CHAPTER 5
KINETICS OF OXIDATION

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5.1 Kinetics of oxidation of cyclohexane by polymer supported Ru (III) and Pd (II) complex catalysts :

5.1.1 Introduction

The oxidation of hydrocarbons is an extremely important commercial reaction for functionalising hydrocarbons to yield products that are either important in themselves or are intermediates en route to other chemicals (1). An explosive growth has been provided in the oxidation reactions using homogeneous catalysts. The activity of the transition metal ions was found to be less as such, while an enhanced activity was observed when the metal ions were either supported on a solid or in the complex form (1).

Platinum group metal complexes have received much attention in recent years because of the structural variety and their role in catalytic oxidation reactions (2, 3). These complexes were found suitable as homogeneous catalysts for the oxidation of hydrocarbons. Recently several Ruthenium (III) complexes of aminopoly carboxylic acids (4), schiff base complexes (5,6) have been used for catalytic oxidation of hydrocarbons in the presence of different oxidants as iodosylbenzene, molecular oxygen as well as hydrogen peroxide. A variety of synthetic metalloporphyrins have been synthesised and used as catalysts in the oxidation of hydrocarbons (7,9). The schiff base complexes of transition metal ions were found to be effective catalysts in the hydroxylation of alkanes and expoxidation of olefins (5,10

- 13). Oxidation of olefins with molecular oxygen has been carried out using Rhodium (III) as a catalyst (14). Group VIII metal side bonded dioxygen complexes have been shown to be reactive towards a variety of organic and inorganic substrates (15 - 18). The palladium dioxygen complex [Pd (P $Ph_3)_2$ (O_2)], has been used for the deoximation of a variety of ketoximes in benzene at 25° C (19).

Oxygenation reactions of saturated and unsaturated substrates by molecular oxygen has been studied by Taqui Khan et al. using ruthenium - EDTA complex in homogeneous system (20). Kinetics of ruthenium (III) catalysed oxidation of cyclohexanol by bromamine - T in HCl was carried out by Singh et al. (21). Takeshi et al. have studied Iron (II) and Ruthenium (III) catalysed oxidation of alkanes with molecular oxygen in the presence of aldehydes and acids (22). Palladium (II) in liquid - phase was used for oxidation of hydrogen peroxide by Zubovich and Co-workers. (23). Selective functionalization of hydrocarbons like cyclohexane, toluene and cyclohexanol have been studied using oxo-ruthenium complexes (24). Manganese (III) amide complexes were used for alkene epoxidation in presence of iodosobenzene (25). Minora et al. have studied palladium (II) catalysed oxygenation of carbon - carbon double bonds by molecular oxygen (26). Enantioselective oxidation of olefins with molecular oxygen and aldehyde catalyzed by optically active Mn (III) complexes has been carried out (27).

However the major disadvantage of homogeneous catalysts is the problem of separating the very expensive catalysts from the products at the end of the reaction. These are thermally unstable and more prone to poisoning by oxygen and moisture. Homogeneous catalysts may also produce corrosion of the reactor walls when used in a commercial scale.

Several references are also available where metal ions supported on either to inorganic oxides or organic polymers have been used as catalysts for oxidation reactions. Selective oxidation of cyclohexane over a titanium silicate molecular sieve has been studied by Sivasankar et al. (28). Bowers and co-workers have studied the oxidation of olefins using zeolite encapsulated Mn (II) complex (29). Iron (III) prorphyrins was used for hydroxylation of cyclohexane with iodosobenzene (30). Effect of a clay support on the catalytic expoxidation of olefins in presence of iodosobenzene of Mn (III) shiff base complex has been seen by Dixit and co-workers (31). Olefin epoxidation and alkane hydroxylation catalyzed by sulphonated Manganese and Iron porphyrins supported on cationic ion -exchange resins were studied by Meunier et al. (32). Co-oxidation of propionaldehyde and cyclohexene catalysed by Fe (II) and Co (III) ions anchored on resins was studied by Chuan et al. (33). Lei and Wang have studied the oxidation of cyclohexene using polymer bound 2 2' bipyridine copper complex. (34).

Cyclohexanone by far the most important cyclic ketone is produced by air oxidation of cyclohexane (35) as well as by hydrogenation of phenol, followed by dehydrogenation of the resulting cyclohexanol. (36). The principal use of cyclohexanone is in the manufacture of γ - caprolactum (by re-arrangement of its oxime) for nylon - 6. A mixture of crude cyclohexanone - cyclohexanol is used to make adipic acid for nylon - 6, 6 (37). It is also used as a solvent for vinyl resins, polystyrene, ethylcellulose, acrylic resins, dyes, insecticides and especially for poly (vinyl chloride) and its copolymers (35).

The oxidation of cyclohexane has been carried out using homogeneous complexes and metal ions supported on inorganic oxides (20, 24, 28). Drago et al., have studied the oxidation of 2, 6 dimethyl phenol using polymer bound cobalt (II) complexes. (38) However the main disadvantage of the above mentioned supported catalysts are their less specificity as well as the considerable leaching of the metal ions from the support during reaction time. (39) Chelated metal complexes are found to be stable and the leaching of the metal ions was found to be negligible even after few cycles of the experiments. In the present investigation, the synthesised polymer bound chelated metal complexes of palladium (II) and ruthenium (III) have been used in order to study the kinetics of oxidation of cyclohexane with molecular oxygen under mild operating conditions.

5.2 Experimental

5.2.1 Measurement of catalytic activity for oxidation reactions :

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

5.2.2 Analysis of kinetic data :

The kinetic data for the oxidation reaction were obtained in a kinetic regime of a stirring speed of 650 rpm at 35^{o} C. The stoichiometry of the reaction was checked by carrying out a few experiments at constant temperature and oxygen pressure at different concentrations of cyclohexane. The initial rate data obtained from oxygen uptake measurements is used to evaluate the kinetic parameters. The products were analysed using a gas chromatograph.

In each kinetic run the uptake of oxygen was measured as a function of time. The initial rates of oxidation were calculated from the slope of the plots of volume of oxygen uptake against time. The influence on the rate of various parameters such as catalyst and substrate concentration, temperature of the system, quantity of solvent used and also the effect of various solvents has been investigated. From the analysis of the rate data, the order of the reaction with respect to the substrate and catalyst concentration have been determined.

5.3 Results and discussion

5.3.1 Effect of concentration of cyclohexane :

The influence of cyclohexane concentration on the rate of oxidation for different catalysts have been studied and an enhancement in the rate was observed with an increase in the concentration of substrate. The results are summarized in Tables 5.3.1 to 5.3.3. The rate of oxidation of cyclohexane increases from 2.58×10^{-2} to 3.65×10^{-2} ml/min as the concentration of cyclohexane varies from 5.94×10^{-3} to 23.9×10^{-3} mol/lit. at 35°C using 15PRu(III)DAP (Ru concentration is 3.22×10^{-5} mol/lit) catalyst. The variation of initial rate was found to be from 2.10×10^{-2} to 5.00×10^{-2} ml/min. for 15PPd(II)DAP catalyst (Pd content 3.66×10^{-5} mol/lit) at 35°C for same concentration of cyclohexane. Similar results were observed in the case of the complex catalysts supported on XAD - 8.

