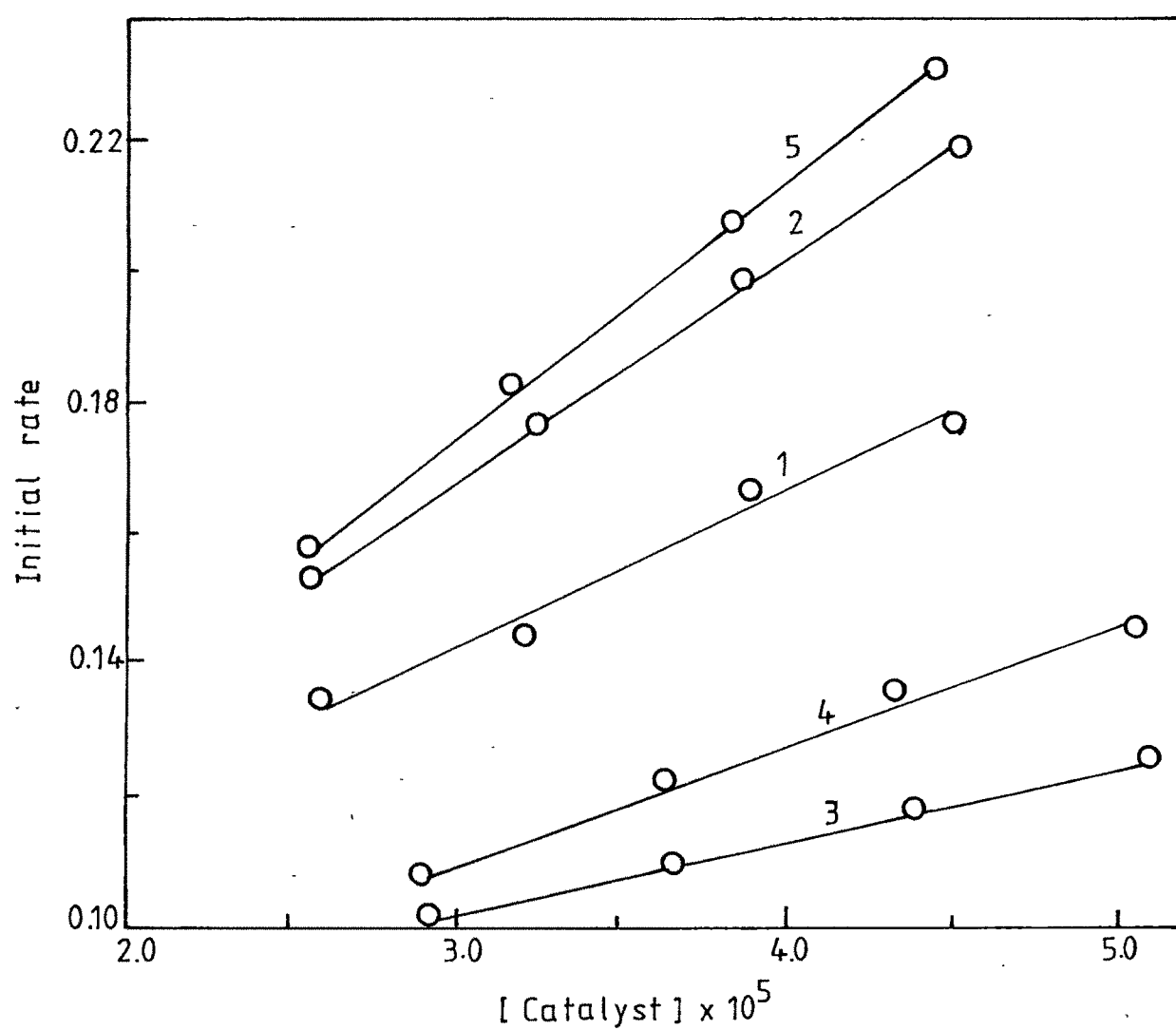


FIG. 4.5 Plot of rate of hydrogen consumption against the catalyst concentration for

[1] 2P[Pd(L2AB)Cl <sub>2</sub> ]	[2] 8P[Pd(L2AB)Cl <sub>2</sub> ]
[3] 8P[Pd(Gly)Cl <sub>2</sub> ]	[4] 14P[Pd(Gly)Cl <sub>2</sub> ]
[5] 14P[Pd(L2AB)Cl <sub>2</sub> ]	

