Chapter - 4

KINETICS OF HYDROGENATION

KINETICS OF HYDROGENATION

4.1 Introduction

Catalytic hydrogenation is one of the most useful broad-scoped reactions for the synthesis of organic compounds as well as to the industries. A number of hydrogenation reactions have been carried out in large scale continuous catalytic operations and in small scale batch operations in the pharmaceutical and fine chemical industries (1). The majority of the industrial hydrogenation reactions have been performed using heterogeneous catalysis (2,3). However, the homogeneous hydrogenation catalysts were found to be suitable for lab-scale reactions, viz, the synthesis of thermally unstable or otherwise sensitive products, applications of prochiral catalysts for the production of optically active products and mechanistic studies (4-7).

The recent development of homogeneous hydrogenation provides the model which are helpful in understanding the various factors in catalytic hydrogenation. In most of the cases, the transition metals of group VIII or their complexes have been used as hydrogenation catalysts (8-12). Effective combinations have resulted from d^8 spin paired (low-spin) configuration arising from strong ligand fields or electron delocalizing (π - acceptor) ligands. The mechanism, by which these homogeneous catalysts activate molecular hydrogen and substrate molecules and transfer ~~of~~ the activated hydrogen to the substrate often with considerable stereospecificity , is well understood (7,13,14).

The platinum group complexes have been widely used as catalysts in homogeneous hydrogenation of olefins (7,15-19). But a few cases have been reported where ruthenium metal ions/complexes have been used in the hydrogenation of olefins (20,21). $RuCl_2$ catalysed the hydrogenation of α, β unsaturated acids but failed to catalyse the olefin hydrogenation (22). However, an enhanced activity was observed in the presence of triphenyl phosphine. It has been found that the hydride complex formed during the reaction is responsible for the higher catalytic activity. Thus the hydrido complex formed readily from $RuCl_2(PPh_3)_3$ and hydrogen in the presence of triethylamine was observed to be most active hydrogenation catalyst (23).

The main disadvantages of these catalysts are the problems of separating these expensive catalysts from the reaction mixture 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. In homogeneous systems, the catalytic activity of metal complexes, active in their monomeric form may be enhanced by attaching them to a rigid inorganic oxide. Thus, the titanocene monomers supported on silica following reduction with BuLi have shown a higher catalytic activity in the hydrogenation of olefins, (3).

Numerous work has been carried out in the hydrogenation reaction of olefins catalysed by metal/metal complexes supported on inorganic oxides (24-29). ~~Thus~~ e.g the hydrogenation of 1-hexene by Pd/zeolite (30), aniline by Rh/Al_2O_3 (31) has been studied. Gattania has used ruthenium clusters suppoted on alumina and silica for CO hydrogenation reaction (32). Taqui Khan et al. have studied the reduction of natural oil using Ru(IV) dihydrido species formed with the interaction of hydrogen and the ruthenium complex on the surface of montmorillonite (33). Other studies include the hydrogenation of toluene and xylenes by Pd and Pd on SiO_2, Al_2O_3, MgO and TiO_3 (34,35) and methyl ester by Pd, Pt, Rh and Ru on activated charcoal (36). Few cases have also been reported in the hydrogenation of olefins by metal ions supported on commercially available polymers / ion exchangers (37-41).

The major disadvantages of these anchored catalysts are the leaching of the metals from the support, surface could deactivate the catalyst as well as the catalyst may be susceptible to ~~the catalys~~t poisoning by the adsorbed species ~~substances~~. These disadvantages can be overcome by heterogenizing the homogeneous catalyst on the polymeric support (42,43). Hydrogenation reactions using polymer bound non-chelated metal complexes have been studied extensively (44,45), but these transition metal complexes are occasionally so labile that the heterogeneous catalysis is not observed (46, 47) or sometimes it results in ~~a~~ singnificant metal leaching in the solution (48).

Metal ions attached to polymer bound chelating ligands were found to be more stable and showed high catalytic activity (49-51). Chelating resins employing phosphine ligands have been widely investigated, not much work has been reported using the ligands containing nitrogen as the donor atom. Neckers and Card (52) have reported the attachment of 2,2'-bipyridine to an insoluble polystyrene support and demonstrated its versability as a polymer bound chelate by preparing a wide variety of transition metal complexes. Recently Ram et al. ( ) have also studied the hydrogenation of 1-octene using Rh(I), Rh(III) and Co(II) anchored on polymer bound chelated ligands and the activity was observed to be higher than the homogeneous counterparts (53-55).

In the present investigation, the polymer bound chelated metal complexes of ruthenium have been used for the kinetics of hydrogenation of cyclohexene as well as nitrobenzene under mild operating conditions. The activity of the catalysts as well as the influence of various parameters such as, catalyst and substrate concentrations, temperature of the system, amount of hydrogen in methanol and also the effect of the various solvents on the rate of the reaction have been investigated. From the analysis of the rate data, the order of the reaction with respect to the susbstrate and the catalyst have been determined. The life cycle of the catalyst have also been studied.

4.2 Measurement of catalytic activity for hydrogenation reactions

The hydrogenation reaction was carried out in a magnetically stirred glass reactor using methanol as the solvent for homogeneous as well as polymer bound ruthenium catalysts. Methanol was found to be the suitable solvent for the hydrogenation reaction catalysed by polymer bound ruthenium catalysts because of better swelling characteristics of the polymer in the solvent (chapter-3). The progress of the reaction was followed by measuring the uptake of hydrogen as a function of reaction time at a constant pressure using a glass manometric apparatus. The experimental set-up and detailed procedure are described in Chapter-2.

4.3 Analysis of kinetic data

The kinetic data for the hydrogenation reaction were obtained in a kinetic regime of a stirring speed of 650 rpm at 35°C. The stoichiometry of the reaction was checked by carrying out a few experiments at constant temperature and hydrogen pressure of one atmosphere at different concentrations of cyclohexene/nitrobenzene for a longer time intervals (i.e. > 4 hours). In all these experiments the amount of hydrogen absorbed was stoichiometrically proportional to the cyclohexene/nitrobenzene converted (calculation based on the GC analysis of the products). This suggests that the formation of any side product is negligible. The initial rate data (based on hydrogen uptake measurements) is used to evaluate the kinetic parameters.

In each kinetic run the uptake of H_2 was measured as a function of time. The initial rates of the hydrogenation were calculated from the slope of the plots of hydrogen uptake against time under different operating conditions.

4.4 HYDROGENATION OF CYCLOHEXENE

4.4 Hydrogenation of cyclohexene

Essentially all high purity cyclohexane is synthesised by hydrogenation of cyclohexene or benzene. Almost all the cyclohexane, produced in the concentrated form is used as a raw material in the manufacturing of the first step of nylon-6 and nylon-6,6. It is an excellent solvent for cellulose ethers, resins, waxes and rubber. When used as a solvent, it is usually in admixture with other hydrocarbons. However, a small amount is used as a reaction diluent in polymer processes (56).

The homogeneous hydrogenation of cyclohexene has been studied widely by using transition metal ions/complexes of Rh(I) , Rh(III) and Ir (I) (57-65), Pd (66,67) and Ru(I) & Ru(III) (68-75) as catalysts. Other metal ions/complexes such as Mn (76), Co (77), Ti (78) and Pt (79) have also been found useful for the hydrogenation of cyclohexene.

The use of noble metals such as Pt, Pd, Rh and Ru supported on Al_2O_3/SiO_2 for the hydrogenation of cyclohexene (80-89) has also been studied. Recently bimetallic catalysts such as Ir-Ru as well as Ir-Rh supported on silica have been introduced to investigate the hydrogenation of cyclohexene (90).

However,

Very few studies on polymer supported catalysts have been noted for the hydrogenation of cyclohexene. Mathew (91) and Uflyand (92) have carried out hydrogenation of cyclohexene by using Pd as a catalyst supported on polymer whereas, Rh was used as catalyst for the same reaction by De Croon (93) supported on polystyrene and an enhanced rate was obtained.

It was therefore planned to investigate the kinetics of the hydrogenation of cyclohexene by using Ru complex supported on functionalised polystyrene-DVB and study the influence on it of various factors which are already mentioned.

4.4.1 Effect of cyclohexene concentration

The influence of cyclohexene concentration on the rate of reaction for different catalysts has been studied and the results are given in Tables 4.4.1 to 4.4.3. The rate of reaction increases with an increase in the concentration of substrate keeping the Ru(III) concentration constant. For example, in the case of 3PRu(III)TMDA catalysts the rate increases from 0.43 x 10^{-2} to 0.62 x 10^{-2} ml/min when the concentration of cyclohexene changes from 2.84 x 10^{-3} to 5.13 x 10^{-3} mol/lit at 35°C and one atmospheric pressure. The plot of log (initial rate) against log [cyclohexene] at a fixed concenration of the catalyst, hydrogen pressure and temperature is found to be linear (Table 4.4.7 and Figures 4.4.1-4.4.2). This indicates that reaction follows first order kinetics with respect to cyclohexene concentration.

For comparision, the hydrogenation reaction was carried out homogeneously using [RuTMDACl_2]Cl under the same reaction conditions as maintained for the heterogeneous reaction. It is noteworthy that for the same Ru concentration the rate was immeasurably low for the homogeneous system. When the concentration of Ru was increased about twentyfive fold a comparable rate of reaction was obtained. The results are summerized in Table 4.4.3. For example, the rates of reaction for the homogeneous

Table-4.4.1

Effect of concentration of cyclohexene on the rate of hydrogenation for poly(Sty-DVB) supported catalysts in methanol at atmospheric pressure.

Reaction temperature (°C) = 35
Qty. of methanol used (ml) = 25

Catalyst	Ru present (mol/lit x 10^6)	[Cyclohexene] (mol/lit x 10^3)	Rate of reaction (ml/min x 10^2)
3PRu(III)TMDA	5.44	2.85	0.43
		3.43	0.47
		3.94	0.50
		4.54	0.56
		5.13	0.62
10PRu(III)TMDA	5.44	2.84	0.89
		3.43	0.94
		3.94	1.02
		4.58	1.23
		5.13	1.40
30PRu(III)TMDA	5.44	1.38	1.25
		2.72	1.75
		3.94	2.13
		5.44	2.37
		6.82	2.59

Table-4.4.2

Effect of concentration of cyclohexene on the rate of hydrogenation for Zeo-Karb 226 supported catalysts in methanol at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of methanol used (ml) = 25

Catalyst	Ru present (mol/lit x 10^6)	[Cyclohexene] (mol/lit x 10^3)	Rate of reaction (ml/min x 10^2)
2.5ZKRu(III)TMDA	10.76	1.69	0.86
		2.80	1.03
		3.94	1.12
		5.09	1.27
		6.19	1.37
20ZKRu(III)TMDA	5.54	2.76	1.18
		3.31	1.34
		3.94	1.45
		4.42	1.62
		4.97	1.93

Table-4.4.3

Effect of concentration of cyclohexene on the rate of hydrogenation for homogeneous catalyst in methanol at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of Methanol used (ml) = 25

Catalyst	Ru present (mol/lit x 10^6)	[cyclohexene] (mol/lit x10^3)	Rate of reaction (ml/min x10^2)
[RuTMDACl$_2$]Cl	130	1.30	1.12
		2.60	1.22
		3.95	1.27
		5.17	1.35
		6.51	1.45

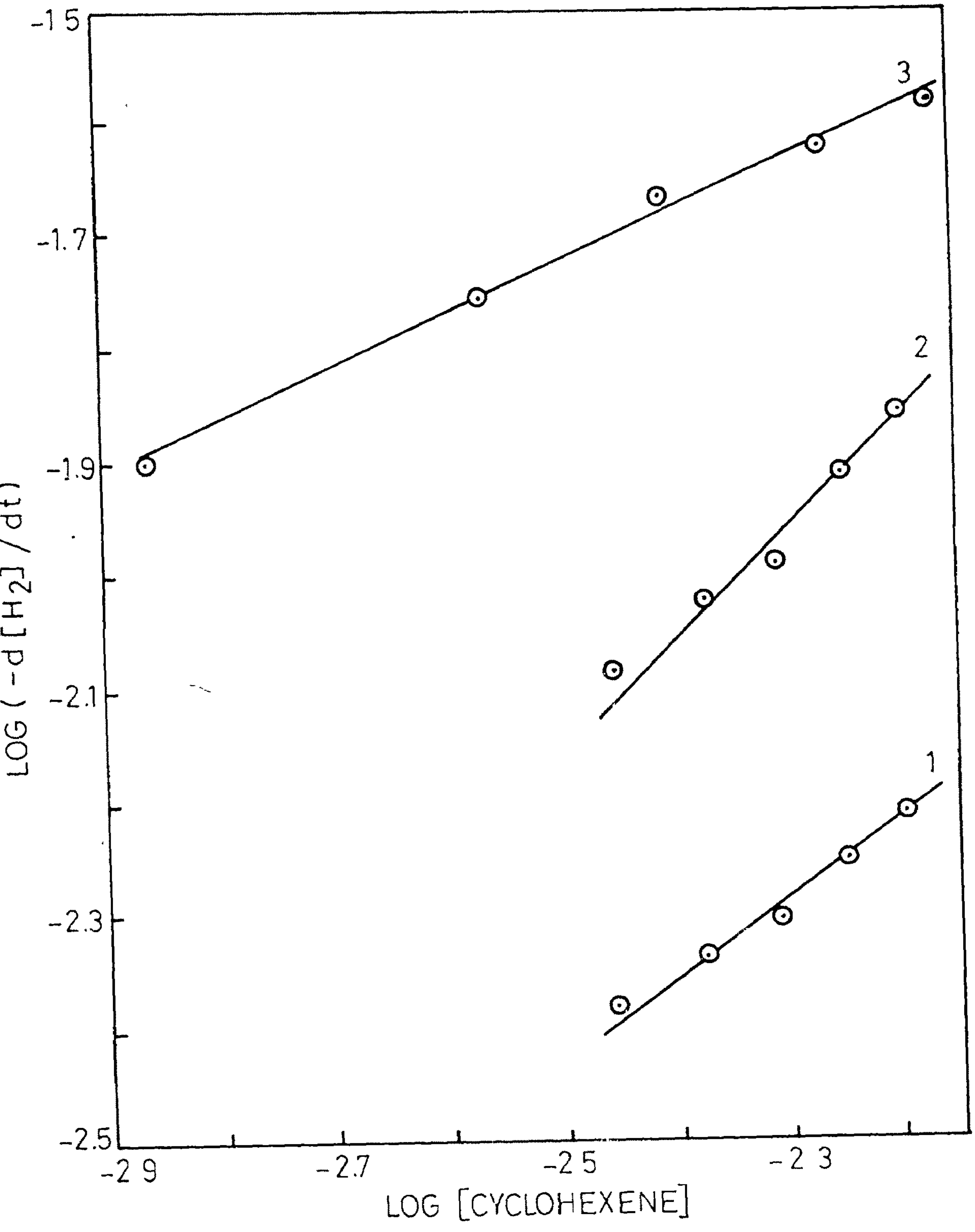

Figure - 4.4.1 Plot of log(-d[H_2]/dt) Vs log [cyclohexene] for catalysts 1) 3PRu(III)TMDA 2) 10PRu(III)TMDA 3) 30PRu(III)TMDA

