CHAPTER - 5

HYDROGENATION OF 1-DECENE

5.0 INTRODUCTION

Catalytic hydrogenation plays an important role to produce a variety of both bulk and fine chemicals Significance of catalytic hydrogenation is highlighted by a number of books, reviews and conference proceedings [1-10] Hydrogenation reaction can be carried out using molecular hydrogen, hydrogen donating substrate or by transfer of hydrogen from the surface of the solid [11] A large number of hydrogenation catalysts are now available and the scope of the hydrogenation has become very large. Most functional groups can be reduced readily, often under mild conditions and frequently with high chemo-, regio- and stereoselectivity A number of heterogeneous catalysts have been used for hydrogenation reactions in chemical as well as in pharmaceutical industries [12-14] Homogeneous catalysts have, however, been found in some cases to be used for hydrogenation reaction e g. the Wilkinson's catalyst [$Rh(PPh_3)_3Cl$] for olefin hydrogenation, synthesis of thermally unstable or otherwise sensitive products, the synthesis of optically active compounds by asymmetric hydrogenation etc.[15-20] The new 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 metal of group (VIII) or their complexes were found suitable as hydrogenation catalysts [21-24] Effective combinations have resulted from d^8 spin paired (low spin) configuration arising from strong ligand fields or electron delocalising by which these homogeneous catalysts activate molecules and transfer the activated hydrogen to the substrate often with considerable stereospecificity is well understood [25-27]

Transition metal ions/complexes have been widely used for catalyzing various reactions including homogeneous hydrogenation of olefins [28-35] The hydrogenation of maleic acid has been studied in aqueous solution using Ru(II) chloride as catalyst [36]. Rhodium complex of water soluble phosphine catalyzed the hydrogenation of olefins dissolved in polar as well as non-polar solvents in single step [37]. The complexes of Ru(II), Pt(II), Co(II), etc. were found to activate molecular hydrogen and were able to catalyze the hydrogenation of olefins under homogeneous condition [38].

Reduction of nitrobenzene was carried out using the metal complexes of Pd [39,40], Rh[41,42], Ru[43,44] and Co[45] and considerable rate enhancement was observed Investigations have also been made for the homogeneous hydrogenation of unsaturated organic compounds using various metal ions/complexes [46-50].

Some of the characteristic properties of the most widely used catalysts for the hydrogenation of organic compounds are given as follows,

1. *Palladium* is a very active catalyst for the hydrogenation of alkenes to alkanes. Palladium has a strong tendency to catalyze isomerizations and double bond migrations.

2. *Platinum* is a very active catalyst for the hydrogenation of double bonds (C=C, C=N, C=O) In contrast to palladium, isomerizations and double bond migrations almost never occur.

3. *Rhodium* catalysts are used for the hydrogenation of aromatic compounds under mild conditions

4. *Ruthenium* is used for the hydrogenation of aromatic compounds and carbonyl functions, normally under higher pressure and at an elevated temperature.

5. *Nickel* catalysts, particularly Raney nickel is especially suited for the hydrogenation of carbonyl functions (ketones, aldehydes) and of nitrites to amines.

6. *Copper* catalysts are used for the hydrogenation of esters to the corresponding alcohols under rather harsh conditions.

The main problem of the homogeneous catalysts are 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 state and 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 co-ordination sites necessary for the 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 have been carried out for olefin hydrogenation catalyzed by metal complexes supported on inorganic oxides [51-57]. The hydrogenation of 1-hexene using Pd/zeolite [58] and aniline by Rh on alumina [59] has been carried out and the reactivity was found to be higher than their homogeneous counterparts Other studies include the hydrogenation of toluene and xylene by Pd on SiO_2, Al_2O_3, MgO [60.61] and methyl ether by Pd, Pt, Rh and Ru on activated charcoal [62]

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 and also the susceptibility of poisoning of the catalyst by absorbed substances This problem could be minimized by heterogenizing the homogeneous catalyst using polymer support [63-65]. A number of studies have been carried out in the hydrogenation of olefins by metal ions/complexes supported on commercial available polymers [66-72]

Reduction of nitrobenzene to aniline has been studied by Drago et al.[73] using polystyrene-bipyridine dispersed palladium metal and it was found to be readily hydrogenated using this catalyst Holy [74] 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 Several other workers [75-78] have also investigated the hydrogenation of nitrobenzene using various metal complexes supported on polymer

The polymer bound nonchelated metal complexes have been studied extensively[79,80] but these transition metal complexes are occasionally so labile and they fail to act as a supported catalyst[81] or some times it results in a significant metal leaching into the solution[82]

Metal ions attached to the polymer bound chelating ligands were found to be more stable and showed higher catalytic activity [83,84] Chelating resins employing phosphine ligands have been widely investigated in several catalytic studies during the past decade[85] Little work has been carried out using nitrogen and oxygen donor groups as a chelating ligand Some of the most versatile chelating system such as 2,2'-dipyridine has been attached to an insoluble polystyrene support and its potential as a polymer bound chelate has been demonstrated[86]

The present investigation deals with the synthesis of polymer bound Schiff base metal complexes to investigate the catalytic activity for the hydrogenation of 1-decene to 1-decane which has been used in many chemical manufacturing processes 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 variation of the solvents have been investigated. On the basis of the kinetic data, thermodynamic parameters have been calculated . A probable reaction mechanism has been suggested.

5.1 EXPERIMENTAL

5.1.1 MEASUREMENT OF CATALYTIC ACTIVITY FOR HYDROGENATION REACTIONS

The hydrogenation reaction was carried out in a glass reactor with magnetic stirrer with stirrer speed of 650 rpm at 40^0C using methanol as solvent. The progress of the reaction was followed by measuring the uptake of the hydrogen as a function of the reaction time at a constant temperature and pressure using a glass manometric apparatus. The experimental set-up and detailed procedures are described earlier **(Chapter 2, Section 3)**

5.2 ANALYSIS OF KINETIC DATA

The hydrogenation was carried out at various temperatures, different concentrations of the catalysts and the substrates as well as by varying the nature of the solvent. The product was analyzed by the use of Gas

Chromatograph using 10% SE-30 column and no side product was observed **(the chromatograms are given in Chapt.2)** The plots of the variation of hydrogen uptake at various interval of time for different concentration of the catalysts and the substrates for catalysts **Pd-A** to **Pd-D** are given in **Fig 5.1- 5.2** and the values for their rates are calculated from the slopes of these plots (only representative plots are given). The results are presented in **Table 5.1- 5.7.**