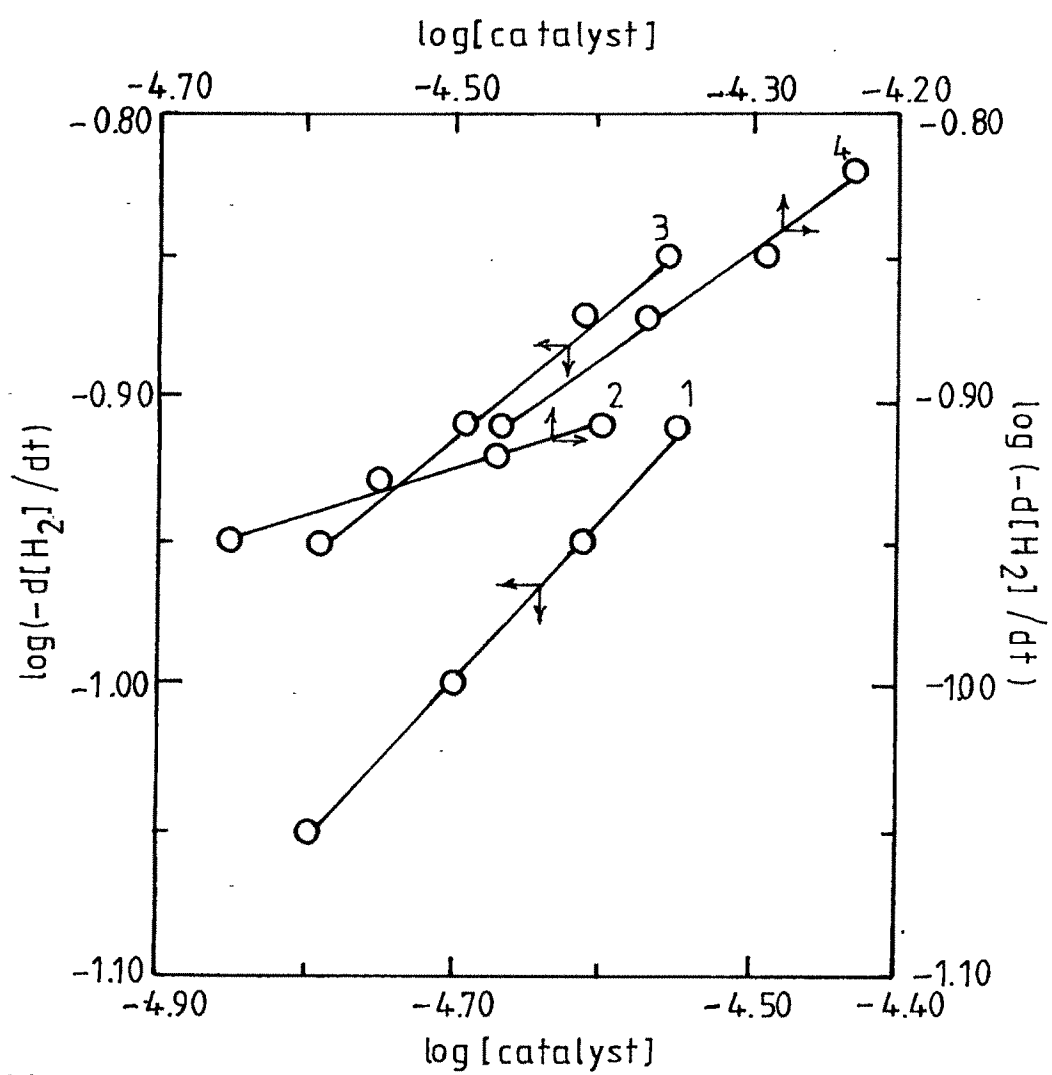


FIG. 4.6  $\log - \log$  plot of the initial rate Vs [ Catalyst ] for  
 [1]  $2\text{P}[\text{Ru}(\text{L2AB})\text{Cl}_3]$  [2]  $2\text{P}[\text{Ru}(\text{Gly})\text{Cl}_3]$   
 [3]  $8\text{P}[\text{Ru}(\text{L2AB})\text{Cl}_3]$  [4]  $8\text{P}[\text{Ru}(\text{Gly})\text{Cl}_3]$

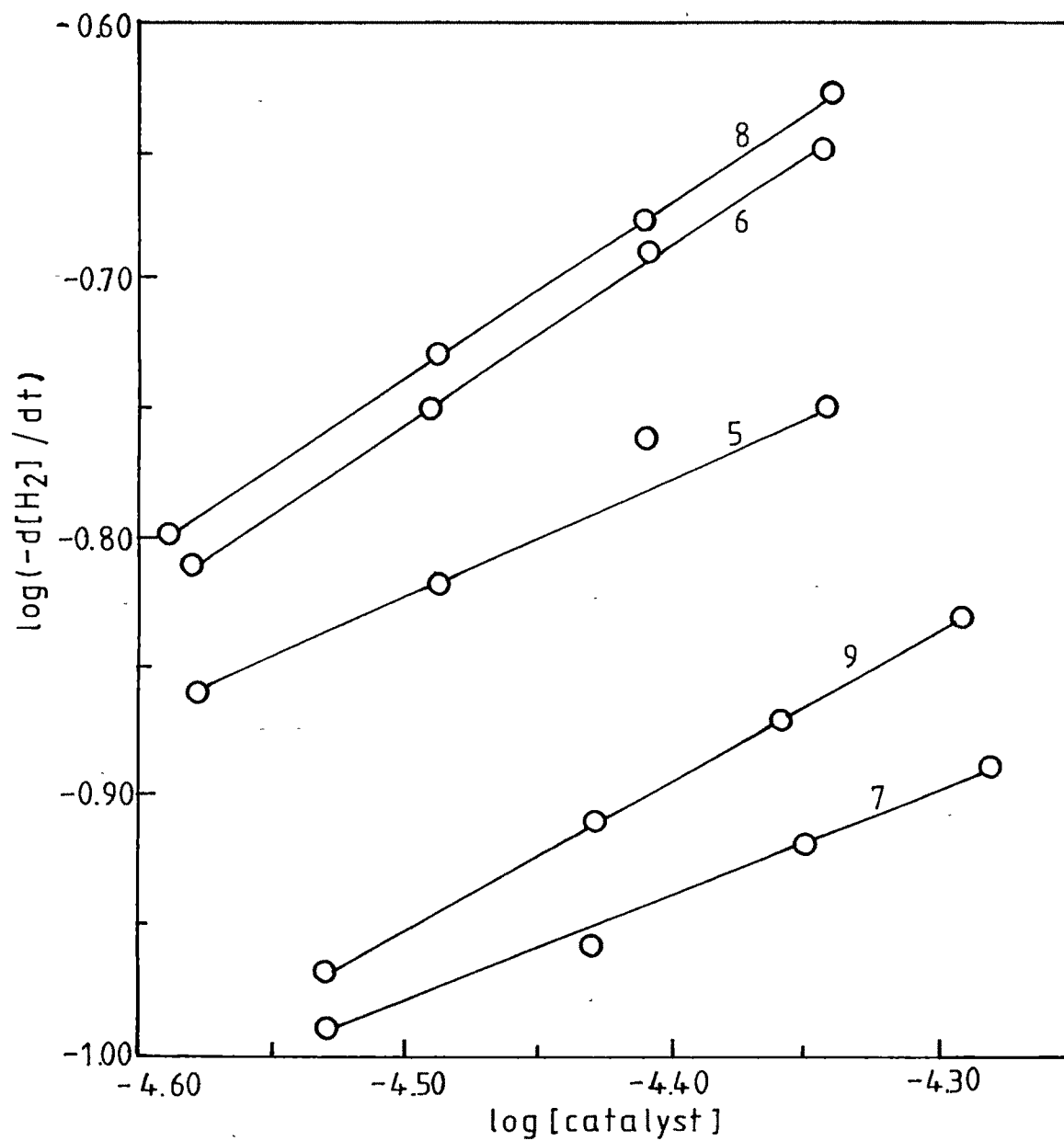


FIG. 4.7 log - log plot of initial rate Vs [Catalyst] for  
 [5]  $2P[\text{Pd}(\text{L2AB})\text{Cl}_2]$  [6]  $8P[\text{Pd}(\text{L2AB})\text{Cl}_2]$   
 [7]  $8P[\text{Pd}(\text{Gly})\text{Cl}_2]$  [8]  $14P[\text{Pd}(\text{L2AB})\text{Cl}_2]$   
 [9]  $14P[\text{Pd}(\text{Gly})\text{Cl}_2]$