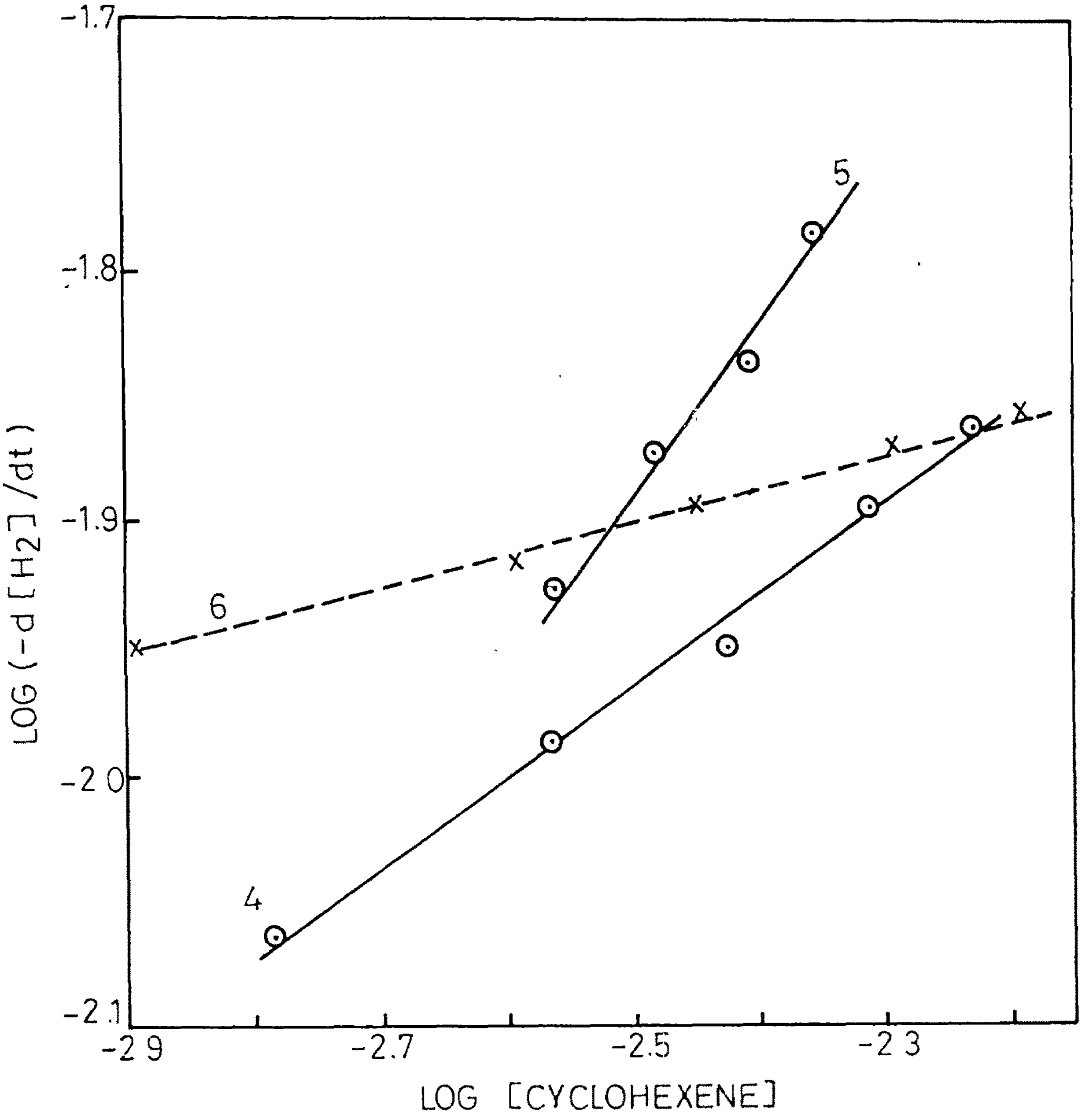

Figure - 4.4.2 Plot of log(-d[H_2]/dt) Vs log [cyclohexene] for catalyts

4) 2.5ZKRu(III)TMDA 5) 20ZKRu(III)TMDA

6) [RuTMDACl_2]Cl

and heterogenized-homogeneous systems are 1.27 $\times 10^{-2}$ ml/min and 2.13 $\times 10^{-2}$ ml/min when the Ru concentration in the catalysts used for the reaction are 1.30 $\times 10^{-4}$ mol/lit and 5.44 $\times 10^{-6}$ mol/lit respectively. This clearly highlights the effectiveness of heterogenizing a homogeneous catalyst in enhancing the catalytic activity.

Effect of the nature of the support

It is seen from the results given in Tables 4.4.1 to 4.4.3 that the rate of the hydrogenation was found to be dependent on the nature of the polymer support used. Increasing the cross-linking of the poly(Sty-DVB) from 3 to 10 to 30% the rate of reaction increased from 0.43 $\times 10^{-2}$ to 0. 9 $\times 10^{-2}$ to 1.25 $\times 10^{-2}$ ml/min for a constant concentration of Ru(III). Similar results have been observed in the case of Zeo-Karb 226, a commercially available polymer. Increase in the rate may be attributed to the higher surface area and hence better dispersion of the active component on the polymer support with the increase in degree of cross-linking of the support. Sokolskii et al. have also reported that the nature of the support considerably affects the rate and mechanism of catalytic processes for hydrogenation of allyl alcohol using poly-2-vinylpyridine-Pd(II) catalyst (94). Dietzmann et al. reported that activity of Rh complexes bound to poly(sty-DVB) of different crosslinking for the hydrosilylation reaction increases with increasing surface area and pore radius (95).

4.4.2 Influence of catalyst concentration

The influence of catalyst concentration on the rate of hydrogenation of cyclohexene has been studied for different catalyst systems. The results are given in Tables 4.4.4 to 4.4.6. In all the cases the rate of reaction is found to increase with the catalyst concentration in the range studied. For example, in the case of 3PRu(III)TMDA catalyst at 35°C and pressure of one atmosphere, when the concentration (in terms of Ru) is varied from 0.544×10^{-5} to 1.629×10^{-5} mol/lit, the rate of reaction increases from 0.50×10^{-2} to 0.61×10^{-2} ml/min.

The order of reaction with respect to concentration of catalyst was calculated from the plots of log (initial rate) versus log [catalyst] at fixed concentration of substrate, hydrogen pressure and temperature and is found to be fractional in all the cases (Table 4.4.7 and Figures 4.4.3, 4.4.4). Although the reaction was carried out in a chemically controlled regime, choosing a suitable swelling agent, the observed fractional order may be due to nonaccessibility of catalytic sites and steric hindrance.

Table-4.4.4

Influence of catalyst concentration on the rate of hydrogenation for poly(Sty-DVB) supported catalyst in methanol at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of methanol used (ml) = 25

[cyclohexene], (mol/lit) = 3.944×10^{-3}

Catalyst	Ru present (mol/lit $\times 10^{5}$)	Rate of reaction (ml/min $\times 10^{2}$)
3PRu(III)TMDA	0.544	0.50
	0.815	0.53
	1.086	0.55
	1.358	0.59
	1.629	0.60
10PRu(III)TMDA	0.544	1.02
	0.816	1.04
	1.088	1.12
	1.360	1.14
	1.631	1.31
30PRu(III)TMDA	0.277	1.75
	0.544	2.13
	0.831	2.25
	1.086	2.39
	1.385	2.55

Table-4.4.5

Influence of catalyst concentration on the rate of hydrogenation for Zeo-Karb 226 supported catalysts in methanol at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of methanol used (ml) = 25

[cylohexene], (mol/lit) = 3.944×10^{-3}

Catalyst	Ru present (mol/lit $\times 10^5$)	Rate of reaction (ml/min $\times 10^2$)
2.5ZKRu(III)TMDA	1.346	0.86
	2.691	1.12
	4.037	1.27
	5.382	1.58
	6.728	1.73
20ZKRu(III)TMDA	0.277	1.25
	0.555	1.45
	1.110	1.59
	1.662	1.88
	2.216	2.05

Table-4.4.6

Influence of catalyst concentration on the rate of hydrogenation for homogeneous catalyst in methanol at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. methanol used (ml) = 25

[cyclohexene], (mol/lit) = 3.944

Catalyst	Ru present (mol/lit x 10^5)	Rate of reaction (ml/min x10^2)
$[RuTMDACl_2]Cl$	8.0	1.06
	9.8	1.15
	13.0	1.27
	19.8	1.49
	39.4	1.73

Table-4.4.7

The values of reaction orders for various catalysts

Catalyst	Order of reaction with respect to [cyclohexene]	Order of reaction with respect to [catalyst]
3PRu(III)TMDA	0.73	0.17
10PRu(III)TMDA	1.02	0.12
30PRu(III)TMDA	0.46	0.22
2.5ZKRu(III)TMDA	0.36	0.43
20ZKRu(III)TMDA	0.61	0.27
$[RuTMDACl_2]Cl$	0.53	0.38

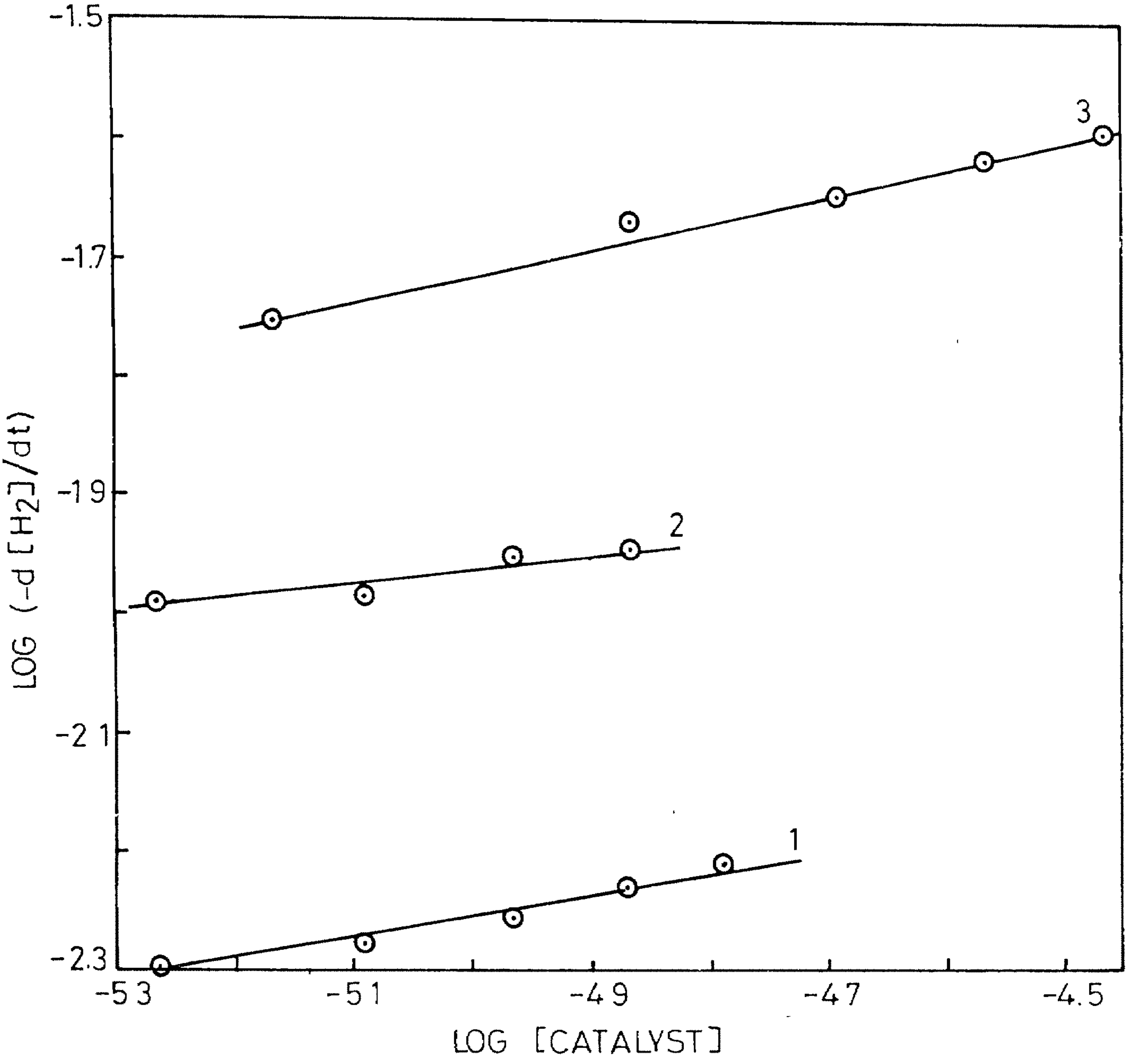

Figure-4.4.3 Plot of log (-d[H_2]/dt) Vs. log [catalyst] for catalysts 1) 3PRu(III)TMDA 2) 10PRu(III)TMDA 3) 30PRu(III)TMDA.

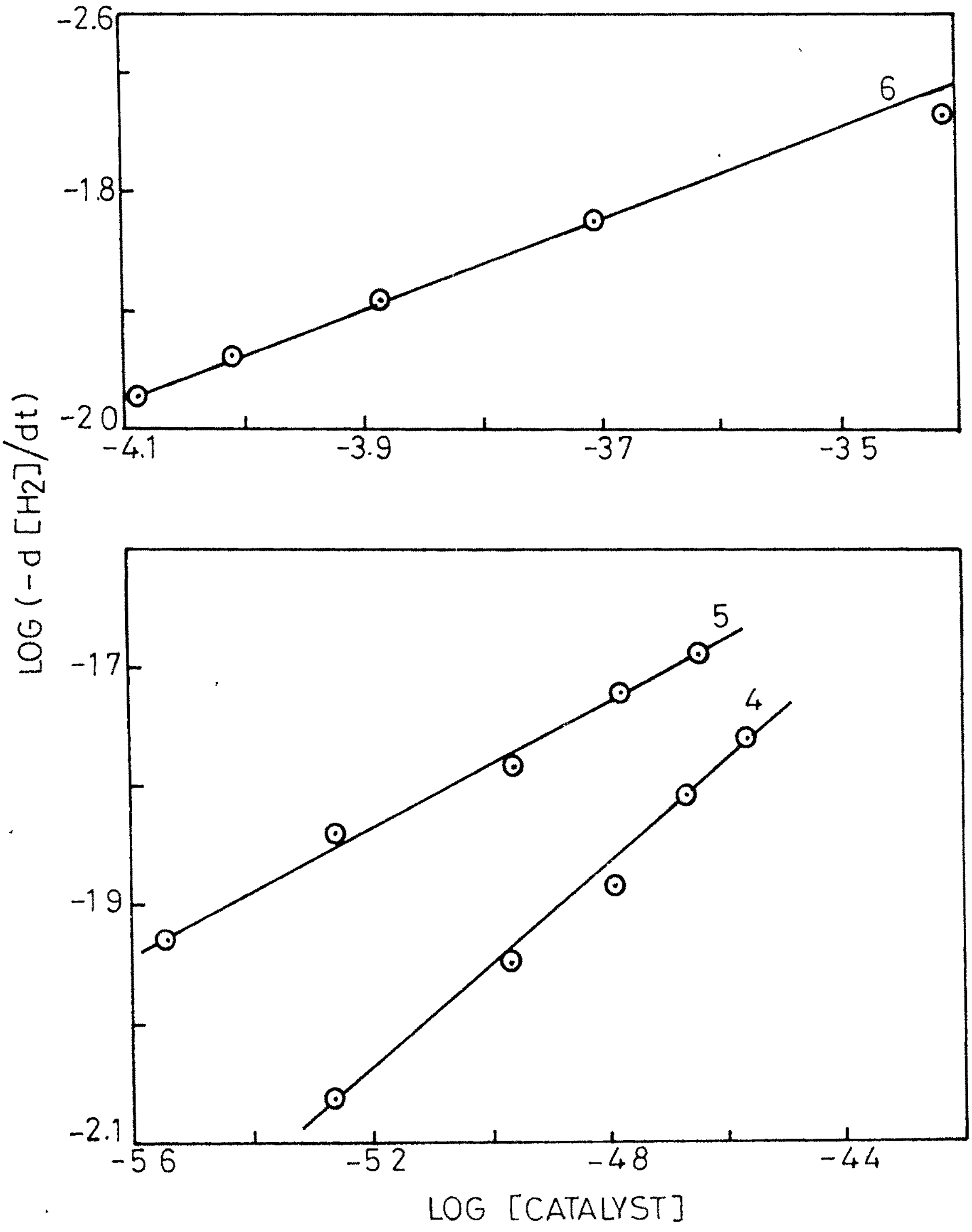

Figure-4.4.4 Plot of log (-d[H_2]/dt) Vs. log[Catalyst] for catalysts
4) 2.5ZKRu(III)TMDA 5) 20ZKRu(III)TMDA
6)[RuTMDACl_2]Cl

4.4.3 Effect of temperature

In any reaction, the rate of molecules undergoing chemical transformation is proportional to the number of molecules that exist in an appropriately activated condition. This number which determines the order of magnitude of the reaction velocity, is an exponential function of temperature. In homogeneous reaction for any ten degree rise in temperature, the rate of reaction is doubled or tripled. In the case of heterogeneous reaction also increase in temperature generally increases the reaction rate.

The effect of temperature on the rate of hydrogenation of cyclohexene has been studied in the range of 30-50°C and results are summarized in Tables 4.4.8 and 4.4.9. For all the catalyst systems, the rate is found to increase with temperature. From the Arrhenius plot i.e. log (initial rate) verses 1/T (Figures 4.4.5, 4.4.6) energy of activation for the reaction has been calculated. The results indicate that the energy of activation is lowest in the case of catalyst with 30% crosslinked polymer support. As mentioned earlier, this support has the maximum surface area and it is only to be expected that this catalyst should have higher activity as a consequence of better dispersion of the active component.

Effect of temperature on the rate of homogeneously catalysed reaction was also studied. As mentioned earlier, the activity of the homogeneous catalyst is very low and hence, the amount of catalyst was so chosen as to maintain rate of reaction comparable to that of heterogeneously catalysed reaction. The results are given in Table 4.4.10.

