CHAPTER 4

KINETICS OF HYDROGENATION OF 1-HEXENE/STYRENE USING POLYMER SUPPORTED Ru(III) AND Pd(II) COMPLEXES

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4.1 Kinetics of hydrogenation of 1-hexene/styrene using polymer-supported Pd(II) and Ru(III) complexes

4.1.1 Introduction

The catalaytic hydrogenation of organic functional groups is probably the most common application of catalysis in the synthesis of organic compounds. Significance of catalytic hydrogenation is highlighted by a number of books, reviews and conference proceedings (1-28). Hydrogenation reaction can be carried out using molecular hydrogen, hydrogen donating substrate or by transfer of hdyrogen from the surface of the solid (29) Hydrogenation using hydrogen donating substances was widely popular because of cost-effectiveness. For example, the hydrogenration of nitrocompounds to amines using Fe-HCl in production of variety of aromatic amines which have applications as intermediates and speciality products (30). However, the problem of waste acid disposal is an environmental hazard. The clean technology revolution has forced to pay attention to better catalytic alternatives (31-33).

Heterogeneous hydrogenation with metal catalysts have been studied extensively (1). However, the design of the catalyst is not easy because the active sites of the catalysts are not well-defined. Only a small portion of the metal is available and effective in catalysis. Catalytic hydrogenation using hydrogen gas with metal catalysts is a reaction familiar to all organic chemists. Discovery of wilkinson's complex provided momentum for work on catalytic hydrogenations using metal complex catalysts (34). Because of well-defined active sites and availability of all metal atoms for catalysis in homogeneous medium, such catalysts gained attention. Many processes were commercialised using such catalysts (Table 1.1, Chapter 1).

The success of homogeneous hydrogenation catalysts has led to a great interest in supporting them in order to combine advantages inherent in their molecular nature with the ease of separation at the end of the reaction that should be possible if an insoluble support is used (35). Therefore, it is not surprising that many supported metal complex catalysts are corresponding homogeneous catalysts linked to a support. The selective hydrogen ation of the olefinic double bond of several compounds present in the gasoline boiling range is of great interest in the petroleum refining industries. Alkenes and dialkenes need to be removed from the feed streams as they enhance the gasoline visocisty and may consume or contaminate the catalyst and also in case of the alkylation processes, they increase the acid consumption (36). Thus hydrogenation of straight chain olefines, cyclic olefins and dialkenes is widely studied as a tool to investigate the catalytic behaviour of the various catalysts . Styrene is a useful compound to investigate the catalytic performance of metal catalysts at a laboratory scale due to the presence of two types of unsaturated groups. During last few years, a large number of studies have been carried out for hydrogenation of styrene in the liquid phase (36).

Ethylbenzene manufacture is very important process in petrochemicals. Shape selective catalysis by zeolites like ZSM-5 to manufacture ethylbenzene is a widely used commercial process (37,38). Hydrogenation of 1-hexene gives n-hexane which is a very useful intermediate in fine chemicals and pharmaceuticals(39).

Many studies were devoted to hydrogenation of olefins and other substrates using inorganic oxide supported catalysts (40-42). Chang and Chau (43) have reported selective hydrogenation of isoprene using Pd as a catalyst supported on various types of alumina and δ-alumina supported Pd catalyst was found to be having the highest activity among catalysts studied for the hydrogenation reaction. Anderson et al (36) have studied hydrogenation of styrene over Ni/sepiolite catalysts with a higher activity. Fan and Fujimoto (44) have reported synthesis of methanol from CO_2 and H_2 on supported Pd catalysts and investigated the reaction mechanism. Devisse et al (44a) have studied butyne hydrogenation using Pd-Mo/υ-Al_2O_3 catalyst with 100% selectivity and significant improvement in hydrogenation activity. Kotker and Thakkar (45) have studied hydrogenation of cycloalkanes using montmorillonite supported Rh(III) complexes and found it to be an efficient catalyst. Mahata and Vishwanathan (46) have reported hydrogenation of phenol to cyclohexanone using Pd/Al_2O_3 and Pd/MgO as the catalysts. However Pd/MgO catalyst was found to be a better catalyst than Pd/Al_2O_3. Rode and Chaudhary (47) have reported kinetics of hydrogenation of m-nitrochlorobenzene to m-chloroaniline using sulfided Pt on carbon and proposed a langmuir Hinshelwood type rate model on the basis of the rate data obtained in the kinetic regime. Notheisz et al (48) have studied determination of mass-trasnfer problems and maximum rate during hydrogenation of cyclohexene using silica supported Pt and Pd catalysts. Huang and Kang (49) have reported hydrogenation of napthalene using platinum as a catalyst supported on Υ-Al_2O_3 as well as on alumina-aluminium phosphate : the latter one was found to be having a better activity. Bond and Stone (50) have carried out hydrogenation of propanenitrile to ethanenitrile using Fe/MgO catalysts which showed higher selectivity.

The main difficulty with the inorganic oxide supported catalysts is the leaching of the metal ions from the surface which could deactivate the catalysts. This problem could be minimised by heterogenizing the homogeneous catalysts using polymeric matrix as a support (51). Catalytic hydrogenation using polymer-bound chelated metal complexes have been studied extensively and such complexes were found to be valuable catalytic material for selective hydrogenation of olefins (52-67). Ruthenium and palladium complexes supported on phosphinated polystyrene were studied widely for olefin hydrogenation (68-72).

Terasawa et al. (73) investigated hydrogenation of olefins and acetylenes using polymer-bound Pd(II) complexes and the activity was noted to be higher than that of the homogeneous counterpart. Guyot et al (74) attempted to determine the influence of the texture of phosphinated polystyrene resin supported Rh complexes on the hydrogenation of 1-hexene and the catalytic activity was observed to be dependent on metal content and localisation of the sites which depends on the preparation process. However, phosphinated polymer-bound catalysts were found to be very sensitive to air (75). Therefore, other polymer supports were employed. MacDonald et al. (76) studied the hydrogenation of some unsaturated hydrocarbons in liquid phase at 50-70°C and 1 atm pressure using Pd on Nylon 66 and the activity was observed to be dependent on the nature of reactant and solvent. Kinetics of hydrogenation of various substrates was carried out by the use of Pt and Pd as catalysts anchored on hydrogel copolymers under mild conditions (77) and no significant decrease in the catalytic activity was found even after 10 cycles.

As the polymer-bound hydrogenation catalysts generated a lot of interest, different studies were carreid out on innovative methods of preparation of such catalysts and attempts were made to further enhance the catalytic activity of such catalysts. Huang and He (78) investigated catalaytic hydrogenation of olefins using polymer-supported colloidal palladium catalysts prepared by a one-step preparation method (OSPM) and a higher catalytic activity was observed for the hydrogenation of olefins. This might be due to uniform dispersion as well as the effective protection of the active metal by the polymer. Teranishi and Toshima (79) reported catalytic hydrogenation by polymer-supported bimetallic catalysts. Polystyrene resin functionalized by tridentate iminodiacetate (ida) moities was employed for the purpose. It was found that the palladium particles supported on chelate resin-lanthanide complexes had higher catalytic activity. Thus lanthanide ions were found to enhance the activity of polymer-bound catalysts.

The main problem of these types of the catalysts is the leaching from the surface.

The N containing ligands have not been used widely. Only few cases have been reported (80). It was therefore planned to synthesise stable catalysts using N containing ligands.

Thus polymer-supported hydrogenation catalysts were found to be very promising. However, each system must be studied and optimized independently (81).

In the present investigation, synthesised polymer-bound schiffbase and EDTA complexes of Ru(III) and Pd(II) have been used to study the kinetics of hydrogenation of 1-hexene and styrene under mild operating conditions. The influence of various parameters such as concentration of catalyst and substrate, temperature of the system as well as nature of solvent used on the rate of the reaction has been invetigated. On the basis of the kinetic data, thermodynamic parameters have been calculated. The life cycle of catalyst has also been studied. A probable reaction mechanism has been suggested.

4.2 Experimental

4.2.1 Measurement of catalytic activity for hydrogenation reactions

The hydrogenation reactions were carried out at atmospheric pressure in a magnetically stirred glass reactor using methanol as solvent. It was chosen as a solvent on the basis of detailed studies of swelling behaviour of catalysts (Tables 3.5 to 3.7, Chapter 3). 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 set-up and detailed procedure are described in chapter 2.

4.2.2 Analysis of Kinetic data

The kinetic data for the hydrogenation reaction were obtained in a kinetic regime at a speed of 650 rpm. Temperature of the reaction was varied from 25-45°C at one atmospheric pressure. In each case, the uptake of hydrogen was measured as a function of time. The plots of variation of hydrogen uptake at various interval of time for catalyst

2PPd(II)Salen is given in Fig. 4 2.1 and the values for their rates are calculated from the slopes of these plots (other plots are not given only to avoid the repetition). The results are given in Tables 4.3.1 to 4.3.11. The initial rate data, thus obtained were used to evaluate the kinetic parameters. The products were analysed using a gas chromatograph with carbowax column and flame ionization detector. 1-hexene was hydrogenated to n-hexane and styrene was converted to ethylbenzene and no side products were formed as revealed by GC analysis.

4.3 Results and discussion

4.3.1 Effect of substrate concentration

The influence of concentration of 1-hexene and styrene on the rate of reaction for different catalysts has been investigated and the results are summarised in tables 4.3.1 to 4.3.3. It was observed that the rate of the reaction increases with an increase in substrate concentration keeping the catalysts concentration constant. Thus, in the case of 2PRu(III) Salen catalyst, the rate increases from 0.05 to 0.11 ml min^{-1} when the concentration of 1-hexene was varied from 2.00x10^{-3} to 8.00x10^{-3} mol l^{-1} at 35°C and 1 atm pressure. In the case of 2PPd(II)Salen the rate was found to increase from 0.05 to 0.08 ml min^{-1}. Similar results were obtained in the case of catalysts 8PRu(III) EDTA, 8PPd(II)EDTA and 14PPd(II)EDTA and are given in table 4.3.1. Investigation of styrene hydrogenation using catalysts 8PRu(III)Salen, 8PPd(II)Salen, 14PRu(III)Salen and 14PPd(II)Salen also revealed similar trends.

The plot of log(initial rate) against log[substrate] at a fixed concentration of the catalysts, hydrogen pressure and temperature was found to be linear (Figs.4.3.2 to 4.3.5) The order of reaction calculated from the slopes of these plots are given in Tables 4.3.1 to 4.3.3. The order of reaction was found to be unity for polymer-bound EDTA complexes.