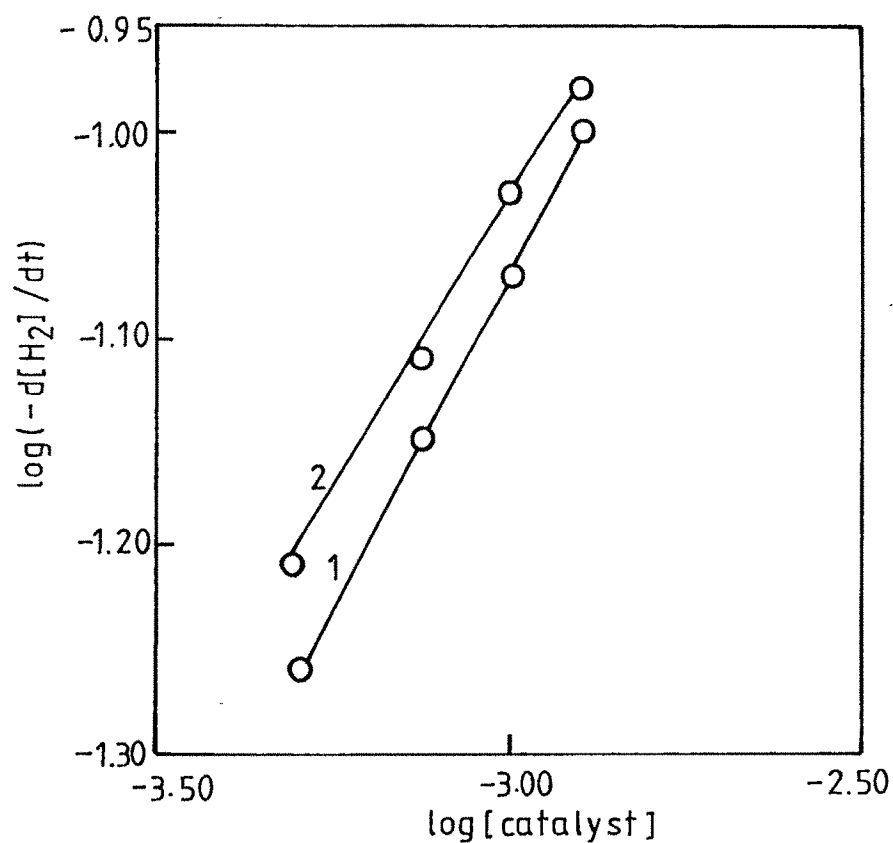


Fig. 4.8(a) log-log Plot of initial rate Vs. [catalyst] for [1]  $[Ru(L2AB)Cl_3]$  [2]  $[Pd(L2AB)Cl_2]$

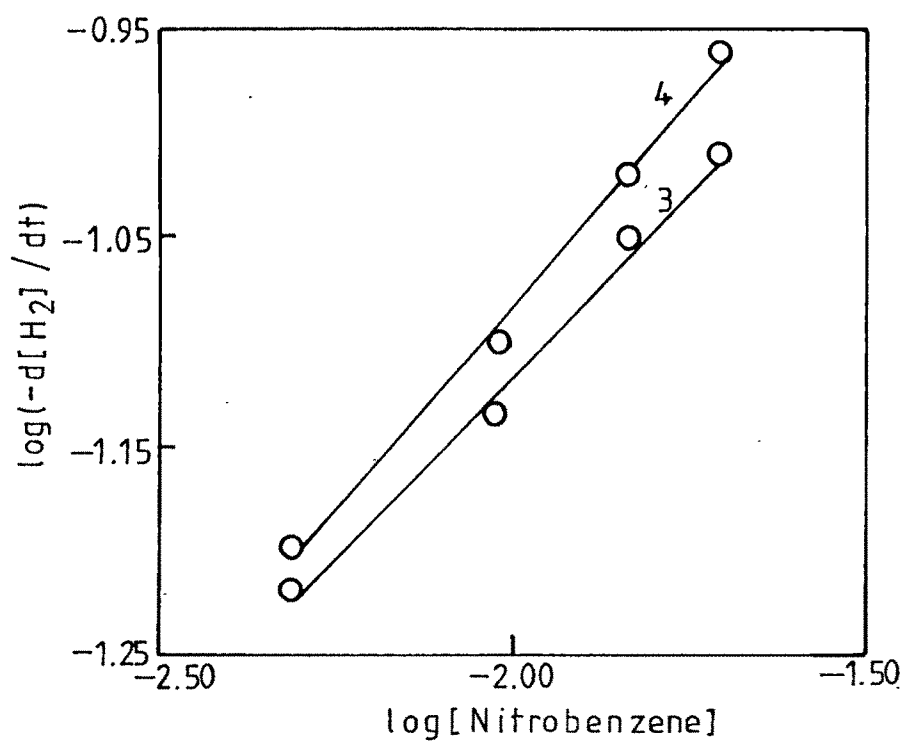


Fig. 4.8(b) log-log Plot of initial rate Vs. [nitrobenzene] for (3)  $[Ru(L2AB)Cl_3]$  (4)  $[Pd(L2AB)Cl_2]$

The experiments were repeated for homogeneous hydrogenation using Pd(II) and Ru(III) complexes in solution and the results are given in Table 4.6. On increasing the concentration of Ru(III) ions from  $5.0 \times 10^{-4}$  to  $12.5 \times 10^{-4}$  mol.lit<sup>-1</sup>, the rate of hydrogenation was observed to increase from  $5.4 \times 10^{-2}$  to  $10.0 \times 10^{-2}$  ml.min<sup>-1</sup> for a nitrobenzene concentration of  $9.72 \times 10^{-3}$  mol lit<sup>-1</sup> at 35°C and at one atmospheric pressure. Similar results were also observed for Pd(II) complex in homogeneous system. An increase in the rate with amount of the catalyst is an indicative of the fact that there is no dimerization of metal complexes either in homogeneous system or in heterogenised system in the range studied.

#### 4.4.3 EFFECT OF TEMPERATURE

The effect of temperature on the rate of hydrogenation of nitrobenzene was studied in the range of 35-45°C and the results are summarised in Tables 4.7 to 4.9. An enhanced rate was observed on increasing the temperature of the reaction system for all the catalysts. Thus the rate varies from  $7.5 \times 10^{-2}$  to  $13.0 \times 10^{-2}$  ml.min<sup>-1</sup> as the temperature is changed from 35 to 45°C using  $2P[Ru(L2AB)Cl_3]$  catalyst (Table 4.7). Similar results were obtained with other homogeneous as well as heterogenised homogeneous catalysts.

The values for the energy of activation was calculated from the slope of the plot of log (initial rate) against  $1/T$  (Figs. 4.9 to 4.11). In case of polymer bound Ru(III) complexes the energy of activation was found to be in the range of 4.0 to 7.0 kcal.mole<sup>-1</sup> while in case of Pd(II) complexes it was found to

Table 4.7

Effect of temperature on hydrogenation of nitrobenzene using polymer supported ruthenium catalysts in methanol at atmospheric pressure.

[Nitrobenzene](mol.lit<sup>-1</sup>) :  $9.72 \times 10^{-3}$

Volume of methanol : 20 ml

Catalyst	[Catalyst] (mol.lit <sup>-1</sup> )x10 <sup>5</sup>	Tempe- rature (°C)	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Energy of Activation kcal.mole <sup>-1</sup>	Entropy of acti- vation (eu)
2P[Ru(L2AB)Cl <sub>3</sub> ]	1.58	30	7.5	6.6	-52.0
		35	8.8		
		40	10.8		
		45	13.0		
8P[Ru(L2AB)Cl <sub>3</sub> ]	1.60	30	8.9	7.0	-50.2
		35	11.2		
		40	13.0		
		45	14.8		
2P[Ru(Gly)Cl <sub>3</sub> ]	2.22	30	8.3	6.7	-51.4
		35	11.0		
		40	12.8		
		45	13.5		
8P[Ru(Gly)Cl <sub>3</sub> ]	3.34	30	11.6	4.0	-60.0
		35	12.1		
		40	13.7		
		45	14.9		

Table 4.8

Effect of temperature on hydrogenation of nitrobenzene using polymer supported palladium catalysts in methanol at atmospheric pressure.