Table-4.4.8

Effect of temperature on cyclohexene hydrogenation reaction for poly-(Sty-DVB) supported catalyst in methanol at atmospheric pressure.

[cyclohexene], (mol/lit) = 9.86×10^{-3}

Qty. of methanol used (ml) = 10

Ru present (mol/lit) = 1.36×10^{-5}

Catalyst	Temperature (°C)	Rate of reaction (ml/min x 10^2)	Activation energy (kcal/mol)
3PRu(III)TMDA	30	0.45	
	35	0.50	
	40	0.68	10.71
	45	0.84	
	50	1.12	
10PRu(III)TMDA	30	0.93	
	35	1.02	
	40	1.32	9.67
	45	1.59	
	50	2.13	
30PRu(III)TMDA	30	1.45	
	35	1.75	
	40	2.15	5.89
	45	2.37	
	50	2.60	

Table-4.4.9

Effect of temperature on cyclohexene hydrogenation reaction for Zeo-karb 226 supported catalysts in methanol at atmospheric pressure.

[cyclohexene], (mol/lit) = 9.86×10^{-3}

Qty. of methanol used (ml) = 10

Catalyst	Ru present (mol/lit $\times 10^5$)	Temperature (°C)	Rate of Reaction (ml/min $\times 10^2$)	Activation energy (kcal/mol)
2.5ZKRu(III)TMDA	2.69	30	0.86	
		35	1.03	
		40	1.32	8.49
		45	1.72	
		50	2.08	
20ZKRu(III)TMDA	1.39	30	1.10	
		35	1.22	
		40	1.42	5.15
		45	1.62	
		50	1.85	

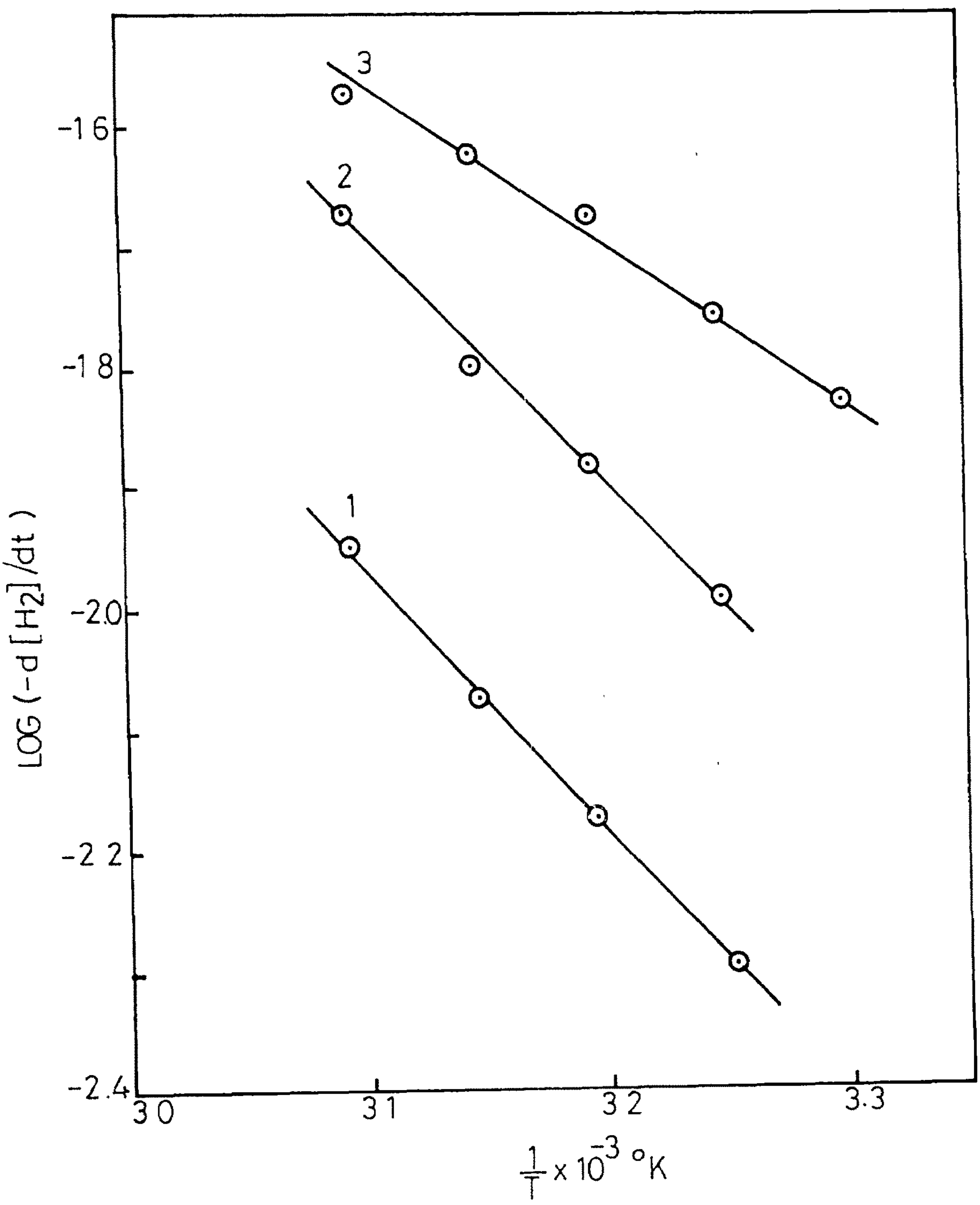

Figure - 4.4.5 Arrhenius plot for catalyst 1) 3PRu(III)TMDA 2) 10PRu(III)TMDA 3) 30PRu(III)TMDA

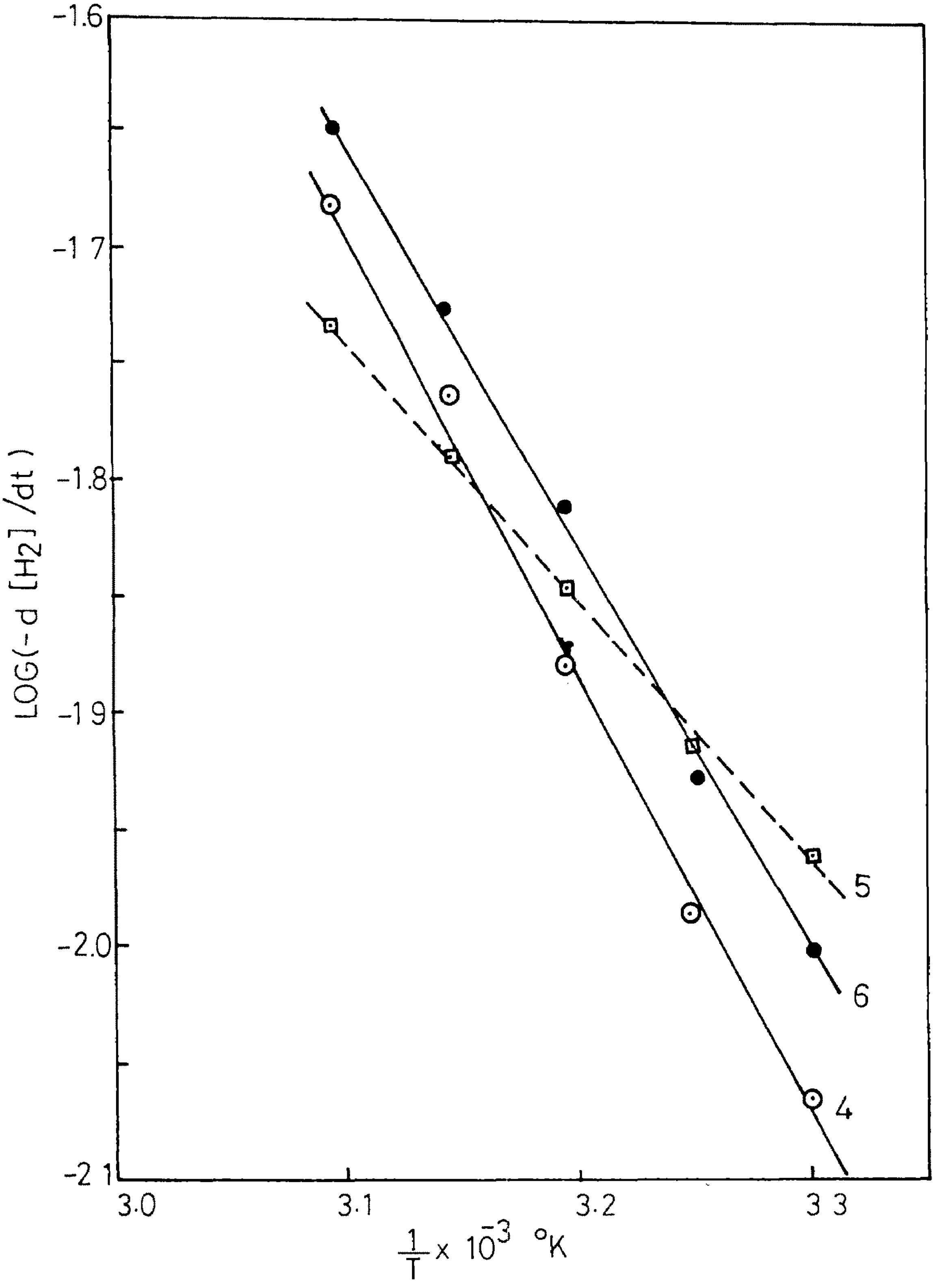

Figure - 4.4.6 Arrhenius plot for the catalysts 4) 2.5ZKRu(III)TMDA 5) 20ZKRu(III)TMDA 6) [RuTMDACl$_2$]Cl

Table-4.4.10

Effect of temperature on cyclohexene hydrogenation reaction for homogeneous catalyst in methanol at atmospheric pressure.

[Cyclohexene], (mol/ lit) = 9.86×10^{-3}

Qty. of methanol used (ml) = 10

Ru present (mol/lit) = 32.5×10^{-5}

Catalyst	Temperature (°C)	Rate of reaction (ml/lit $\times 10^{2}$)	Activation energy (kcal/mol)
$[RuTMDACl_2]Cl$	30	1.00	
	35	1.18	
	40	1.56	7.64
	45	1.80	
	50	2.23	

4.4.4 Effect of solvents

The nature of the solvent can be varied in order to control the activity and selectivity of the polymer supported hydrogenation catalyst. Firstly, the coordinating solvents often take part in the mechanism of the reaction being coordinated to and displaced from the active sites during the catalytic cycle. The second way in which a solvent can influence a reaction is through its ability to swell the support. Thirdly, the polarity of the solvent will lead to a polarity gradient between the bulk solvent and the local environment of the catalytic site. Hence, the suitable solvent would be the one that combines the good swelling ability and high polarity.

The influence of five different solvents (methanol, ethanol, dioxane, THF and benzene) on the rate of reaction has been studied. An increase in the rate was observed when the nature of the solvent is changed from non-polar to polar. In the case of benzene, the rate was found to be 0.06 x 10^{-2} ml/min while in the case of methanol it was 0.50 x 10^{-2} ml/min with 3PRu(III)TMDA catalyst. Similar results are obtained for other catalysts and are given in Tables 4.4.11 to 4.4.13.

Plots of solvent strength ε_o Vs initial rate (Figures 4.4.7 and 4.4.8) gave S-shaped curves (98, 99) for all catalysts, from which it is evident that higher yield of cyclohexane is obtained in methanol, ethanol and dioxane than in solvents of low polarity like THF and benzene.

Table - 4.4.11

Solvent dependence of the hydrogenation of cyclohexene by poly(Sty-DVB) supported catalysts at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of solvent used (ml) = 25

[Cyclohexene], (mol/lit) = 3.944×10^{-3}

Catalyst	Ru present (mol/lit $\times 10^{6}$)	Solvent	Rate of reaction (ml/min $\times 10^{2}$)
3PRu(III)TMDA	5.44	Methanol	0.50
		Ethanol	0.46
		Dioxane	0.40
		THF	0.33
		Benzene	0.06
10PRu(III)TMDA	5.44	Methanol	1.02
		Ethanol	0.99
		Dioxane	0.89
		THF	0.81
		Benzene	0.61
30PRu(III)TMDA	5.44	Methanol	2.13
		Ethanol	2.02
		Dioxane	1.80
		THF	1.45
		Benzene	1.17

Table-4.4.12

Solvent dependence of the hydrogenation of cyclohexene by Zeo-Karb 226 supported catalysts at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of solvent used (ml) = 25

[Cyclohexene], (mol/lit) = 3.944×10^{-3}

Catalyst	Ru present (mol/lit $\times 10^{6}$)	solvent	Rate of reaction (ml/min $\times 10^{2}$)
2.5ZKRu(III)TMDA	10.76	Methanol	1.14
		Ethanol	1.12
		Dioxane	0.83
		THF	0.73
		Benzene	0.37
20ZKRu(III)TMDA	5.54	Methanol	1.14
		Ethanol	1.38
		Dioxane	1.29
		THF	1.25
		Benzene	0.97

Table-4.4.13

Solvent dependence of the hydrogenation of cyclohexene by homogeneous catalyst at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of solvent used (ml) = 25

[Cyclohexene], (mol/lit) = 3.944×10^{-3}

Catalyst	Ru present (mol/lit $\times 10^{6}$)	Solvent	Rate of reaction (ml/min $\times 10^{2}$)
$[RuTMDACl_2]Cl$	130	Methanol	1.27
		Ethanol	1.06
		Dioxane	0.91
		THF	0.79
		Benzene	0.35

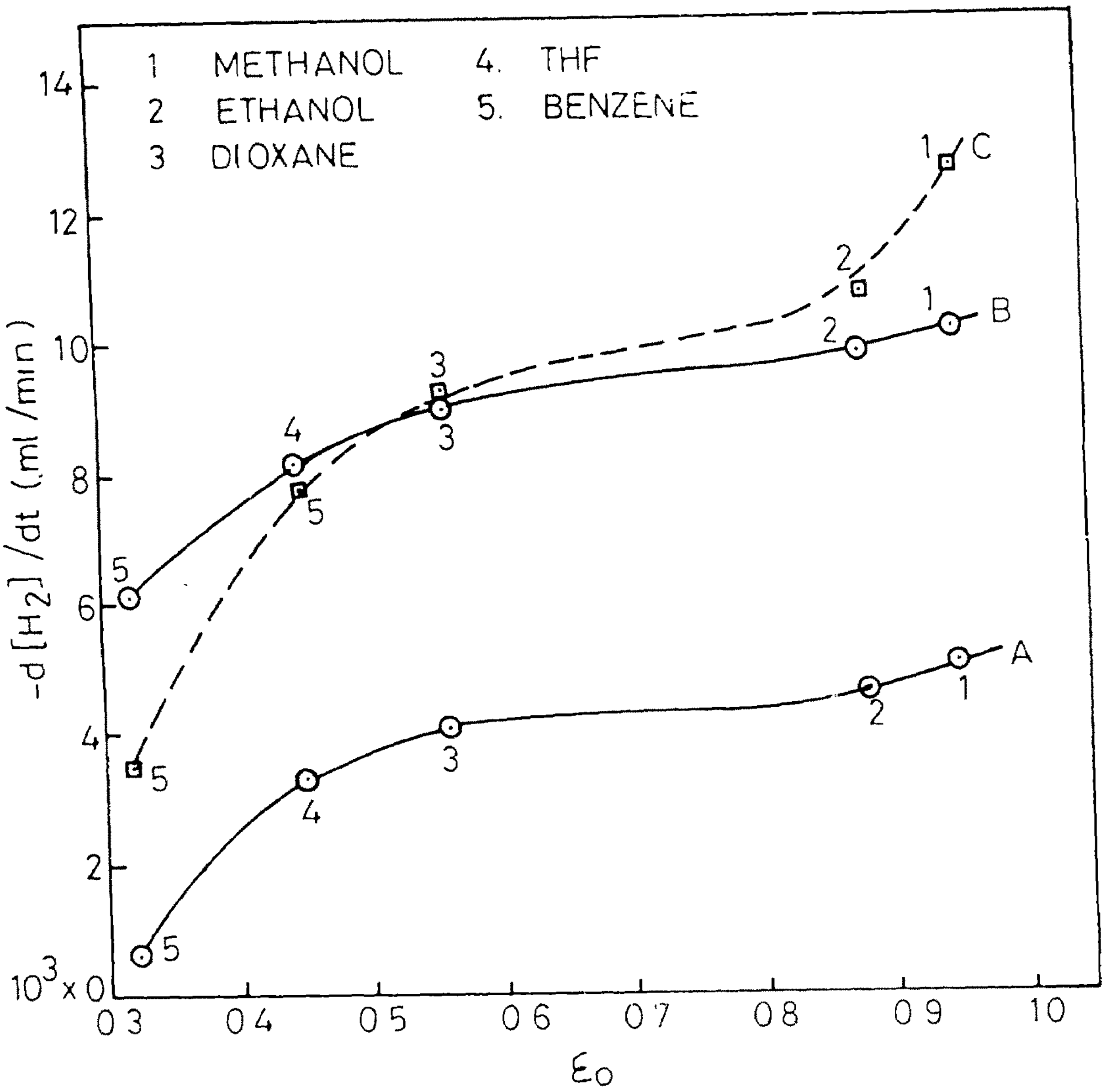

Figure - 4.4.7 Solvent dependence of the hydrogenation of cyclohexene for catalysts A) 3PRu(III)TMDA B) 10PRu(III)TMDA C) 30PRu(III)TMDA