The plot of reciprocal of substrate concentration against reciprocal of rate of

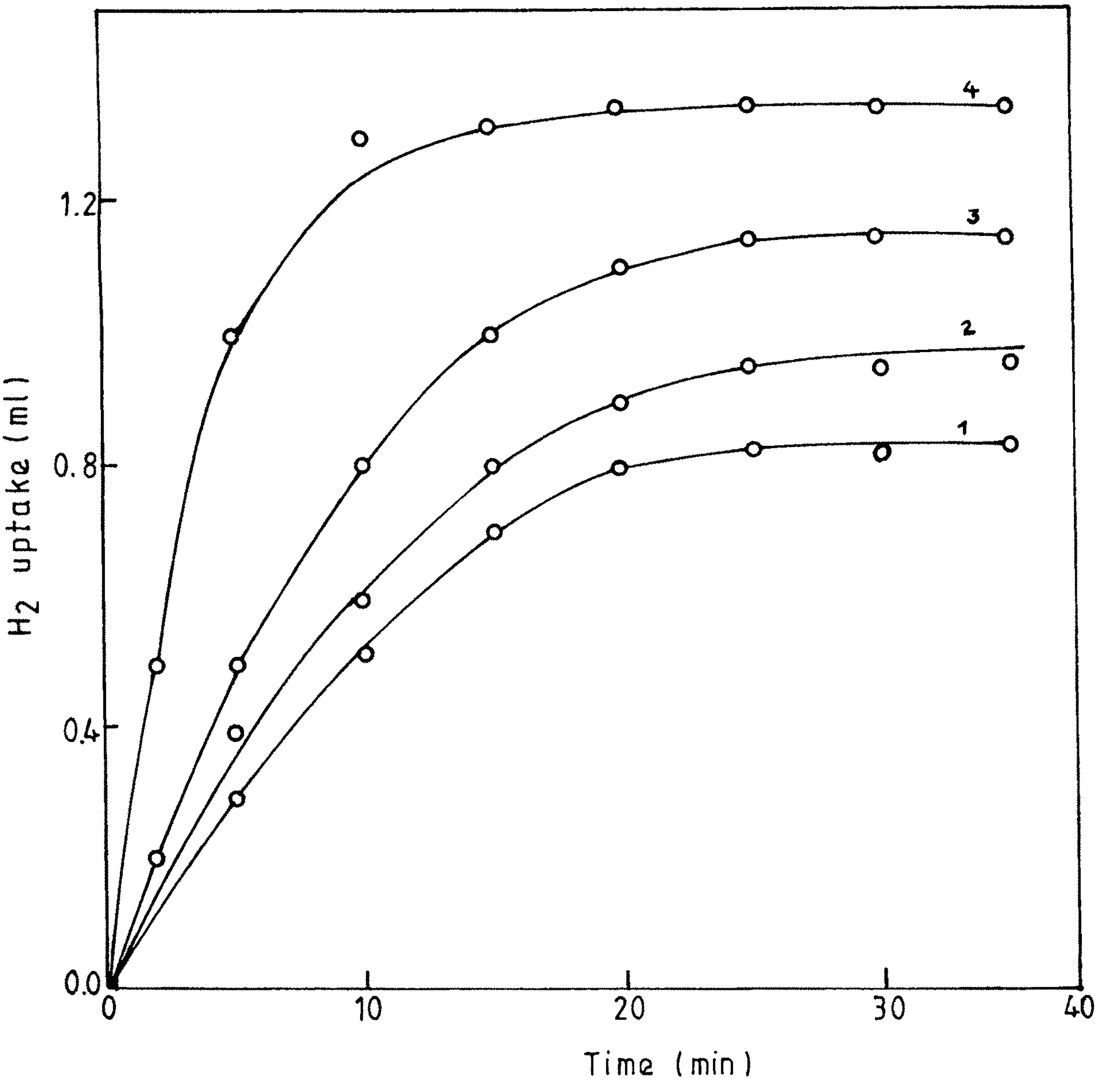


Fig. 4.2.1 Plot of hydrogen uptake vs time for catalyst 2PPd(II)Salen for various amount of the catalyst
[Catalyst] (mol l^{-1} x10^{-6}) : (1) 5 74 (2) 7.66 (3) 9.57 (4) 11.49

reaction (Figs.4.3.6 and 4.3.7) was found to be linear with a positive intercept. This indicates that the rate of hydrogenation, R, is related to the substrate concentration, [S] by the relationship

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

where a and b are the slope and intercept of the plot respectively. Similar results are reported earlier by Terasawa et al (63) and Taquikhan et al (71).

The hydrogenation reaction was carried out using homogeneous complexes of Ru(III) and Pd(II) under similar conditions and no considerable consumption of hydrogen gas was observed. However, the study was made with a higher concentration of metal complexes and the rate of the reaction was found to be lower which is indicative of the fact that the anchored metal complexes have higher catalytic activity than their homogeneous analogoues. The results are summarised in Tables 4.3.3.

Table 4.3.1

Effect of [1-hexene] on the rate of hydrogenation using polymer supported catalysts at 35°C and 1 atm pressure.

Volume of methanol = 20 ml

Catalyst	[Catalyst] $(\mathrm{mol.l^{-1}})10^{6}$	[1-hexene] $(\mathrm{mol\ l^{-1}})10^{3}$	Rate of reaction $(\mathrm{ml\ min^{-1}})$	Order of reaction
2PRu(III)Salen	8.16	2.00	0.05	0.85
		4.00	0.07	
		6.00	0.09	
		8.00	0.11	
2PPd(II)Salen	9.57	2.00	0.05	0.20
		4.00	0.07	
		6.00	0.08	
		8.00	0.08	
8PRu(III)EDTA	0.49	4.00	0.23	1.15
		6.00	0.29	
		8.00	0.54	
		10.00	0.68	
8PPd(II)EDTA	0.75	2.00	0.17	1.00
		4.00	0.24	
		6.00	0.35	
		8.00	0.48	
14PPd(II)EDTA	1.32	2.00	0.10	1.00
		4.00	0.16	
		6.00	0.25	
		8.00	0.45	

Table 4.3.2

Effect of [styrene] on the rate of hydrogenation using polymer supported catalysts at 35°C and 1 atm pressure

Volume of methanol = 20 ml

Catalyst	[Catalyst] (mol l^{-1})	[1-hexene] (mol l^{-1})10^3	Rate of reaction (ml min^{-1})	Order of reaction
8PRu(III)Salen	$7.12x10^{-5}$	4.36	0.15	0.69
		8.73	0 22	
		13.09	0.28	
		17.46	0.35	
8PPd(II)Salen	$1.16x10^{-6}$	4.36	0.43	0.23
		8.73	0.45	
		13.09	0.48	
		17.46	0 52	
14PRu(III)Salen	$2.97x10^{-6}$	4.36	0.07	1.5
		8.73	0.22	
		13.09	0.38	
		17.46	0.54	
14PPd(II)Salen	$0.45x10^{-6}$	4.36	0.34	0.44
		8.73	0.42	
		13.09	0.50	
		17.46	0 61	

Table 4.3.3

Effect of [substrate] on the rate of hydrogenation using homogeneous complexes at 35°C and 1 atm pressure

Volume of methanol = 20 ml

Catalyst	[Catalyst] (mol l^{-1})10^3	[1-hexene] (mol l^{-1})10^3		Rate of reaction (ml min^{-1})		Order of reaction	
		a	b	a	b	a	b
(Ru(III)Salen Cl]	1 03	4.00	4.36	0.15	0.12	0.75	0.59
		8.00	8.73	0.23	0.21		
		12.00	13.09	0.31	0.32		
		16.00	17.46	0.40	0.41		
[Pd(II)Salen]	0.83	4.00	4.36	0.07	0 09	0.91	0.95
		8.00	8.73	0.15	0 18		
		12.00	13.09	0.26	0.29		
		16.00	17.46	0.36	0.39		

a for hydrogenation of 1-hexene b for hydrogenation of styrene

4.3.2 Influence of catalyst concentration

The influence of catalyst concentration on the rate of hydrogenation of 1-hexene/ styrene has been studied for polymer-bound catalysts and the rate was found to increase from 0.07 to 0.11 ml min^{-1} for catalyst 2PRu(III)Salen on changing the ruthenium concentration from 2.72×10^{-6} to 10.88×10^{-6} mol l^{-1}, at 35°C and 1 atm pressure, at a constant concentration of 1-hexene (4.00×10^{-3}); in case of 2PPd(II)Salen catalyst, an increase in rate was observed from 0.05 to 0.09 ml min^{-1} as the concentration of palladium varied from 5.74×10^{-6} to 11.49×10^{-6} mol l^{-1} under similar condition. Similar results have also been found for the hydrogenation of styrene. The other results are given in Tables 4.3.4 to 4.3.6.

The variation of the rate of the reaction with the concentration of the catalyst was found to be linear (as shown in Tables 4.3.4 to 4 3.6) which is indicative of the fact that the mass transfer effect could be neglected under the reaction conditions (73). An increase in the rate of reaction with an increase in the amount of the catalyst is also indicative of the

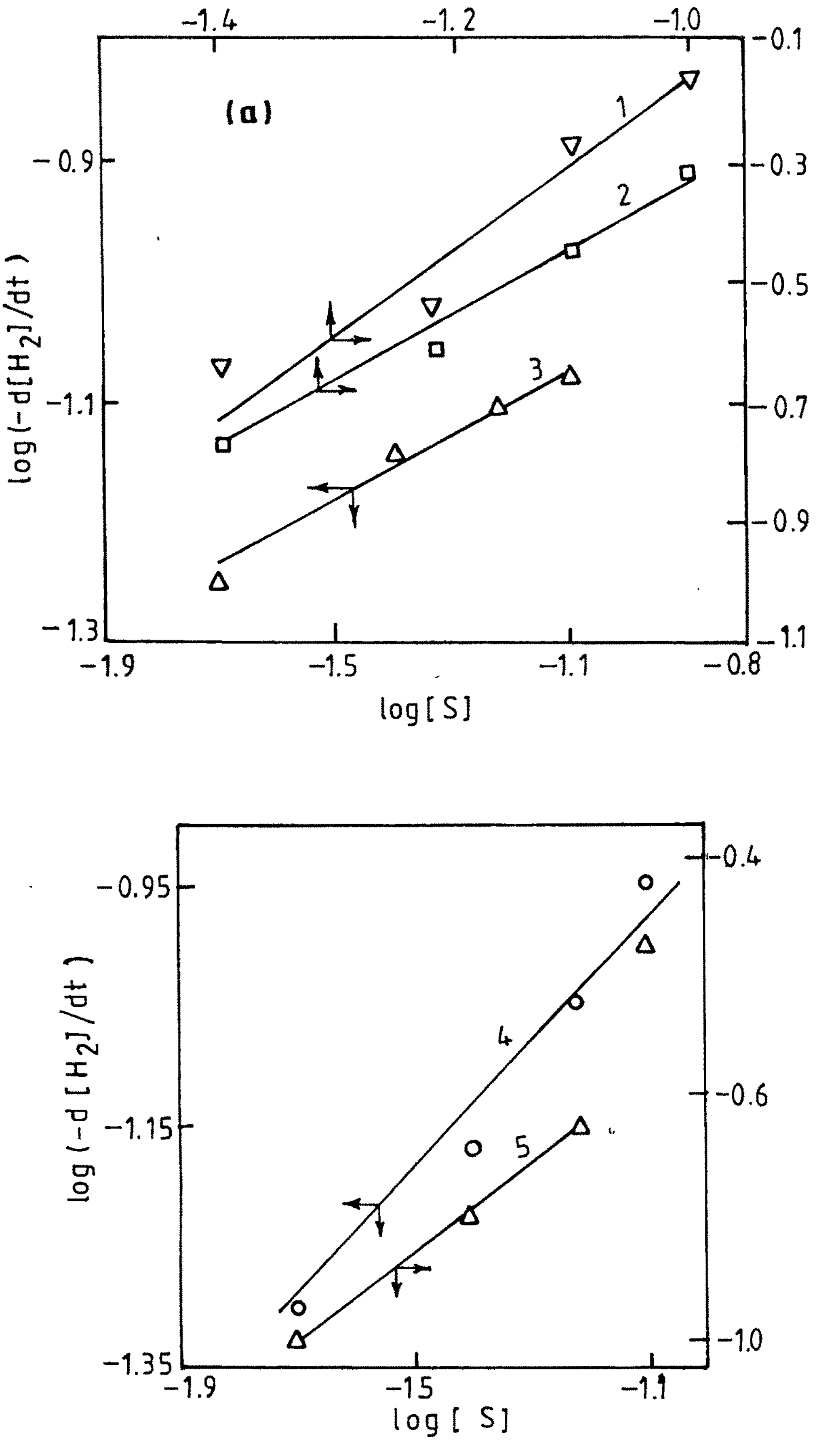


Fig. 4.3 2 (a) and (b) Plot of log(initial rate) vs log[1-hexene] for polymer supported catalysts (1) 8PRu(III)EDTA (2) 8PPd(II)EDTA (3) 2PPd(III)Salen (4) 2PRu(III)Salen and (5) 14PPd(II)Salen

