STUDIES IN OXIDATIVE CARBONYLATION AND HYDROFORMYLATION REACTIONS USING TRANSITION METAL CATALYSTS

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FORM - A

CERTIFIED that the work incorporated in this thesis entitled - **STUDIES IN OXIDATIVE CARBONYLATION AND HYDROFORMYLATION REACTIONS USING TRANSITION METAL CATALYSTS**, submitted by Mr. S. Kanagasabapathy was carried out by him under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

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(S.Kanagasabapathy)

TO

MY ATTHAI and MAMA

MRS. & MR. P. SHANMUGARAJ

SUMMARY OF THE THESIS

The reactions involving carbonylation, hydroformylation, oxidative carbonylation and hydrocarbonylation are very important in several industrial processes for the manufacture of bulk and speciality chemicals. Transition metal complexes have been extensively used as catalysts for such reactions due to their ability to activate some important substrates (CO, H_2, olefin etc.), universal choice of ligands, and variability of the co-ordination number and the oxidation states. Some of the important industrial processes developed involving carbon monoxide and using transition metal complex catalysts in solution are a) Carbonylation of methanol to acetic acid (Monsanto process), b) Carbonylation of butadiene to adipic acid (BASF process), c) Hydroformylation (Oxo-process) of propylene to butyraldehyde (Davy Mckee, Union Carbide process), d) Oxidative carbonylation of methanol to dimethyl carbonate (ENICHEM process), e) Hydrocarbonylation of methyl acetate to vinylacetate (Halcon process). The recent developments in carbonylation reactions have been reviewed in several books and articles(Falbe 1980, Parshall 1980, Sheldon 1983).

Considering the industrial significance of the carbonylation reactions, further research on catalysis, reaction kinetics and mechanism of these reactions is most essential. The present thesis aims at investigations on the following reaction systems using transition metal catalysts in soluble and solid states.

- Oxidative carbonylation of amines to dialkyl and diaryl ureas and carbamates
- Synthesis of novel water soluble ligands and catalysts and evaluation of their performance in hydroformylation reactions.

- Hydroformylation of ethylene using a water soluble Rh catalyst in homogeneous and biphasic medium.

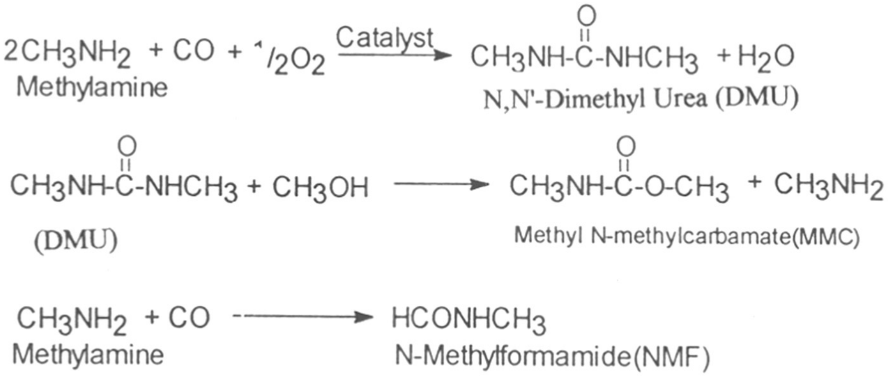
Oxidative carbonylation of amines gives urea derivatives and carbamates, which have wide ranging applications in pesticides and polymer industry. These are conventionally prepared by phosgenation route, which has serious problems due to toxic nature of phosgene and handling hazards. The carbonylation route eliminates the use of toxic phosgene. Moreover, the oxidative carbonylation reaction has the added advantage of mild operating conditions of temperature and pressure. This process employs transition metal catalyst, in particular, palladium complexes as catalyst with NaI as a promoter. This thesis presents a detailed investigation on catalysis aspects.

Hydroformylation of olefins to aldehydes in the presence of homogeneous transition metal catalysts is also important in industry. The present work has been undertaken with the objective of investigating the role of various catalysts and reaction conditions in hydroformylation reactions. Particularly, the reaction using water soluble metal complex catalysts have been studied.

Part I: Oxidative carbonylation of aliphatic using transition metal catalysts.

Chapter 1 presents a complete literature survey on the oxidative carbonylation of aliphatic and aromatic amines in the presence of transition metal catalysts. It was observed from the literature reports that transition metals such as Pd, Pt, Rh, Ru, Co, Cu and Ni in homogeneous and heterogeneous forms as catalysts have been studied for oxidative carbonylation reactions. However, Pd based catalysts are very active for this reaction. A promoter consisting of alkali metal halide is necessary to initiate the reaction. The effect of catalyst precursors, solvents, promoters, co-catalyst, reaction conditions as well as the kinetics and mechanisms of oxidative carbonylation of aromatic amines are reviewed. Though, the patented literature established the feasibility of oxidative carbonylation of aliphatic amines, a limited literature is available on the reaction mechanism, catalytic cycle and activity and selectivity behavior. The scope of the present thesis is also outlined.