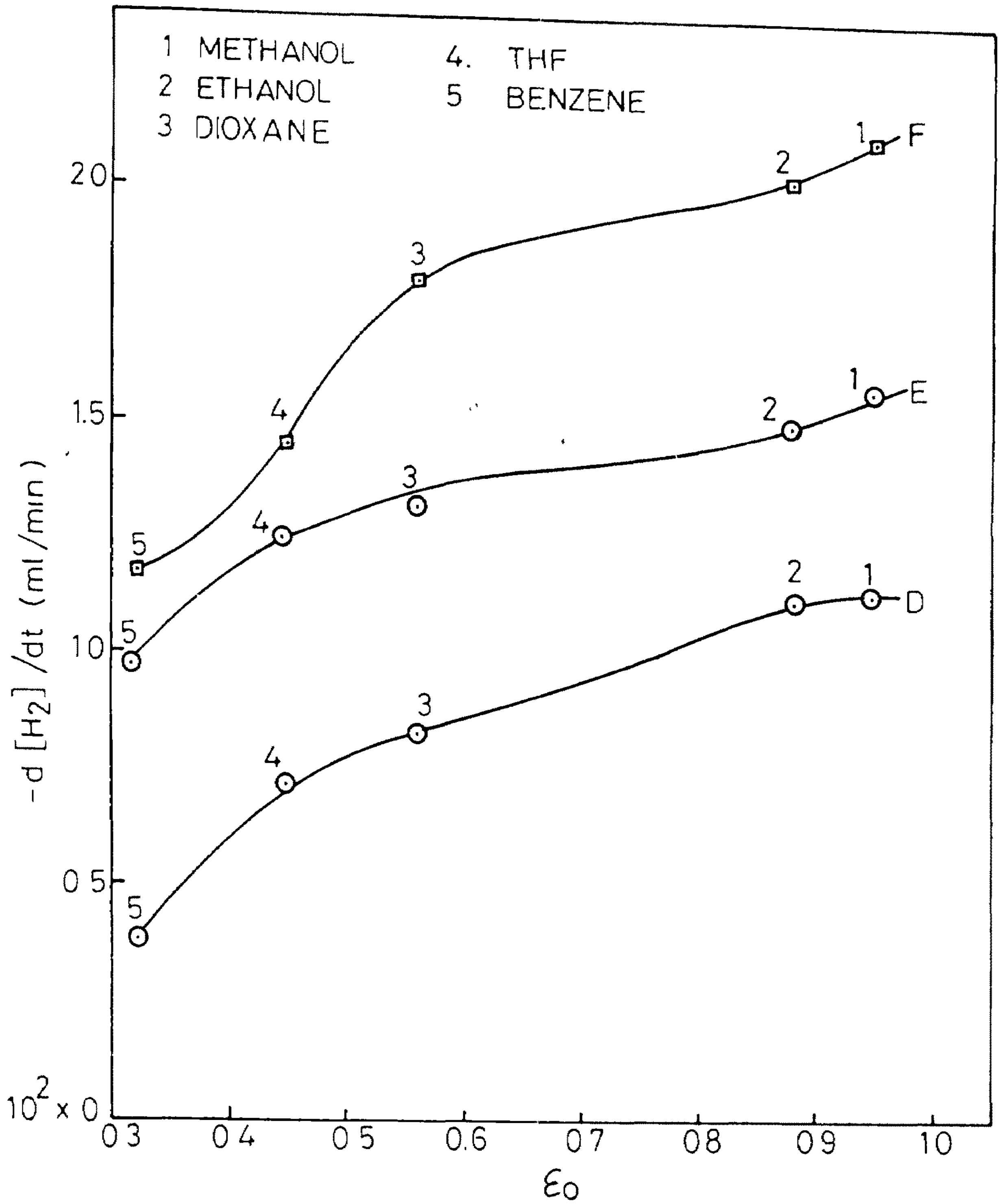

Figure - 4.4.8 Solvent dependence of the hydrogenation of cyclohexene for catalysts D) 2.5ZKRu(III)TMDA E) 20ZKRu(III)TMDA F) [RuTMDACl$_2$]Cl

A knowledge of solubility of gases in liquid is very essential in interpreting the gas-liquid-solid reactions. It is therefore necessary to know the solubility of the gas, especially in the reaction medium (96). A detailed study of the solubility of hydrogen in methanol has been made at various pressures and temperatures (97).

Figures 4.4.9 and 4.4.10 illustrate the influence of amount of hydrogen in methanol on the rate of reaction for all the catalysts at a constant concentration of catalyst and that of the substrate at 35°C.

As the amount of reaction medium i.e. methanol, is increased, the amount of hydrogen available for the reaction in the liquid phase increases. This is found to influence the rate of hydrogenation of cyclohexene as evident from the data given in Tables 4.4.14 to 4.4.16, where the volume of methanol was increased from 10 to 40 ml keeping the amount of cyclohexene and catalyst constant. For example, the rate increases from 0.50×10^{-2} to 0.61×10^{-2} ml/min as the volume of methanol is raised from 10 to 40 ml when 3PRu(III)TMDA used as a catalyst. Similar results have also been observed in the case of Ru complex catalyst supported on Zeo-Karb 226. In case of $[RuTMDACl_2]Cl$, used as a homogeneous catalyst, the rates of reaction obtained were 1.18×10^{-2} to 1.40×10^{-2} ml/min respectively.

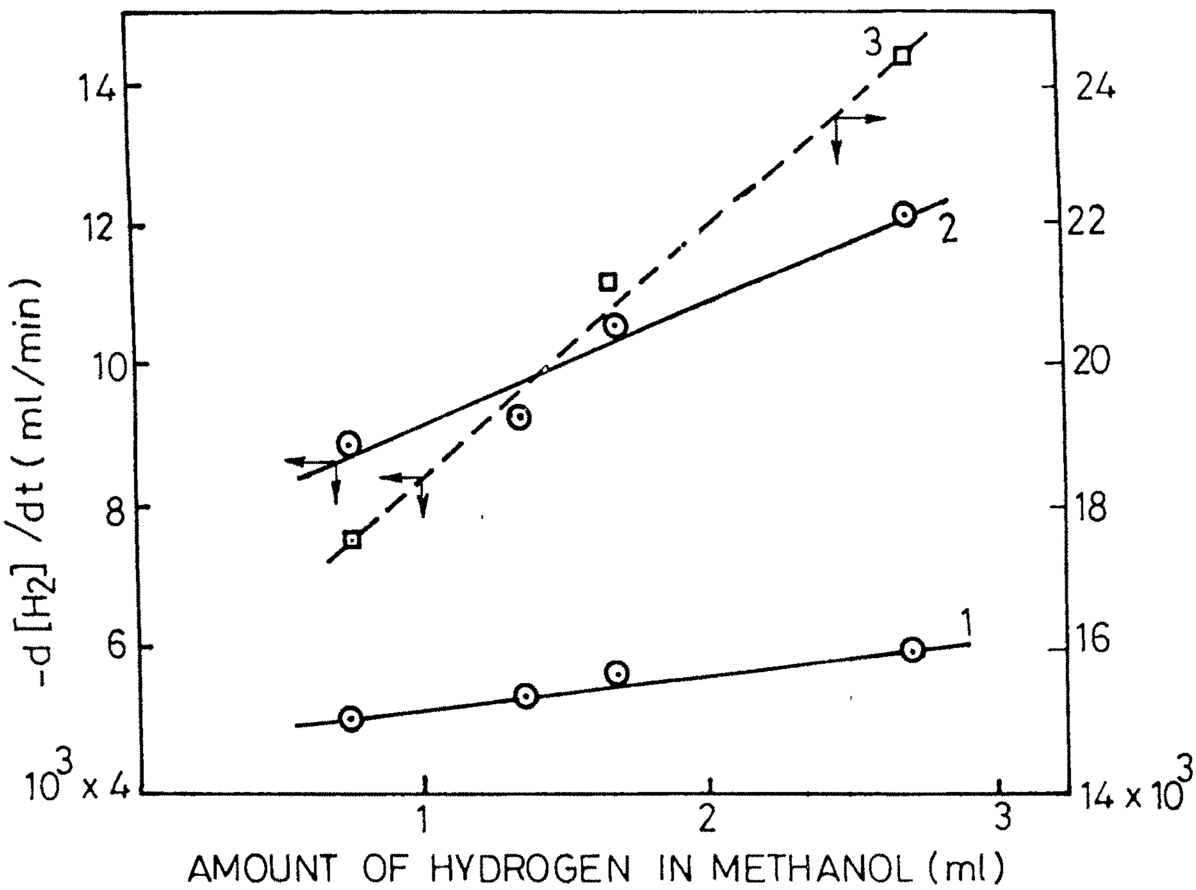

Figure - 4.4.9 Influence of amount of hydrogen on the rate of hydrogenation of cyclohexene for catalysts 1) 3PRu(III)TMDA 2) 10PRu(III)TMDA 3) 30PRu(III)TMDA

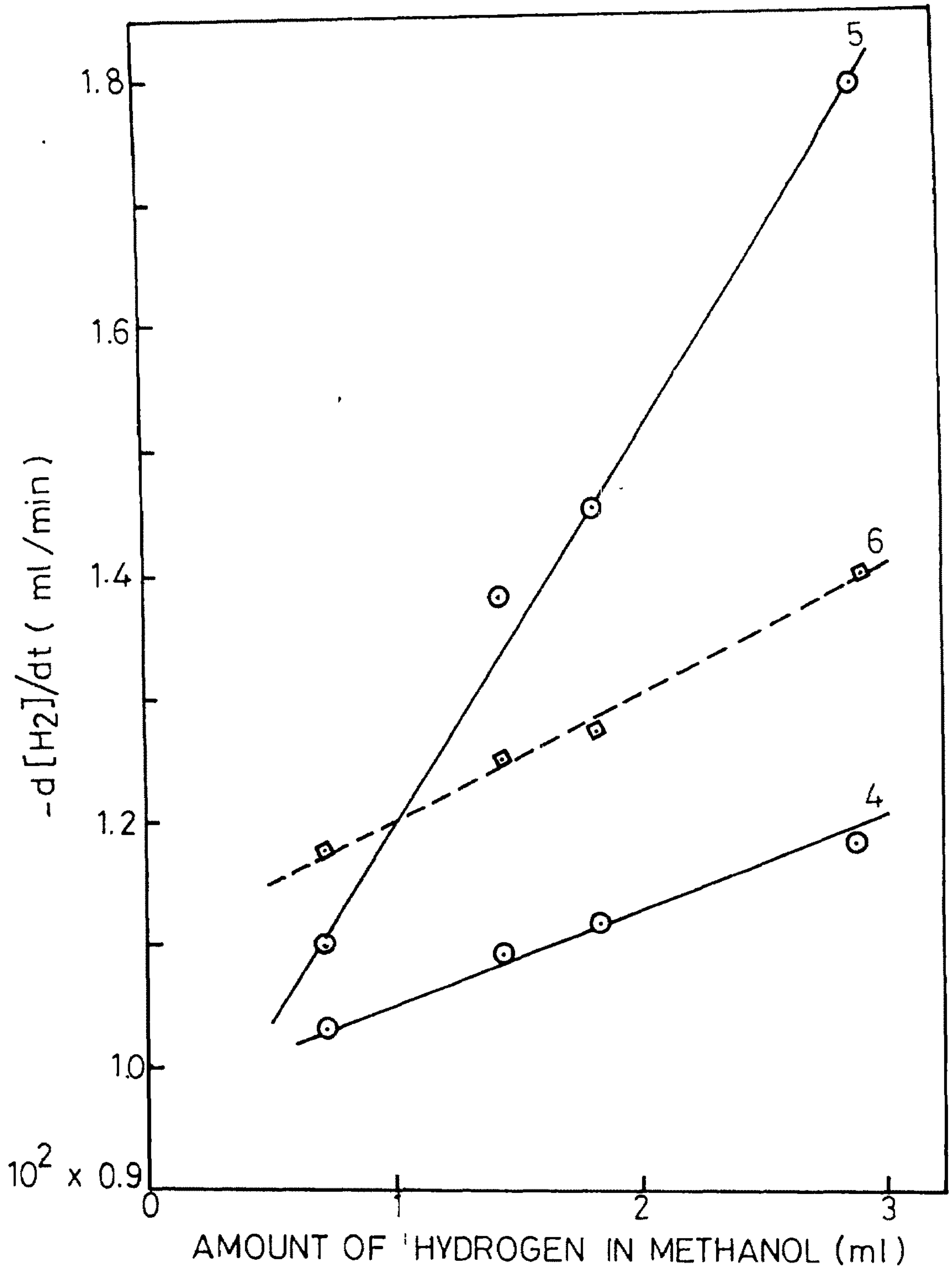

Figure - 4.4.10 Influence of amount of hydrogen on the rate of hydrogenation of cyclohexene for catalysts

4) 2.5ZKRu(III)TMDA 5) 20ZKRu(III)TMDA 6) $[RuTMDACl_2]Cl$

Table-4.4.14

Effect of amount of hydrogen in methanol on the rate of hydrogenation for poly(Sty-DVB) supported catalyst at atmospheric pressure.

Reaction temperature (°C) = 35

[Cyclohexene], (mol/lit) = 3.944×10^{-3}

Catalyst	Ru present (mol/lit $\times 10^6$)	Qty. of methanol (ml)	Rate of reaction (ml/min $\times 10^2$)
3PRu(III)TMDA	5.44	10	0.50
		20	0.53
		25	0.56
		40	0.61
10PRu(III)TMDA	5.44	10	0.89
		20	0.91
		25	1.05
		40	1.21
30PRu(III)TMDA	5.44	10	1.75
		20	1.92
		25	2.13
		40	2.45

Table - 4.4.15

Effect of amount of hydrogen in methanol on the rate of hydrogenation for Zeo-Karb 226 supported catalyst at atmospheric pressure.

Reation temperature (°C) = 35

[Cyclohexene], (mol/lit) = 3.944×10^{-3}

Catalyst	Ru present (mol/litx10^6]	Qty. of methanol (ml)	Rate of reaction (ml/minx10^2)
2.5ZKRu(III)TMDA	10.76	10	1.03
		20	1.09
		25	1.12
		40	1.18
20ZKRu(III)TMDA	5.54	10	1.10
		20	1.38
		25	1.45
		40	1.78

Table - 4.4.16

Effect of amount of hydrogen in methanol on the rate of hydrogenation for homogeneous catalyst at atmospheric pressure.

Reaction temperature (°C) = 35

[Cyclohexene], (mol/lit) = 3.944×10^{-3}

Catalyst	Ru present (mol/litx10^{6})	Qty. of methanol (ml)	Rate of reaction (ml/min x10^{2})
[RuTMDACL_2]Cl	130	10	1.18
		20	1.25
		25	1.27
		40	1.40

4.4.5 Life cycle of catalysts

One of the ways in which a polymer-bound catalyst can lose its activity, is by loss of Ru(III), 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 into the solution (100, 101). The effect is enhanced when the complex is anchored through monodentate ligands. However it has been reported by Drago et al. that polymer-anchored complexes through chelating ligands are more stable (100). Pittman et al. have synthesised the rhodium-diphos chelating complexes bound to resins and used them in the hydroformylation of styrene (102) and pent-1-ene (103). In order to study the stability of the catalyst, the recycling efficiency of the catalysts was tested.

The experiment was carried out at 35°C for about 16 hours. In each cycle 10 μl of the substrate was injected. Every time, after the completion of the reaction, 60 minutes were allowed to lapse before the next injection was made. The rate of hydrogenation was measured as function of time for both the used and the fresh catalysts. The results are summarized in Tables 4.4.17 and 4.4.18.

It is seen from the results that in the case of poly(Sty-DVB) supported catalysts, the maximum rate of reaction is maintained for about 10 hours after which the rate decreased slowly. Quantitative estimation showed a loss of 50 % of the metal from the polymer at the end of the reaction.

Table-4.4.17

Life cycle study for poly(Sty-DVB) supported catalysts.