5.3 RESULTS AND DISCUSSION

5.3.1 EFFECT OF SUBSTRATE CONCENTRATION

In all the sets of experiments the hydrogenation uptake is fast during initial stages, slow down later and proceeds gradually toward saturation in 40 min. The influence of substrate on the rate of hydrogenation of 1-decene was determined at constant palladium concentration of 1 41x10^{-5} mol.lit^{-1} for **Pd-A**, 3.55x10^{-5} mol.lit^{-1} for **Pd-B** , 2.78x10^{-5} mol.lit^{-1} for **Pd-C** and 2.38x10^{-5} mol lit^{-1} for **Pd-D** at 40^{0} C. It was observed that the rate of reaction increased with an increase in substrate concentration [87,88]. The results are shown in **Table 5.1.**

The order of the reaction calculated from the slope of the linear plots of log(initial rate) Vs log(substrate) at a fixed concentration of catalysts **(Fig. 5.3),** hydrogen pressure and temperature, is of fractional order with respect to the substrate [89]

The hydrogenation reaction was also carried out in homogeneous system using Pd(II) complexes of Schiff base under similar condition and the rate was found to be slow as compared to the heterogenized homogeneous catalysts. In order to compare the results, the experiments were carried out keeping the same concentration of the catalyst in homogeneous system as was present on polymer support, however a measurable hydrogen uptake was not observed On the basis of the few trial experiments higher concentration of the catalyst was chosen and the measurable rate of consumption of hydrogen was obtained in homogeneous system. The results are shown in **Table 5.2.**

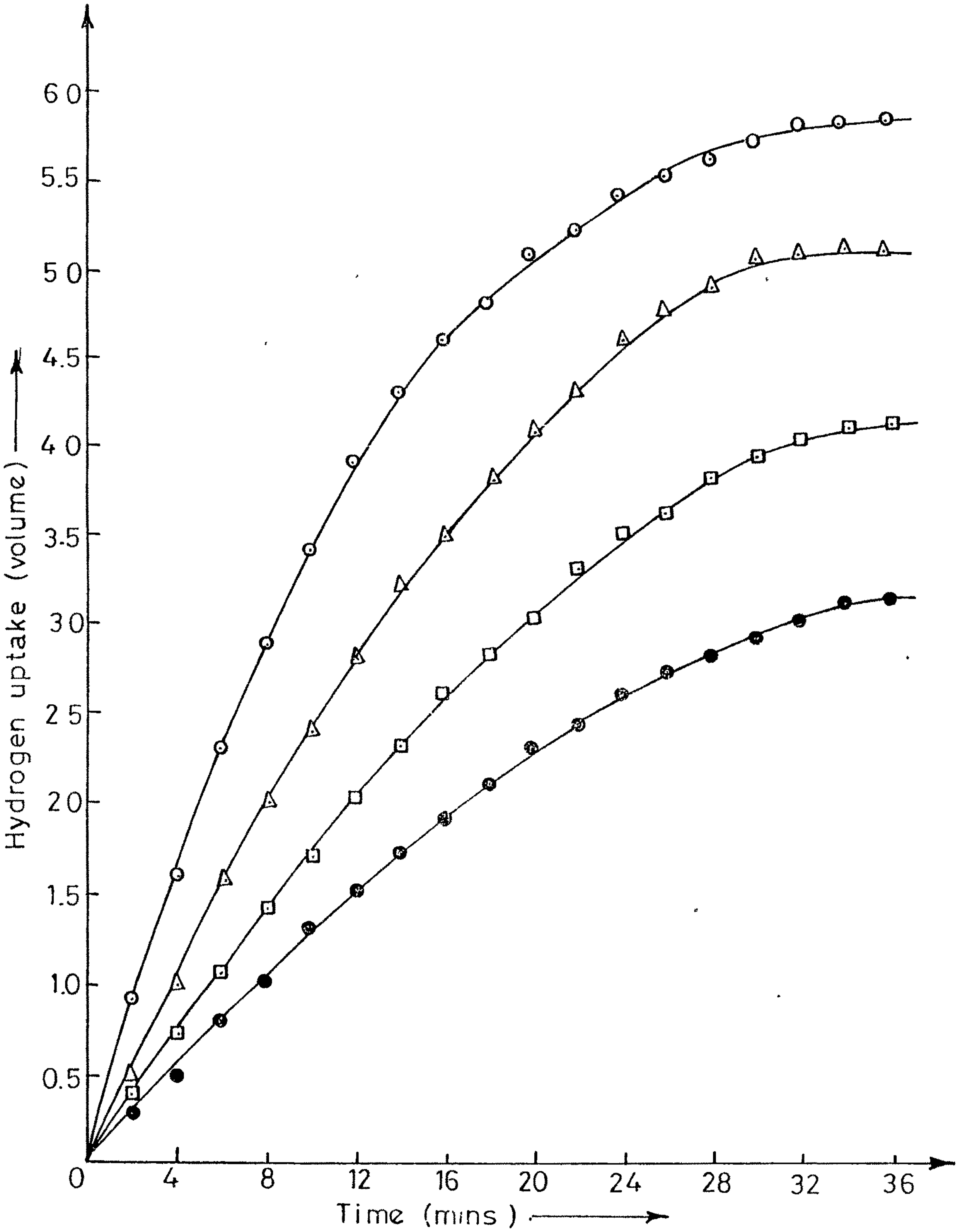

Fig. 5.1 Plot of hydrogen uptake *VS* time for different concentration of 1-decene