The plot of log (initial rate) against log (Cyclohexane) at fixed concentration of the catalyst was found to be linear (Figures 5.3.1 and 5.3.2) and the order of reaction calculated from the slopes of the above plots was found to be fractional (Table 5.3.7) with respect to cyclohexane concentration.

In the case of homogeneous system inspite of using larger amount of Ru (III) / Pd (II) to catalyse the reaction a lower rate is observed as compared to heterogenised - homogeneous system. Thus at a constant concentration of cyclohexane (i.e, 11.8 x 10^{-3} mol/lit) at 35° C, the rate of reaction was found to be 2.01 x 10^{-2} ml/min with $[RuDAPCl_2]Cl$, (Ru concentration is 1.60 x 10^{-3} mol/lit) catalyst and by the use of $[PdDAP]Cl_2$, (Pd concentration 1.80 x 10^{-3} mol/lit) the rate was observed to be 2.69 x 10^{-2} ml/min. (Table 5.3.3). It is evident from the above results that heterogenising a homogeneous catalyst on a polymeric support has higher activity than its homogeneous counterparts. Similar results have been reported by Verlaan et al. in the oxidation of 2, 6 dimethylphenol using copper (II) supported on a copolymer of styrene and 4 - vinyl pyridine (40).

Table 5.3.1

Effect of cyclohexane concentration on the rate of oxidation for polymer supported catalyst at atmospheric pressure.

Reaction temperature = 35° C
Quantity of methanol used = 20 ml.

Catalyst	Ru/Pd Present (mol/lit)	(Cyclohexane) (mol/litx10^3)	Reaction rate (ml/minx10^2)
15PRu(III)DAP	3.22×10^{-5}	5.94	2.58
		11.80	2.69
		14.80	3.05
		17.80	3.24
		23.00	3.65
15PPd(II)DAP	3.66×10^{-5}	5.94	2.10
		11.80	3.53
		14.80	4.00
		17.80	4.57
		23.00	5.00

Table 5.3.2

Effect of cyclohexane concentration on the rate of oxidation for polymer supported catalysts at atmospheric pressure.

Reaction temperature = 35° C
Qty. of methanol used = 20 ml.

Catalyst	Ru/Pd Present (mol/litx10^6	(Cyclohexane) (mol/litx10^3)	Reaction rate (ml/minx10^2)
8XRu(III)DAP	1.55	5.94	3.06
		11.80	3.36
		14.80	3.72
		17.80	4.10
		23.00	4.50
8XPd(II)DAP	1.97	5.94	3.02
		11.80	3.82
		14.80	4.17
		17.80	4.29
		23.00	4.40

Table 5.3.3

Effect of cyclohexane concentration on the rate of oxidation for homogeneous catalysts at atmospheric pressure.

Reaction temperature = 35°C
Qty. of methanol used = 20 ml.

Catalyst	Ru/Pd Present (mol/litx10^3)	(Cyclohexane) (mol/litx10^3)	Reaction rate (ml/minx10^2)
[RuDAPCl$_2$]Cl	1.60	5.94	2.01
		11.80	3.16
		14.80	3.34
		17.80	3.50
		23.00	3.98
[PdDAP]Cl$_2$	1.80	5.94	2.69
		11.80	3.01
		14.80	3.19
		17.80	3.34
		23.00	3.54

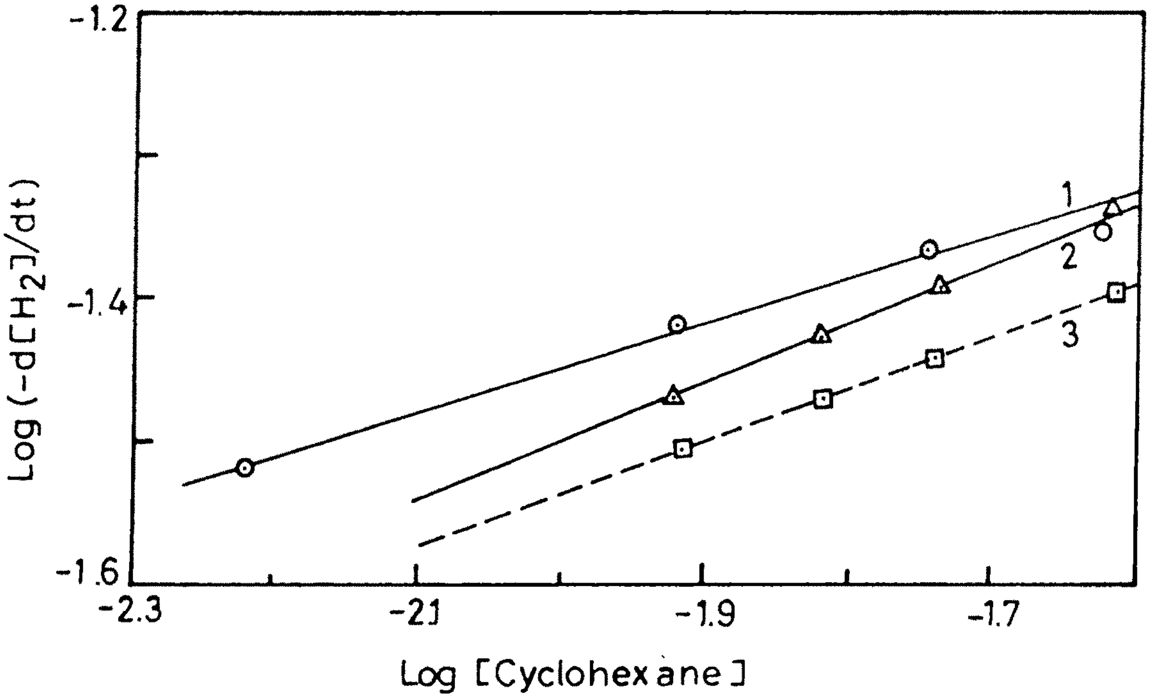


Fig. 5.3.1 Plot of log ($-d[H_2]/dt$) vs log[cyclohexane] for catalysts 1. 8XPd(II)DAP
2. 8XRu(III)DAP 3. $[RuDAPCl_2]Cl$