Reaction temperature (°C) = 35   Qty. of methanol used (ml) = 25

Fresh catalyst		Used catalyst	
Time (min)	Rate of reaction (ml/min $\times 10^2$)	Time (min)	Rate of reaction (ml/min $\times 10^2$)
	3PRu(III)TMDA[a]		
140	0.71	140	0.70
340	0.71	340	0.70
535	0.71	555	0.65
720	0.64	775	0.38
940	0.56	-	-
	10PRu(III)TMDA[b]		
90	1.88	90	1.88
40	1.88	240	1.88
390	1.88	390	1.88
540	1.88	540	1.19
690	1.50	690	1.00
840	1.10	840	0.96
970	0.81	-	-
	30PRu(III)TMDA[c]		
60	2.85	70	2.56
220	2.21	220	1.97
360	1.89	340	1.43
480	1.42	-	-

a Amount of catalyst 0.7 gm (7.62 x 10^{-5} Ru mol/lit);
Total time on stream 16.25 h (14-40 h)*

b Amount of catalyst 0.7gm (7.75 x10^{5} Ru mol/lit);
Total time on stream 15.45 h (14.45 h)*

c Amount of catalyst 1.120gm (7.76 x10^{-5}) Ru mol/lit);
Total time on stream 8.5 h (6.4 h)*

* Values given in parentheses indicate data for used catalyst.

Table-4.4.18

Life cycle study for Zeo-Karb 226 supported catalysts.

Reaction temperature (°C) = 35

Qty. of methanol used (ml) = 25

Fresh catalyst		Used catalyst	
Time (min)	Rate of reaction (ml/min x 10^2)	Time (min)	Rate of reaction (ml/min x10^2)
	2.5ZKRu(III)TMDA[d]		
65	3.08	85	2.73
200	3.06	2.05	1.84
355	2.14	-	-
475	1.15	-	-
	20ZKRu(III)TMDA[e]		
80	2.12	80	2.02
220	1.91	230	1.62
370	1.60	350	1.28
490	1.36	-	-

d Amount of catalyst 0.57 gm (7.67 x10^{-5} Ru mol/lit);
Total time on stream 8.45 h (4.01 h)*

e Amount of catalyst 1.75 gm (3.88 x10^{-5} Ru mol/lit);
Total time on stream 9.00 h (8.40 h)*

* Values given in parentheses indicate data for used catalyst.

In the case of Zeo-Karb 226 supported catalysts, the maximum rate of reaction is maintained for about 3 hours after which the rate declined slowly. In this case, a 70 % loss of the metal was observed at the end of the reaction.

The loss in activity may be due to low mechanical strength of the polymer support and also due to polymer-bound complexes and polymer-bound non-coordinated ligand molecules leaching out in solution and forming stable complexes in solution which are ineffective in catalysing the reaction.

4.4.6 Rate equation

In the present investigation, the partial pressure of hydrogen and the concentration of hydrogen in solution is kept constant by carrying out the reaction at constant hydrogen pressure and using the fixed amout of the catalyst. In all the experiments, the solvent along with the catalyst was initially saturated with hydrogen followed by the injection of olefin and hence the actual consumption of hydrogen was measured.

The mechanism of olefin hydrogenation using ruthenium catalyst has been extensively studied (20,42,65). The formation of hydrido species, and preferential attack of olefin on the hydrido complex of ruthenium have been well established by various experimental studies and thermodyanmic properties (57,65). On the basis of above literature evidence, the following mechanism and thereby, the rate equation, are proposed:

$$[RuTMDACl_2]Cl + H_2 \underset{}{\overset{K_1}{\rightleftharpoons}} [RuTMDA(H)Cl]Cl + HCl$$

$$[RuTMDA(H)Cl]Cl + S \xrightarrow[slow]{k'} [RuTMDA(HS)Cl]Cl$$

$$[RuTMDA(HS)Cl]Cl + H_2 \xrightarrow{fast} [RuTMDA(H)Cl] + Alkane$$

where K_1 represents the equilibrium contant, k' the rate constant, S is the cyclohexene and C is the catalyst (i.e. $[RuTMDACl_2]Cl$) then rate law can be written as:

$$\text{Rate (R)} = \frac{K_1\, k'\, [C]\, [H_2]\, [S]}{1 + K\, [S]}$$

where K is constant.

The order of reaction with respect to cyclohexene concentration is first order and that with respect to the catalyst concentration and hydrogen concentration are both fractional.

4.5 HYDROGENATION OF NITROBENZENE

4.5 Hydrogenation of nitrobenzene

Aniline is produced commercially by catalytic hydrogenation of nitrobenzene. About 300 chemical products and intermediates are currently manufactured from aniline. Some are produced by a single process; many others, especially dyes and pharmaceuticals, require several steps (104).

Aniline is widely used in the polymer, rubber, agricultural and dye industries, primarily for the manufacture of isocyanates to synthesise polyurethanes (105). It is also utilised in the pharmaceutical industries in the manufacturing of sulfa drugs, acetanilide, antipyretic and sweetening agents.

The homogeneous hydrogenation of nitrobenzene has been studied widely by using transition metal ions/complexes of Pd (106-108) and Rh (109,110). Other metal ions/complexes of Ru (111, 112), Co (113) and Pt (114) have also been found useful for the hydrogenation of nitrobenzene.

Studies ~~has~~ have been carried out utilising transition metals such as Pd, Pt (115-120), Cu, Ni and Cr (121-123) supported on Al_2O_3 and SiO_2 as catalyst. Raney nickel (126, 127), Pt-Sn (128), Ni-Cu (124, 125) as bimetallic catalysts and Pd supported on activated charcoal have also been found to be a suitable as catalyst for this reaction.

However, the catalytic activity using palladium ion/complexes and ?
also that of Rh using a polymer support has been reported in the literature for hydrogenation of nitrobenzene. M.V. Klyuev et al. have reported the

use of chloromethylated poly(butadiene-styrene) and polyvinylimidazole supported palladium (132-133). Hely (134) has used Pd supported on chloromethylated polystyrene beads (XAD-4) and Nasibulin (135) used polymer-bound Pd (cross-linked aminated, chloromethylated styrene-DVB copolymer) for hydrogenation of nitrobenzene. M.V. Klyuev et al. (136) have also carried out the reaction by using Pd-supported on anion exchangers like AN 221, AN 511 and AN 541. Yakerson et al. (137) have studied the hydrogenation of nitrobenzene using polymer-supported $RhCl_3$ catalysts modified by methylpyrazole, imidazole and benzimidazole. It was, therefore, planned to investigate the hydrogenation of nitrobenzene by using ruthenium-TMDA complex supported on functionalised poly(Sty-DVB).

4.5.1 Effect of the concentration of nitrobenzene

The influence of nitrobenzene concentration on the rate of hydrogenation for different catalysts have been studied and an enhancement in the rate was observed on increasing the concentration of the substrate. The results are summarized in Tables 4.5.1 to 4.5.3. Thus the rate of the hydrogenation of nitrobenzene increases from 1.07×10^{-2} to 1.45×10^{-2} ml/min as the concentration of nitrobenzene varies from 2.759×10^{-3} to 4.974×10^{-3} mol/lit at 35°C and at one atmospheric pressure by using 3PRu(III)TMDA (Ru concentration is 5.65×10^{-6} mol/lit) catalyst. The plot of log (initial rate) against log [nitrobenzene] at fixed concentration of the catalyst, hydrogen pressure and temperature is found to be linear (Figures 4.5.1, 4.5.2) and the order of reaction calculated from the slopes of the above plots was found to be fractional (Table 4.5.7) with respect to nitrobenzene concentration.

Table-4.5.1

Effect of nitrobenzene concentration on the rate of hydrogenation for poly (Sty-DVB) supported catalysts in methanol at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of methanol use (ml) = 25

Catalyst	Ru present (mol/lit x10^5)	[Nitrobenzene] (mol/lit x10^3)	Rate of Reaction (ml/min x10^2)
3PRu(III)TMDA	0.565	2.759	1.07
		3.342	1.17
		3.886	1.27
		4.430	1.66
		4.974	1.45
10PRu(III)TMDA	0.555	2.759	1.28
		3.342	1.50
		3.886	1.79
		4.430	1.97
		5.013	2.25
30PRu(III)TMDA	0.554	2.759	1.17
		3.342	1.34
		3.886	1.51
		4.430	1.17
		4.974	1.85

Table-4.52

Effect of nitrobenzene concentration on the hydrogenation for Zeo-Karb 226 supported catalysts in methanol at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of methanol used (ml) = 25

Catalyst	Ru present (mol/lit $\times 10^5$)	[Nitrobenzene] (mol/lit $\times 10^3$)	Rate of Reaction (ml/min $\times 10^2$)
2.5ZKRu(III)TMDA	1.110	1.044	1.25
		1.724	1.67
		2.429	1.91
		3.133	2.35
		3.813	2.65
20ZKRu(III)TMDA	0.554	2.759	1.20
		6.342	1.30
		6.886	1.45
		4.430	1.54
		4.974	1.65

Table-4.5.3

Effect of nitrobenzene concentration on the hydrogenation for homogeneous catalyst in methanol at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of Methanol used (ml) = 25

Catalyst	Ru present (mol/lit x10^4)	[Nitrobenzene] (mol/lit x10^3)	Rate of Reaction (ml/min x10^2)
$[RuTMDACl_2]Cl$	1.30	1.438	1.10
		2.720	1.23
		3.886	1.35
		5.674	1.51
		7.072	1.65

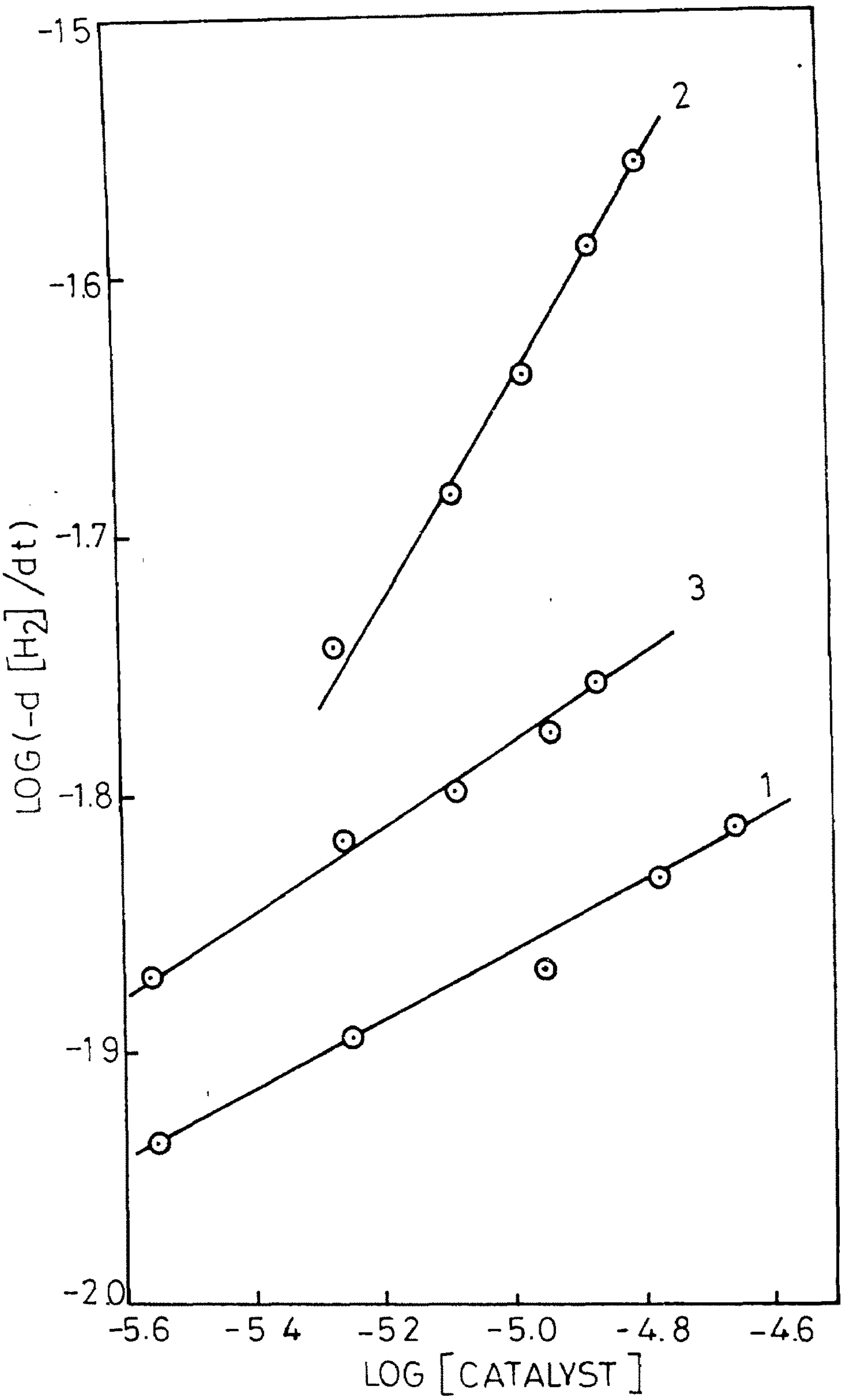

Figure - 4.5.1 Plot of log(-d[H_2]/dt) Vs log [nitrobenzene] for catalysts 1) 3PRu(III)TMDA 2) 10PRu(III)TMDA 3) 3CP Ru(III)TMDA

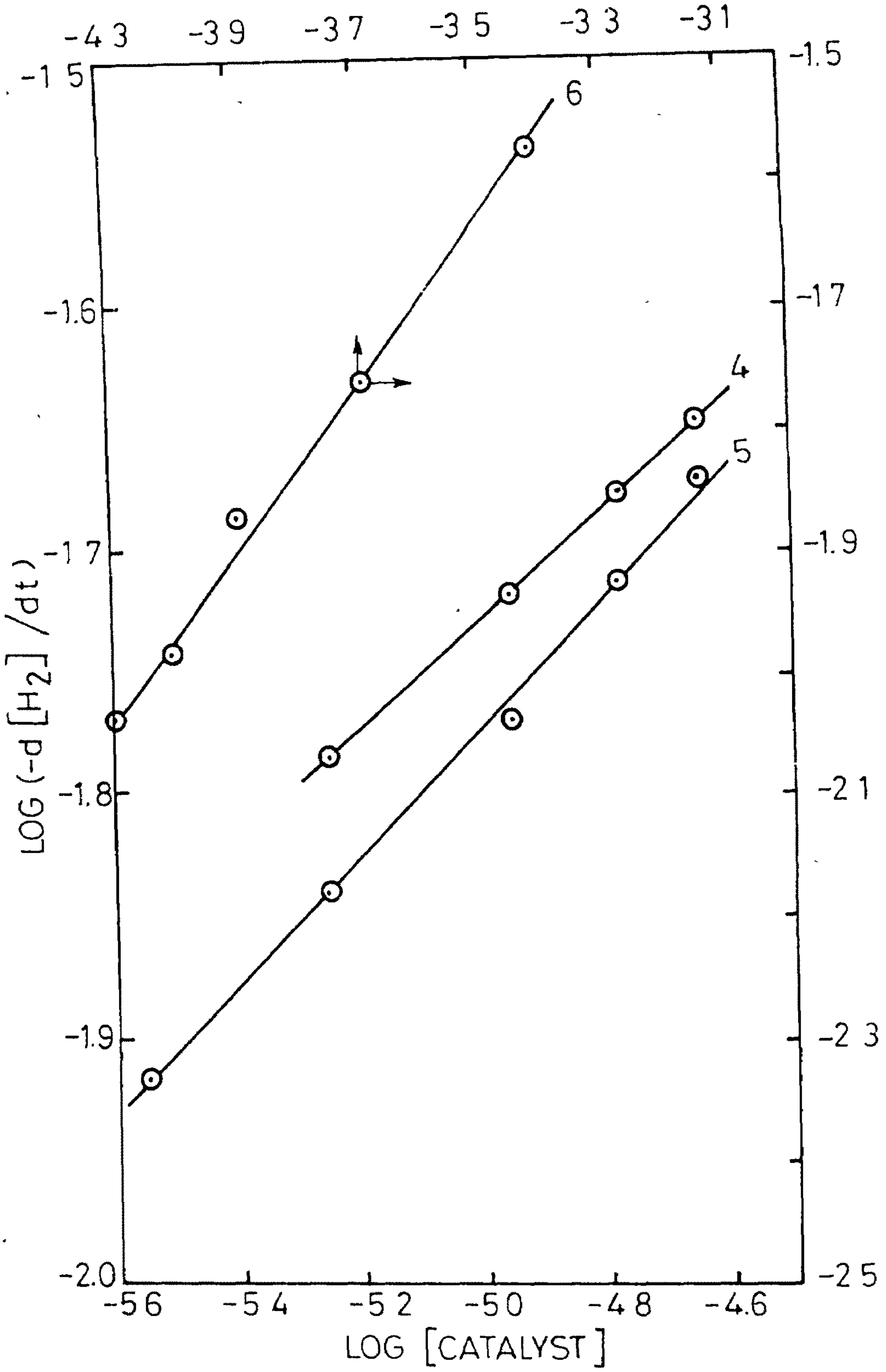

Figure - 4.5.2 Plot of log(-d[H_2]/dt) Vs log [nitrobenzene] for catalyts

4) 2.5ZKRu(III)TMDA 5) 20ZKRu(III)TMDA

6) [RuTMDACl$_2$]Cl

In the case of the homogeneous system inspite of using larger amount of Ru to catalyse the reaction a lower rate was observed. Thus, keeping the concentration of nitrobenzene at 2.72 $\times 10^{-3}$ mol/lit, the rate of the reaction was found to be 1.23 $\times 10^{-2}$ ml/min as the amount of the catalyst present is 1.30 $\times 10^{-4}$ mol/lit. This indicates that heterogenizing the catalyst by supporting it on a polymer has higher activity than the homogeneous system.