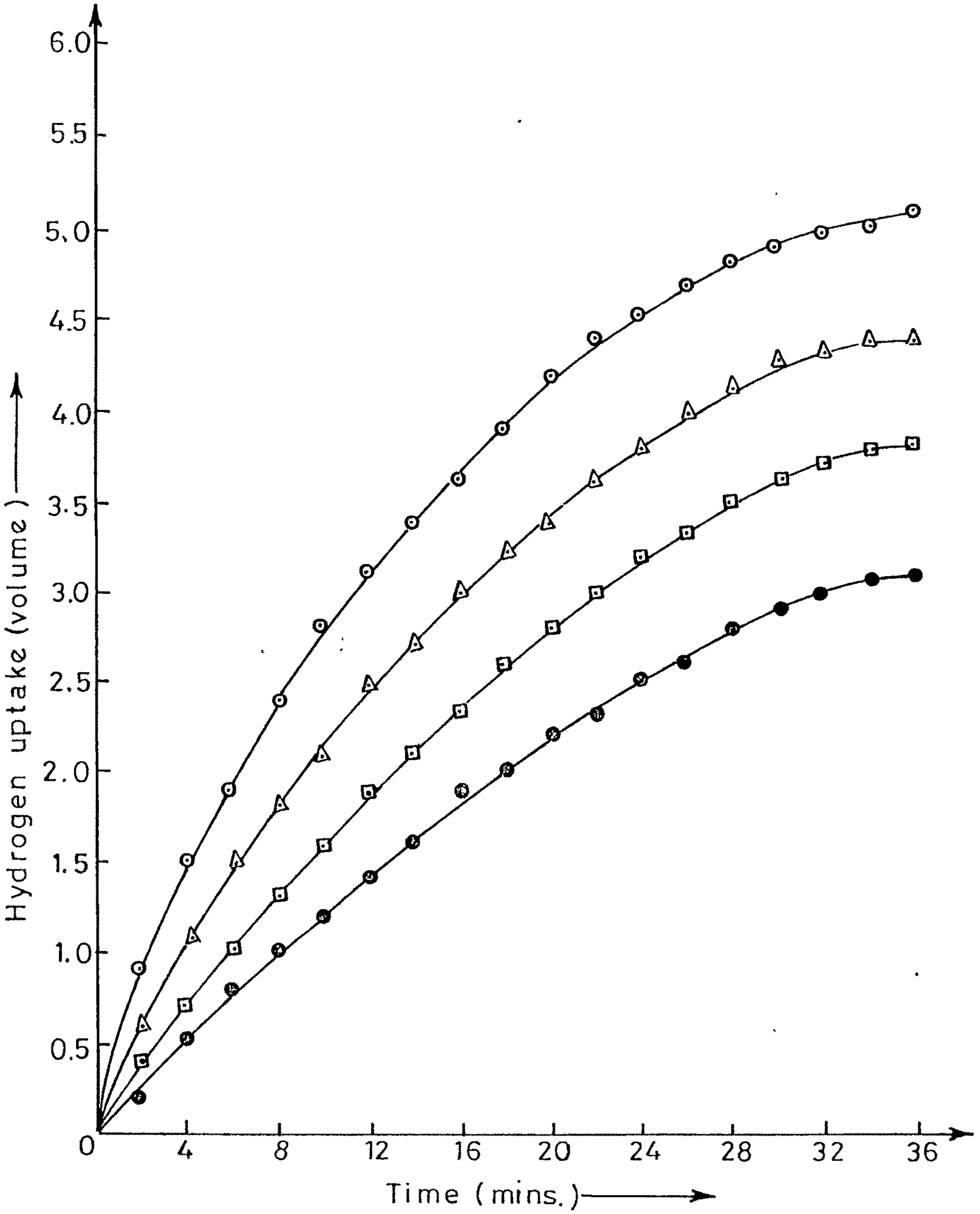

Fig. 5.2 Plot of hydrogen uptake *VS* time for different concentration of catalyst

Table 5.1
Effect of 1-decene on rate of hydrogenation for polymer supported palladium catalysts.

Catalyst	Pd content (mol.lit^{-1})x10^5	1-Decene (mol.lit^{-1})x10^3	Rate of reaction (ml.min^{-1})x10^2	Order of reaction w.r.t.(1-decene)
Pd-A	1.41	2.65	10.4	0.34
		5.29	13.1	
		7.94	15.0	
		10.58	18.7	
Pd-B	3.55	2.65	09.6	0.48
		5.29	13.0	
		7.94	16.2	
		10.58	22.8	
Pd-C	2.78	2.65	10.4	0.31
		5.29	13.1	
		7.94	15.1	
		10.65	16.5	
Pd-D	2.38	2.65	11.4	0.48
		5.29	14.8	
		7.94	19.2	
		10.65	25.0	

Reaction condition . Solvent = 20ml methanol P_{H2} *= 1 kg/cm^2,*
Temp = 40^{0}C

Table 5.2
Influence of substrate on the rate of hydrogenation for homogeneous catalysts.

Catalyst	1-Decene $(mol.lit^{-1})x10^3$	Initial rate of reaction $(ml.min^{-1})x10^2$	Order of reaction w.r.t.(1-decene)
[Pd(1,3-dap-SB)Cl_2]	02.65	10 4	0.34
	05.29	13 1	
	07 94	14 8	
	10 58	18 4	
[Pd(4,4'-dabp-SB)Cl_2]	02 65	10.4	0.35
	05 29	13 2	
	07 94	15.3	
	10.58	16 6	

Reaction condition *Catalyst [Pd(dap-SB)Cl_2] = 3.1$(mol.lit^{-1})x10^3$*
[Pd(dabp-SB)Cl_2] = 3.3$(mol\ lit^{-1})x10^3$
Solvent = Methanol(20 ml), Temp. = 40^0C,
P_{H2} = 1 kg/cm^2