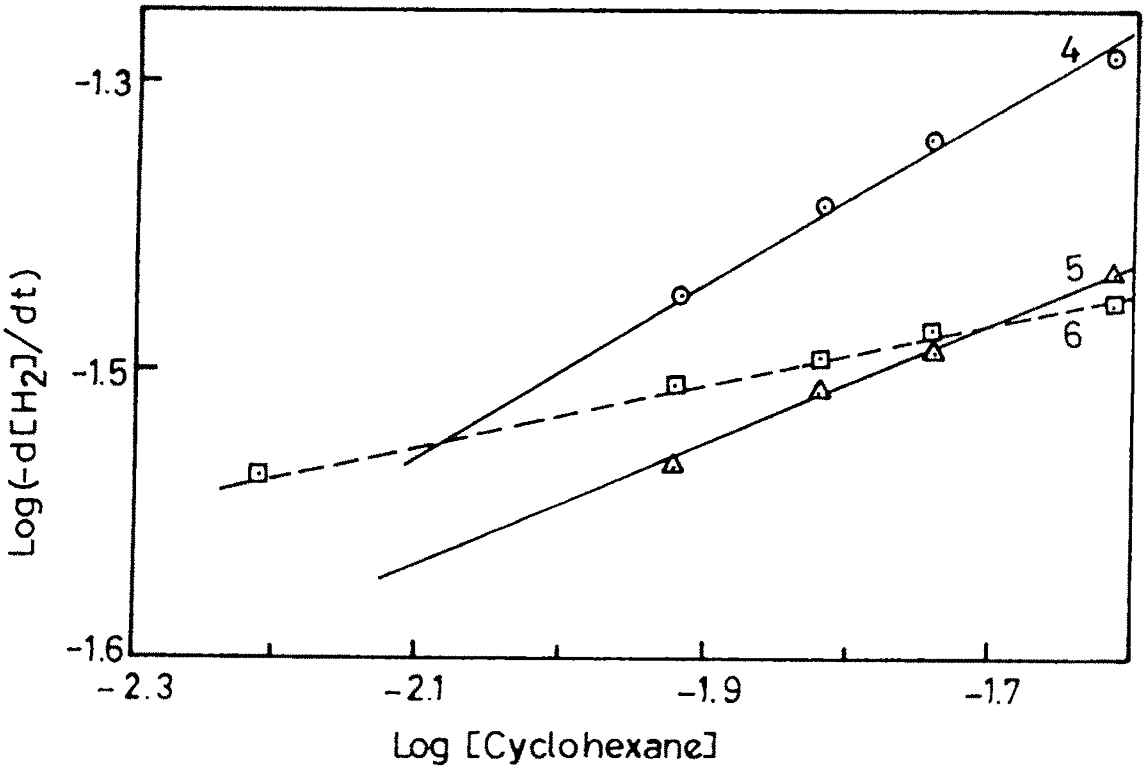


Fig. 5.3.2 Plot of log ($-d[H_2]/dt$) vs log [cyclohexane] for
4. 15PPd(II)DAP 5. 15PRu(III)DAP 6. $[PdDAP]Cl_2$

5.3.2 **Influence of catalyst concentration :**

The influence of the catalyst concentration on the rate of oxidation of cyclohexane for different catalysts has been investigated. An incerease in the rate of oxidation was observed as the concentration of Ru (III) and Pd (II) are increased on the surface of the polymer. The results are summarized in Tables 5.3.4 to 5.3.6. Thus an enhanced rate of oxidation of cyclohexane was observed from 2.69×10^{-2} to 4.64×10^{-2} ml/min as the concentration of Ru (III) varies from 1.61×10^{-5} to 6.43×10^{-5} mol/lit. in the case of 15 P Ru(III)DAP catalyst at 35°C at a fixed concentration of cyclohexane (11.8×10^{-3} mol/lit). Similarly in the case of 15PPd(II)DAP catalyst the rate was found to increase from 2.88×10^{-2} to 4.82×10^{-2} ml/min when the concentration of the catalyst varies from 1.83×10^{-5} to 7.33×10^{-5} mol/lit of Pd (II) keeping the same concentration of the substrate.

The study was carried out using the homogeneous complexes under similar conditions and an enhanced rate was observed by varying the concentration of the catalysts. The rate of oxidation in the case of [RuDAPCl$_2$]Cl was found to be in the range of 1.90×10^{-2} to 2.34×10^{-2} ml/min as the concentration of catalyst varies from 0.643×10^{-3} to 1.6×10^{-3} mol/lit at 35°C at a constant concentration of cyclohexane (11.8×10^{-3} mol/lit). The other results are given in Table 5.3.6.

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 and was found to be fractional in all cases. (Table 5.3.7 and Figures 5.3.3, 5.3.4). Though the reaction was carried out in a chemically controlled regime, choosing a suitable swelling agent, the observed fractional order might be due to non accessibility of catalytic sites and steric hindrance because of the complex nature of the catalyst.

5.3.3 Effect of temperature :

The effect of temperature on the rate of oxidation of cyclohexane has been studied in the range of 30 - 45°C and the results are summarised in Tables 5.3.8 to 5.3.10. The rate of oxidation was found to increase with an increase in temperature for all the systems. Thus an enhanced rate of oxidation was observed from 2.52×10^{-2} to 3.93×10^{-2} ml/min by using 15PRu(III)DAP catalyst as the temperature is raised from 30 to 45°C. In a similar way by the use of 15PPd(II)DAP catalyst the rate varies from 3.09×10^{-2} to 5.50×10^{-2} ml/min at a constant concentration of the substrate (11.8×10^{-3} mol/lit).

Table 5.3.4

Effect of catalyst concentration in the rate of oxidation for supported catalysts in methanol at atmospheric pressure.

Reaction temperature = 35°C
Qty. of methanol used = 20 mol.

Catalyst	(Cyclohexane) ($mol/lit x 10^3$)	Ru/Pd Present ($mol/lit x 10^5$)	Reaction rate ($ml/min x 10^2$)
15PRu(III)DAP	11.80	1.61	2.69
		3.02	3.11
		4.01	3.85
		4.83	4.25
		6.43	4.64
15PPd(II)DAP	11.80	1.83	2.88
		3.66	3.23
		4.58	3.91
		5.50	4.10
		7.33	4.82

Table 5.3.5

Effect of catalyst concentration in the rate of oxidation for supported catalysts in methanol at atmospheric pressure.

Reaction temperature = 35°C
Qty. of methanol used = 20 ml.

Catalyst	(Cyclohexane) (mol/litx10^3)	Ru/Pd Present (mol/litx10^6)	Reaction rate (ml/minx10^2)
8XRu(III)DAP	11.80	0.776	2.77
		1.550	2.98
		1.940	3.78
		2.330	4.40
		3.100	4.60
8XPd(II)DAP	11.80	0.986	2.69
		1.970	3.11
		2.460	3.85
		2.960	4.29
		3.940	4.64

Table 5.3.6

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

Reaction temperature = 35°C
Qty. of methanol used = 20 ml.