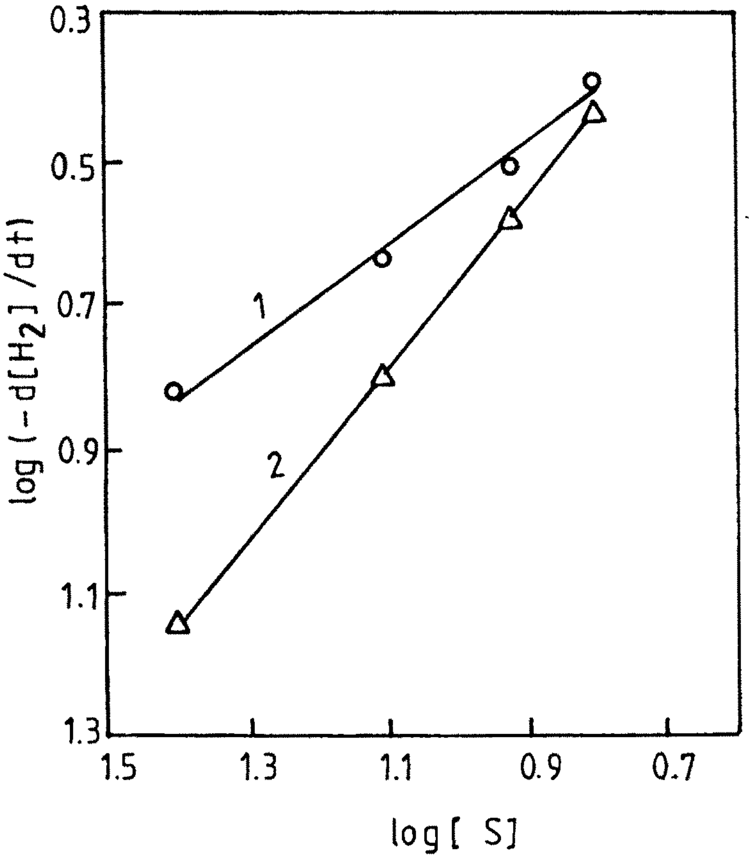


Fig. 4.3.3 Plot of log(initial rate) vs log[1-hexene] for homogeneous complexes
(1) [Ru(III)Salen Cl] (2) [Pd(II)Salen]

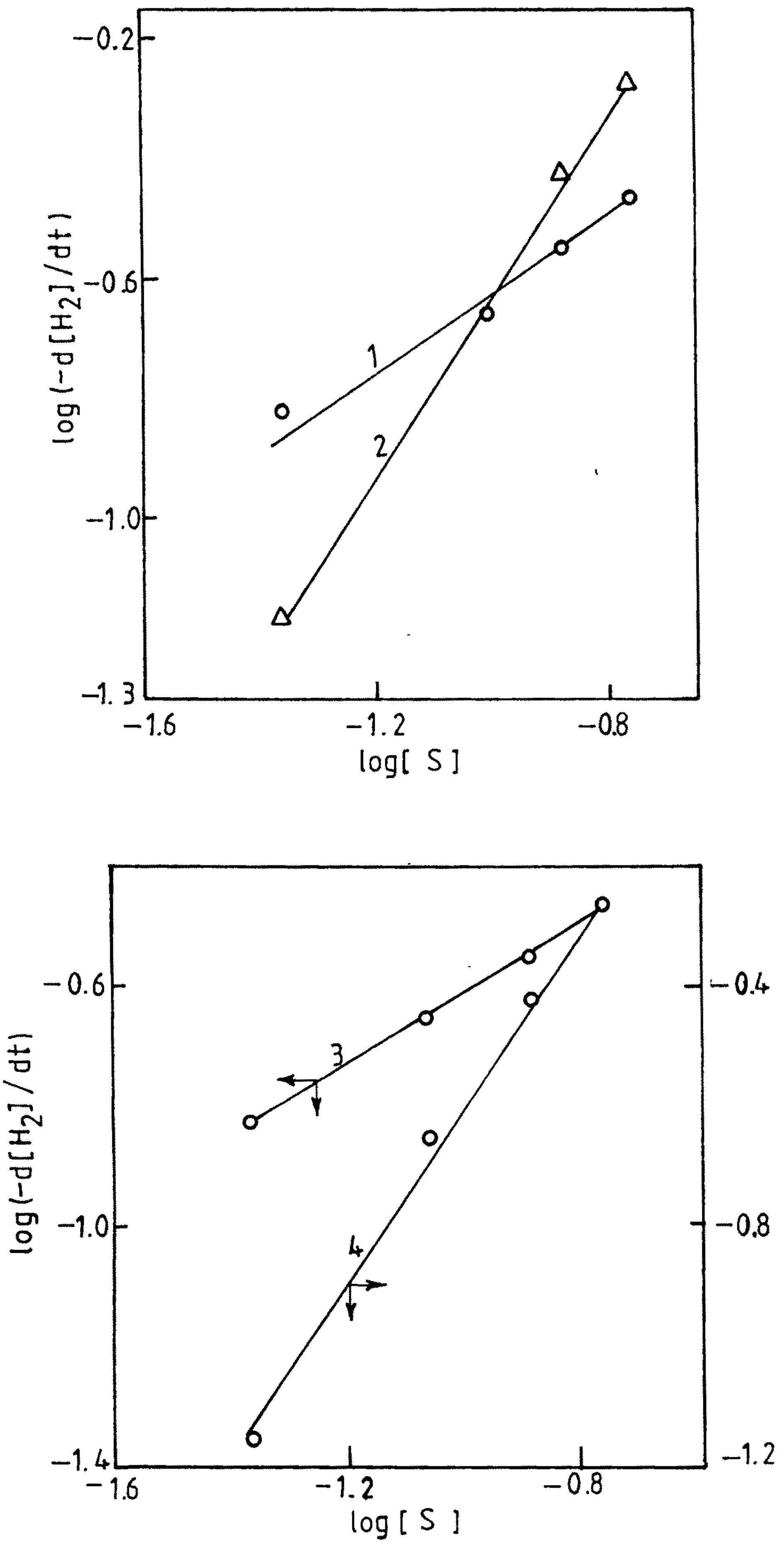


Fig.4.3.4 (a) and (b) Plot of log(initial rate) vs log [styrene] for polymer supported catalysts (1) 8PRu(III)Salen (2) 14PRu(III)Salen and homogeneous complexes (3) [Ru(III)Salen Cl] (4) [Pd(II)Salen]

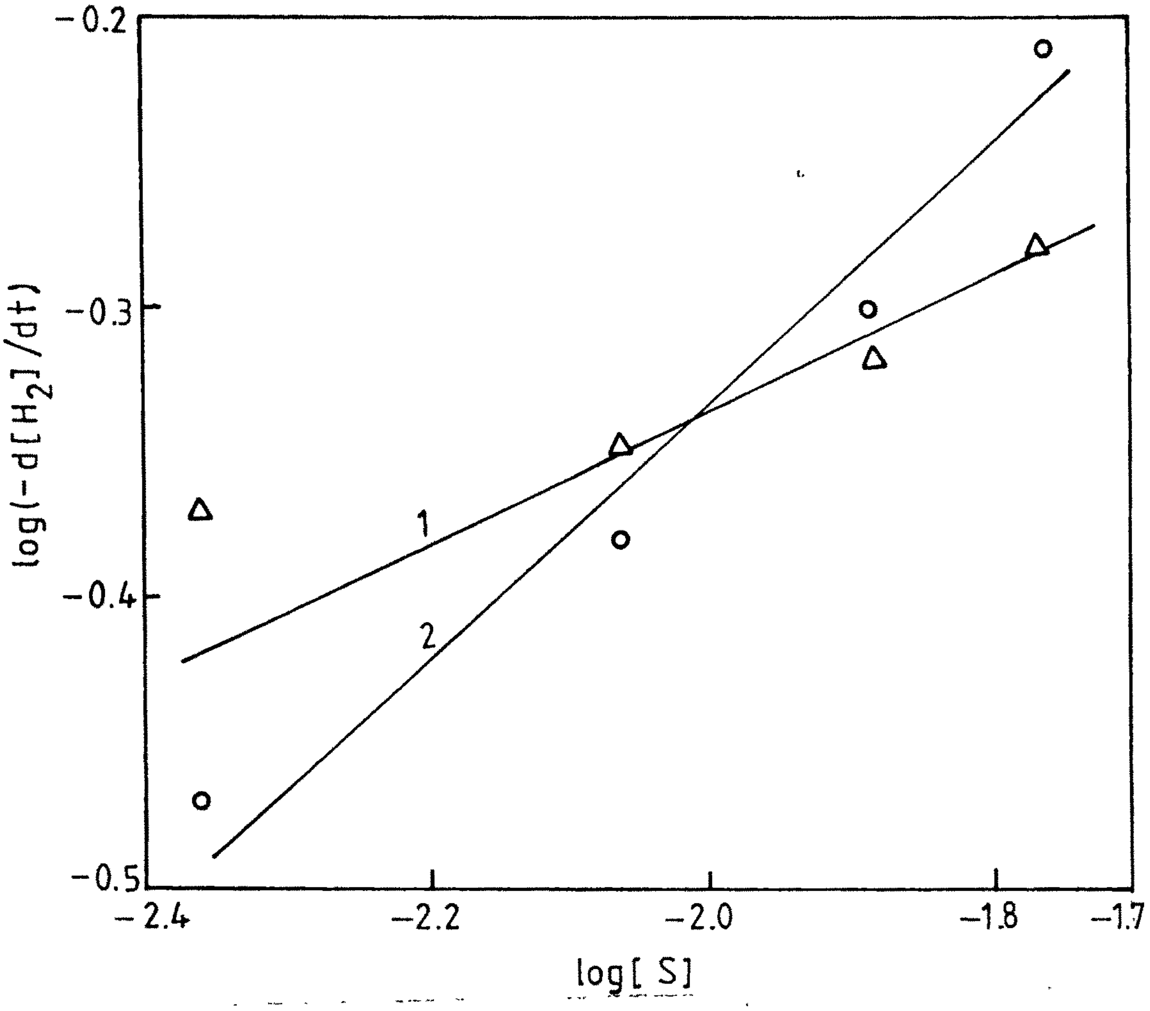


Fig. 4.3.5 Plot of log(initial rate) vs log[styrene] for polymer supported catalysts
(1) 8PPd(II)Salen (2) 14PPd(II)Salen