[Nitrobenzene] (mol.lit<sup>-1</sup>) : 9.72 x 10<sup>-3</sup>

Volume of methanol : 20 ml

Catalyst	[Catalyst] (mol.lit <sup>-1</sup> )x10 <sup>5</sup>	Tempe- rature (°C)	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Energy of Activation kcal.mole <sup>-1</sup>	Entropy of acti- vation (eu)
2P[Pd(L2AB)Cl <sub>2</sub> ]	2.58	30	9.0		
		35	13.6	2.9	-63.2
		40	15.0		
		45	15.7		
8P[Pd(L2AB)Cl <sub>2</sub> ]	2.58	30	14.5		
		35	15.3	3.9	-59.9
		40	18.2		
		45	20.3		
8P[Pd(Gly)Cl <sub>2</sub> ]	2.93	30	8.2		
		35	10.1	4.2	-59.8
		40	10.6		
		45	11.6		
14P[Pd(Gly)Cl <sub>2</sub> ]	2.90	30	9.0		
		35	10.7	4.1	-59.7
		40	11.0		
		45	12.5		
14P[Pd(L2AB)Cl <sub>2</sub> ]	2.55	30	15.0		
		35	15.8	5.8	-53.5
		40	18.7		
		45	21.2		

Table 4.9

Effect of temperature on hydrogenation of nitrobenzene using homogeneous catalysts in methanol at atmospheric pressure.

[Nitrobenzene] (mol.lit<sup>-1</sup>) :  $9.72 \times 10^{-3}$

Volume of methanol : 20 ml

Catalyst	[Catalyst] (mol.lit <sup>-1</sup> )x10 <sup>4</sup>	Tempe- rature (°C)	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Energy of Activation kcal.mole <sup>-1</sup>	Entropy of acti- vation (eu)
[Ru(L2AB)Cl <sub>3</sub> ]	7.5	30	5.6		
		35	6.6	7.2	-51.2
		40	8.4		
		45	10.0		
[Pd(L2AB)Cl <sub>2</sub> ]	7.5	30	6.6		
		35	7.7	6.1	-54.5
		40	9.6		
		45	10.6		

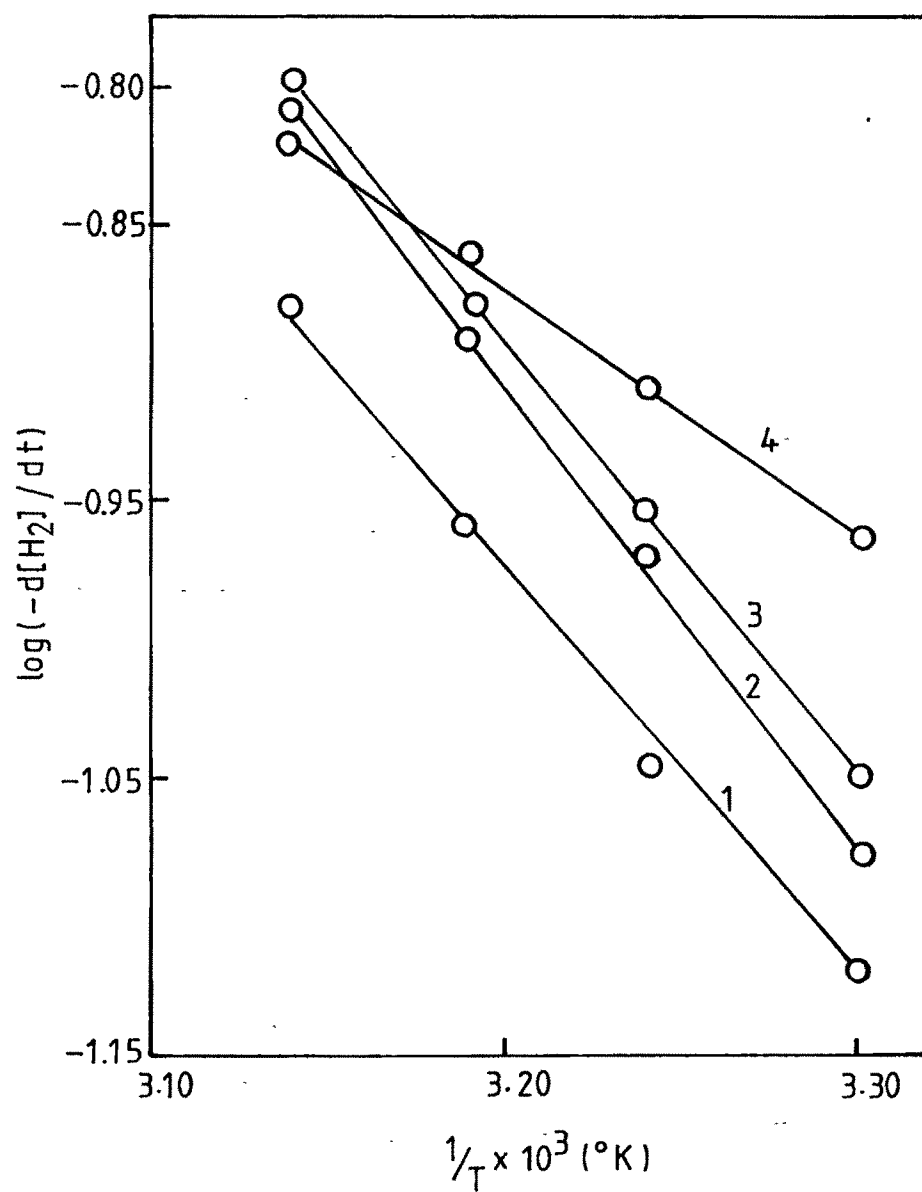


FIG. 4.9 Arrhenius plot for catalysts

[1] $2P[Ru(L2AB)Cl_3]$	[2] $2P[Ru(Gly)Cl_3]$
[3] $8P[Ru(L2AB)Cl_3]$	[4] $8P[Ru(Gly)Cl_3]$