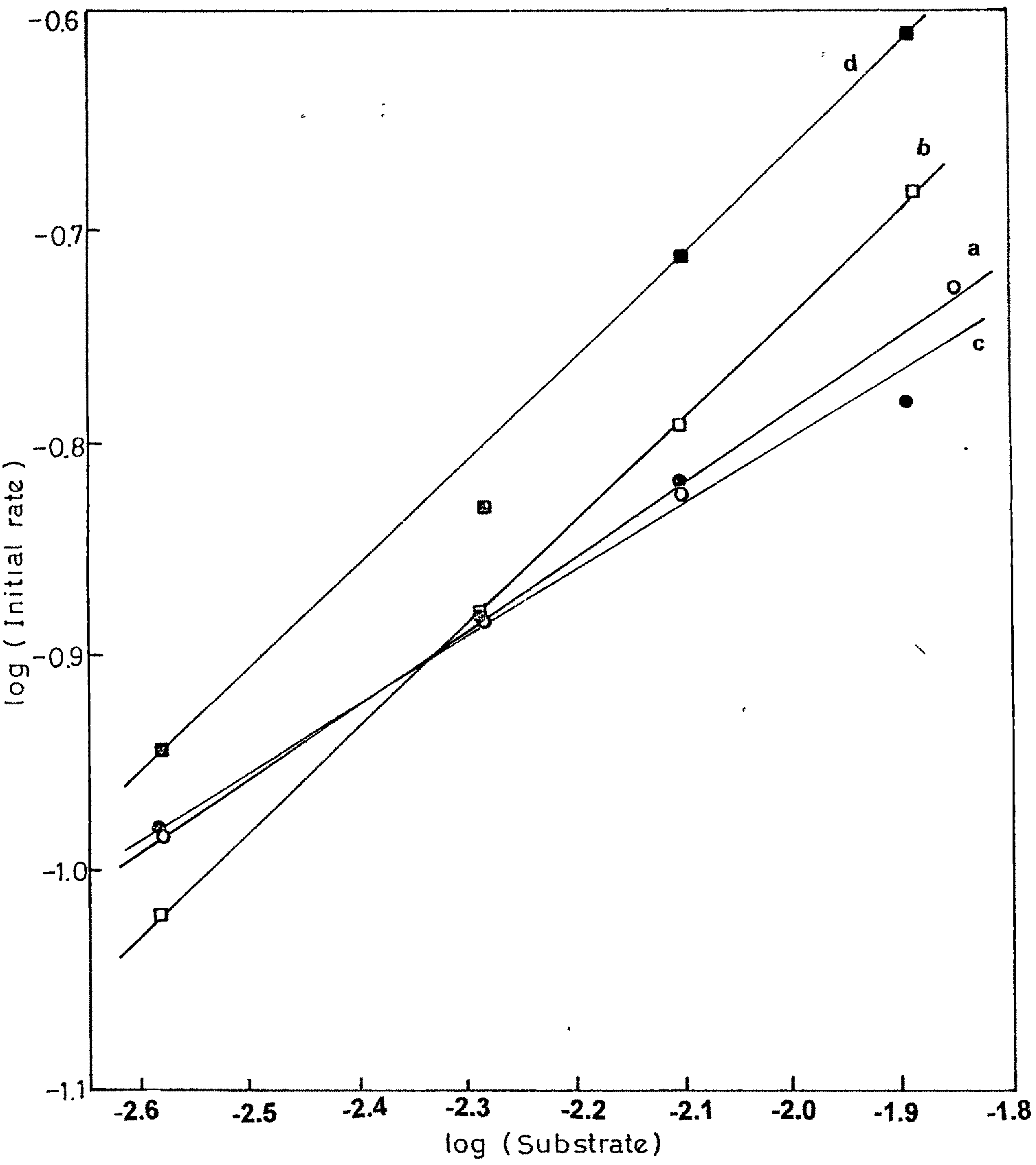

Fig. 5.3(a) log-log plot of the initial rate *VS* substrate [1-decene] for (a) Pd-A (b) Pd-B (c) Pd- C (d) Pd-D

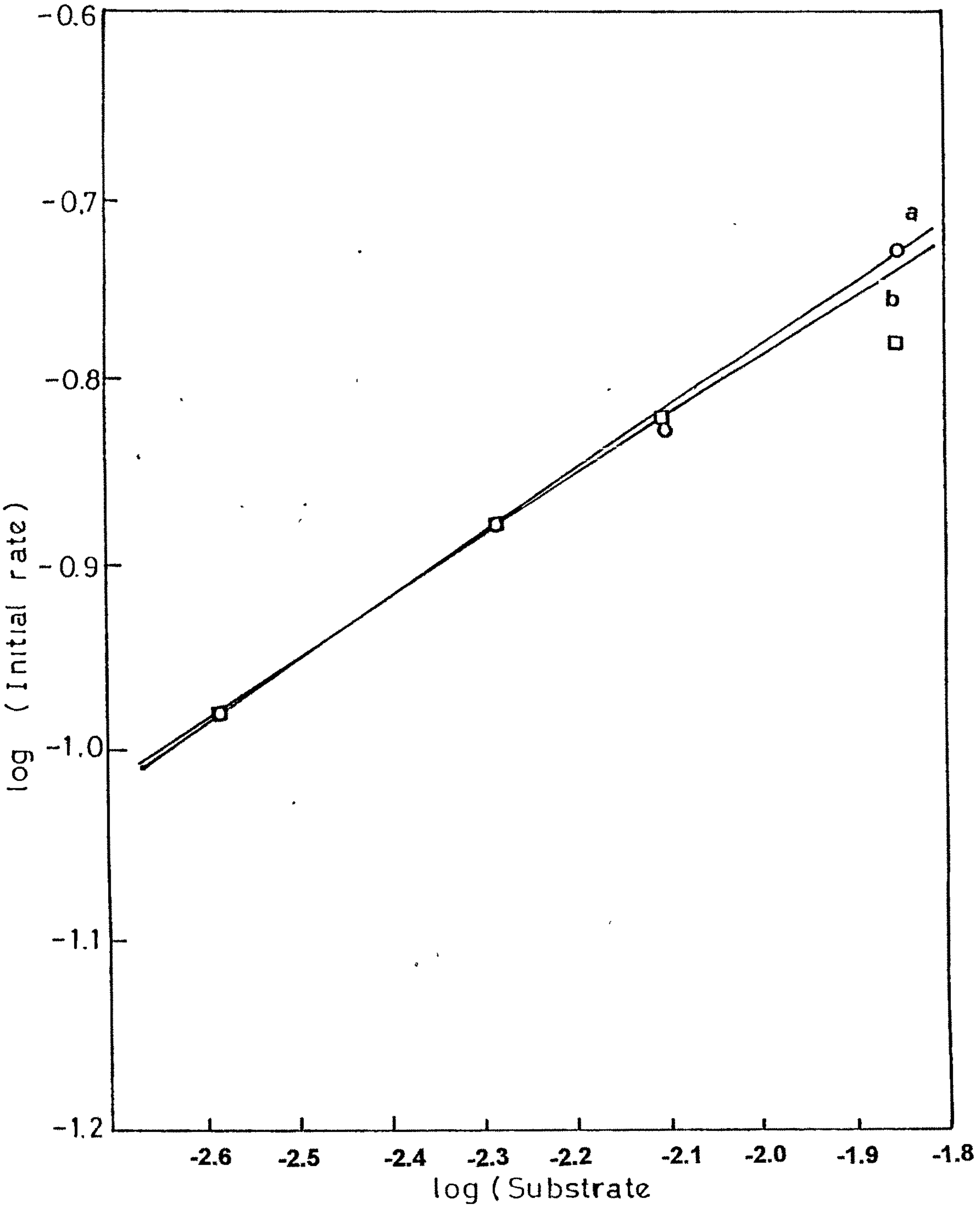

Fig. 5.3(b) log-log plot of the initial rate *VS* substrate [1-decene] for homogeneous complexes(a) [Pd(dap-SB)Cl_2] (b) [Pd(dabp-SB)Cl_2]