Catalyst	[Cyclohexane] (mol/litx10^3)	Ru/Pd present (mol/litx10^3)	Reaction rate (ml/minx10^2)
$[RuDAPCl_2]Cl$	11.80	0.643	1.90
		0.803	1.99
		0.960	2.08
		1.28	2.18
		1.60	2.34
$[PdDAP]Cl_2$	11.80	0.790	1.99
		0.980	2.22
		1.18	2.45
		1.58	2.75
		1.80	2.95

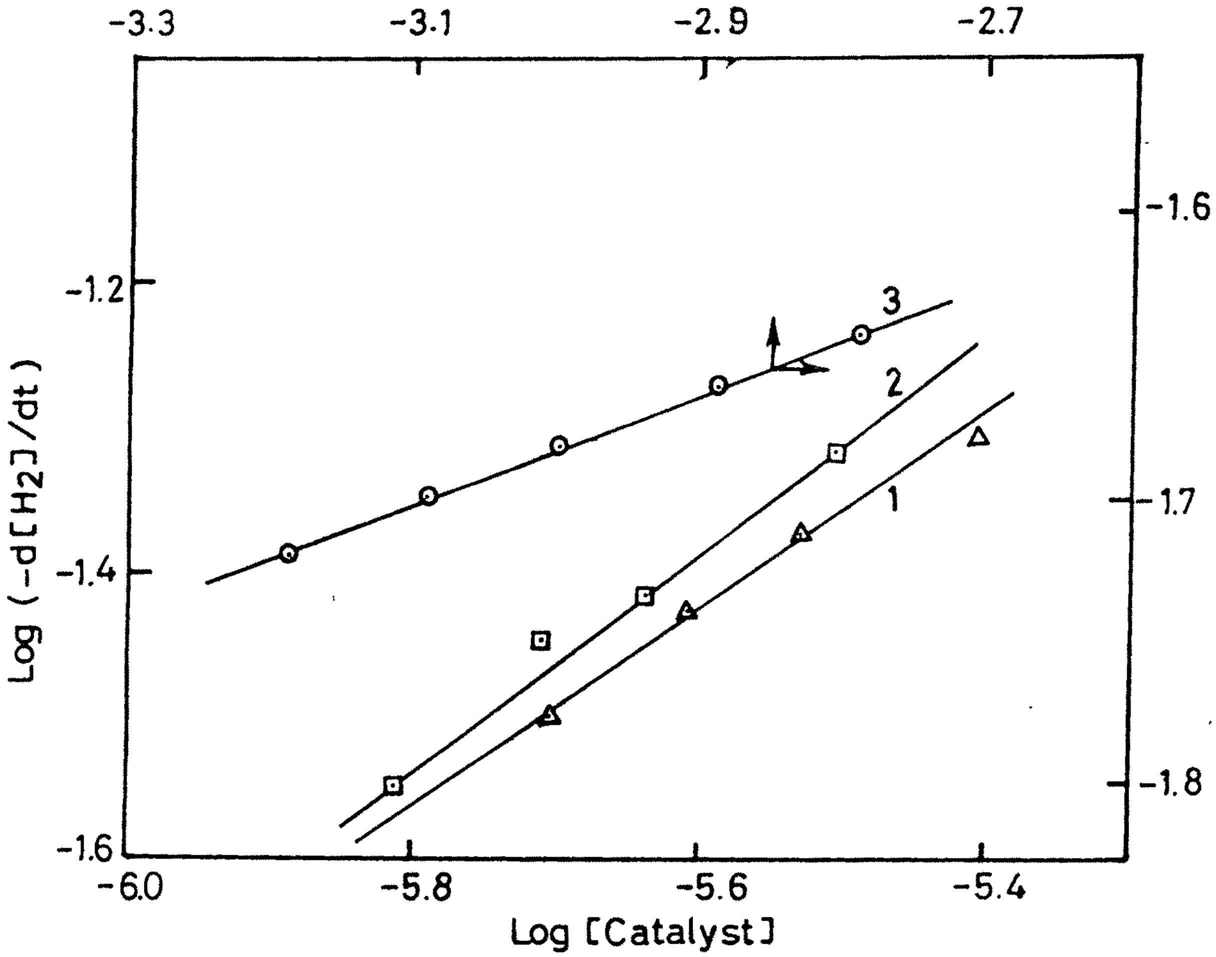


Fig. 5.3.3 Plot of log (-d[H_2]/dt) vs log [catalyst] for catalysts 1. 8XPd(II)DAP 2. 8XRu(III)DAP 3. [RuDAPCl_2]Cl

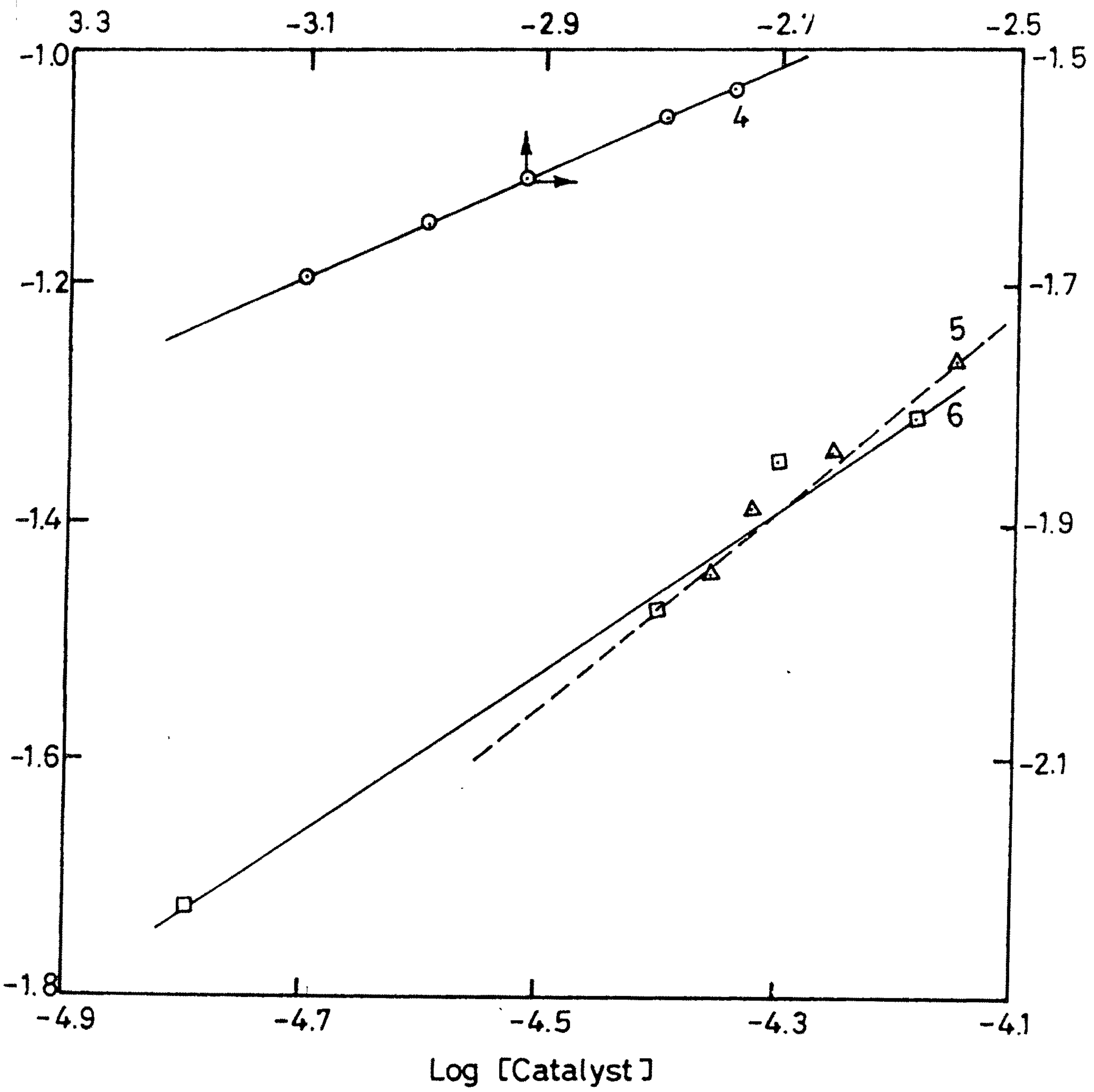


Fig. 5.3.4 Plot of log (-d[H]/dt) vs log [catalyst] for catalysts 4. $[PdDAP]Cl_2$ 5. 15PPd(II)DAP 6. 15PRu(III)DAP

Table 5.3.7

The values of reaction order for various catalysts.