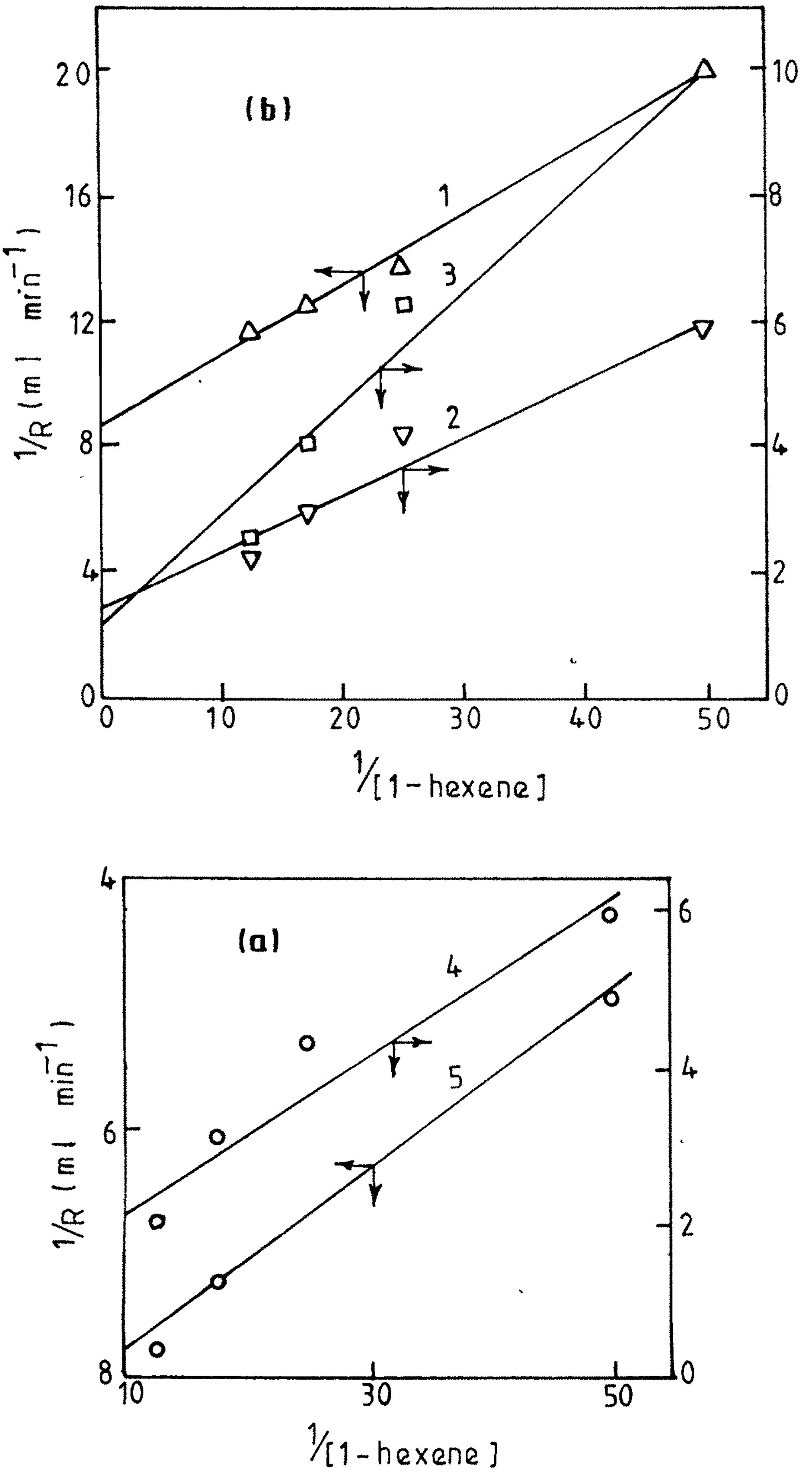


Fig. 4.3.6(a) and (b) Plot of 1/Rate vs 1/[1-hexene] for polymer supported catalysts (1) 2PPd(II)Salen (2) 8PRu(III) EDTA (3) 14PPd(II) EDTA (4) 8PPd(II) EDTA (5) 2PRu(III)Salen

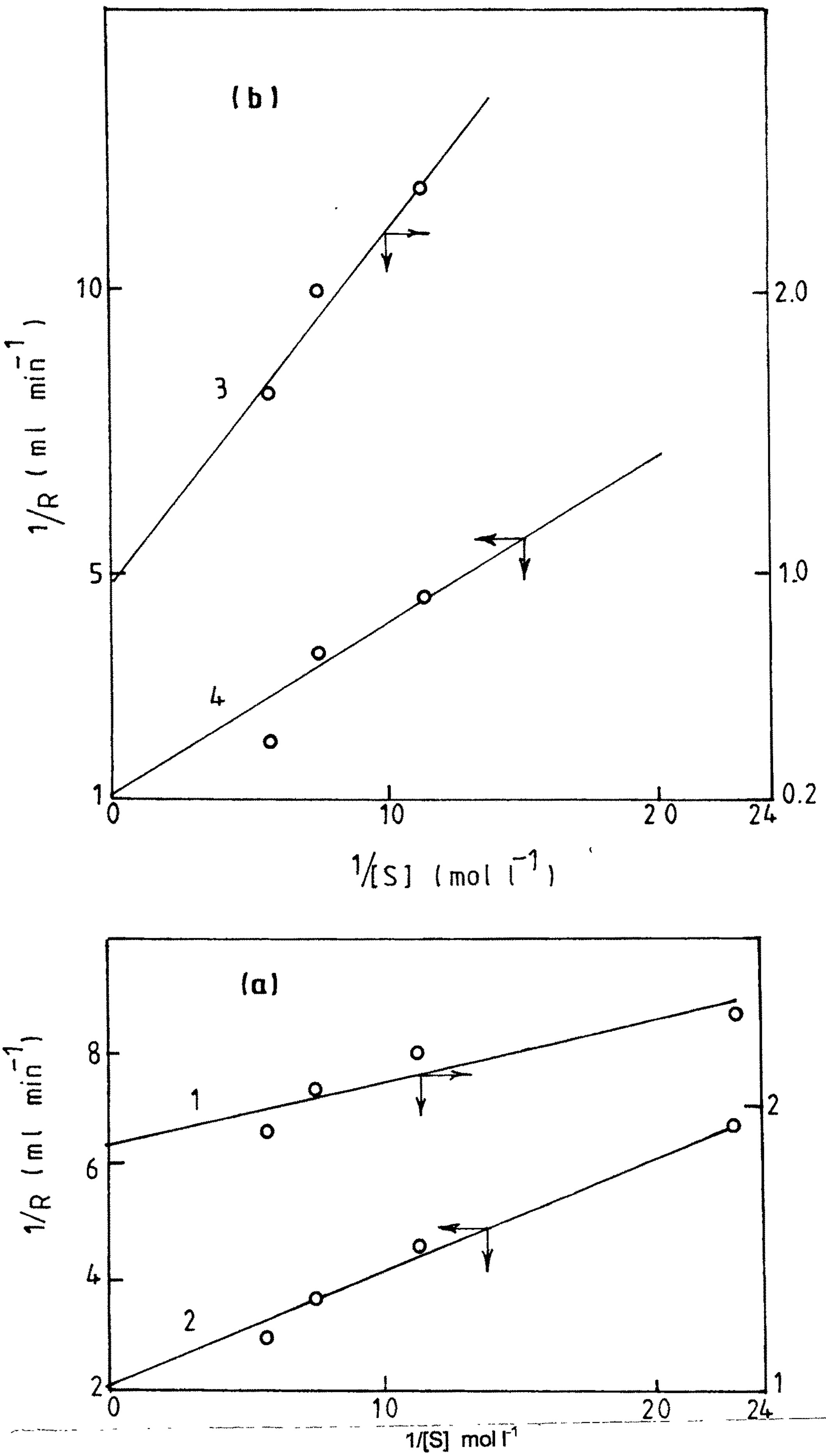


Fig. 4.3.7 (a) and (b) Plot of 1/Rate vs 1/[styrene] for polymer-supported catalysts (1) 14PPd(II)Salen (2) 14PRu(III)Salen (3) 8PPd(II)Salen (4) 8PRu(III)Salen

fact that there is no dimerization of the metal complex in the range studied (82).

The order of reaction with respect to the catalyst concentration was calculated from the plots of log (initial rate) vs log[catalyst] (Figs.4.3.8 to 4.3.10) at a fixed concentration of substrate at 35°C. It was found to be fractional in the case of all polymer-bound schiff-base complexes. However in the case of polymer-bound EDTA complexes, the order was found to be unity. The fractional order of reaction obtained in heterogenized homogeneous system indciates that all the active sites may not be available on the surface to catalyse the reaction because of the swellability of polymer matrix and the ligand molecules might have caused steric hinderance.

The experiments were carried out in homogeneous medium using Ru(III) and Pd(II) metal complexes and the results are summarised in Table 4.3.6. For the sake of convenience in measuring the rate of reaction, a higher amount of metal ions were used, however, a lower rate was observed which indicates that heterogenized homogeneous catalysts are efficient for 1-hexene and styrene hydrogenation compared to homogeneous analogues.

4.3.3 Effect of temperature

Influence of temperature on the rate of reaction is well established. The increase in the rate of reaction of homogeneously or heterogeneously catalyzed reaction with an increase in temperature is well known (83).

The effect of temperature on the rate of hydrogenation of 1-hexene/styrene by polymer-bound catalysts has been studied in the range of 25-45°C and the results are summarised in Tables 4.3.7 to 4.3.8. The rate of hydrogenation was found to increase with an increase in temperature for all the catalysts studied. Thus the rate of reaction varied from 0.06 to 0.13 ml min^{-1} for catalyst 2PRu(III)Salen, as the temperature is increased from 30 to 45°C at a fixed catalyst concentration of $8.6x10^{-6}$ mol l^{-1} and a fixed

Table 4.3.4

Effect of [catalyst] on the rate of hydrogenation of 1-hexene using polymer supported catalysts at 35°C and 1 atm pressure

Volume of methanol = 20 ml

Catalyst	[Catalyst] (mol l^{-1})10^6	[1-hexene] mol 1^{-1}x10^3	Rate of reaction (ml min^{-1})	Order of reaction
2PRu(III)Salen	2.72	4.00	0.06	0.13
	5.44		0.07	
	8.16		0.08	
	10.88		0.11	
2PPd(II)Salen	5.74	4.00	0.05	0.38
	7.66		0.08	
	9.57		0.08	
	11.49		0.09	
8PRu(III)EDTA	0.37	8.00	0.32	1.63
	0.49		0.54	
	0.62		0.72	
	0.74		0.95	
8PPd(II)EDTA	0.38	8.00	0.30	1.00
	0.75		0.48	
	1.13		0.73	
	1.50		0.98	
14PPd(II) EDTA	0.33	8.00	0.30	0.30
	0.66		0.34	
	0.99		0.40	
	1.32		0.45	

Table 4.3.5

Effect of [Catalyst] on the rate of hydrogenation of styrene using polymer supported catalysts at 35°C and 1 atm pressure

Volume of methanol = 20 ml
[Styrene] = 8.73×10^{-3} mol l^{-1}

Catalyst	[Catalyst] (mol l^{-1})	Rate of reaction (ml min^{-1})	Order of reaction
8PRu(III)Salen	3.66×10^{-5}	0.18	0.30
	7.12	0.22	
	10.68	0.25	
	14.24	0.30	
8PPd(II)Salen	0.58×10^{-6}	0.32	0.50
	0.87	0.39	
	1.16	0.45	
	1.45	0.50	
14PRu(III)Salen	1.48×10^{-6}	0.09	1.14
	2.97	0.22	
	4.45	0.36	
	5.94	0.50	
14PPd(II)Salen	0.22×10^{-6}	0.37	0.20
	0.45	0.42	
	0.67	0.45	
	0.89	0.48	