5.3.2 EFFECT OF CATALYST CONCENTRATION

The influence of the catalyst concentration on the rate of hydrogenation of 1-decene for different catalyst was investigated. The results are shown in **Table 5.3.** An enhanced rate of hydrogenation was observed on increasing the concentration of the catalysts keeping the substrate concentration constant at a constant temperature[90]. The order of reaction with respect to the concentration of catalyst calculated from the plots of log(initial rate) Vs log(catalyst concentration) at fixed concentration of substrate at 40°C was found to be fractional order in all cases. The plots are given in **Fig. 5.4.**

The experiments were repeated for homogeneous hydrogenation using Pd(II) complexes and the results are given in **Table 5.4.** An increase in the rate with amount of catalyst is indicative of the fact that there is no dimerization of metal complexes either in homogeneous system or in heterogenized homogeneous system

5.3.3. EFFECT OF TEMPERATURE

The effect of temperature on the rate of hydrogenation of 1-decene was studied in the range of 30 to 45°C with fixed catalyst and substrate concentration and the results are summarized in **Table 5.5.** The initial rate of hydrogenation was found to increase with increase in the temperature for all the catalysts. The values for the energy of activation were calculated from the slope of the plot of log(initial rate) Vs 1/T (Arrhenius Plots) **(Fig 5.5)** and was found to be 7.14 kcal/mole for (Pd-A), 8.42 kcal/mole for (Pd-B), 6 99 kcal/mole for (Pd-C) and 5.59 kcal/mole for (Pd-D). The calculated activation energy for the reaction is low compared to bond dissociation energy of hydrogen molecules [91,92] This is attributed to the formation of an alternative low energy path for the reaction.

In the case of homogeneous system, the energy of activation was found to be 8.7 kcal/mole for [Pd(dap-SB)Cl_2] and 7.3 kcal/mole for [Pd(dabp-SB)Cl_2] catalysts and is shown in **Table 5.6.** The catalytic activity however can not be compared on the basis of the energy of activation of both the system because of the lower activity in homogeneous system, a higher concentration of catalyst was used to obtain a considerable rate of reaction.

5.3.4 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 catalyst [93]. It is therefore apparent that the nature of the solvent can be of great importance in directing the course of reaction

The hydrogenation of 1-decene was studied using different solvents such as methanol, ethanol, THF and benzene and the results are summarized in **Table 5.7.**

An increase in the rate was observed when nature of the solvent was changed from non-polar to a polar . An enhanced rate may be due to higher swelling of catalyst as well as moderate coordinating ability of the solvent with metal species. Thus the optimum solvent would be one that combines good swelling ability and high polarity. Methanol was, therefore, chosen as the solvent for the reaction system.

Table 5.3
Effect of catalyst on rate of hydrogenation for polymer supported palladium catalysts.

Catalyst	Pd content (mol.lit^{-1})x10^{5}	1-Decene (mol.lit^{-1})x10^{3}	Rate of reaction (ml.min^{-1})x10^{2}	Order of reaction w.r.t.(catalyst)
Pd-A	0.47	7.94	10.1	0.33
	0.94		14.0	
	1.41		15.0	
	1.88		15.5	
Pd-B	1.18	7.94	10.0	0.46
	2.36		14.8	
	3.55		16.2	
	4.74		19.2	
Pd-C	0.92	7.94	10.7	0.20
	1.85		14.5	
	2.78		15.2	
	3.78		18.6	
Pd-D	0.79	7.94	12.5	0.47
	1.59		17.2	
	2.38		19.2	
	3.18		23.5	

Reaction condition Solvent = 20ml methanol P_{H2} *= 1 kg/cm*^{2}*,*
Temp = 40^{0}*C*

Table 5.4
Influence of catalyst on the rate of hydrogenation for homogeneous catalysts.

Catalyst	Pd content $(\mathrm{mol.lit}^{-1})\mathrm{x}10^{3}$	Initial rate of reaction $(\mathrm{ml.min}^{-1})\mathrm{x}10^{2}$	Order of reaction w.r.t.(catalyst)
$[Pd(1,3dap\text{-}SB)Cl_2]$	1.0	10.2	0.35
	2.1	13.1	
	3.1	14.8	
	4.1	16.6	
$[Pd(4,4'\text{-}dabp\text{-}SB)Cl_2]$	1.1	10.7	0.40
	2.2	13.8	
	3.3	15.3	
	4.4	18.6	

Reaction condition : 1-Decene = 7.94 (mol lit $^{-1}$)x10^{3} ,Solvent = Methanol(20 ml),
Temp. = 40^{0}C, P_{H2} = 1 kg/cm^{2}