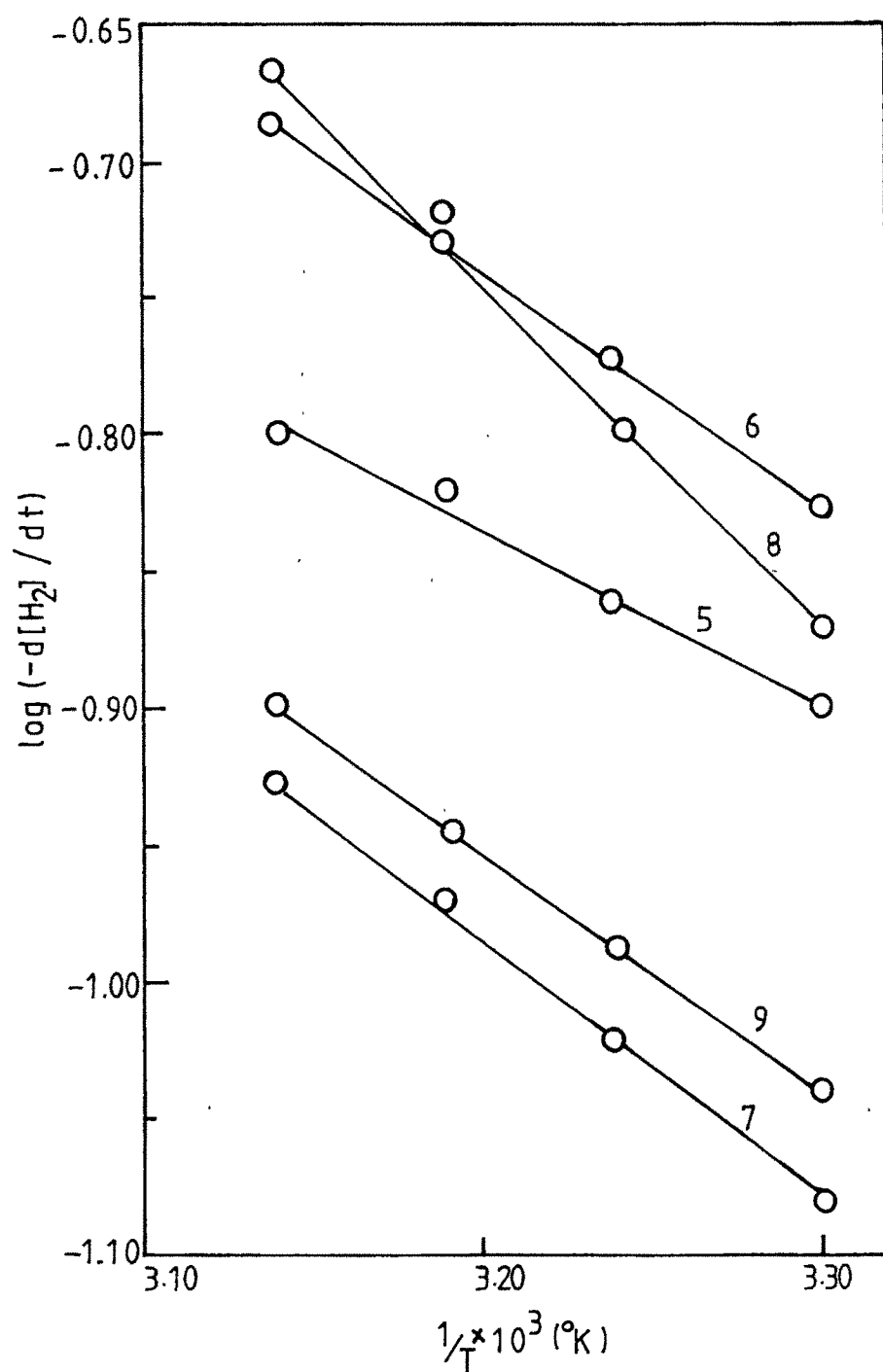


FIG. 4.10 Arrhenius plot for catalysts

[5]  $2P[Pd(L2AB)Cl_2]$

[7]  $8P[Pd(Gly)Cl_2]$

[9]  $14P[Pd(Gly)Cl_2]$

[6]  $8P[Pd(L2AB)Cl_2]$

[8]  $14P[Pd(L2AB)Cl_2]$

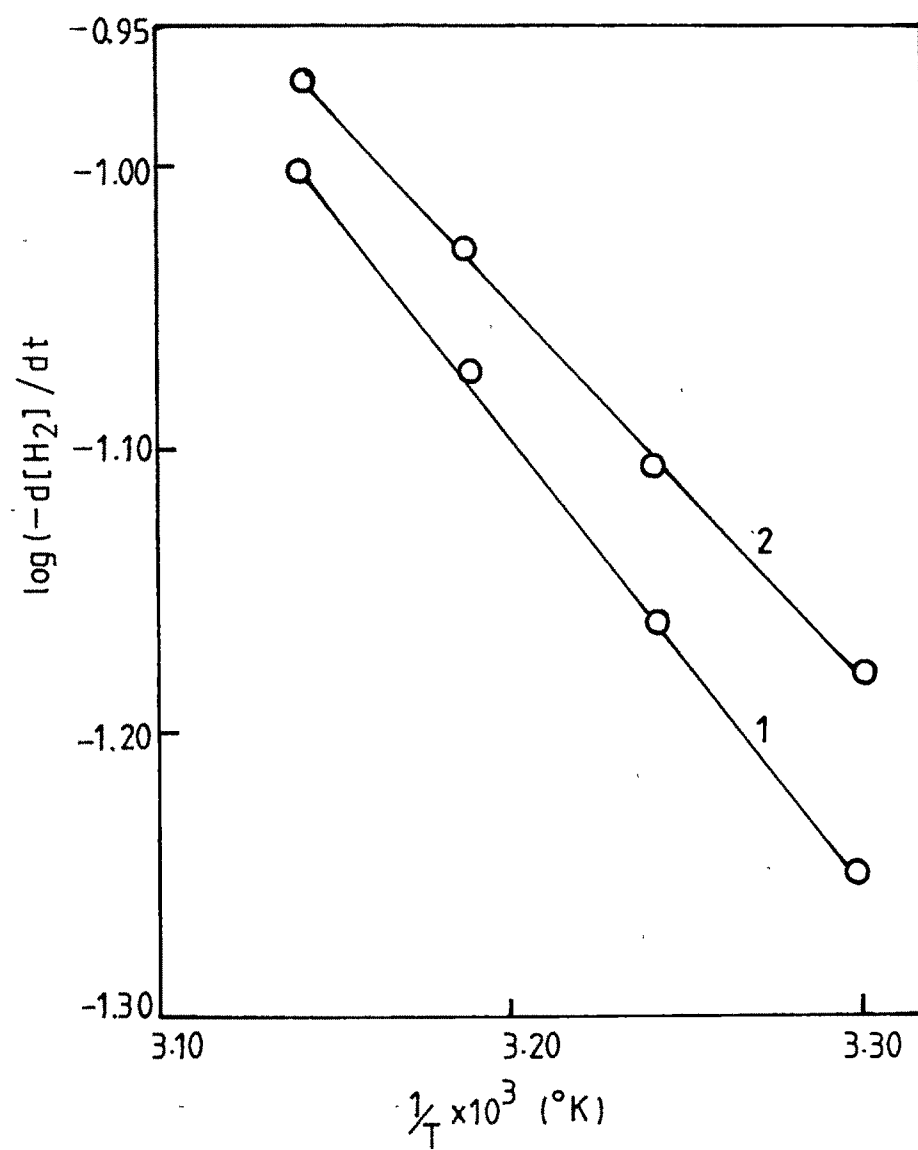


Fig. 4.11. Arrhenius plot for catalysts.