Table 4.3.6

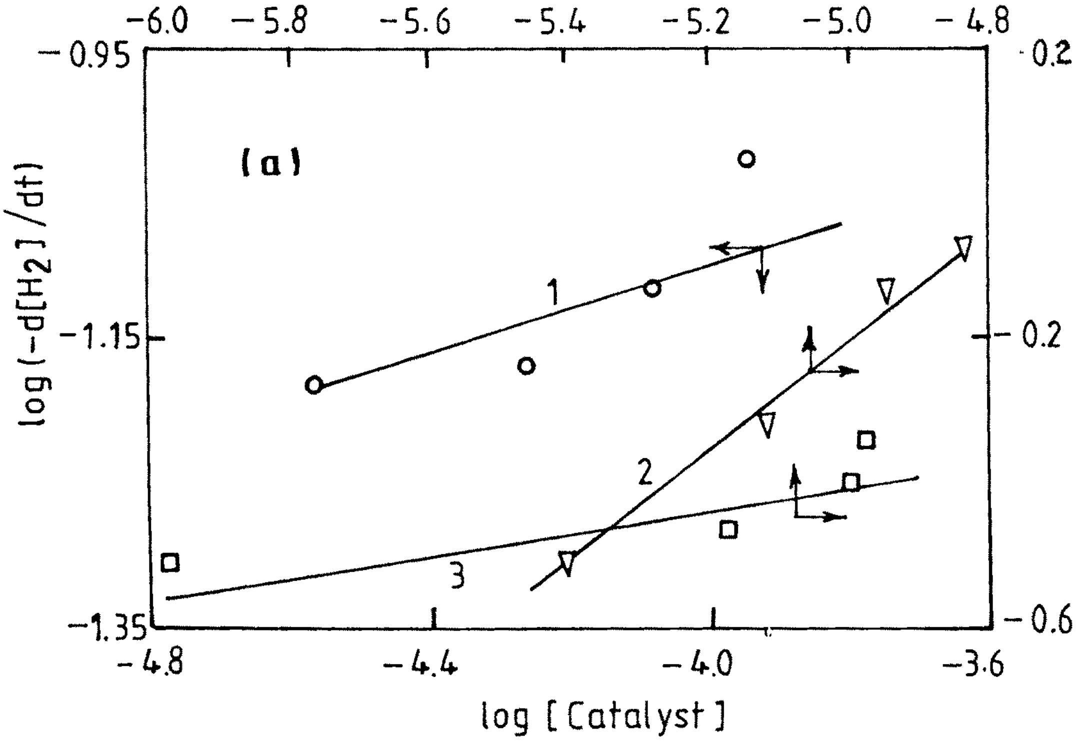
Effect of [Catalyst] on the rate of hydrogenation of 1-hexene/styrene using metal complex catalysts in homogeneous medium at 35°C and 1 atm pressure

Volume of methanol = 20 ml
a = 1-hexene
b = styrene

Catalyst	Ru/Pd present (mol l^{-1})10^3	[Substrate] (mol l^{-1})10^3		Rate of reaction (ml min^{-1})		Order of reaction	
		a	b	a	b	a	b
[Ru(III)Salen Cl]	1.03	8.00	8.73	0.23	0.21	0.45	0.44
	2.05			0.29	0.26		
	3.08			0.35	0.31		
	4.10			0.41	0.40		
[Pd(II)Salen]	0.83	8.00	8.73	0.15	0.18	1.16	0.77
	1.67			0.30	0.30		
	2.50			0.45	0.41		
	3.30			0.62	0.51		

1-hexene concentration of 4.00×10^{-3} mol l^{-1}. Similar results were obtained in all other cases. In case of catalyst 2PPd(II)Salen containing 9.57×10^{-6} mol l^{-1} of Pd, the rate of reaction was observed to increase from 0.05 to 0.10 ml min^{-1} when the temperature was varied from 25 to 40°C. Similar results were obtained in hydrogenation of styrene.

The values for the energy of activation calculated from the slope of the straight line plot of log(initial rate) against 1/T (Figs. 4.3.11 to 4.3.14) are given in Tables 4.37 to 4.3.10. In the case of polymer-bound Ru catalysts, the energy of activation was found to be in the range of 30.5 to 70.8 kJ mol^{-1} for 1-hexene hydrogenation. For the hydrogenation of styrene it was observed to be in the range of 38.3 to 104.7 kJ mol^{-1}. Homogeneous hydrogenation was carried out with higher catalyst concentration for



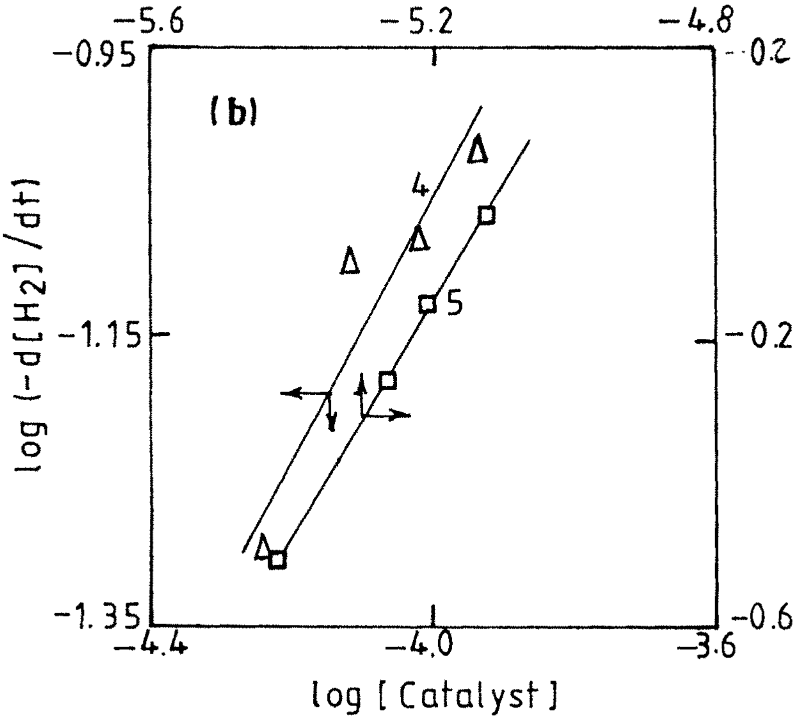


Fig 4.3.8(a) and (b) Plot of log (initial rate) vs log[catalyst] for polymer-supported catalysts (1) 2PRu(III)Salen (2) 8PPd(II) EDTA (3) 14PPd(II)EDTA (4) 2PPd(II)Salen and (5) 8PRu(III)EDTA

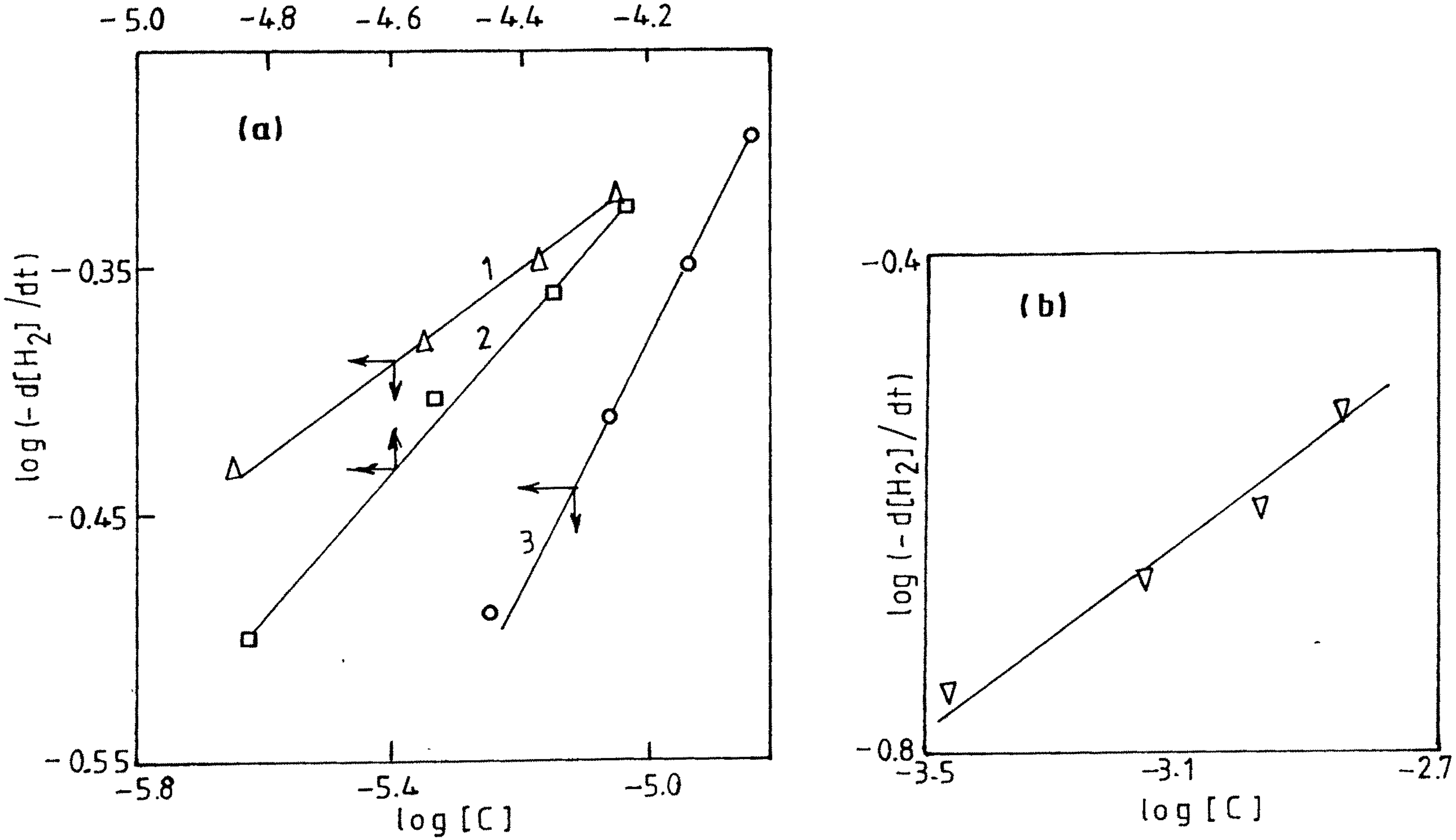
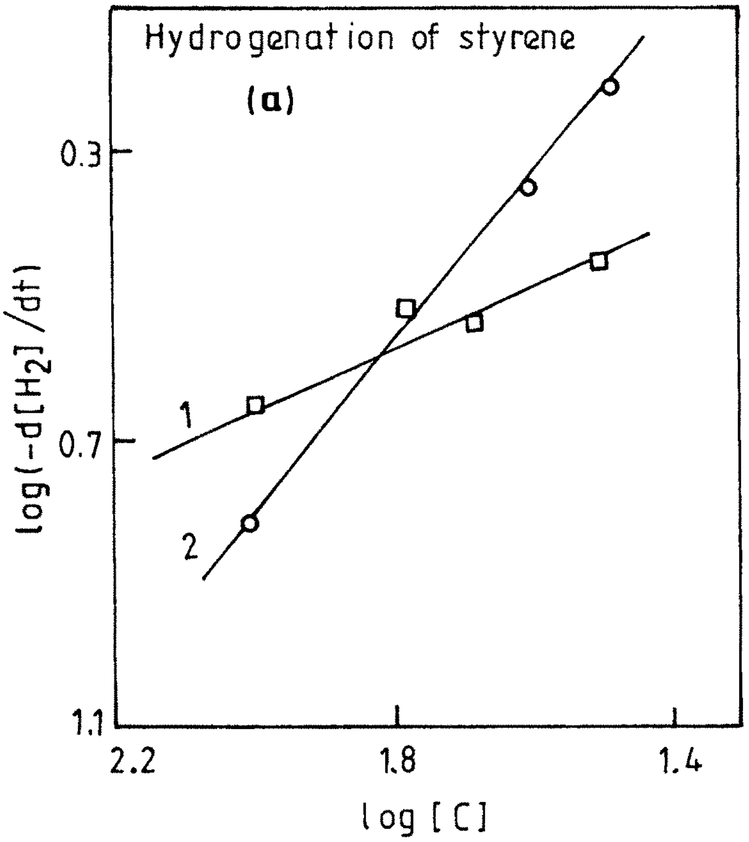