4.5.2 Influence of the catalyst concentration

The influence of the catalyst concentration on the rate of hydrogenation of nitrobenzene for the different catalysts has been investigated. It was observed that in the case of polymer supported ruthenium complex catalysts the rate of the hydrogenation increases linearly with an increase in the amount of the catalysts in the range studied (Tables 4.5.4 to 4.5.6). Thus in case of 3PRu(III)TMDA, rate of reaction increases from 1.16 $\times 10^{-2}$ to 1.53 $\times 10^{-2}$ ml/min when the concentration of the catalyst varies from 0.283 $\times 10^{-5}$ to 2.261 $\times 10^{-5}$ mol/lit at constant concentration of nitrobenzene (i.e. 3.886 $\times 10^{3}$ mol/lit). Linear relation of rate with catalyst concentration indicates that there are no complications such as dimerisation of the catalyst in the concentration range studied.

In the case of homogeneous catalysts, the rate of hydrogenation increased from 0.92 $\times 10^{-2}$ to 2.66 $\times 10^{-2}$ ml/min as concentration of catalyst increased from 0.80 $\times 10^{-4}$ to 3.94 $\times 10^{-4}$ mol/lit at a constant concentration

Table-4.5.4

Effect of catalyst concentration on the rate of hydrogenation for poly(Sty-DVB) supported catalyst in methanol at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of methanol used (ml) = 25

Catalyst	[Nitrobenzene] (mol/lit x10^3)	Ru present (mol/lit x10^5)	Rate of Reaction (ml/min x10^2)
3PRu(III)TMDA	3.886	0.283	1.16
		0.565	1.27
		1.130	1.33
		1.695	1.46
		2.261	1.53
10PRu(III)TMDA	3.886	0.555	1.79
		0.833	2.07
		1.110	2.29
		1.388	2.58
		1.665	2.76
30PRu(III)TMDA	3.886	0.277	1.34
		0.554	1.51
		0.831	1.58
		1.168	1.67
		1.385	1.78

Table-4.5.5

Effect of catalyst concentration of the rate of hydrogenation for Zeo-Karb 226 supported catalyst in methanol at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of methanol used (ml) = 25

Catalyst	[Nitrobenzene] (mol/lit x10^{5})	Ru present (mol/lit x10^{5})	Rate of Reaction (ml/min x10^{2})
2.5ZKRu(III)TMDA	3.886	0.555	1.64
		1.110	1.91
		1.661	2.10
		2.220	2.25
		2.777	2.58
2.0ZKRu(III)TMDA	3.886	0.277	1.22
		0.554	1.45
		1.108	1.69
		1.662	1.95
		2.216	2.13

Table-4.5.6

Effect of catalyst concentration on the rate of hydrogenation for homogeneous catalyst in methanol at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of methanol used (ml) = 25

Catalyst	[Nitrobenzene] (mol/lit x10^3)	Ru Present (mol/lit x10^4)	Rate of Reaction (ml/min x10^2)
$[RuTMDACl_2]Cl$	3.886	0.80	0.92
		0.98	1.04
		1.30	1.35
		1.98	1.74
		3.94	2.66

of nitrobenzene i.e. 3.886×10^{-3} mol/lit.

The order of reaction with respect to concentration of catalyst was calculated from the plots of log (initial rate) versus log [catalyst] at fixed concentration of substrate, hydrogen pressure and temperature and is found to be fractional in all the cases (Table 4.5.7 and Figures 4.5.3, 4.5.4). Although the reaction was carried out in a chemically controlled regime, choosing a suitable swelling agent, the observed fractional order may be due to nonaccessibility of catalytic sites and steric hindrance.

4.5.3 Effect of temperature

The effect of temperature on the rate of hydrogenation of nitrobenzene has been studied in the range of 30-50°C and The results are summarized in Tables 4.5.8 to 4.5.10. For all the catalyst systems, the rate is found to increase with temperature. Thus an increase in the rate of the hydrogenation was found from 1.15×10^{-2} to 1.79×10^{-2} ml/min by the use of 3PRu(III)TMDA catalyst, as the temperature is raised from 30 to 50 °C The corresponding results were also obtained in the case of 10PRu(III)TMDA where the rate increased from 1.40×10^{-2} to 2.72×10^{-2} ml/min. Similar results have also been observed in the case of Zeo-Karb 226 supported ruthenium catalysts. The values for the energy of activation calculated from the Arrhenius plots were found in the range of 2.56 - 5.49 kcal/mol. (Figures 4.5.5, 4.5.6)

In case of $[RuTMDACl_2]Cl$ (where Ru is present in a large quantity) used as a homogeneous catalyst, the rate of the reaction obtained was from

Table-4.5.7

The values of reaction order for various catalysts

Catalyst	Order of reaction with respect to [nitrobenzene]	Order of reaction with respect to [catalyst]
3PRu(III)TMDA	0.54	0.14
10PRu(III)TMDA	0.94	0.41
30PRu(III)TMDA	0.81	0.16
2.5ZKRu(III)TMDA	0.58	0.23
20ZKRu(III)TMDA	0.59	0.26
$[RuTMDACl_2]Cl$	0.31	0.34

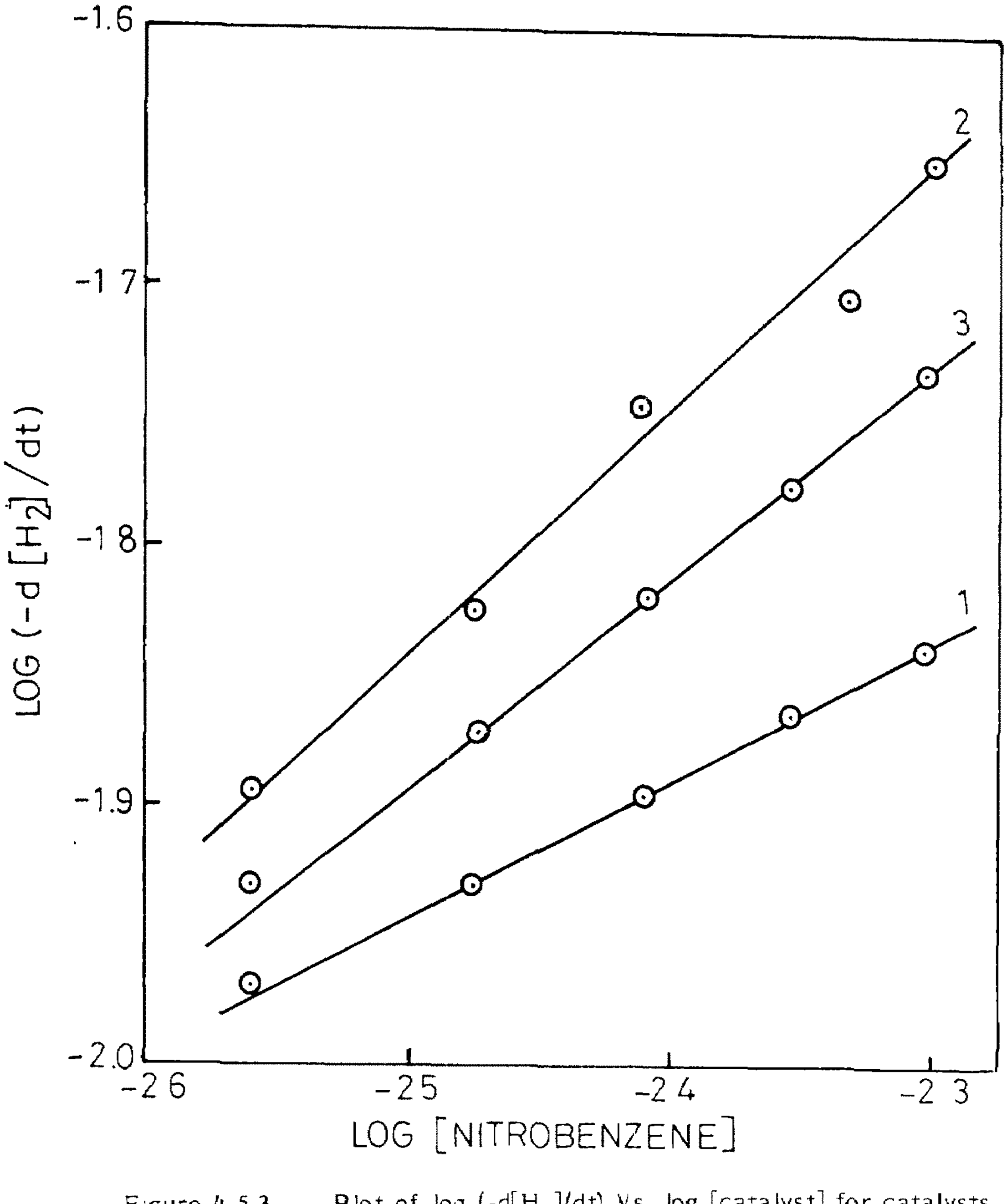

Figure-4.5.3 Plot of log ($-d[H_2]/dt$) Vs. log [catalyst] for catalysts 1) 3PRu(III)TMDA 2) 10PRu(III)TMDA 3) 30PRu(III)TMDA.

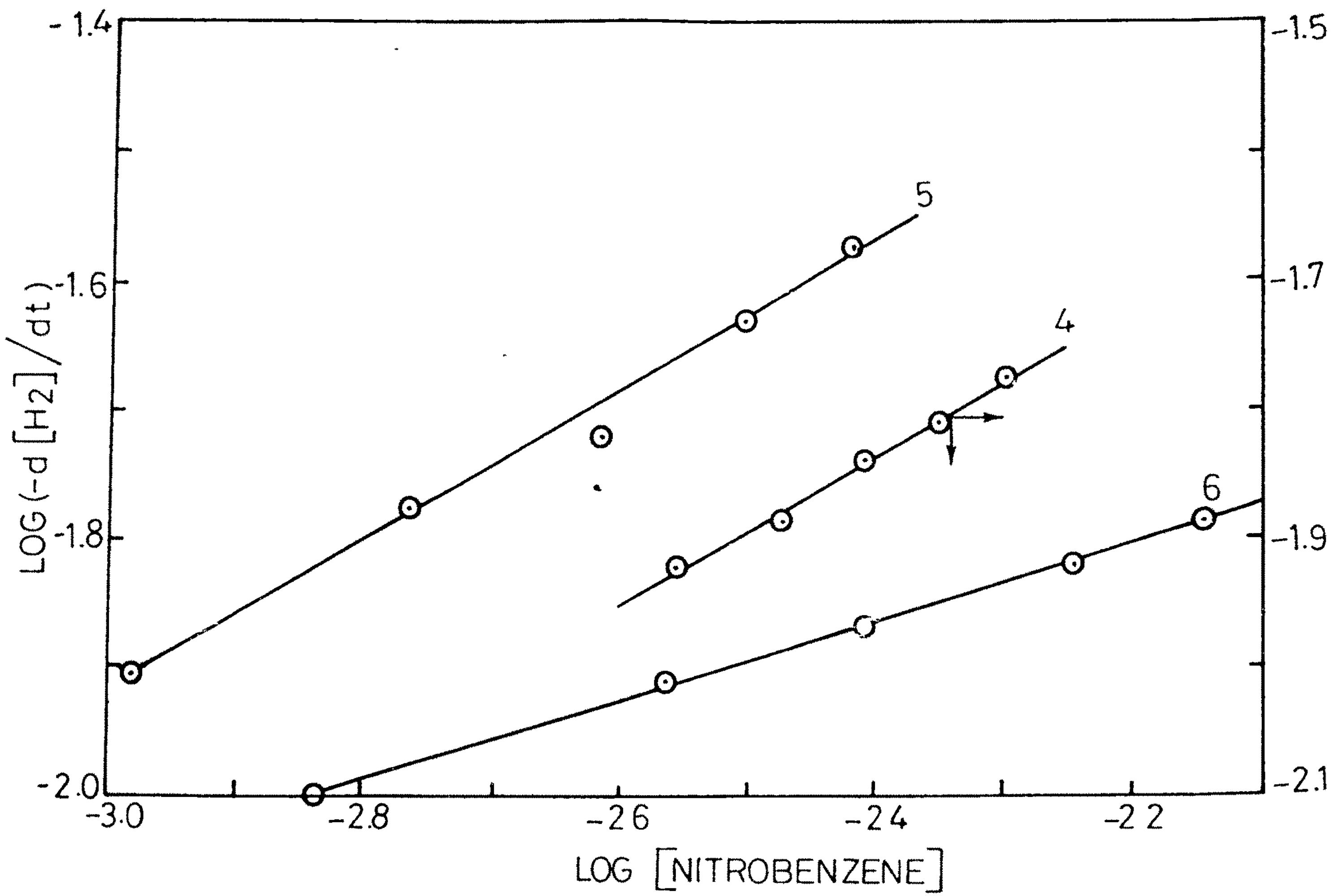

Figure-4.5.4 Plot of log (-d[H_2]/dt) Vs. log [catalyst] for catalysts 4) 2.5ZKRu(III)TMDA 5) 20ZKRu(III)TMDA 6) [RuTMDACl_2]Cl

Table-4.5.8

Effect of temperature on nitrobenzene hydrogenation reaction for poly(Sty-DVB) supported catalysts in methanol at atmospheric pressure.

[Nitrobenzene], (mol/lit) = 9.715×10^{-3}

Qty. of methanol used (ml) = 10

Catalyst	Ru present (mol/lit $\times 10^5$)	Temperature (°C)	Rate of Reaction (mol/min $\times 10^2$)	Activation energy (kcal/mol)
3PRu(III)TMDA	1.413	30	1.15	
		35	1.22	
		40	1.36	2.58
		45	1.61	
		50	1.79	
10PRu(III)TMDA	1.388	30	1.40	
		35	1.56	3.24
		40	1.91	
		45	2.33	
		50	2.72	
30PRu(III)TMDA	1.385	30	1.08	
		35	1.23	3.43
		40	1.46	
		45	1.74	
		50	2.06	

Table-4.5.9

Effect of temperature on nitrobenzene hydrogenation reaction for Zeo-Karb 226 supported catalysts in methanol at atmospheric pressure.

[Nitrobenzene] (mol/lit) = 9.715×10^{-3}

Qty. of methanol used (ml) = 10

Catalyst	Ru present (mol/lit $\times 10^5$)	Temperature (°C)	Rate of Reaction (ml/lit $\times 10^2$)	Activation energy (kcal/mol)
2.5ZKRu(III)TMDA	2.775	30	1.25	
		35	1.58	
		40	2.10	5.49
		45	3.04	
		50	3.81	
20ZKRu(III)TMDA	1.385	30	1.05	
		35	1.22	3.05
		40	1.45	
		45	1.65	
		50	1.97	

Table-4.5.10

Effect of temperature on nitrobenzene hydrogenation reaction for homogeneous catalyst in methanol at atmospheric pressure.