(1)  $[\text{Ru}(\text{L2AB})\text{Cl}_3]$  (2)  $\text{Pd}(\text{L2AB})\text{Cl}_2$



be in the range of 2.9 to 5.8 kcal.mole<sup>-1</sup>. In case of homogeneous system, the energy of activation was obtained to be 7.2 and 6.1 kcal.mole<sup>-1</sup> for [Ru(L2AB)Cl<sub>3</sub>] and [Pd(L2AB)Cl<sub>2</sub>] catalysts respectively. The catalytic activity however can not be compared on the basis of the energy of activation of both the systems because of the lower activity in homogeneous system, a higher concentration of the catalyst was used to obtain a considerable rate of reaction.

The entropy of activation was calculated using following equation.

$$k = \frac{KT}{h} \cdot e^{\frac{\Delta S/R}{}} \cdot e^{-\frac{\Delta E/RT}{}}$$

(Where K and h are plank's and Boltzman constants respectively;  $\Delta S$  and  $\Delta E$  are entropy and energy of activation) and the values for all sets of experiments were found to be negative (Tables 4.7 to 4.9). The negative values of entropy correspond to a considerable loss of freedom due to fixation of the catalyst molecule on the polymer matrix (94). The formation of dihydrido complex with the substrate and subsequent fast insertion and elimination of the product may also be taken into consideration. Similar results have been reported by Taquikhan et al (92) in the case of homogeneous hydrogenation of 1 - heptene catalysed by Rh (I) complex.

On the basis of the above results it can be seen that the heterogenised homogenous catalysts have a higher catalytic activity than their homogeneous counterparts though a higher concentration of metal content is present in the later one e.g in case of 14P[Pd(L2AB)Cl<sub>2</sub>] (Pd content :  $2.55 \times 10^{-5}$  mol.lit<sup>-1</sup>)

the rate of hydrogenation was found to be  $14.7 \times 10^{-2} \text{ ml.min}^{-1}$  at  $35^\circ\text{C}$  while using  $[\text{Pd}(\text{L2AB})\text{Cl}_2]$  in homogeneous system (Pd content :  $7.5 \times 10^{-4} \text{ mol.lit}^{-1}$ ) the rate was found to be  $6.3 \times 10^{-2} \text{ ml.min}^{-1}$  for same concentration of nitrobenzene ( $4.83 \times 10^{-3} \text{ mol.lit}^{-1}$ ). The results are given in Tables 4.2 and 4.3 respectively. The other results are also summarized in Tables 4.1 to 4.9. This may be due to the formation of the coordinatively unsaturated metal species which can be more easily obtained in the polymer bound moiety than in the monomeric analogs. The presence of coordinative unsaturation giving higher activity was proposed by Pittman and Collman(95) for transition metal complexes attached to phosphinated polystyrene resin.

#### 4.4.4 EFFECT OF SOLVENT

The nature of the solvent is an important factor in order to control the activity and the selectivity of polymer supported catalysts. It can be modified by coordinating the metal species with solvents. The polymer swelling is another important parameter which is able to influence the reaction and to control the activity of the catalysts (96). It is therefore apparent that the nature of the solvent can be of great importance in directing the course of reaction.

The hydrogenation of nitrobenzene was studied using different solvents such as methanol, ethanol, THF and benzene and the results are summarised in Tables 4.10 and 4.11. An increase in the rate was observed when solvent varies from a non-polar to a polar character. The rate was found to be  $5.0 \times 10^{-2} \text{ ml.min}^{-1}$  using benzene as a solvent while in case of methanol it was found to be  $8.8 \times 10^{-2} \text{ ml.min}^{-1}$  using

Kinetics of hydrogenation of nitrobenzene by polymer supported ruthenium catalysts at atmospheric pressure using various solvents.

Reaction temperature : 35<sup>0</sup> C

Volume of methanol : 20 ml

[Nitrobenzene] (mol.lit<sup>-1</sup>) : 9.72 x 10<sup>-3</sup>

Catalyst	[Catalyst] (mol.lit <sup>-1</sup> )x10 <sup>5</sup>	Solvent	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>
2P[Ru(L2AB)Cl <sub>3</sub> ]	1.58	Methanol	8.8
		Ethanol	7.0
		THF	6.6
		Benzene	5.0
8P[Ru(L2AB)Cl <sub>3</sub> ]	1.60	Methanol	11.2
		Ethanol	10.2
		THF	8.8
		Benzene	6.5
2P[Ru(Gly)Cl <sub>3</sub> ]	2.22	Methanol	11.0
		Ethanol	8.2
		THF	6.4
		Benzene	5.5
8P[Ru(Gly)Cl <sub>3</sub> ]	3.34	Methanol	12.1
		Ethanol	10.6
		THF	9.6
		Benzene	9.2

Table 4.11

Kinetics of hydrogenation of nitrobenzene by polymer supported palladium catalysts at atmospheric pressure using various solvents.

Reaction temperature : 35° C

Volume of methanol : 20 ml

[Nitrobenzene] (mol.lit<sup>-1</sup>) : 9.72 x 10<sup>-3</sup>

Catalyst	[Catalyst] (mol.lit <sup>-1</sup> )x10 <sup>5</sup>	Solvent	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>
2P[Pd(L2AB)Cl <sub>2</sub> ]	2.58	Methanol	13.6
		Ethanol	11.3
		THF	8.5
		Benzene	7.7
8P[Pd(L2AB)Cl <sub>2</sub> ]	2.58	Methanol	15.3
		Ethanol	12.9
		THF	10.8
		Benzene	8.6
8P[Pd(Gly)Cl <sub>2</sub> ]	2.93	Methanol	10.1
		Ethanol	8.6
		THF	6.7
		Benzene	5.1
14P[Pd(Gly)Cl <sub>2</sub> ]	2.90	Methanol	10.7
		Ethanol	9.7
		THF	7.1
		Benzene	5.8
14P[Pd(L2AB)Cl <sub>2</sub> ]	2.55	Methanol	15.8
		Ethanol	13.8
		THF	12.0
		Benzene	10.3

2P[Ru(L2AB)Cl<sub>3</sub>] as a catalyst; in case of 2P[Pd(L2AB)Cl<sub>2</sub>], the rate was found to be  $7.7 \times 10^{-2}$  and  $13.6 \times 10^{-2}$  ml.min<sup>-1</sup> respectively. An enhanced rate may be due to the higher swelling of catalyst as well as moderate coordinating ability of the solvent with the metal species. Thus the optimum solvent would be one that combines good swelling ability and high polarity. Methanol was therefore chosen as a suitable solvent for the reaction system.