Fig 4.3.9 (a) and (b) Plot of log(initial rate) vs log[catalyst] for polymer-bound catalysts
(1) 14PPd(II)Salen (2) 14PRu(III)Salen (3) 8PPd(II)EDTA (4) 8PRu(III)Salen



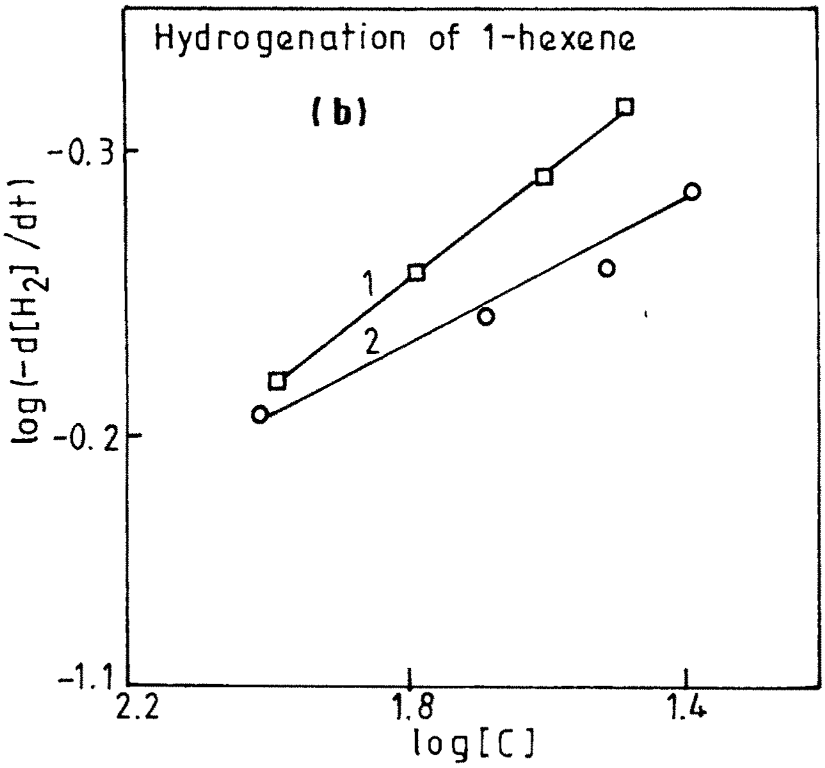


Fig 4 3.10(a) and (b) Plot of log(initial rate) vs log[catalyst] for homnogeneous complexes (1) [Ru(III)Salen Cl] (2) [Pd(II)Salen] conveniently measuring the rate. In the case of homogeneous ruthenium complex, energy of activation was found to be 53.6 kJ mol^{-1} for hydrogenation of 1-hexene and 72.8 kJ mol^{-1} for hydrogenation of styrene whereas for palladium complex it was found to be 87.5 and 71.5 kJ mol^{-1} respectively.

The entropy of activation was calculated using the equation:

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

where K and h are Boltzmann and Plank's constant respectively. ΔS is the entropy of activation. Values of entropy of activation for polymer-bound catalysts are given in Tables 4.3.7 and 4.3.8. Negative values of ΔS obtained for polymer-bound catalysts indicate the loss of freedom of motion due to fixation of catalyst molecule on the polymer matrix (84). Similar results were reported by Terasawa et al. in the study of hydrogenation of styrene using polymer-bound palladium complex (73). The formation of dihydrido complex with the substrate and subsequent fast insertion and elimination of the product may also be taken into consideration.

4.3.4 Effect of solvents

The nature of solvent used can influence catalytic activity of polymer-bound complexes, because of swellability of polymer support. Polymer swelling is a very useful parameter to control both specificity and slectivity in a batch reactor. The activity and selectivity of supported catalysts may be varied by nature of solvent used (85). Choice of better swelling agent is essential in catalytic reactions using polymer-bound complexes (86-91). Solvent can influence a reaction through its ability to swell the support. Polarity of the solvent can lead to a polarity gradient between the bulk solvent and the local environment of the catalytic site. Thus a suitable solvent is one that would combine better swellability and high polarity.

Table 4.3.7

Kinetics of hydrogenation of 1-hexene at various temperatures using polymer supported metal complex catalysts at 1 atm pressure

Volume of methanol = 20 ml

Catalyst	[Catalyst] (mol l^{-1})10^{6}	[1-hexene] (mol l^{-1})10^{3}	Temp. (°C)	Rate of reaction (ml min^{-1})	Energy of activation (kJ mol^{-1})	Entropy of activation (eu)
2PRu(III)Salen	8.16	4.00	30	0.06	30.5	-45.8
			35	0.07		
			40	0.08		
			45	0.13		
2PPd(II)Salen	9.57	4.00	25	0.05	36.1	-41.1
			30	0.07		
			35	0.08		
			40	0.10		
8PRu(III)EDTA	0.49	8.00	25	0.25	70.8	-10.4
			30	0.35		
			35	0.54		
			40	0.86		
8PPd(II)EDTA	0.75	8.00	30	0.35	71.4	-14.8
			35	0.48		
			40	0.86		
			45	1.26		
14PPd(II)EDTA	1.32	8.00	25	0.25	59.1	-27.5
			30	0.33		
			35	0.45		
			40	0.63		

Table 4 3 8

Kinetics of hydrogenation of styrene at various temperatures using polymer supported metal complex catalysts at 1 atm pressure

[Styrene] = 8.73×10^{-3} mol l^{-1}
Volume of methanol = 20 ml

Catalyst	[Catalyst] (mol l^{-1})	Temp. (°C)	Rate of reaction (ml min^{-1})	Energy of activation (kJ mol^{-1})	entropy of activation (eu)
8PRu(III)Salen	7.12×10^{-5}	30	0.14	61.3	-19.6
		35	0 22		
		40	0.30		
		45	0.38		
8PPd(II)Salen	1.16×10^{-6}	30	0.37	38.3	-36.0
		35	0.45		
		40	0.60		
		45	0 70		
14PRu(III)Salen	2.97×10^{-6}	30	0.09	104.7	-148.4
		35	0 22		
		40	0.40		
		45	0.55		
14PPd(II)Salen	0.45×10^{-6}	30	0.32	39.0	-35.7
		35	0.42		
		40	0.52		
		45	0 63		

Table 4.3.9

Kinetics of hydrogenation of 1-hexene at various temperatures using metal complex catalysts in homogeneous medium

Volume of methanol = 20 ml
[1-hexene] = 8.00x10^{-3} mol l^{-1}

Catalyst	[Catalyst] (mol l^{-1})10^3	Temp (°C)	Rate of reaction (ml min^{-1})	Energy of activation (kJ mol^{-1})	Entropy of activation (eu)
[Ru(III)Salen Cl]	1.03	30	0.16	53.6	-25.48
		35	0.23		
		40	0.36		
		45	0.38		
[Pd(II)Salen]	0.83	30	0.07	87 5	-00.03
		35	0.15		
		40	0.25		
		45	0.36		

Table 4.3.10

Kinetics of hydrogenation of styrene at various temperatures using metal complex catalysts in homogeneous medium.

Volume of methanol = 20 ml
[Styrene] = 8.73x10^{-3} mol l^{-1}

Catalyst	[Catalyst] (mol l^{-1})10^3	Temp (°C)	Rate of reaction (ml min^{-1})	Energy of activation (kJ mol^{-1})	Entropy of activation (eu)
[Ru(III)Salen Cl]	1.03	30	0.12	72.8	-10 8
		35	0.21		
		40	0.31		
		45	0.40		
[Pd(II)Salen]	0.83	30	0.10	71.5	-12.1
		35	0.18		
		40	0.27		
		45	0.39		

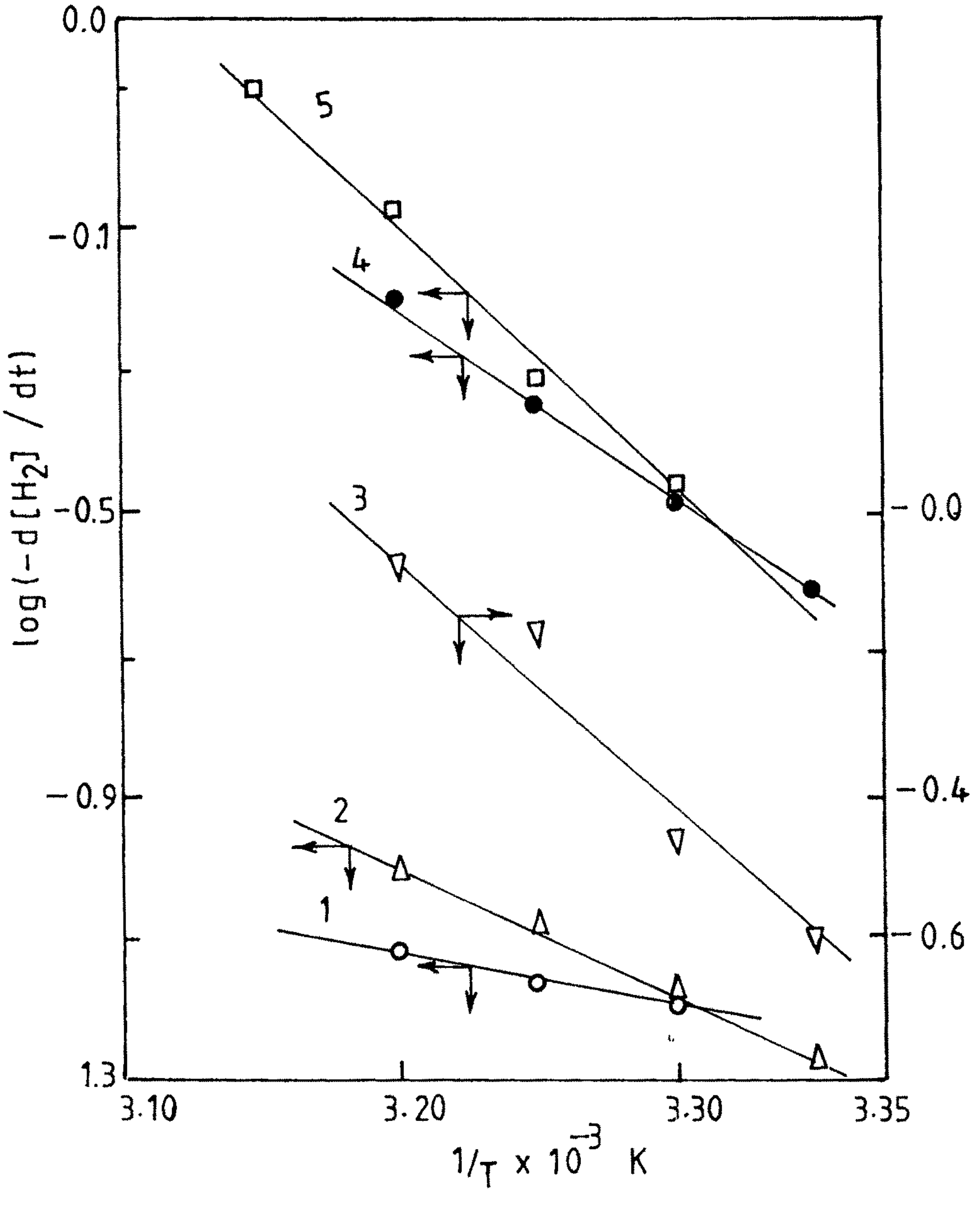


Fig. 4.3.11 Arrhenius plots for polymer supported catalysts (1) 2PRu(III)Salen (2) 2PPd(II)Salen (3) 8PRu(III)Salen (4) 14PPd(II)Salen (5) 8PPd(II)EDTA