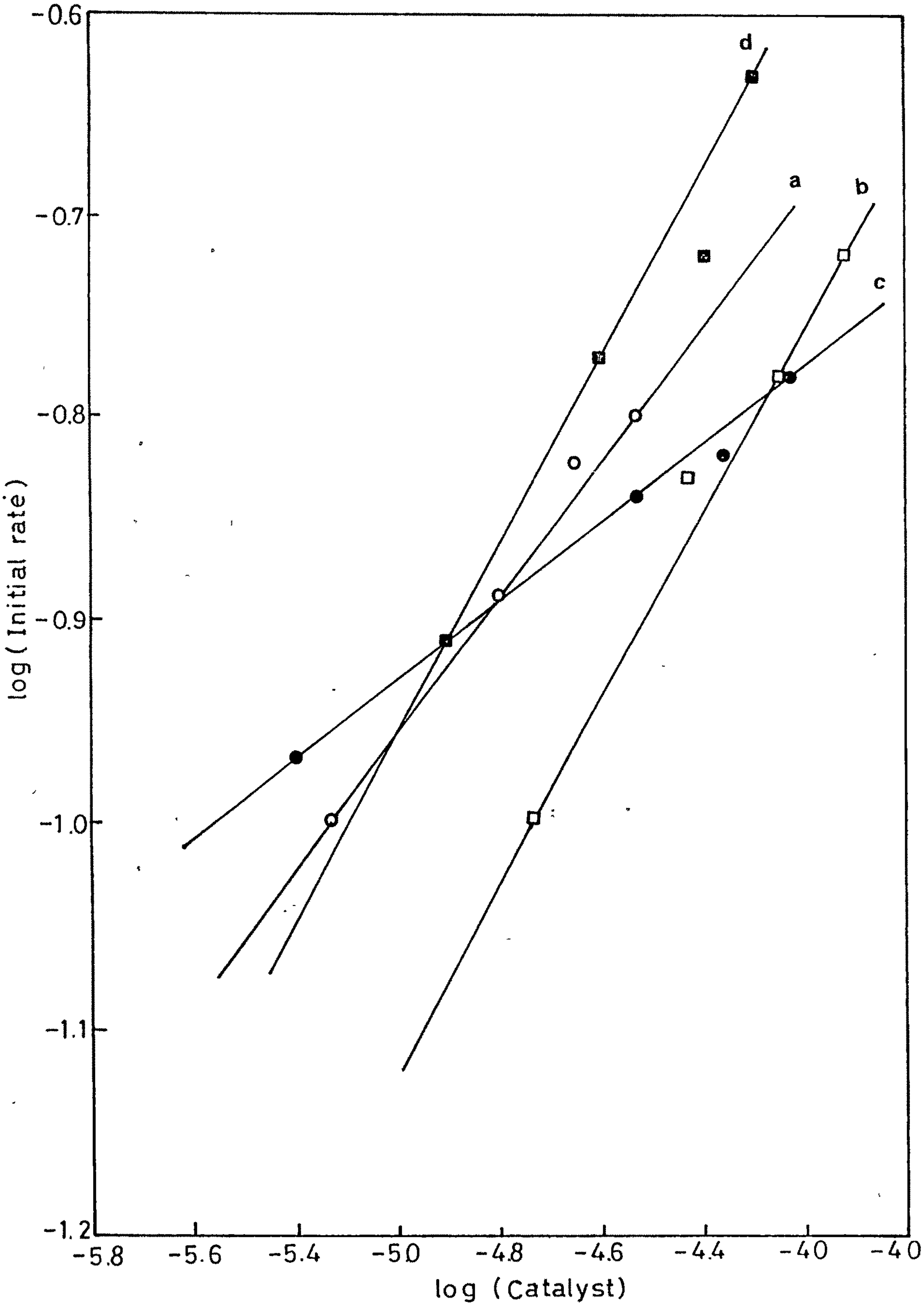

Fig. 5.4(a) log-log plot of the initial rate *VS* catalyst for (a) Pd-A (b) Pd-B (c) Pd- C (d) Pd-D

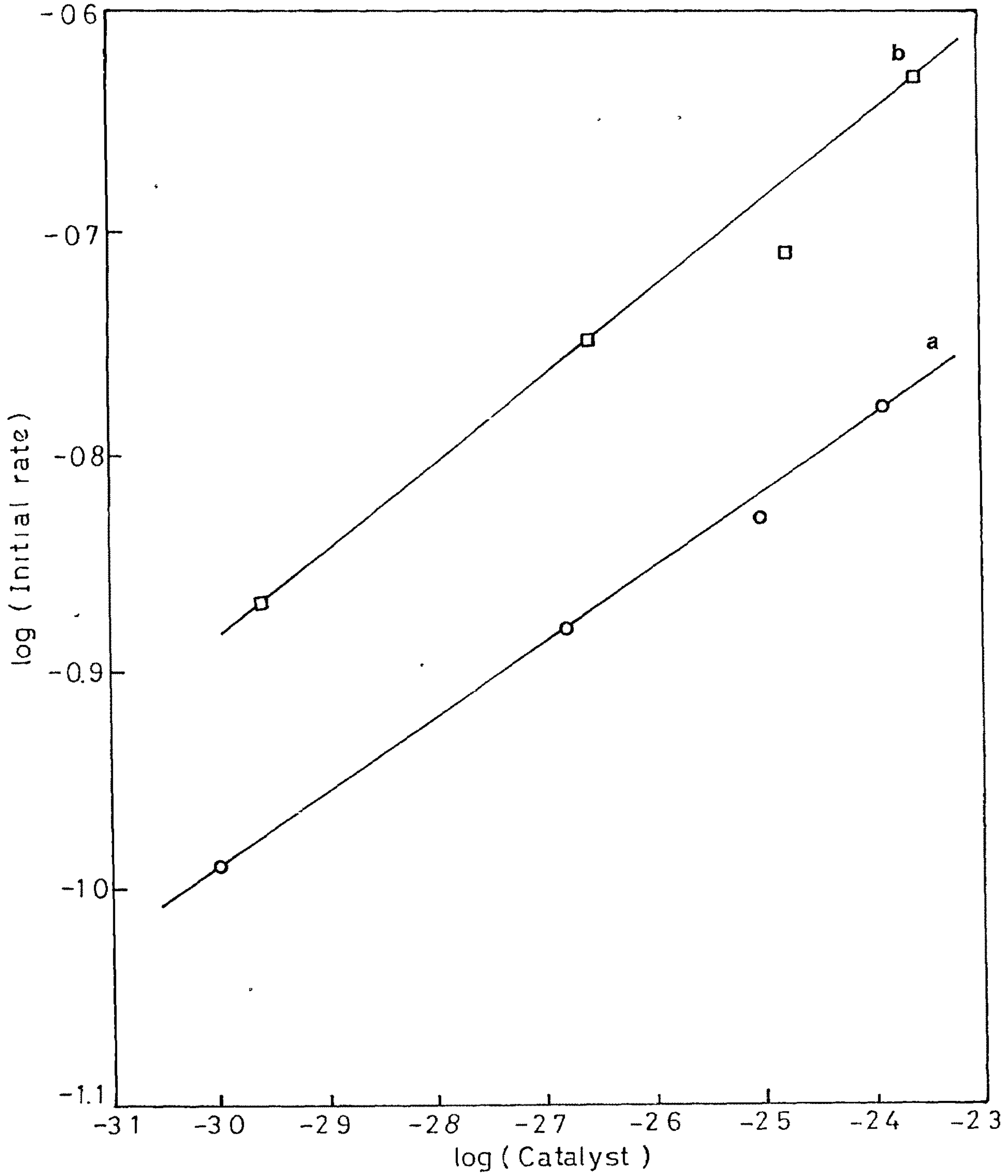

Fig. 5.4(b) log-log plot of the initial rate *VS* catalyst for homogeneous complexes(a) [Pd(dap-SB)Cl_2] (b) [Pd(dabp-SB)Cl_2]

Table 5.5

Effect of temperature on rate of hydrogenation for polymer supported palladium catalysts.