Catalyst	Order of reaction with respect to (Cyclohexane)	Order of reaction with respect to (Catalyst)
15PRu(III)DAP	0.41	0.67
15PPd(II)DAP	0.61	0.80
8XRu(III)DAP	0.41	0.76
8XPd(II)DAP	0.32	0.70
$[RuDAPCl_2]Cl$	0.34	0.30
$[PdDAP]Cl_2$	0.22	0.43

In the case of [RuDAPCl_2]Cl, (Ru content 1.60 x 10^{-3} mol/lit) used as a homogeneous catalyst, the rate was found to be in the range of 2.81 x 10^{-2} to 4.84 x 10^{-2} ml/min by varying the temperature from 30 - 45° C at a constant concentration of cyclohexane (11.8 x 10^{-3} mol/lit); In the case of [PdDAP]Cl_2 (Pd content 1.80 x 10^{-3} mol/lit), the rate increases from 2.70 x 10^{-2} to 4.60 x 10^{-2} ml/min (Table 5.3.10).

The values of energy of activation calculated from the Arrhenius plots were found to be in the range of 6.0 to 9.4 K cal/mol for ruthenium catalysts and 5.0 to 9.0 Kcal/mol for palladium catalysts (figures 5.3.5 and 5.3.6). On the basis of the above data, the synthesized polymer supported complex catalysts have higher catalytic activity than their homogeneous counterparts.

5.3.4 Effect of solvents :

The infleuence of five different solvents (as mentioned in Table 5.3.11) on the rate of oxidation has been studied. The rate of oxidation was found to increase when the nature of solvent is changed from non-polar to polar. In the case of benzene the rate was found to be 8.9 x 10^{-3} ml/min and in the case of methanol it was 3.24 x 10^{-2} min/min with 15PRu(III)DAP catalyst. Similar results were obtained while using other catalysts for the oxidation of cyclohexane. The results are given in Tables 5.3.11 to 5.3.13.

Table 5.3.8

Effect of temperature in the oxidation of cyclohexane using supported catalysts in methanol at atmospheric pressure.

[Cyclohexane], mol/lit) = 11.8×10^{-3}
Qty. of methanol used = 20 mol.

Catalyst	Ru/Pd Present (mol/lit)	Temperature (°C)	Rate of reaction (ml/min $\times 10^2$)	Energy of activation (Kcal/mol)
15PRu(III)DAP	3.22×10^{-5}	30	2.52	
		35	2.66	6.06
		40	3.50	
		45	3.93	
15PPd(II)DAP	3.66×10^{-5}	30	3.09	
		35	3.47	6.00
		40	3.75	
		45	5.50	

Table 5.3.9

Effect of temperature in the oxidation of cyclohexane for supported catalysts in methanol at atmospheric pressure.

[Cyclohexane], (mol/lit) = 11.8×10^{-3}
Qty. of methanol used = 20 ml.

Catalyst	Ru/Pd Present (mol/lit)	Temperature (^{o}C)	Rate of reaction (ml/min x 10^2)	Energy of activation (Kcal/mol)
8XRu(III)DAP	1.55×10^{-6}	30	2.79	
		35	2.90	
		40	3.56	9.36
		45	4.61	
8XPd(II)DAP	1.97×10^{-6}	30	2.94	
		35	3.14	5.05
		40	3.43	
		45	4.22	

Table 5.3.10

Effect of temperature on cyclohexane oxidation for homogeneous catalysts in methanol at atmospheric pressure.

[Cyclohexane] (mol/lit) = 11.8×10^{-3}.
Qty. of methanol used = 20 ml.

Catalyst	Ru/Pd Present (mol/lit)	Temperature (^{o}C)	Rate of reaction (ml/min $\times 10^{2}$)	Energy of activation (Kcal/mol)
$[RuDAPCl_2]Cl$	1.6×10^{-3}	30	2.81	7.04
		35	3.38	
		40	3.98	
		45	4.84	
$[PdDAP]Cl_2$	1.8×10^{-3}	30	2.70	8.99
		35	3.54	
		40	4.20	
		45	4.60	

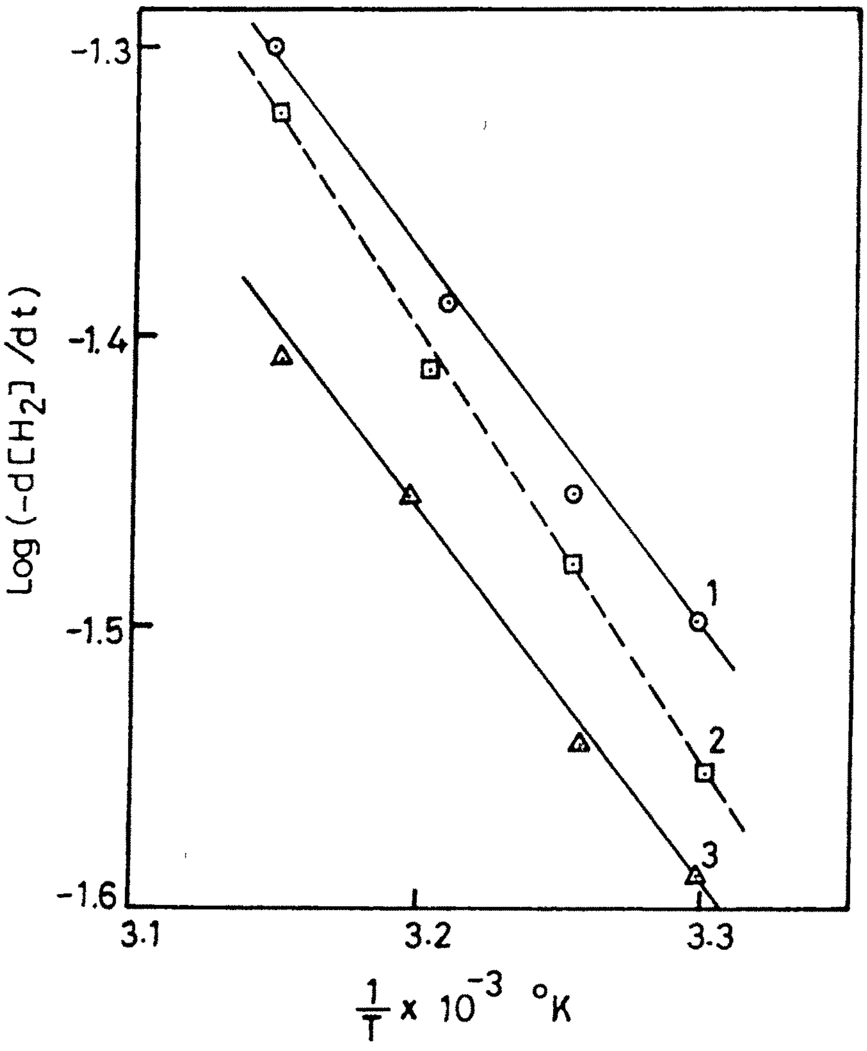


Fig. 5.3.5 Arrhenius plots for catalysts
1. 15PPd(II)DAP 2. [RuDAPCl$_2$]Cl 3. 15PRu(III)DAP