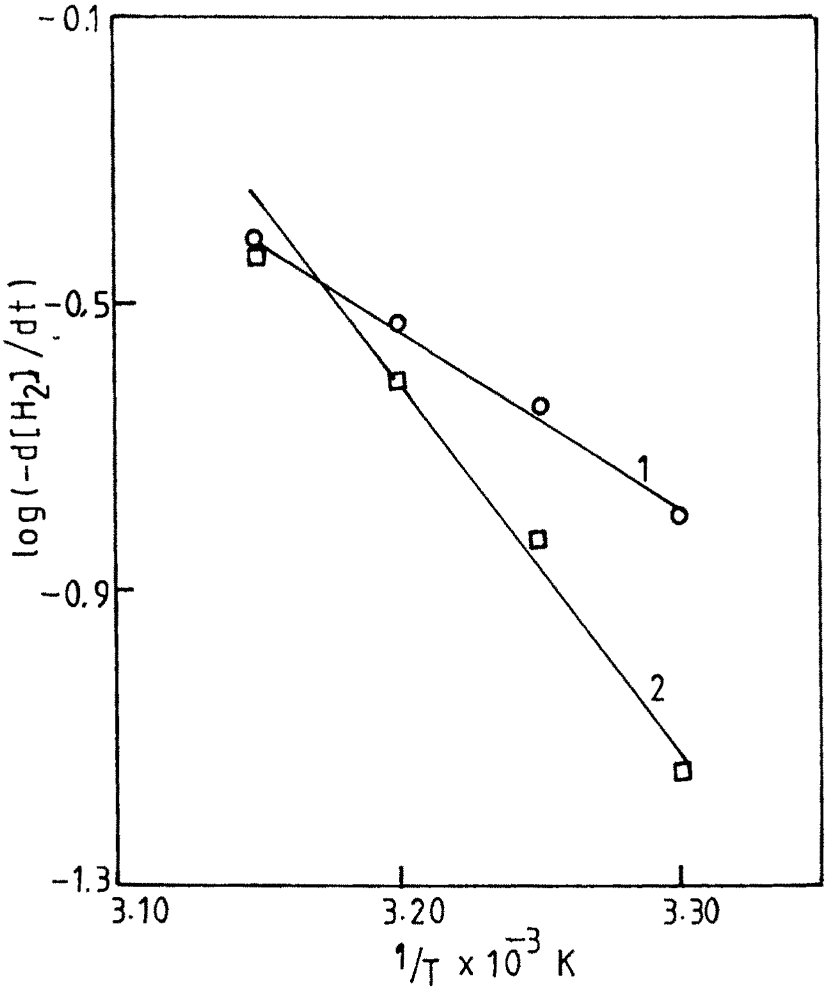


Fig.4.3.12 Arrhenius plots for hydrogenation of 1-hexene (1) [Ru(III)Salen Cl]
(2) [Pd(II)Salen]

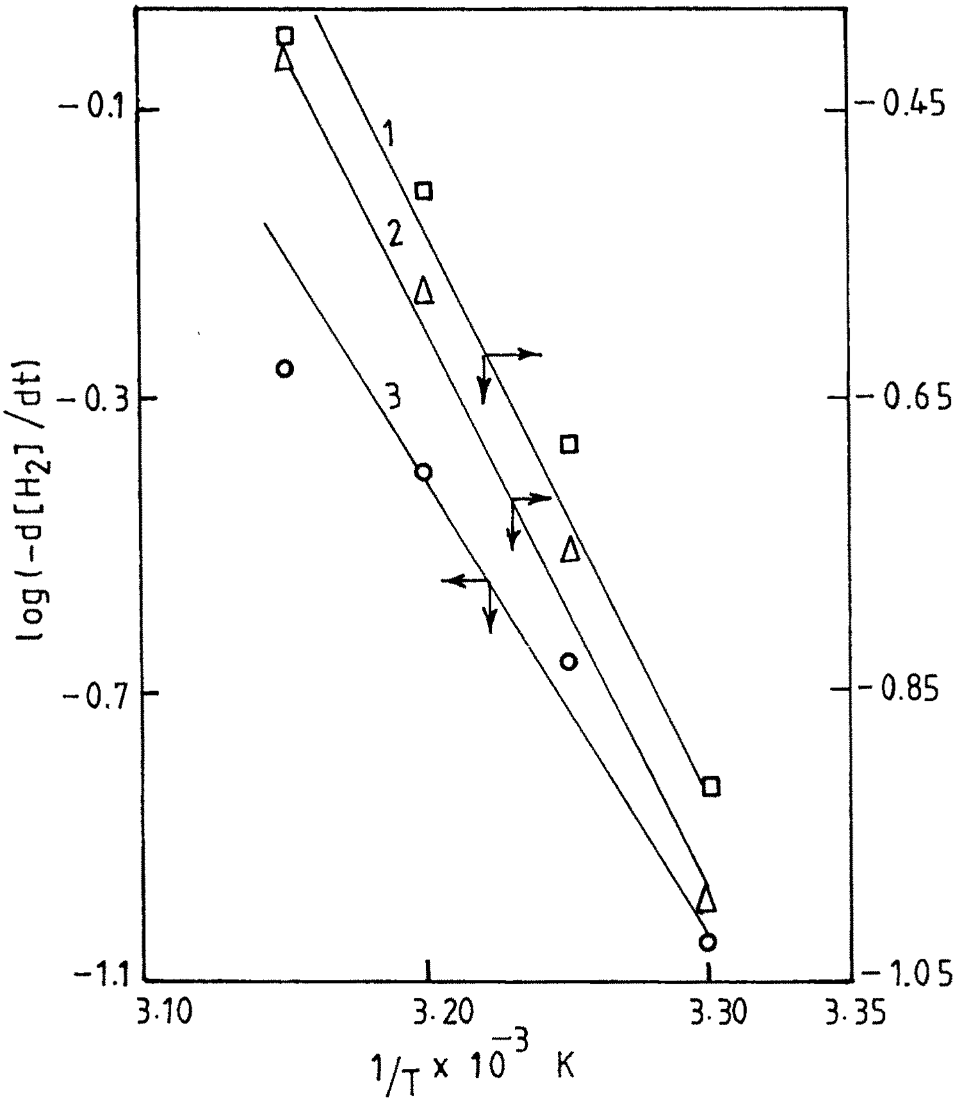


Fig. 4.3 13 Arrhenius plots for hydrogenation of styrene
(1) [Ru(III)Salen Cl] (2) [Pd(II)Salen] (3) 14PRu(III)Salen

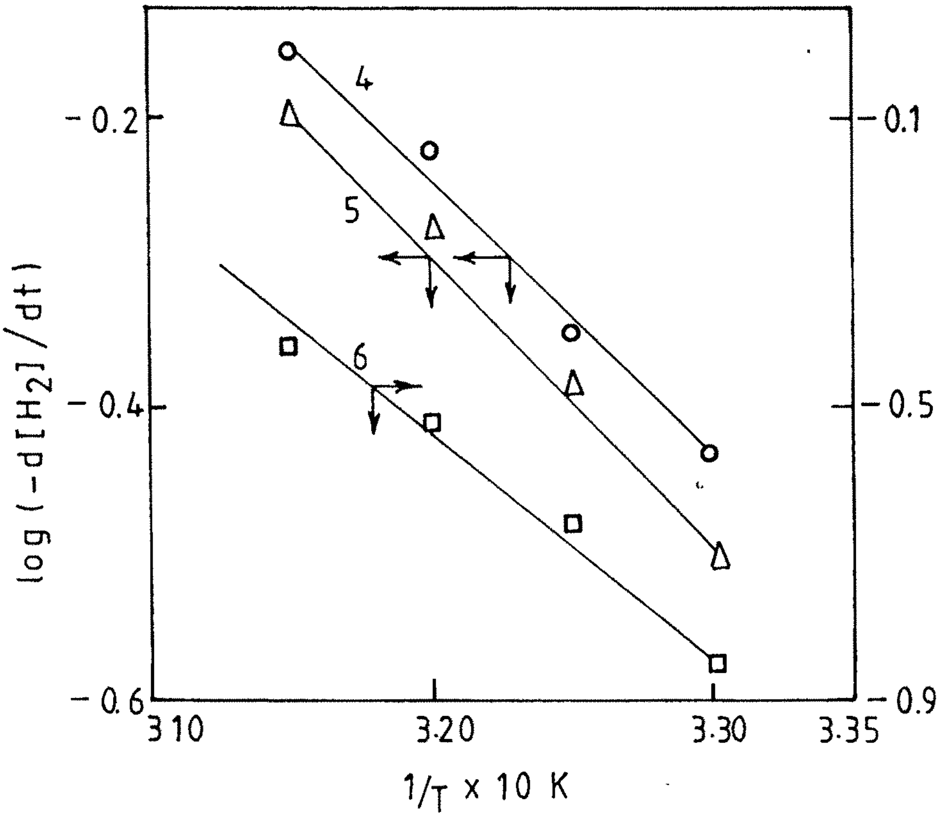


Fig. 4.3.14 Arrhenius plots for hydrogenation of styrene (4) 8PPd(II)Salen (5) 14PPd(II)Salen (6) 8PRu(III)Salen

The influence of different solvents on the rate of hydrogenation of 1-hexene/ styrene was studied and the results are summarised in Tables 4.3 11 and 4 3 12.

It was observed that the rate of hydrogenation increases with an increase in the polarity of the solvent. Thus for the catalyst 2PRu(III)Salen, the rate was found to be 0.025 ml min^{-1} in benzene whereas in methanol it was observed to be 0.068 ml min^{-1} in hydrogenation of 1-hexene at 35°C and constant catalyst concentration. Similar results were obtained in all other cases which are given in Tables 4 3.11 to 4.3.12 This may be probably due to the higher swelling and therefore more sites are available for the reacting system.