Catalyst	Pd content $(mol.lit^{-1})x10^5$	Temperature (°C)	Rate of reaction $(ml.min^{-1})x10^2$	E_A Kcal/mole
Pd-A	1.41	30	09.1	7.1
		35	12.6	
		40	15.0	
		45	18.5	
Pd-B	3.55	30	12.3	8.4
		35	15.6	
		40	16.2	
		45	20.5	
Pd-C	2.78	30	10.7	7.0
		35	14.1	
		40	15.2	
		45	19.4	
Pd-D	2.38	30	13.3	5.6
		35	15.5	
		40	19.2	
		45	21.0	

Reaction condition : Solvent = 20ml methanol P_{H2} *= 1 kg/cm*^{2}*,*

1-decene = 7.94 $(mol.lit^{-1})x10^3$

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Table 5.6
Influence of temperature on the rate of hydrogenation for homogeneous catalysts.

Catalyst	Temperature (°C)	Initial rate of reaction $(ml.min^{-1})x10^2$	E_A Kcal/mole
$[Pd(1,3\text{-dap-SB})Cl_2]$	30	10 0	8 7
	35	11 8	
	40	14 8	
	45	17.5	
$[Pd(4,4'\text{-dabp-SB})Cl_2]$	30	10.4	7 3
	35	14 1	
	40	15 3	
	45	18 2	

Reaction condition : 1-Decene = 7.94 $(mol\ lit^{-1})x10^3$ *,Solvent = Methanol(20 ml),*
Catalyst $[Pd(dap\text{-}SB)Cl_2] = 3.1(mol.lit^{-1})x10^3$
$[Pd(dabp\text{-}SB)Cl_2] = 3.3(mol\ lit^{-1})x10^3$
$P_{H2} = 1\ kg/cm^2$