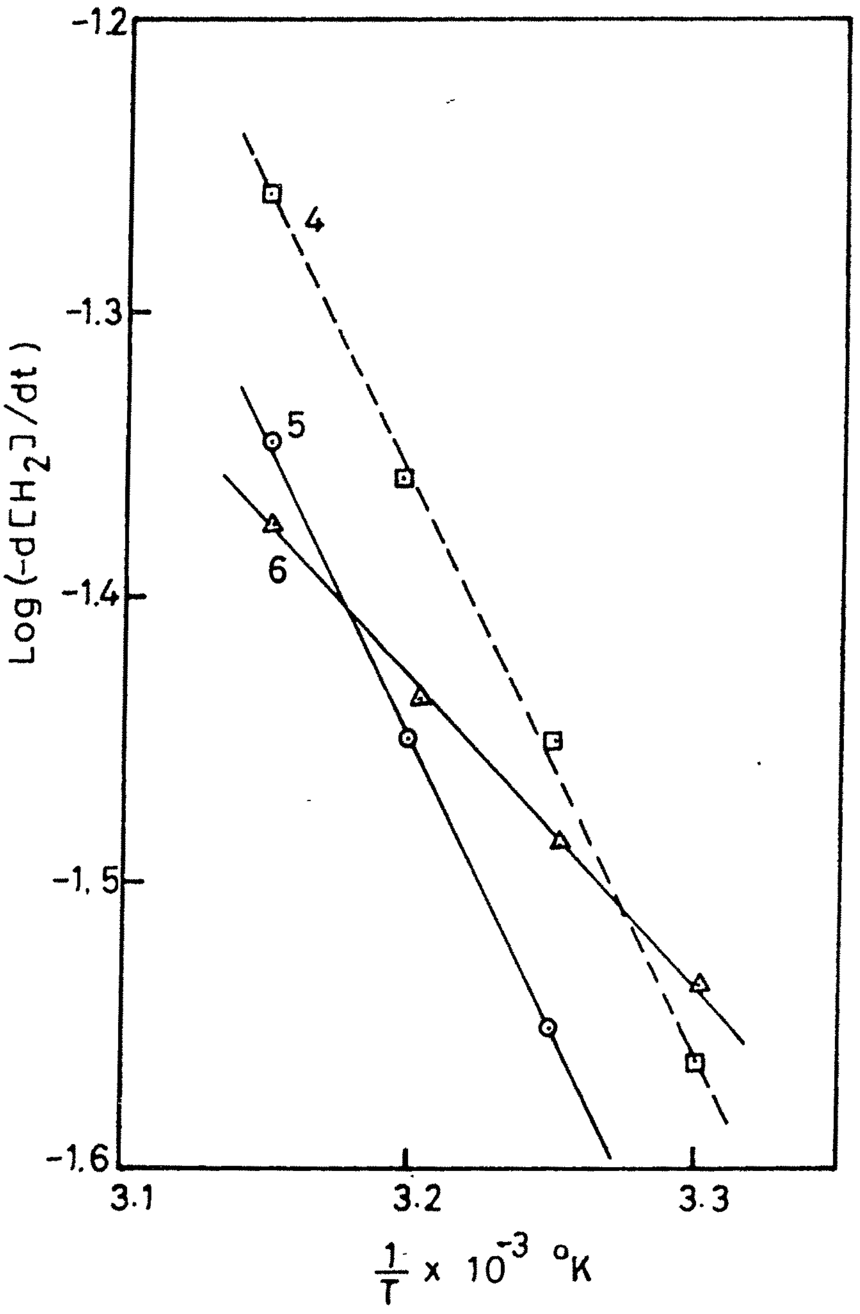


Fig. 5.3.6 Arrhenius plots for catalysts
4. [PdDAP]Cl_2 5. 8XRu(III)DAP 6. 8XPd(II)DAP

In the case of 15PPd(II)DAP catalyst the rate of reaction was found to be 2.90×10^{-2} ml/min using methanol as a solvent and 0.92×10^{-2} ml/min as benzene was used as a solvent. In the case of homogeneous catalysts, where the metal concentration is more than the anchored catalysts, the rate was found to be 2.98×10^{-2} ml/min and 1.00×10^{-2} ml/min using methanol and benzene as solvents respectively for $[RuDAPCl_2]Cl$ catalyst. Similar results have been reported by Ford et al. in the reaction of 1-bromooctane with aqueous sodium cyanide catalysed by polystyrene - bound butyl phosphonium ion where the rate of reaction increases with swelling power of the solvent (41). The more swollen the catalyst, the faster the intra particle diffusion and the faster reaction. Hence selection of a good swelling agent is essential to achieve maximum efficiency with polymer bound catalysts.

The influence of amount of oxygen in methanol for all the catalysts at a constant concentration of catalyst and substrate at 35° C has been studied. It was observed that as the amount of solvent used is increased, the dissolution of the quantity of oxygen in the liquid phase increases which may be responsible for the enhancement of the rate of oxidation of cyclohexane as evident from the data given in Table 5.3.14 to 5.3.16. In this case the volume of methanol was increased from 10 to 40 ml, keeping the amount of cyclohexane and catalyst constant. An enhancement in the rate was observed on increasing the amount of methanol. The rate

Table 5.3.11

Solvent dependence in the oxidation of cyclohexane by supported catalysts at atmospheric pressure.

Reaction temperature = 35°C
Qty. of solvent used = 20 ml.
[Cyclohexane] (mol/lit) = 11.8×10^{-3}.

Catalyst	Ru/Pd present (mol/lit x 10^5)	Solvent	Rate of reaction (ml/min x 10^2)
15PRu(III)DAP	3.22	Methanol	3.24
		Ethanol	3.16
		Dioxane	2.90
		THF	1.98
		Benzene	0.89
15PPd(II)DAP	3.66	Methanol	2.90
		Ethanol	2.60
		Dioxane	2.00
		THF	1.62
		Benzene	0.92

Table 5.3.12

Solvent dependence in the oxidation of cyclohexane by supported catalysts at atmospheric pressure.

Reaction temperature = 35°C
Qty. of solvent used = 20 ml.
[Cyclohexane] (mol/lit.) = 11.8×10^{-3}

Catalyst	Ru/Pd present (mol/lit $\times 10^6$)	Solvent	Rate of reaction (ml/min $\times 10^2$)
8XRu(III)DAP	1.55	Methanol	3.57
		Ethanol	3.40
		Dioxane	2.72
		THF	2.28
		Benzene	0.85
8XPd(II)DAP	1.97	Methanol	3.7
		Ethanol	3.16
		Dioxane	2.22
		THF	2.07
		Benzene	1.05

Table 5.3.13

Solvent dependence in the oxidation of cyclohexane by homogeneous catalysts at atmospheric pressure.