[Nitrobenzene], (mol/lit) = 9.715×10^{3}

Qty. of methanol used (ml) = 10

Catalyst	Ru present (mol/lit $\times 10^{4}$)	Temperature (°C)	Rate of Reaction (ml/min $\times 10^{2}$)	Activation energy (kcal/mol)
$[RuTMDACl_2]Cl$	3.25	30	0.89	
		35	1.11	
		40	1.36	4.13
		45	1.69	
		50	2.09	

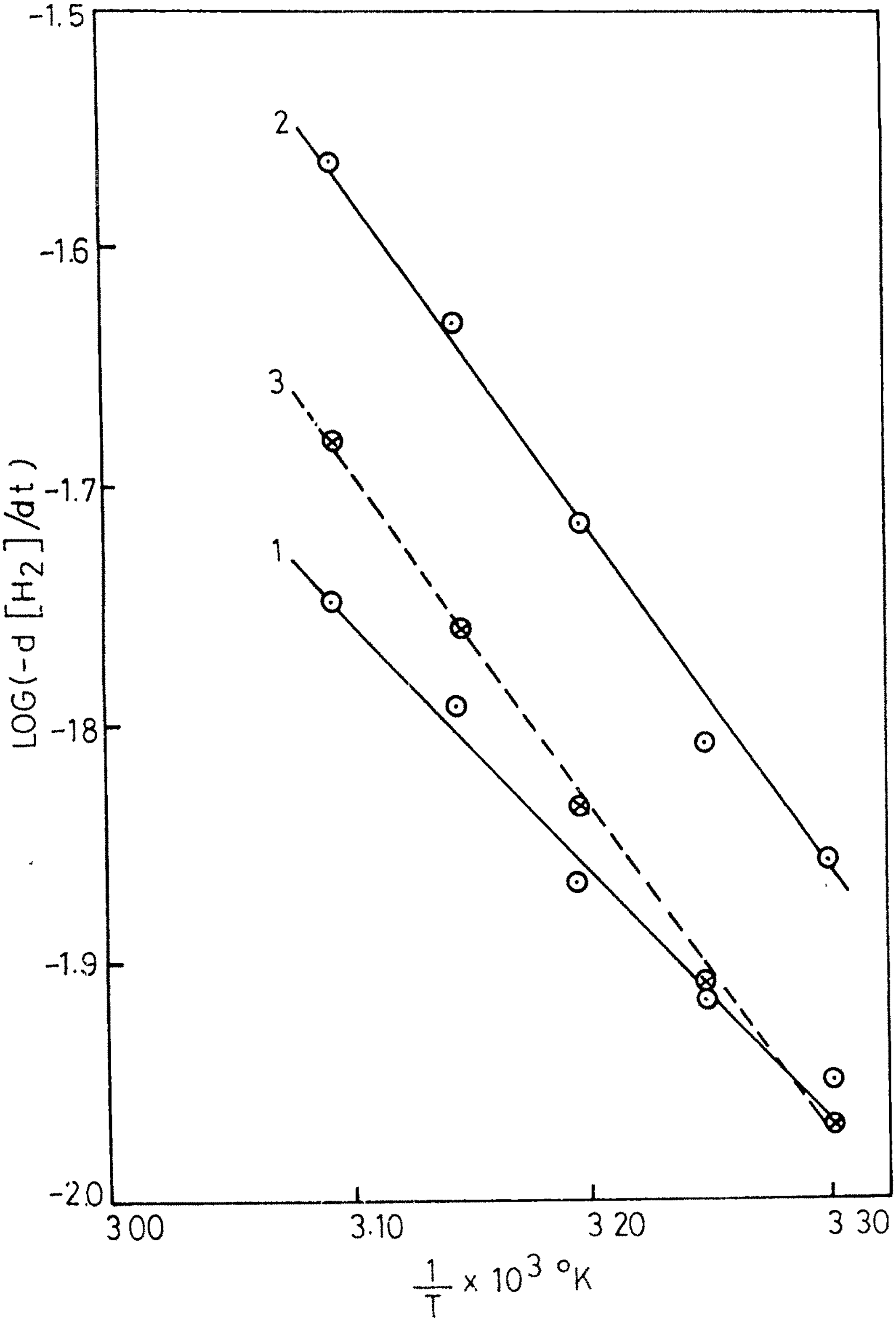

Figure - 4.5.5 Arrhenius plot for catalyst 1) 3PRu(III)TMDA 2) 10PRu(III)TMDA 3) 30P Ru(III)TMDA

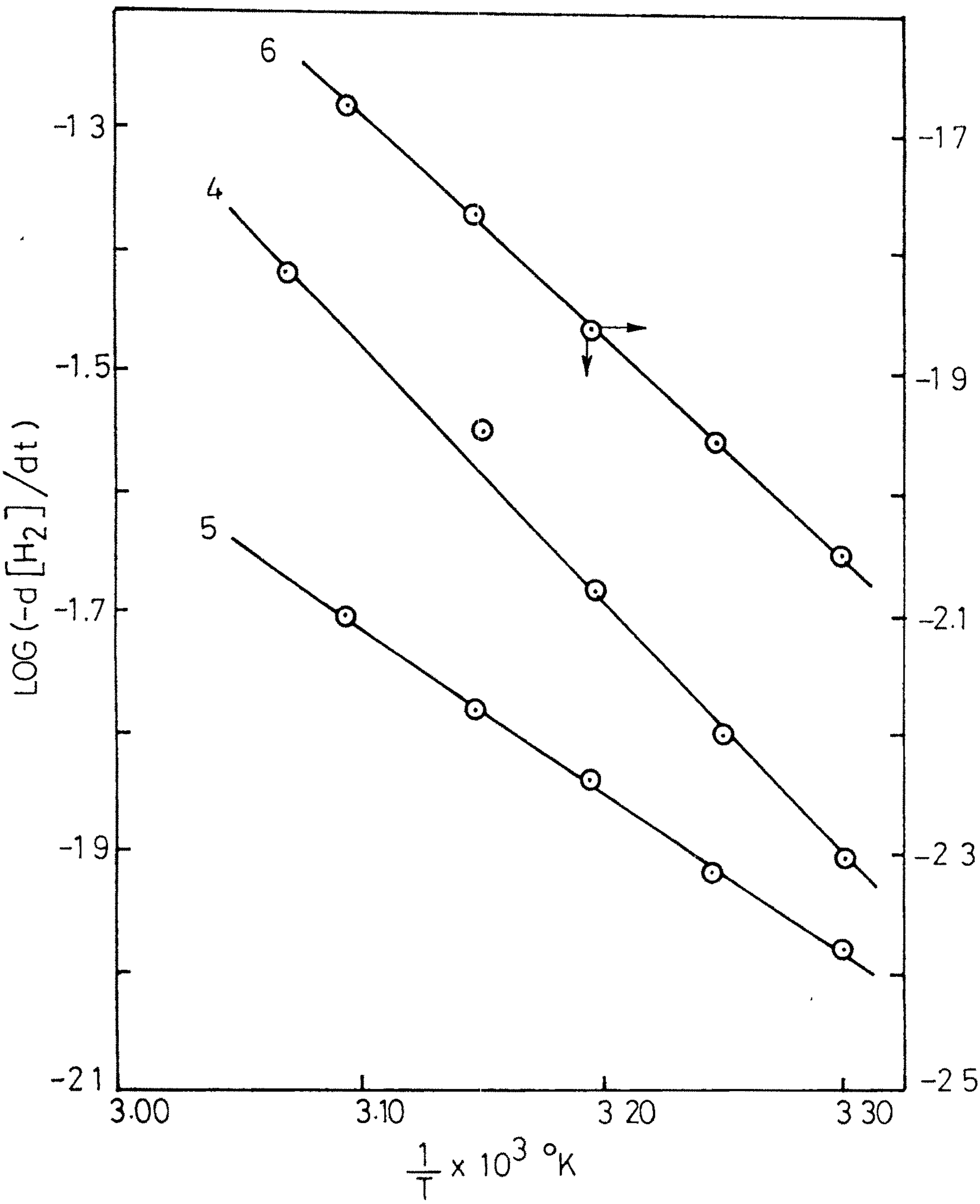

Figure - 4.5.6 Arrhenius plot for the catalysts 4) 2.5ZKRu(III)TMDA

5) 20ZKRu(III)TMDA 6) $[RuTMDACl_2]Cl$

0.89×10^{-2} to 2.09×10^{-2} ml/min when the temperature is raised from 30 to 50°C. On the basis of the above results, it may be concluded that the hydrogenation of nitrobenzene is faster in the case of polymer supported ruthenium complex catalysts.

4.5.4 Effect of solvents

The influence of five different solvents (methanol, ethanol, dioxane, THF and benzene) on the rate of reaction has been studied. An increase in the rate was observed when the nature of the solvent is changed from non-polar to polar. In the case of benzene, the rate was found to be 1.00 $\times 10^{-2}$ ml/min while in the case of methanol, it was 1.27×10^{-2} ml/min with 3PRu(III)TMDA catalyst. In the case of 2.5ZKRu(III)TMDA catalyst, the rate increases from 1.12×10^{-2} ml/min to 1.91×10^{-2} ml/min as solvent changes from benzene to methanol. Similar results for other systems are given in Tables 4.5.11 to 4.5.13

Plots of solvent strength ε_o Vs. initial rate (Figure 4.5.7 and 4.5.8) gave S-shaped curves (98,99) for all catalysts. From which it is evident that higher yield of aniline is obtained in methanol, ethanol and dioxane than in solvent of low polarity like THF and benzene.

Figures 4.5.9 to 4.5.10 illustrate the influence of amount of hydrogen in methanol for all the catalysts at a constant concentration of the catalyst and the substrate at 35°C. As the amount of reaction medium i.e. methanol, is increased the amount of hydrogen available for the reaction in the liquid phase increases. This is found to influence the rate of hydrogenation of

Table-4.5.11

Solvent dependence of the hydrogenation of nitrobenzene by poly(Sty-DVB) supported catalysts at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of solvent used (ml) = 25

[Nitrobenzene], (mol/lit) = 3.886 x10^{-3}

Catalyst	Ru present (mol/lit x10^5)	Solvent	Rate of reaction (ml/min x10^2)
3PRu(III)TMDA	0.565	Methanol	1.27
		Ethanol	1.23
		Dioxane	1.19
		THF	1.08
		Benzene	1.00
10PRu(III)TMDA	0.555	Methanol	1.79
		Ethanol	1.64
		Dioxane	1.58
		THF	1.43
		Benzene	1.13
30PRu(III)TMDA	0.554	Methanol	1.51
		Ethanol	1.41
		Dioxane	1.37
		THF	1.34
		Benzene	1.21

Table-4.5.12

Solvent dependence of the hydrogenation of nitrobenzene by Zeo-Karb 226 support catalysts at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of solvent used (ml) = 25

[Nitrobenzene], (mol/lit) = 3.886×10^{-3}

Catalyst	Ru present (mol/lit $\times 10^5$)	Solvent	Rate of Reaction (ml/min $\times 10^2$)
2.5ZKRu(III)TMDA	1.110	Methanol	1.91
		Ethanol	1.70
		Dioxane	1.63
		THF	1.25
		Benzene	1.12
20ZKRu(III)TMDA	0.554	Methanol	1.45
		Ethanol	1.48
		Dioxane	1.30
		THF	1.28
		Benzene	0.86

Table-4.5.13

Solvent dependence of the hydrogenation of nitrobenzene by homogeneous catalysts at atmospheric pressure.

Reaction temperature (°C) = 35

Qty. of solvent used (ml) = 25

[Nitrobenzene], (mol/lit) = 3.886×10^{-3}

Catalyst	Ru present (mol/lit $\times 10^{4}$)	Solvent	Rate of Reation (ml/min $\times 10^{2}$)
$[RuTMDACl_2]Cl$	1.30	Methanol	1.35
		Ethanol	1.15
		Dioxane	1.11
		THF	1.00
		Benzene	0.52

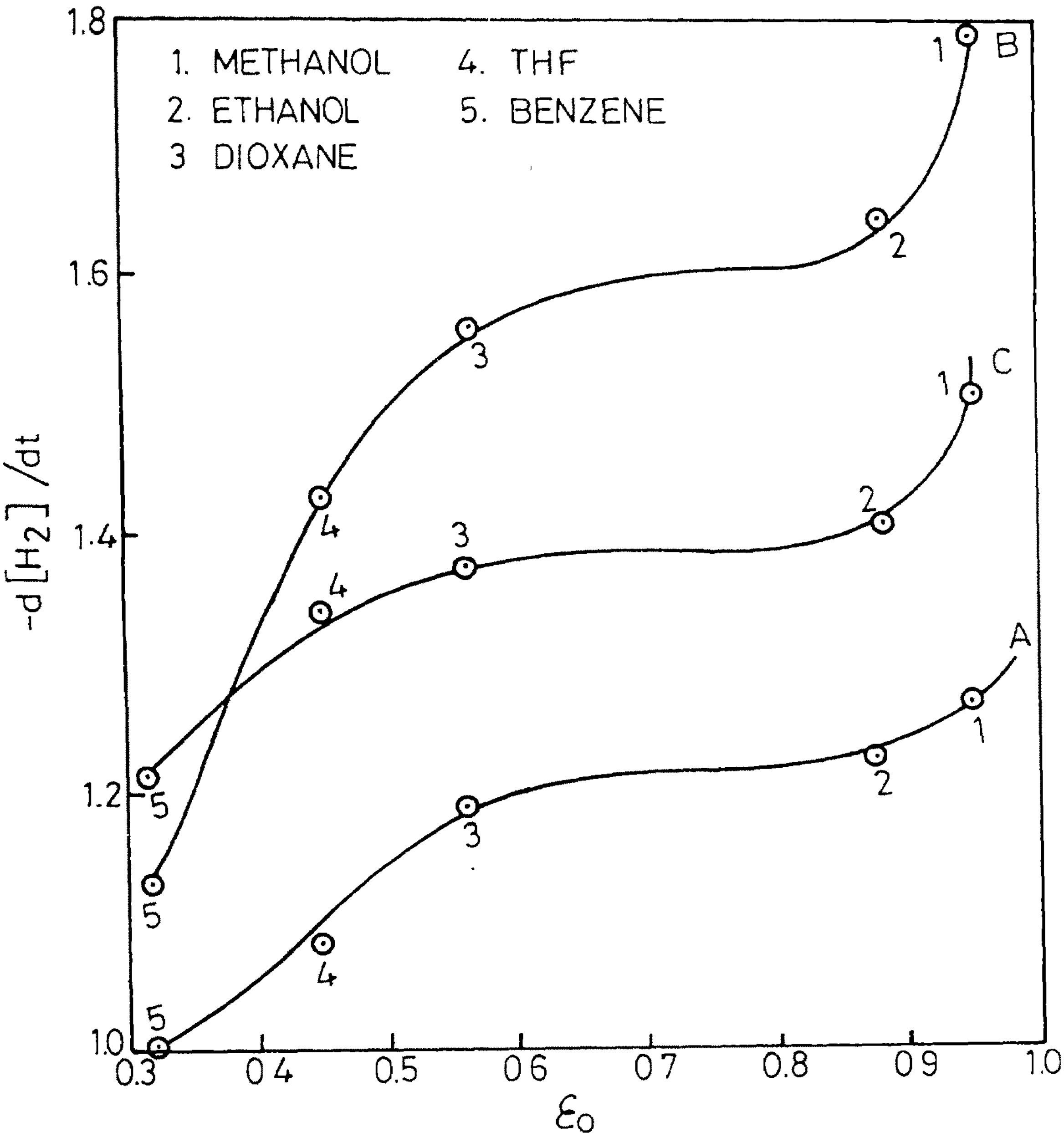

Figure - 4.5.7 Solvent dependence of the hydrogenation of nitrobenzene for catalysts A) 3PRu(III)TMDA B) 10PRu(III)TMDA C) 30PRu(III)TMDA