Chapter 2 deals with the investigations on oxidative carbonylation of methylamine to methyl N-methylcarbamate in the presence of Pd metal/ NaI catalyst system at 443 K and 60 atm. pressure. The stoichiometric reaction is given below.



$$\underset{\text{Methylamine}}{2CH_3NH_2} + CO + {}^1/_2O_2 \xrightarrow{\text{Catalyst}} \underset{\text{N,N'-Dimethyl Urea (DMU)}}{CH_3NH\text{-}\overset{\overset{O}{||}}{C}\text{-}NHCH_3} + H_2O$$

$$\underset{\text{(DMU)}}{CH_3NH\text{-}\overset{\overset{O}{||}}{C}\text{-}NHCH_3} + CH_3OH \longrightarrow \underset{\text{Methyl N-methylcarbamate(MMC)}}{CH_3NH\text{-}\overset{\overset{O}{||}}{C}\text{-}O\text{-}CH_3} + CH_3NH_2$$

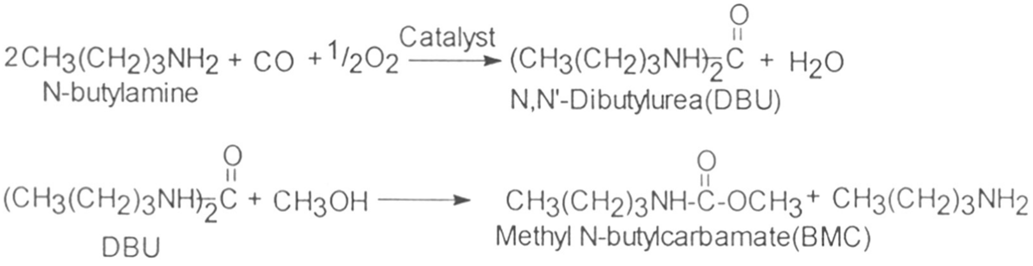
$$\underset{\text{Methylamine}}{CH_3NH_2} + CO \longrightarrow \underset{\text{N-Methylformamide(NMF)}}{HCONHCH_3}$$

Oxidative carbonylation reactions were carried out in a 300 ml stirred high pressure reactor. The reaction products were analyzed by GC, and confirmed by IR and NMR technique. The effect of promoters and screening of transition metal catalysts, temperature, catalyst concentration, methylamine concentration, Pd:NaI ratio on oxidative carbonylation of methylamine was studied.

The following conclusions were drawn based on this work.

- The product distribution was found to be sensitive to the reaction conditions in oxidative carbonylation of methylamine and DMU was found to be an intermediate product in MMC synthesis.
- It was found that the selectivity pattern was strongly dependent on the type of catalyst used, concentration of methylamine, $CO:O_2$ ratio and temperature.
- At lower temperatures and higher methylamine concentrations, DMU was the major product, while at a higher $CO:O_2$ ratio NMF was the major product.
- A possible mechanism based on the results is discussed and an active species of the following type has been proposed.

In Chapter 3, the results on oxidative carbonylation of n-butylamine with Pd/NaI catalyst system have been studied at 373 to 443 K at 60 atm total pressure of CO and O_2 in the presence of methanol as a solvent. Several homogeneous and heterogeneous transition metal catalysts have been tested for their activity and selectivity. The effect of promoters, solvents and temperature has been investigated. Oxidative carbonylation of n-butylamine proceeds through the formation of N,N'-dibutylurea(DBU) to methyl N-butylcarbamate. The reactions involved are shown below.



$$\underset{\text{N-butylamine}}{2CH_3(CH_2)_3NH_2} + CO + {}^1/_2O_2 \xrightarrow{\text{Catalyst}} \underset{\text{N,N'-Dibutylurea(DBU)}}{(CH_3(CH_2)_3NH)_2\overset{\overset{O}{\parallel}}{C}} + H_2O$$

$$\underset{\text{DBU}}{(CH_3(CH_2)_3NH)_2\overset{\overset{O}{\parallel}}{C}} + CH_3OH \longrightarrow \underset{\text{Methyl N-butylcarbamate(BMC)}}{CH_3(CH_2)_3NH\text{-}\overset{\overset{O}{\parallel}}{C}\text{-}OCH_3} + CH_3(CH_2)_3NH_2$$

A summary of the important observations is given below.