#### 4.4.5 LIFE CYCLE OF CATALYSTS

One of the ways in which a polymer bound catalyst can deactivate its activity by loss of metal ions, which is brought about by leaching of the active component or reduction to free metal. In most of the cases, the polymer anchored metal complexes detach and the metal is leached out in the reaction system (97,98). The loss of the metal ion/complexes due to leaching could be avoided by using the bidentate chelating ligands or to ensure a larger ligand to metal ratio. It has been reported by Wang and Neckers (99) as also by Li and Frechet (100) that palladium complexes anchored on polyamides or polybenzimidazole (where the ligand/Pd ratio are large) showed a negligible or no loss of metal ions even after 5-10 cycles of use. Drago et. al. have also synthesised the stable supported metal complex catalysts using bidentate chelating ligands (98). We have also synthesised few catalysts using bidentate ligands and the recycling efficiency of the catalysts was tested as given below.

The experiment was carried out at 35°C for about 10 hours. For this, a fixed quantity of the catalyst was kept in contact with the solvent for about half an hour and flushed

with hydrogen gas. To this, 20.0 $\mu$ l of the substrate was injected and the consumption of H<sub>2</sub> was measured at different interval of time. After reaching saturation, the reaction was allowed to keep as such at least for 30 minutes in order to check the hydrogen uptake (if any) and then the next injection was made. The study was carried out for both fresh as well as used catalysts and the results are summarised in Tables 4.12 to 4.14. In each case the rate was found to remain unchanged at least upto five cycles and after that a decrease was observed in both the cases. This may be due to the loss of the metal ions from the polymer surface. The metal content was thus estimated at the end of the reaction (i.e. after 10 hours) and a 50% loss of metal content was observed. A decrease in catalytic activity may be due to low mechanical strength of the polymer support as well as polymer bound complexes and polymer bound non-coordinated ligand molecules leaching out and forming stable complex in solution which are less effective in catalyzing the reaction (101). It is clear from the above study that the catalysts can be used at least upto five cycles.

#### 4.4.6 RATE EQUATION

In the present investigation the partial pressure as well as the concentration of hydrogen in solution is kept constant. Thus the reaction was carried out at a fixed amount of the catalyst and at constant amount of hydrogen. The actual quantity of hydrogen consumed is obtained by saturating the solvent alongwith the catalyst with before injecting the substrate.

The hydrogenation of olefins and nitro compounds has been studied extensively using the ruthenium and palladium

Table 4.12

Life cycle study for the polymer supported catalysts

Reaction temperature : 35<sup>o</sup> C

Volume of methanol : 20 ml

Total time on stream : 10 h

[Nitrobenzene] (mol.lit<sup>-1</sup>) : 9.72 x 10<sup>-3</sup>

Catalyst	Time (min)	Fresh catalyst Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Used catalyst Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>
2P[Ru(L2AB)Cl <sub>3</sub> ] <sup>a</sup>	60	8.8	8.6
	120	8.8	8.5
	180	8.6	8.2
	240	8.3	8.0
	300	7.6	7.3
8P[Ru(L2AB)Cl <sub>3</sub> ] <sup>b</sup>	60	11.0	10.8
	120	11.0	10.7
	180	10.8	10.2
	240	10.3	9.7
	300	10.1	9.3
2P[Ru(Gly)Cl <sub>3</sub> ] <sup>c</sup>	60	11.0	10.9
	120	10.9	10.9
	180	10.9	10.3
	240	10.1	9.7
	300	10.0	9.4

a : Amount of catalyst :- 1.58 X 10<sup>-5</sup> mol.lit<sup>-1</sup> Ru present on the surfaceb : Amount of catalyst :- 1.60 X 10<sup>-5</sup> mol.lit<sup>-1</sup> Ru present on the surfacec : Amount of catalyst :- 2.22 X 10<sup>-5</sup> mol.lit<sup>-1</sup> Ru present on the surface

Table 4.13

Life cycle study for the polymer supported catalysts

Reaction temperature : 35<sup>o</sup> C

Volume of methanol : 20 ml

Total time on stream : 10 h

[Nitrobenzene] (mol.lit<sup>-1</sup>) : 9.72 x 10<sup>-3</sup>

Catalyst	Time (min)	Fresh catalyst	Used catalyst
		Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>
8P[Ru(Gly)Cl <sub>3</sub> ] <sup>d</sup>	60	12.1	12.0
	120	12.0	11.8
	180	12.0	11.6
	240	11.4	11.3
	300	11.1	10.7
2P[Pd(L2AB)Cl <sub>2</sub> ] <sup>e</sup>	60	13.6	12.6
	120	13.4	12.4
	180	13.3	12.0
	240	13.0	11.1
8P[Pd(L2AB)Cl <sub>2</sub> ] <sup>f</sup>	60	15.3	15.3
	120	15.3	15.3
	180	15.1	15.0
	240	14.8	14.4

d : Amount of catalyst :- 3.34 X 10<sup>-5</sup> mol.lit<sup>-1</sup> Ru present on the surfacee : Amount of catalyst :- 2.58 X 10<sup>-5</sup> mol.lit<sup>-1</sup> Pd present on the surfacef : Amount of catalyst :- 2.58 X 10<sup>-5</sup> mol.lit<sup>-1</sup> Pd present on the surface



Table 4.14

Life cycle study for the polymer supported catalysts

Reaction temperature : 35° C

Volume of methanol : 20 ml

Total time on stream : 10 h

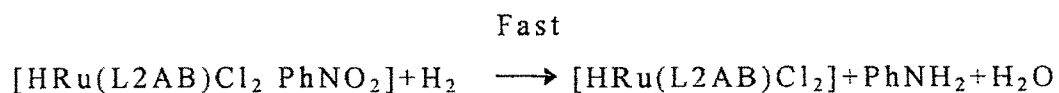
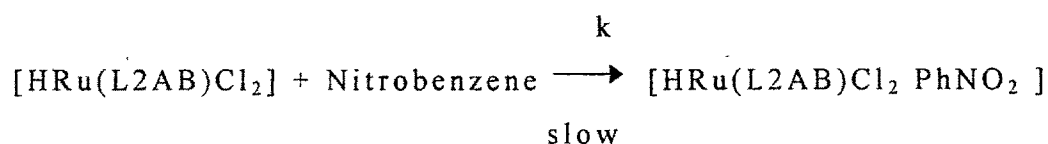
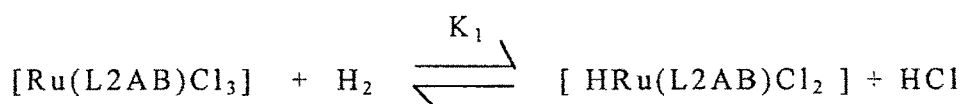
[Nitrobenzene] (mol.lit<sup>-1</sup>) : 9.72 x 10<sup>-3</sup>