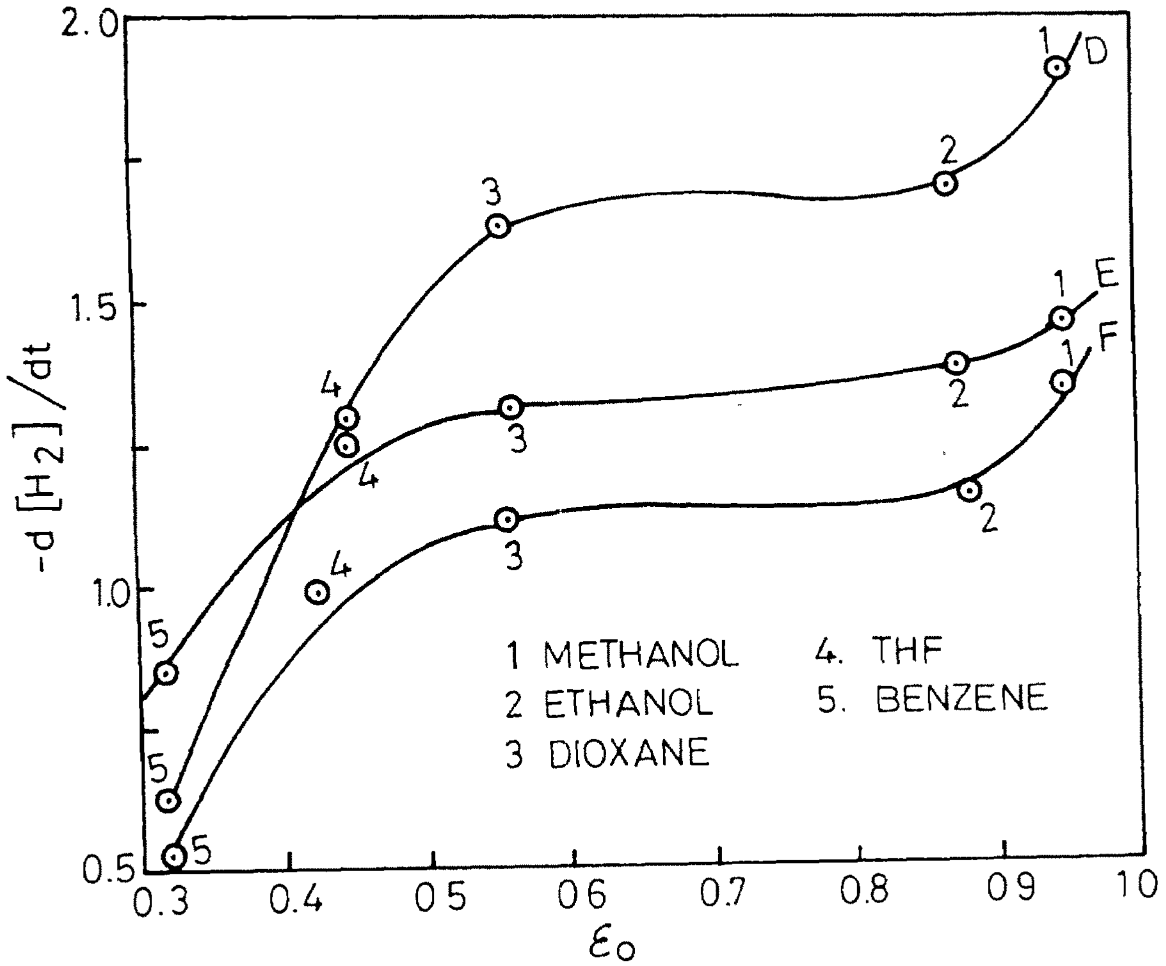

Figure - 4.5.8 Solvent dependence of the hydrogenation of nitrobenzene for catalysts D) 2.5ZK Ru(III)TMDA E) 2 0ZKRu(III)TMDA F) [RuTMDACl$_2$]Cl

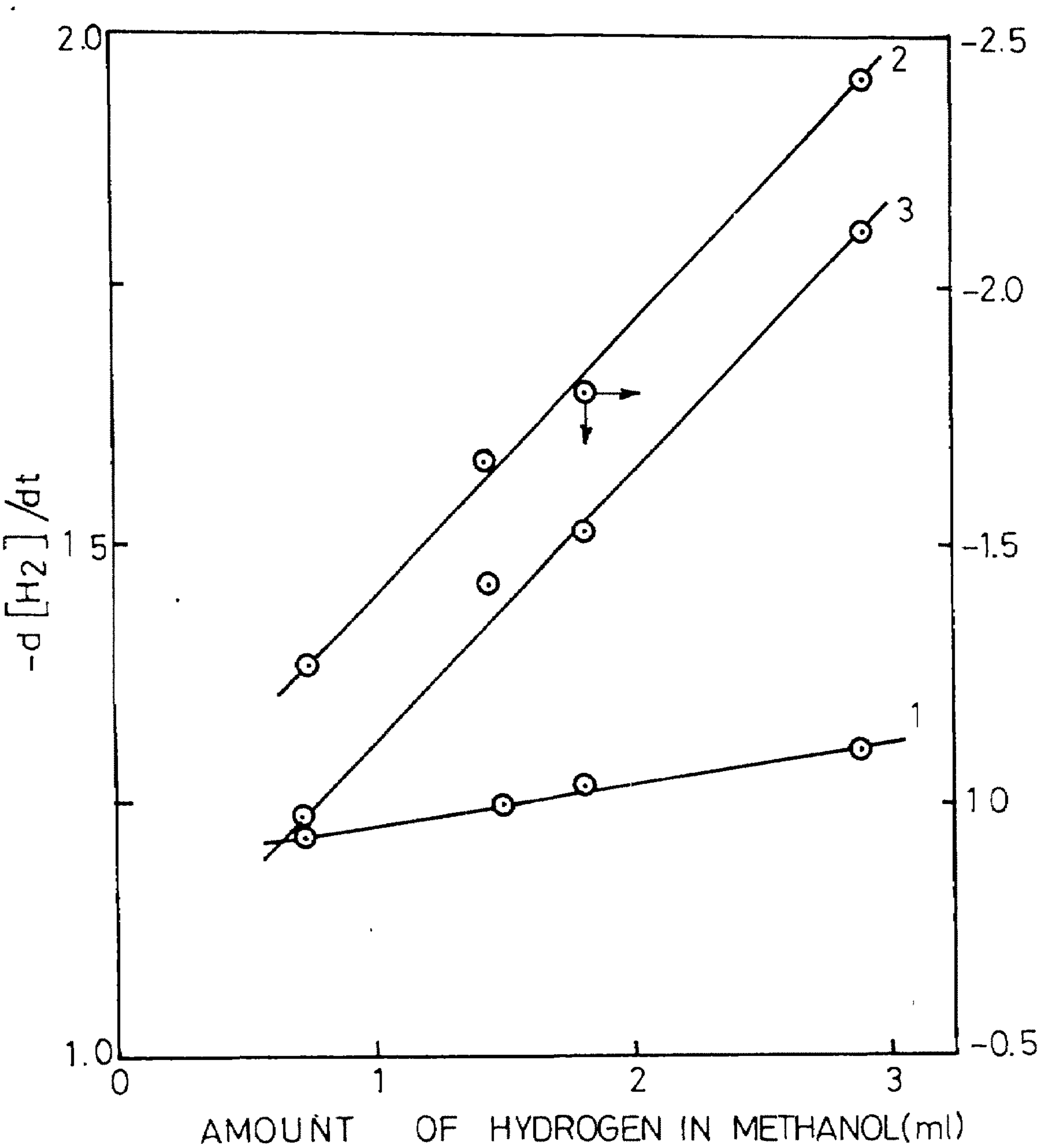

Figure - 4.5.9 Influence of amount of hydrogen on the rate of hydrogenation of nitrobenzene for catalysts

1) 3PRu(III)TMDA 2) 10PRu(III)TMDA

3) 30PRu(III)TMDA

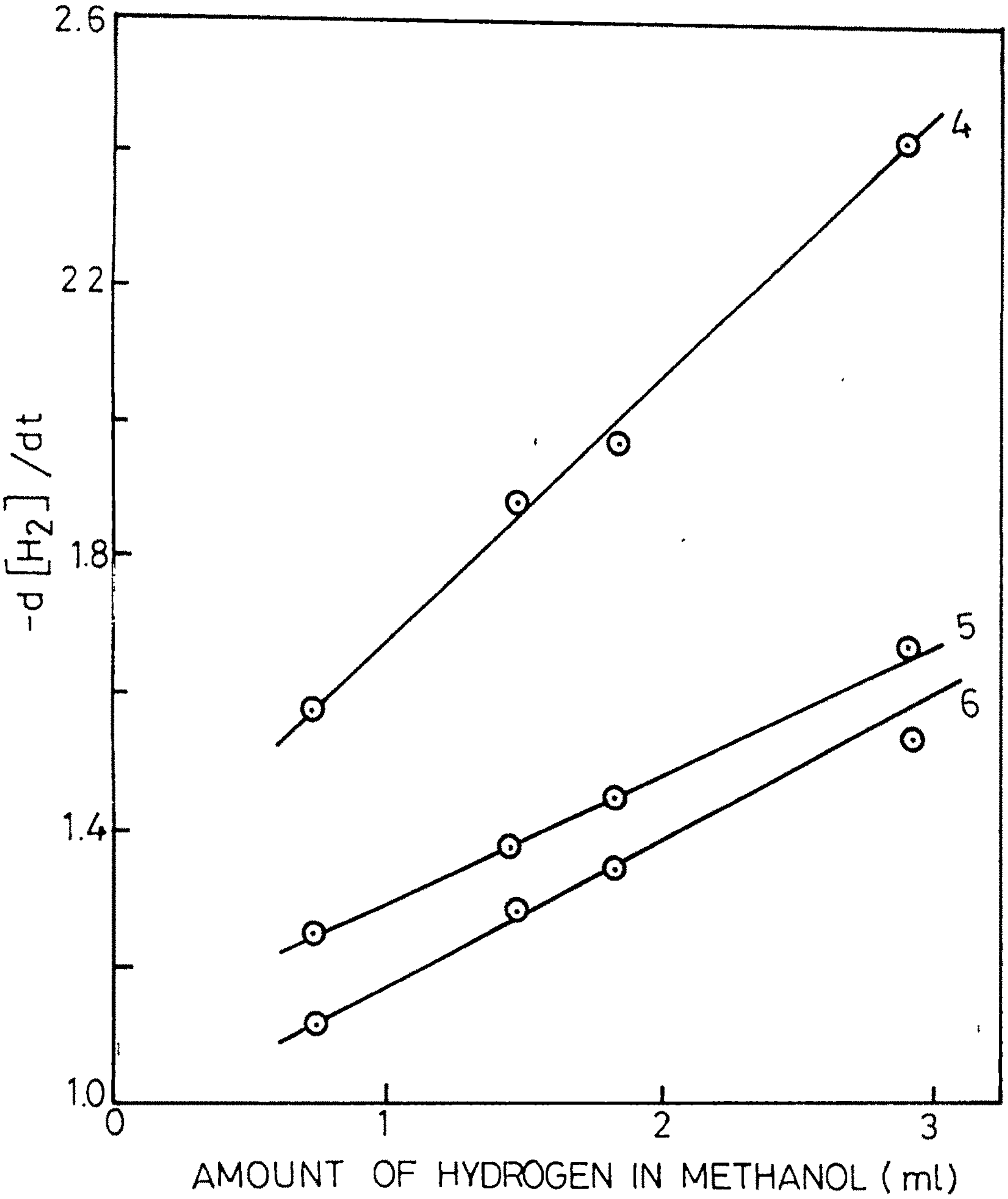

Figure - 4.5.10 Influence of amount of hydrogen on the rate of hydrogenation of nitrobenzene for catalysts

4) 2.5ZKRu(III)TMDA 5) 20ZKRu(III)TMDA

6) [RuTMDACl_2]Cl

nitrobenzene as evident from the data given in Tables 4.5.14 to 4.5.16, where the volume of methanol was increased from 10 to 40 ml keeping the amount of nitrobenzene and catalyst constant. An enhanced rate of the reaction was observed on increasing the amount of hydrogen in methanol. For example, the rate increased from 1.22×10^{-2} to 1.39×10^{-2} ml/min as the volume of methanol is raised from 10 to 40 ml when 3PRu(III)TMDA is used as a catalyst. Similar results have also been observed in the case of Zeo-Karb 226 supported ruthenium complexes.

In case of $[RuTMDACl_2]Cl$ used as a homogeneous catalyst, the rate of the reaction obtained was from 1.11×10^{-2} to 1.54×10^{-2} ml/min though a large quantity of Ru(III) is present in the system (i.e. 13.0×10^{-4} mol/lit). It indicates that even at various amount of hydrogen in methanol polymer supported metal complex catalysts have a higher activity then the homogeneous counterparts.

Table-4.5.14

Effect of amount of hydrogen in methanol on the rate of hydrogenation for poly(Sty-DVB) supported catalysts at atmospheric pressure.

Reaction temperature (°C) = 35

Catalyst	[Nitrobenzene] (mol/lit x10^3)	Ru present (mol/lit x10^5)	Qty.of methanol (ml)	Rate of Reaction (ml/min x10^2)
3PRu(III)TMDA	3.886	0.565	10	1.22
			20	1.25
			25	1.27
			40	1.39
10PRu(III)TMDA	3.886	0.555	10	1.26
			20	1.66
			25	1.79
			40	2.41
30PRu(III)TMDA	3.886	0.554	10	1.23
			20	1.46
			25	1.51
			40	1.80

Table-4.5.15

Effect of amount of hydrogen in methanol on the rate of hydrogenation for Zeo-Karb 226 supported catalysts at atmospheric pressure.

Reaction temperature (°C) = 35

Catalyst	[Nitrobenzene] (mol/lit x10^3)	Ru present (mol/lit x10^5)	Qty. of Methanol (ml)	Rate of Reaction (ml/min x10^2)
2.5ZKRu(III)TMDA	3.886	1.110	10	1.58
			20	1.89
			25	1.98
			40	2.43
20ZKRu(III)TMDA	3.886	0.554	10	1.25
			20	1.38
			25	1.45
			40	1.68

Table-4.5.16

Effect of amount of hydrogen in methanol on the rate of hydrogenation for homogeneous catalyst at atmospheric pressure.

Reaction temperature (°C) = 35

Catalyst	[Nitrobenzene] (mol/lit x 10^3)	Ru present (mol/lit x 10^4)	Qty. of Methanol (ml)	Rate of Reaction (ml/min x 10^2)
$[RuTMDACl_2]Cl$	3.886	1.30	10	1.11
			20	1.29
			25	1.35
			40	1.54

4.5.5 Life cycle of catalysts

For the study of the life cycle of the catalyst, the experiment was carried out at 35°C for about 10 hours. In each cycle 10 μl of the substrate was injected. Every time after the completion of the reaction, 60 minutes were allowed to lapse before the next injection was made. The rate of hydrogenation of nitrobenzene was measured as function of time for both the used and the fresh catalysts. The results are summarized in Tables 4.5.17 and 4.5.18.

It is seen from the results that in case of poly(Sty-DVB) supported catalyst, the maximum rate of reaction is maintained for about 4 hours after which the rate was found to decrease slowly. After the metal estimation, a loss of 54% of the metal complex was observed from the polymer at the end of the reaction.

In the case of Zeo-Karb 226 supported catalysts, the maximum rate of reaction is maintained for about 3 hours after that the rate decreases slowly; where 60-65% loss of the metal was observed at the end of the reaction.

The loss in activity may be due to low mechanical strength of the polymer support and also due to the polymer-bound complexes and polymer-bound non-coordinated ligand molecules leaching out in solution and forming stable complexes in solution which are ineffective in the catalysing reaction.

Table-4.5.17

Life cycle study for poly(Sty-DVB) supported catalysts

Reaction temperature (°C) = 35 Qty. of methanol used (ml) = 25

Fresh catalyst: Time (min)	Fresh catalyst: Rate of Reaction (ml/ min x10^2)	Used catalyst: Time (min)	Used catalyst: Rate of reaction (ml/min x10^2)
	30Ru(III) TMDA[a]		
80	2.56	80	2.40
220	2.56	230	2.14
370	2.20	390	1.94
540	1.90	570	1.57
	10PRu(III)TMDA[b]		
50	4.27	50	4.26
160	4.27	170	3.96
280	3.94	300	2.80
410	3.21	440	2.50
550	2.45	580	2.00
	30PRu(III)TMDA[c]		
60	2.84	60	2.66
180	2.84	190	2.50
310	2.59	330	2.12
450	2.17	480	1.79

a Amount of catalyst 0.491gm (3.44 x10^{-5} Ru mol/lit)
Total time on stream 9.00 h (9.30 h)*

b Amount of catalyst 0.5 gm (5.442 x 10^{-5} Ru mol/lit)
Total time on stream 9.10 h (9.40 h)*

c Amount of catalyst 0.785 gm (5.43 x 10^{-5} Ru mol/lit)
Total time on stream 7.30 h (8.0 h)*

* Values given in parentheses indicate data for used catalyst.

Table-4.5.18

Life cycle study for Zeo- Karb226 supported catalysts.

Reaction temperature (°C) = 35

Qty. of methanol used (ml) = 25

Fresh catalyst		Used catalyst	
Time (min)	Rate of reaction ($ml/min \times 10^2$)	Time (min)	Rate of reaction ($ml/min \times 10^2$)
	2.5ZKRu(III)TMDA[d]		
45	4.71	50	4.44
150	4.71	175	3.90
270	3.94	315	2.18
420	2.35	-	-
	20ZKRu(III)TMDA[e]		
60	3.02	60	2. 5
180	3.02	190	2.75
310	2.58	340	1.55
460	1.88	-	-

d Amount of catalyst 0.5775 gm (7.771×10^{-5} Ru mol/lit)
Total time on stream 5.25 h (5.20 h)*

e Amount of catalyst 1.38 gm (7.728×10^{-5} Ru mol/lit)
Total time of stream 7.40 h (5.40 h)*

* Values given in parentheses indicate data for used catalyst.

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