- Selectivity of N,N'-dibutylurea(DBU) and methyl N-butylcarbamate(BMC) was influenced by the type of catalyst used and the process parameters employed.
- Palladium based catalysts gave higher selectivity for BMC while higher yields of DBU were obtained when homogeneous ruthenium complex catalysts [$Ru(CO)_3(PPh_3)_2$, $Ru(Cl)_2(PPh_3)_2$ $Ru(Cl)_2(PPh_3)_3$ etc.] were used.
- The activity of the catalyst was found to vary with the kind of promoter used. NaI was found to be the best promoter for this system.
- At temperatures below 373 K, DBU was obtained as a major product, while above 423K, BMC was selectively produced.
- A possible reaction mechanism has also been proposed which shows that the oxidative carbonylation of amines to carbamate does not proceed via formamide and isocyanate intermediates.

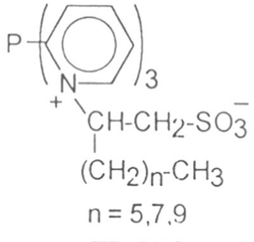
Part II : Hydroformylation of olefins using homogeneous and biphasic catalysis:

Chapter 4 involves a detailed literature survey on the hydroformylation of olefins. Variety of transition metals such as Rh, Co, Ir and Ru in homogeneous and heterogeneous forms have been suggested, however, Rh and Co metal complexes are extensively studied for hydroformylation reactions because of their better activity and selectivity. Processes using cobalt and rhodium carbonyl catalysts for hydroformylation reactions and their advantages and disadvantages have been critically reviewed.

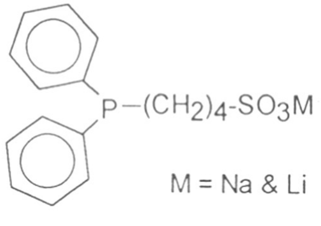
The Co and Rh carbonyl catalysts were modified with trialkyl and triaryl phosphines as ligands. The great advantage of the modified rhodium catalysts: it operates under mild reaction conditions moreover this catalyst gives excellent selectivity for formation of the desired linear aldehydes. Despite the advantages of the modified rhodium catalyst, the high cost of rhodium and difficulty in separation of the catalyst limit its use. The application of this catalyst system is limited to the hydroformylation of lower olefins such as propylene wherein volatile products are found which are easy to separate.

A major breakthrough in hydroformylation technology is the use of water soluble catalysts in a biphasic medium to overcome the separation problem associated with the catalyst recycle. A brief summary of the concept of biphasic catalysis has been discussed. The first water soluble (Rh-TPPTS) complex catalyst was used for hydroformylation reaction by Kuntz in 1975. This methodology was extended further to synthesize different water soluble ligands consisting of sulphonated mono and diphosphine derivatives like sodium salts of monosulphonated triphenylphosphine(NaTPPMS), Sulphoalkyltris(2-pyridyl)phosphine, sulphonated chiral phosphines(BISBIS) etc. A complete literature report on the synthesis of such ligands and its rhodium complexes and their applications to hydroformylation reactions has been given in this chapter.

Chapter 5 deals with the experimental studies on the activity and selectivity of the various water soluble rhodium complex catalysts in homogeneous and biphasic hydroformylation of 1-tetradecene, 1-hexene and styrene. The ligands of following type



TPyPTS



NaBSDP & LiBSDP

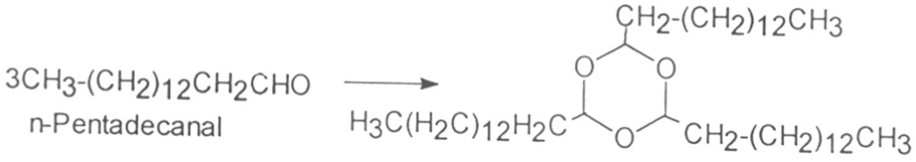
and their rhodium complexes have been prepared. The ligand TPyRnPTS has several advantages including carries the reaction even at mild temperatures.

The advantage of NaBSDPP and LiBSDPP are that these are having surfactant properties and acting as water soluble as well as organic(methanol) soluble ligands. Due to these properties, the reaction can be performed in homogeneous medium and the catalysts can be separated by filtration at 0°C. The synthesis of NaBSDPP was reported earlier, but it was not studied earlier for hydroformylation reactions. Therefore the role of these ligands with respect to the catalyst concentration, temperature, pressure, P/Rh ratio and surfactant on hydroformylation of higher (1-tetradecene), middle(1-hexene) and substituted(styrene) olefins in homogeneous and biphasic reactions. A summary of the important observations is given below.