Catalyst	Time (min)	Fresh catalyst	Used catalyst
		Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>	Initial rate of reaction (ml.min <sup>-1</sup> )x10 <sup>2</sup>
8P[Pd(Gly)Cl <sub>2</sub> ] <sup>g</sup>	60	10.1	10.0
	120	10.0	9.6
	180	9.7	9.2
	240	9.5	9.1
	300	9.4	9.0
14P[Pd(Gly)Cl <sub>2</sub> ] <sup>h</sup>	60	10.7	10.6
	120	10.7	10.4
	180	10.5	10.2
	240	10.3	10.1
	300	10.1	9.8
14P[Pd(L2AB)Cl <sub>2</sub> ] <sup>i</sup>	60	15.8	15.6
	120	15.7	15.5
	180	15.6	15.4
	240	15.2	15.0
	300	15.0	14.7

g : Amount of catalyst :- 2.93 X 10<sup>-5</sup> mol.lit<sup>-1</sup> Pd present on the surfaceh : Amount of catalyst :- 2.90 X 10<sup>-5</sup> mol.lit<sup>-1</sup> Pd present on the surfacei : Amount of catalyst :- 2.55 X 10<sup>-5</sup> mol.lit<sup>-1</sup> Pd present on the surface

complexes as catalysts in homogeneous medium (102 - 106). The formation of the hydrido complex was probably found to be responsible for a higher catalytic activity. In a separate experiment, hydrogen gas was passed through a solution of ruthenium as well as unbound palladium metal complexes. In case of ruthenium a change in colour was observed from grayish to violet while a disappearance of yellow colour in case of palladium was found. If these complex solutions are mixed with a small quantity of the substrate, the catalysts regained their original colour slowly. This indicates the probability of the formation of the hydrido complex followed by a transfer of hydrogen to the substrate. The above fact has been established by many other workers in the hydrogenation of olefins and other unsaturated compounds (107,108).

On the basis of the experimental evidences and literature support a probable reaction mechanism may be suggested.



Considering the production of HCl to be constant, the initial rate (R) of the reaction can be suggested as follows:

$$R = \frac{K_1 k [\text{catalyst}] [\text{H}_2] [\text{substrate}]}{1 + K_1 [\text{S}]}$$

The reciprocal of the above equation is

$$\begin{aligned} \frac{1}{R} &= \frac{1}{K_1 k [\text{catalyst}] [\text{H}_2] [\text{S}]} + \frac{K_1 [\text{S}]}{K_1 k [\text{catalyst}] [\text{H}_2] [\text{S}]} \\ &= \frac{1}{K_1 k [\text{catalyst}] [\text{H}_2] [\text{S}]} + \frac{1}{k [\text{catalyst}] [\text{H}_2]} \end{aligned}$$

Where, 'S' is the substrate. [This mechanism is applicable for all the catalysts used for hydrogenation reaction.]

The straight line plot of reciprocal of the initial rate against reciprocal of [S] is indicative of the complex formation at the intermediate state which is in agreement with the experimental results.

On the basis of the above studies, a probable reaction path can be suggested. As can be seen from fig. 4.12 that a hydrogen molecule may go through the gas/liquid interface to dissolve in the liquid phase. It migrates through the solution and passes through the liquid/solid barrier before it can reach the catalyst particle where it has to find an active site on which to adsorb and be activated. On the otherhand, the substrate molecules present in the solution will go through the

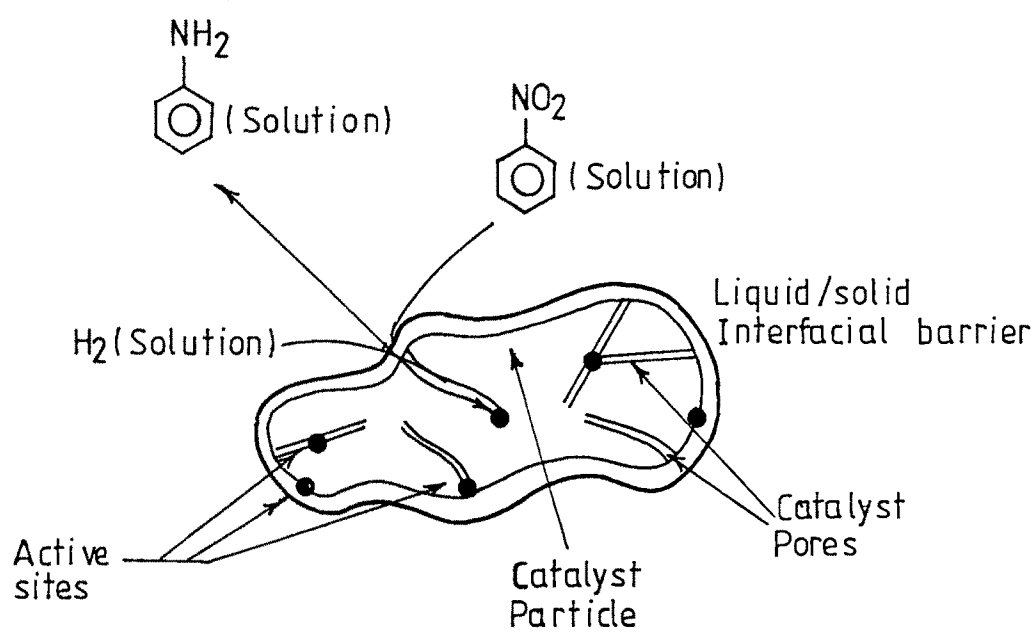
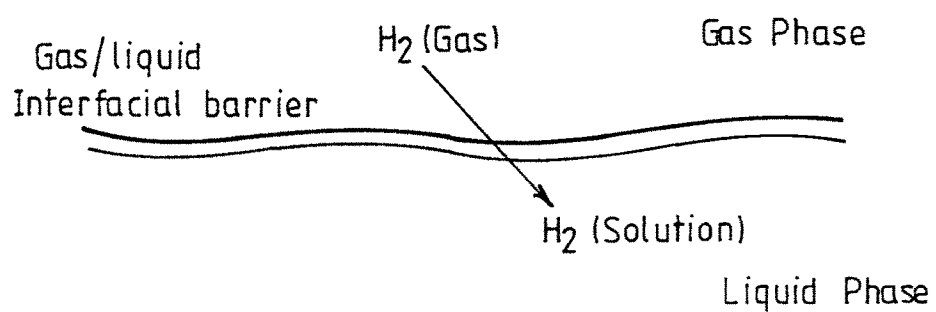


Fig. 4.12. Reaction path in the liquid phase hydrogenation of nitrobenzene.

liquid/solid interface and migrate through the catalyst particle to react the active sites. Reaction thus takes place on the catalyst surface to produce the product. This then desorbs, migrates out of the catalyst particle, passes through the solid/liquid interface and finally goes into the solution.

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