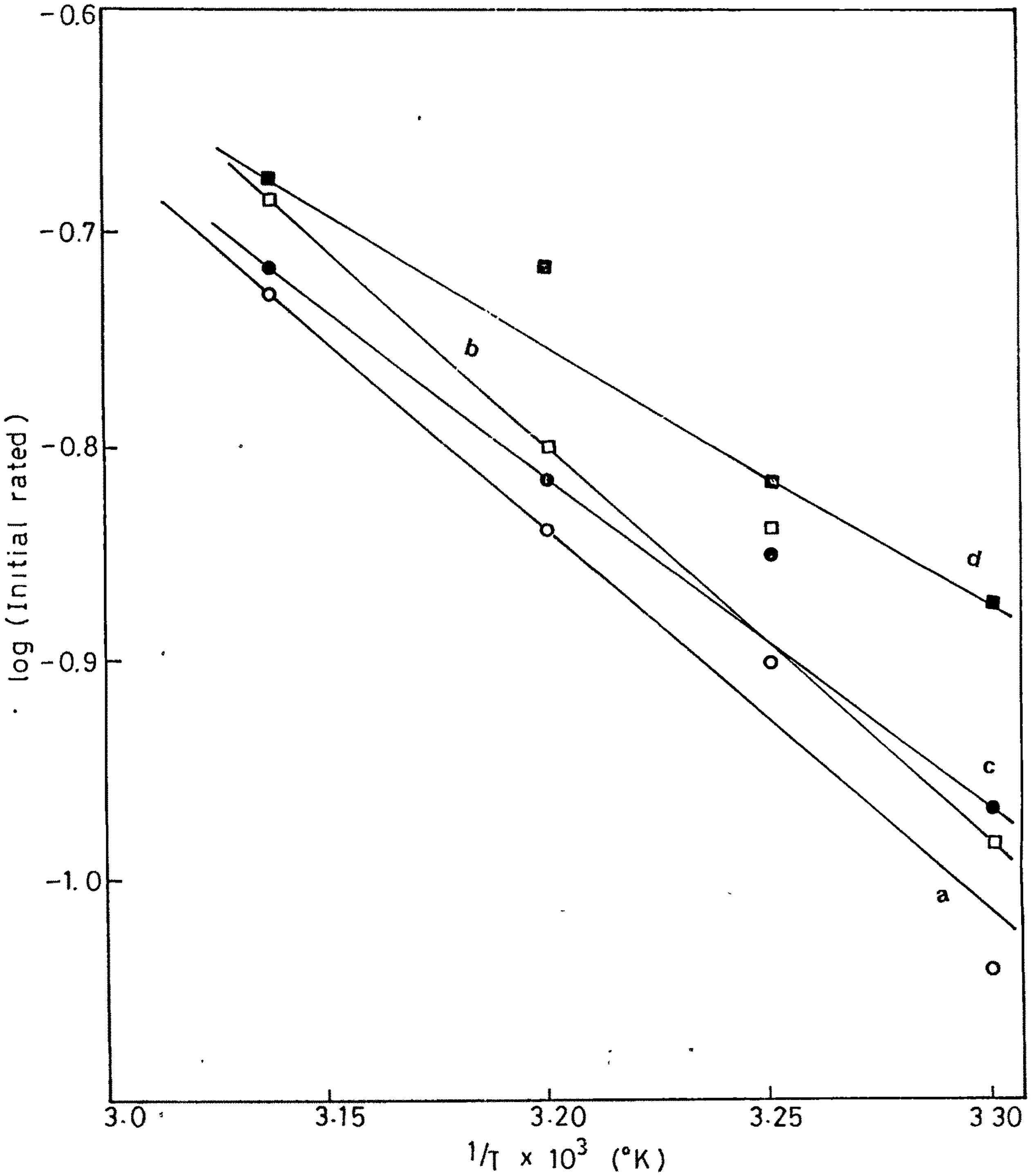

Fig. 5.5(a) Arrhenius plot for catalysts (a) Pd-A (b) Pd-B (c) Pd- C (d) Pd-D

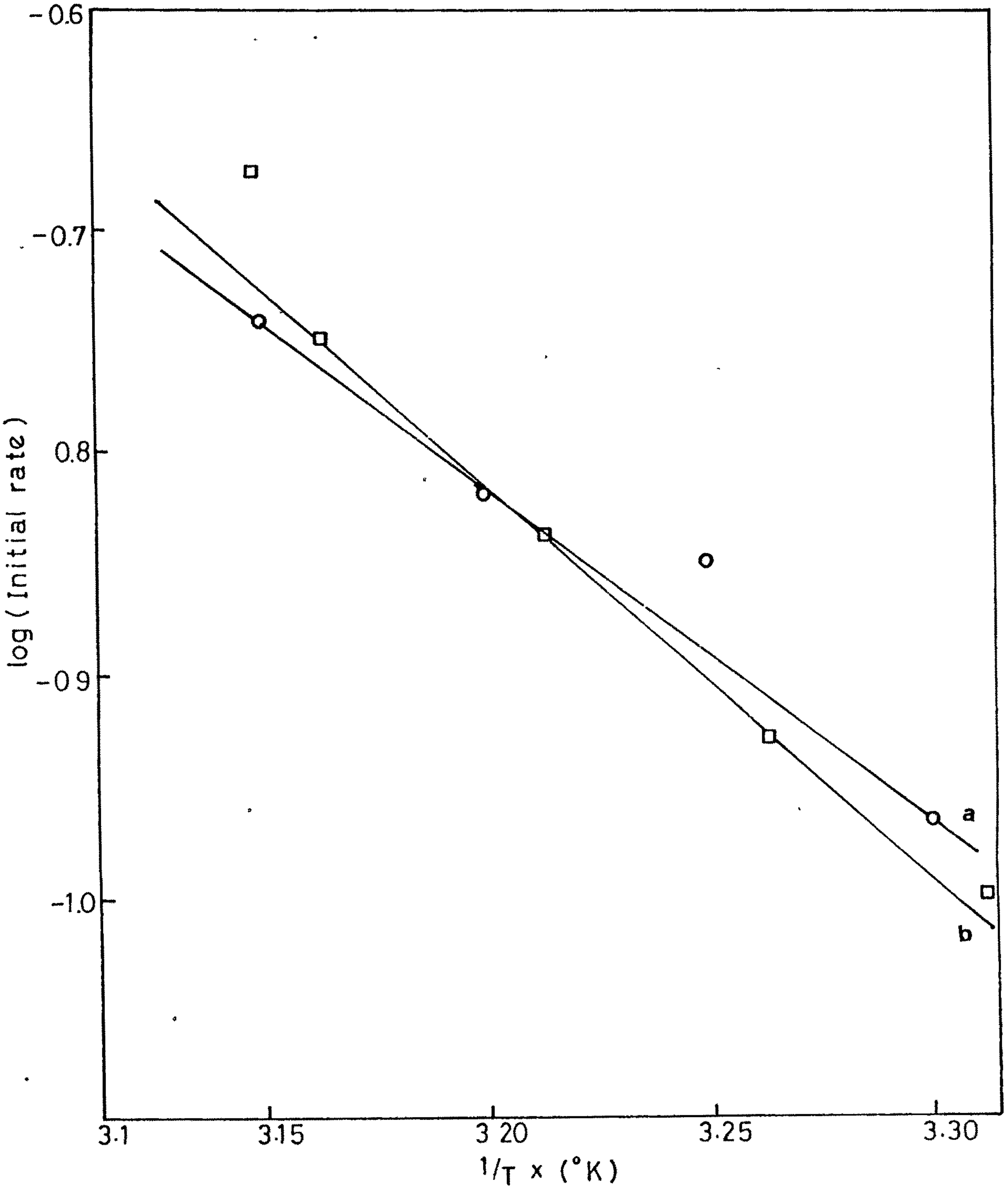

Fig. 5.5(b) Arrhenius plot for homogeneous complexes (a) [Pd(dap-SB)Cl_2] (b) [Pd(dabp-SB)Cl_2]

Table 5.7
Effect of solvent on rate of hydrogenation for polymer supported palladium catalysts.

Catalyst	Pd content (mol.lit^{-1})x10^{5}	1-Decene (mol.lit^{-1})x10^{3}	Solvent (20 ml)	Rate of reaction (ml.min^{-1})x10^{2}
Pd-A	1 41	7 94	Methanol	15 0
			Ethanol	14 3
			THF	12 8
			Benzene	09 9
Pd-B	3 55	7.94	Methanol	16.2
			Ethanol	15 5
			THF	10 0
			Benzene	05 5
Pd-C	2.78	7 94	Methanol	15 2
			Ethanol	13 3
			THF	10 3
			Benzene	08 5
Pd-D	2 38	7 94	Methanol	19 2
			Ethanol	17 8
			THF	14 3
			Benzene	11 4

Reaction conditions : $P_{H2} = 1\ kg/cm^2$, *Temp.* = 40^0C

5.3.5 RATE OF REACTION

The mechanism of olefin hydrogenation over polymer bound palladium catalysts has been extensively studied [94]. On the basis of experimental results and evidence from the literature, the following mechanism and rate equation are proposed

$$X\text{-}PdCl_2 + H_2 \longrightarrow X\text{-}PdHCl + HCl$$

$$\text{Olefin} + X\text{-}PdHCl \underset{\substack{k_{-1}\\ \text{slow}}}{\overset{k_1}{\rightleftharpoons}} X\text{-}Pd\,(alkyl)Cl$$

$$X\text{-}Pd\,(alkyl)Cl + H_2 \xrightarrow[\text{fast}]{k_2} \text{Paraffin} + X\text{-}PdHC$$

where X is the polymer modified with the ligand and k_1, k_{-1} and k_2 are the rate constants

$$\text{Rate}(R) = \frac{k_1 k_2 [S] [H_2][C]}{k_{-1} + k_1 [S] + k_2 [H_2]}$$

where S is substrate and C is the catalyst

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