Reaction temperature = 35°C
Qty. of solvent used = 20 ml.
[Cyclohexane] (mol/lit.) = 11.8×10^{-3}.

Catalyst	Ru/Pd present ($mol/lit \times 10^3$)	Solvent	Rate of reaction ($ml/min \times 10^2$)
$[RuDAPCl_2]Cl$	3.22	Methanol	2.98
		Ethanol	2.42
		Dioxane	2.01
		THF	1.42
		Benzene	1.00
$[PdDAP]Cl_2$	3.66	Methanol	3.05
		Ethanol	2.66
		Dioxane	1.72
		THF	1.69
		Benzene	0.93

increased from 2.85 x 10^{-2} to 3.77 x 10^{-2} ml/min when 15 P Ru (III) DAP is used as catalyst. Similar results have been noted for other catalysts also. For 15 P Pd (II) DAP used as catalyst the rate changes from 2.96 x 10^{-2} to 4.00 x 10^{-2} ml/min when the amount of methanol increased from 10 to 40 ml. (Table 5.3.14 and 5.3.15).

In the case of homogeneous catalyst $[RuDAPCl_2]Cl$, the rate increases from 3.00 x 10^{-2} to 3.44 x 10^{-2} ml/min. as the volume of methanol increased from 10 to 40 ml keeping a constant concentration of Ru (III) as 1.60 x 10^{-3} mol/lit for $[PdDAP]Cl_2$ (Pd Content 1.80 x 10^{-3} mol/lit) catalyst an increase in the rate was observed from 3.10 x 10^{2} to 3.52 x 10^{-2} ml/min. The results are given in Table 5.3.16. The corresponding plots are shown in Fig. 5.3.7.

Table 5.3.14

Effect of amount of methanol on the rate of oxidation of cyclohexane for supported catalysts at atmospheric pressure.

Reaction temperature = 35°C.
[Cyclohexane] (mol/lit) = 11.8×10^{-3}.

Catalyst	Ru/Pd Present (mol/lit x 10^5)	Qty. of methanol (ml)	Rate of reaction (ml/min x10^2)
15PRu(III)DAP	3.22	10	2.85
		20	3.20
		25	3.30
		30	3.42
		40	3.77
15PPd(II)DAP	3.66	10	2.96
		20	3.28
		25	3.50
		30	3.79
		40	4.00

Table 5.3.15

Effect of amount of methanol on the rate of oxidation of cyclohexane for supported catalysts at atmospheric pressure.

Reaction temperature = 35°C
[Cyclohexane] (mol/lit) = 11.8 x 10^{-3}.

Catalyst	Ru/Pd Present (mol/lit x 10^6)	Qty. of methanol (ml)	Rate of reaction (ml/min x10^2)
8XRu(III)DAP	1.55	10	3.20
		20	3.60
		25	3.71
		30	3.82
		40	3.96
8XPd(II)DAP	1.97	10	3.14
		20	3.70
		25	3.89
		30	3.92
		40	4.20

Table 5.3.16

Effect of amount of methanol on the rate of oxidation of cyclohexane for homogeneous catalysts at atmospheric pressure.

Reaction temperature = 35°C.
[Cyclohexane] (mol/lit) = 11.8×10^{-3}.

Catalyst	Ru/Pd Present (mol/lit x 10^3)	Qty. of methanol (ml)	Rate of reaction (ml/min x10^2)
$[RuDAPCl_2]Cl$	1.60	10	3.00
		20	3.12
		25	3.20
		30	3.28
		40	3.44
$[PdDAP]Cl_2$	1.80	10	3.10
		20	3.24
		25	3.32
		30	3.36
		40	3.52

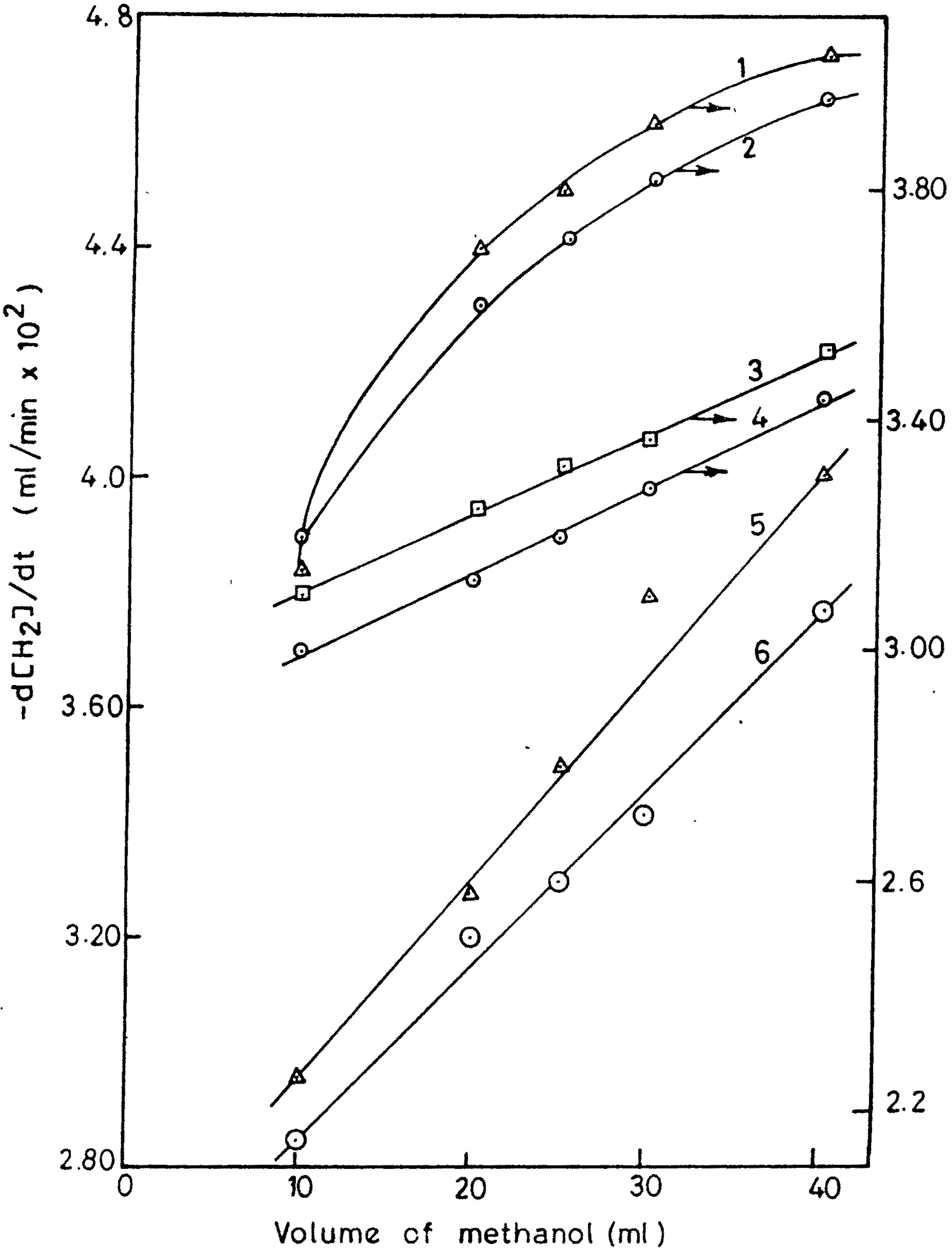


Fig. 5.3.7 Influence of amount of solvent on the rate of oxidation of cyclohexane for catalysts
1. 8XPd(II)DAP 2. 8XRu(III)DAP 3. [PdDAP]Cl_2
4. [RuDAPCl_2]Cl 5. 15PPd(II)DAP 6. 15PRu(III)DAP

5.3.5 **Rate equation :**

In the present study the partial pressure of oxygen and the amount of catalyst are kept constant. In all the experiments, the solvent along with the catalyst was initially saturated with oxygen followed by the injection of cyclohexane and hence actual uptake of oxygen was measured.