4.3.5 Life cycle study of catalyst

Catalyst recycle is the main objective of supporting metal ions onto a polymer support. Catalyst recycle without significant loss of catalytic activity is very important and necessary as the noble metals are costly. However, it was observed that the polymer-bound catalyst can lose its activity by loss of metal ions, which is brought about by leaching of the active component or reduction to free metal (92) Usually the metal ions get leached out in solution (93-95), especially when they are under reaction condition. The leaching of these metal ions could be controlled by attaching it to the support through a chelating ligand (80).

Stability of the polymer-bound catalyst was tested under repeated catalytic cycles and the results are summarised in Tables 4.3.13 and 4.3.14. The experiment was carried out at 35°C for about 10 hours. In each cycle 20 μl of the substrate was injected The rate of hydrogenation was measured as a function of time for both used and fresh catalysts.

It was observed that the maximum rate of reaction was retained upto four cycles for catalyst 2PPd(II)Salen and 8PPd(II)EDTA, thereafter a decrease was found slowly. The estimation of metal content at the end of the reaction shows a loss of about 35% of

Table 4.3.11

Solvent dependence in the hydrogenation of 1-hexene using polymer supported catalysts at 35°C and 1 atm pressure

Quantity of the solvent used = 20 ml

Catalyst	[Catalyst] (mol l^{-1})10^6	[1-hexene] (mol l^{-1})10^3	Solvent	Rate of reaction (ml min^{-1})
2PRu(III)Salen	8.16	4.00	Methanol	0.07
			Ethanol	0.06
			THF	0.05
			Benzene	0.03
2PPd(II)Salen	9.57	4.00	Methanol	0.08
			Ethanol	0.08
			THF	0.06
			Benzene	0.04
8PRu(III)EDTA	0.49	8.00	Methanol	0.54
			Ethanol	0.48
			THF	0.32
			Benzene	0.15
8PPd(II)EDTA	0.75	8.00	Methanol	0.48
			Ethanol	0.44
			THF	0.35
			Benzene	0.15
14PPd(II)EDTA	1.32	8.00	Methanol	0.34
			Ethanol	0.30
			THF	0.23
			Benzene	0.16

Table 4.3.12

Solvent dependence in the hydrogenation of styrene using polymer-supported catalysts at 35°C and 1 atm pressure

Quantity of the solvent used = 20 ml
[Styrene] = 8.73×10^{-3} mol l^{-1}

Catalyst	[Catalyst] (mol l^{-1})	Solvent	Rate of reaction (ml min^{-1})
8PRu(III)Salen	7.12×10^{-5}	Methanol	0.22
		Ethanol	0.20
		THF	0.11
		Benzene	0.08
8PPd(III)Salen	1.16×10^{-6}	Methanol	0.45
		Ethanol	0.39
		THF	0.30
		Benzene	0.12
14PRu(III)Salen	2.97×10^{-6}	Methanol	0.22
		Ethanol	0.19
		THF	0.10
		Benzene	0.07
14PPd(II)Salen	0.45×10^{-6}	Methanol	0.42
		Ethanol	0.37
		THF	0.22
		Benzene	0.09

Table 4.3.13

Life cycle study of polymer-bound catalysts in the hydrogenation of 1-hexene at 35°C and 1 atm pressure

[1-hexene] = 8.00×10^{-3} mol l^{-1}
Volume of methanol = 20 ml

Time	Rate of reaction (ml min^{-1})
2PRu(III)Salen ([Ru(III)] = 8.16×10^{-6} mol l^{-1})	
60	0.11 (0.11)
120	0.11 (0.11)
165	0.11 (0.09)
210	0.09 (0.07)
265	0.08 (0.05)
2PPd(II)Salen ([Pd(II)]=9.57×10^{-6} mol l^{-1})	
60	0.08 (0.08)
120	0.08 (0.08)
165	0.08 (0.08)
210	0.08 (0.08)
265	0.08 (0.07)
8PPd(II)EDTA ([Pd(II)]=0.75×10^{-6} mol l^{-1})	
45	0.50 (0.50)
90	0.50 (0.50)
180	0.50 (0.50)
240	0.50 (0.47)
300	0.48 (0.43)
400	0.45 (0.40)
8PRu(III)EDTA ([Ru(III)] = 0.49×10^{-6} mol l^{-1})	
45	0.54 (0.54)
90	0.54 (0.54)
165	0.52 (0.50)
210	0.49 (0.45)
265	0.44 (0.39)
14PPd(II)EDTA ([Pd(II)] = 1.32×10^{-6} mol l^{-1})	
45	0.45 (0.40)
90	0.38 (0.36)
165	0.18 (0.14)
210	0.15 (0.11)
265	0.10 (0.08)

Values in parenthesis indicate data for the used catalyst.

Table 4.3.14

Life cycle study of polymer-bound catalysts in the hydrogenation of styrene at 35°C and 1 atm pressure

[styrene] = 8.73×10^{-3} mol l^{-1}
Volume of methanol = 20 ml

Time	Rate of reaction	
8PRu(III)Salen ([Ru(III)]=7.12×10^{-5} mol l^{-1})		
55	0.22	(0.22)
100	0.22	(0.22)
155	0.22	(0.21)
210	0.22	(0.20)
265	0.20	(0.16)
310	0.17	(0.13)
8PPd(II)Salen ([Pd(II)]=1.16×10^{-6} mol l^{-1})		
55	0.45	(0.45)
100	0.45	(0.45)
155	0.45	(0.45)
215	0.45	(0.42)
270	0.40	(0.38)
315	0.37	(0.33)
14PRu(III)Salen ([Ru(III)]=2.97×10^{-6} mol l^{-1})		
55	0.22	(0.22)
100	0.22	(0.22)
155	0.22	(0.20)
210	0.21	(0.18)
265	0.18	(0.15)
310	0.15	(0.11)
14PPd(II)Salen ([Pd(II)]=0.45×10^{-6} mol l^{-1})		
55	0.42	(0.42)
100	0.42	(0.42)
155	0.42	(0.41)
210	0.41	(0.40)
265	0.39	(0.35)
310	0.36	(0.31)

Values in parenthesis indicate data for the used catalysts metal from the support which brought about the decrease in catalytic activity.

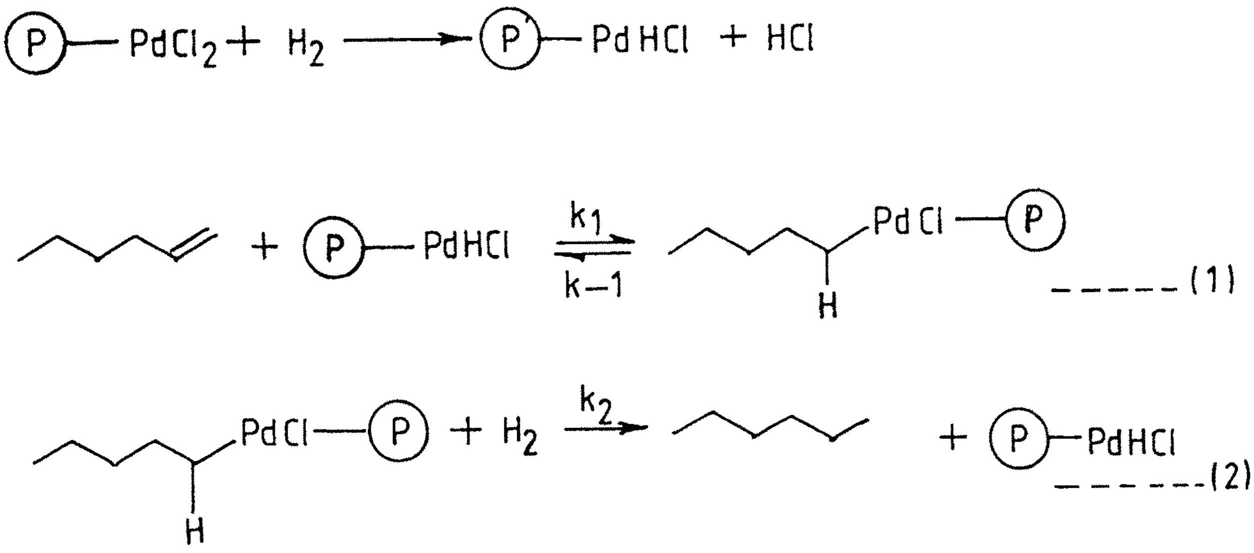
4.3.6 Rate equation

In the present study, the partial pressure of hydrogen is kept constant. In all the experiments, the solvent and the catalyst both were initially saturated with hydrogen gas followed by injection of 1-hexene/styrene and thereafter actual uptake of hydrogen was taken. A slight colour change of the polymer beads was observed during the reaction which is indicative of the surface complex formation responsible for higher catalytic activity

In order to investigate the reaction mechanism of 1-hexene/styrene hydrogenation, in a separate experiment, ruthenium chloride was mixed with salen(1.1) in homogeneous medium and hydrogen was bubbled through it. A change in intensity of colour was observed from dark brown to light brown. As the substrate (1-hexene/styrene) was injected, the reappearance of the dark brown colour was observed. Similarly, in the case of 1:1 mixture of $PdCl_2$ and Salen, yellow colour disappeared completely after passing hydrogen through the solution and reappeared on injecting the substrate. It is indicative of the fact that after passing molecular hydrogen, there is an intermediate complex formation which transfers hydrogen to the substrate and finally catalyst regains its original colour. However, no clear peak was observed in UV-visible spectra probably due to the unstable nature of the intermediate complex formed.

The reaction mechanism for olefin hydrogenation using ruthenium and palladium complexes in the homogeneous and heterogenized medium has been studied by several workers (96-101). The formation of hydrido complex and preferential attack of olefin on the hydrido complex has been established by several authors (73,101). Formation of palladium-hydride intermediate complex and subsequent transfer of hydrogen to the substrate was suggested by Terasawa et al (73) in the polymer-bound palladium (II) complex catalysed hydrogenation of alkenes and alkynes. Kaneda and Imanaka (101) have also suggested similar mechanism in polymer-bound palladium(II) complex catalyzed olefin hydrogenation

On the basis of the above observation and literature data, a probable reaction mechanism may be suggested :



Assuming step 2 is the rate determining step of the reaction, the following rate law may be suggested

$$R = \frac{k_1\, k_2\, [S][H_2][C]}{k_{-1} + k_2\, [H_2]}$$

where S is substrate and C is the catalyst The resiprocal of the above equation is

$$\frac{1}{R} = \frac{k_{-1}}{k_1\, k_2\, [S]\, [H_2]\, [C]} + \frac{k_2\, [H_2]}{k_1\, k_2\, [S]\, [H_2]\, [C]}$$

$$= \frac{k_{-1}}{k_1\, k_2\, [S]\, [H_2]\, [C]} + \frac{1}{k_1\, [S]\, [C]}$$

The straight line plot of reciprocal the initial rate against resiprocal of [S] is thus indicative of the intermediate complex formation (Figs 4.3.6 and 4.3.7).

A probable reaction path may be suggested on the basis of the above studies.

When hydrogen gas is inserted into the solvent containing the catalyst, a hydrido complex is formed on the surface which is unstable in nature. As the substrate is injected, hydrogen is transferred to the substrate and finally there is a formation of the product through some intermediate steps. Finally the product comes out through diffusion and again the surface remains active for the reaction of the other molecules. Thus the metal complexes present on the surface was found to be responsible for higher catalytic activity

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