The reaction mechanism for the oxidation of olefins by the use of metalions / complexes in the homogeneous system has been studied widely (2-8, 20), and the formation of peroxo and oxo complexes was suggested to be responsible for the transfer of oxygen to the substrate. Vaska et al., have reported the formation of peroxo and superoxo complexes when dioxygen is covalently bound to the metal centre (42). The formation of the oxo complex and the transfer of oxygen via this route has been suggested by Taqui Khan et al. in the Ruthenium (III) complex catalysed oxidation of olefins. (43).

The electronic spectra of homogeneous solution of Ru (III) complex of 1,2-diaminopropane showed two bands at 400 and 505 nm. After bubbling oxygen in the solution, the bands shifted to 360 and 450 nm respectively indicating the formation of Ru(V) = O, complex. The bands started disappearing after addition of cyclohexane probably due to transfer of oxygen to the substrate. (Fig. 5.3.8).

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

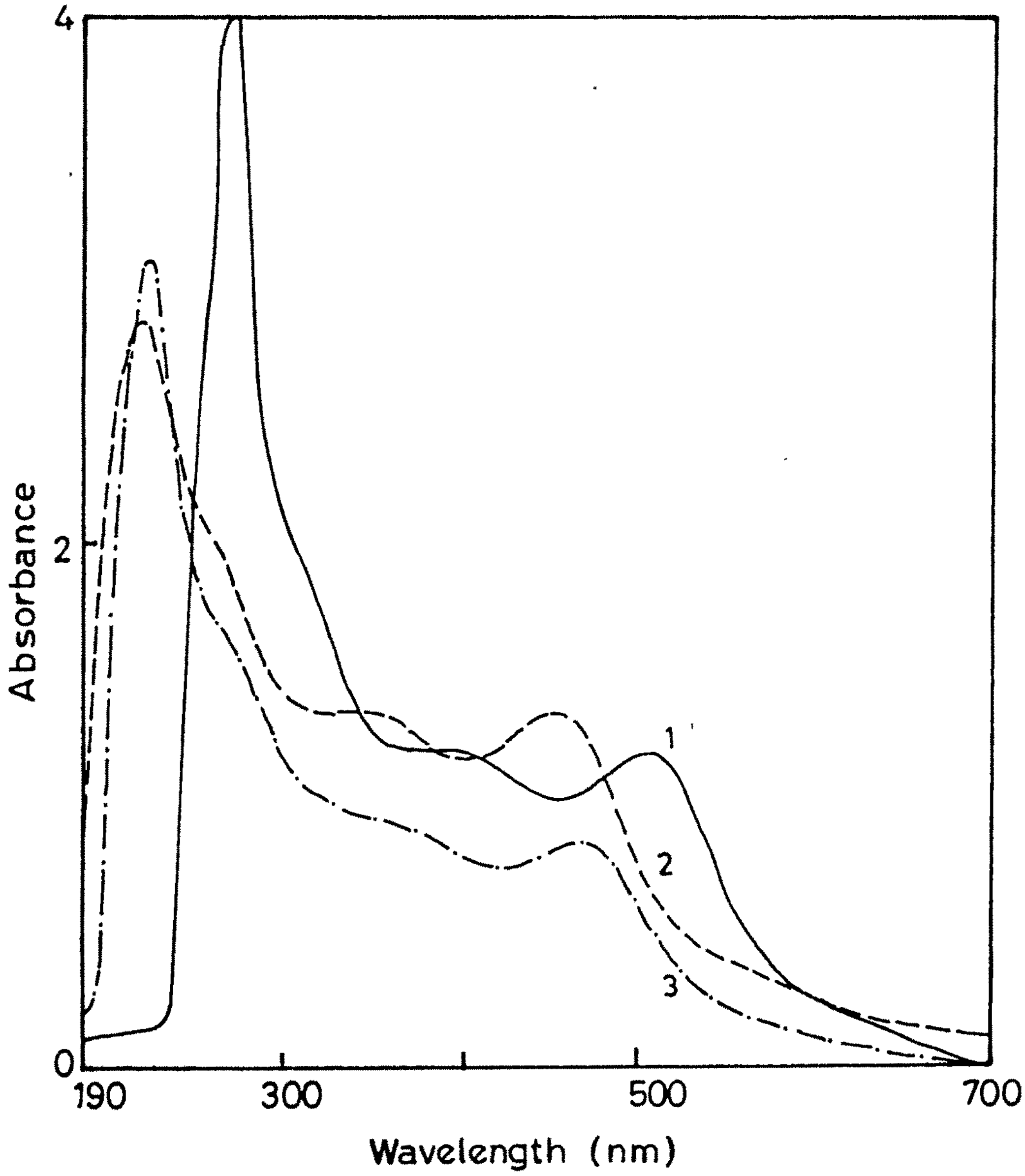
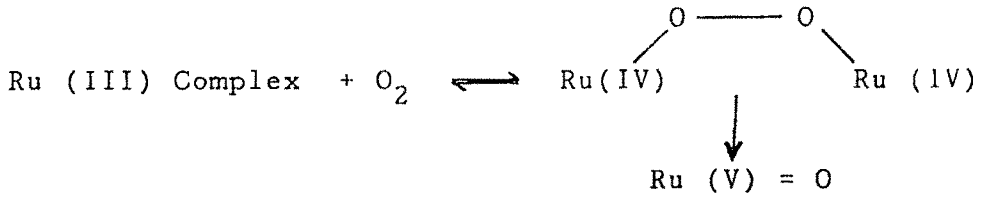


Fig. 5.3.8 UV-vis absorbance spectra in methanol of

1. [RuDAPCl $_2$]Cl
2. After passing oxygen through 1.
3. After adding cyclohexane to 2.



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

$$\text{Ru (V)} = O + \text{Substrate} \longrightarrow \text{Product} + \text{Ru (III) Complex}$$

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

$$'R' = k\,[\text{Catalyst}]\ [\text{Cyclohexane}].$$

Thus on increasing the amount of the catalyst as well as the concentration of cyclohexane an increase in rate is observed (Tables 5.3.1 to 5.3.6).

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