- It was noticed from the study that Rh-TPyPTS catalyst alone was very active for biphasic hydroformylation of 1-tetradecene without any surfactants, but the catalyst of type Rh-NaBSDP and Rh-LiBSDP failed to react with higher olefins. However, Rh-NaBSDP and Rh-LiBSDP were active in the presence of surfactants as binding ligands.
- It was also noted that the catalysts such as Rh-NaBSDP and Rh-LiBSDP were very efficient(100 % conversion and 80 % selectivity towards iso-aldehyde) for the hydroformylation of styrene in homogeneous medium. Complete separation of the catalyst in this system was achieved, and it could be reused several time without the loss in activity.

- The catalysts of type Rh-NaBSDP and Rh-LiBSDP were active only in the presence of surfactants (trialkylmethylammonoium chlorides and bromides). It was observed that the activity of the catalyst increased with increase in the alkyl chain of the surfactant and decreased by further increase in the chain length.

Cyclic ethers were formed during hydroformylation of higher olefins (C_{12} and above) as side products by trimerization of the aldehydes. The trimerization of aldehydes under hydroformylation conditions were observed for the first time.



Trimer

Chapter 6 presents a study on the hydroformylation of ethylene using Rh-TPPTS complex in homogeneous and biphasic media at 303 to 323 K temperatures. The reactions were carried out in a 50 ml capacity microclave reactor. The stoichiometric reaction is given below.

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + CO + H_2 \xrightarrow{\text{Catalyst}} \underset{\text{Propionaldehyde}}{CH_3\text{-}CH_2\text{-}CHO}$$

The mass balance of ethylene, carbon monoxide and hydrogen consumed and the formation of propionaldehyde was greater than 95 %. The role of solvents, co-solvents and pH of the reaction medium at 303 K to 323 K for homogeneous system has been studied.

- In aqueous medium at 303 to 323 K the rate was found to be negative order with respect to CO and ethylene, whereas a linear dependence on hydrogen was observed.
- At higher catalyst concentrations (> 1×10^{-3}, kmol/m^3), the rate was found to be strongly dependent on agitation speed indicating mass transfer limitations, while at lower concentration (5×10^{-4}, kmol/m^3) the rate was independent of agitation, indicating kinetic control.

REFERENCES :

Falbe., Carbon monoxide in organic systhesis, Springer Verlag, Berline, (1980).

Kuntz E.G.,Fr.Patent 2,314,910 to Rhone-Poulenc Industries(1975).

Parshall G.W., Homogeneous Catalysis, Wiley-Interprise Publication, New York, (1980).

Pruett R., and Smith J. A., J.Org. Chem., 34, 327, (1969).

Sheldon R. A., Chemicals from synthesis gas, D. Reidel Publishing Company, Dordrecht, (1983).

LIST OF CONTENTS

PART I : OXIDATIVE CARBONYLATION OF AMINES

CHAPTER 1 : GENERAL INTRODUCTION AND LITERATURE SURVEY ON OXIDATIVE CARBONYLATION OF AMINES

CHAPTER 2 : OXIDATIVE CARBONYLATION OF METHYLAMINE TO METHYL N-METHYL CARBAMATE USING pd-Nal CATALYST SYSTEM

CHAPTER 3 : OXIDATIVE CARBONYLATION OF N-BUTYLAMINE USING pd-NaI CATALYST SYSTEM

PART II : HYDROFORMYLATION OF OLEFINS USING HOMOGENEOUS AND BIPHASIC CATALYSIS

CHAPTER 4 : HYDROFORMYLATION OF OLEFINS : A LITERATURE SUMMARY

CHAPTER 5 : HYDROFORMYLATION OF 1-HEXENE, 1-TETRADECENE AND STYRENE USING WATER SOLUBLE RHODIUM COMPLEX CATALYSTS

CHAPTER 6 : KINETICS OF HYDROFORMYLATION OF ETHYLENE USING WATER SOLUBLE Rh-TPPTS CATALYST

PART I

OXIDATIVE CARBONYLATION OF AMINES

CHAPTER 1

GENERAL INTRODUCTION AND LITERATURE SURVEY ON OXIDATIVE CARBONYLATION OF AMINES

1.1 GENERAL INTRODUCTION

Catalysis plays an important role in a wide range of industrial processes in the manufacture of petroleum and chemical products with end applications in plastics, agrochemicals, fine chemicals, Pharmaceuticals and fertilizers (Parshall and Nugent 1988 a,b,c and Satterfield 1981). The type of catalyst used in industries are generally classified as heterogeneous or homogeneous, depending on the form in which they are used. Large number of chemical processes are based on heterogeneous catalysts (Satterfield 1980). However, the homogeneous catalysts used in the liquid phase have also important applications in the industry (Nakamura and Tsutsui 1980, Parshall 1980). For example, hydroformylation of olefins to aldehydes invented by Rollen made a major impact on applications of homogeneous catalysts in chemical industry. The major disadvantage of homogeneous catalysis is that they are not easily separable from the products. However, the advantages in high activity, selectivity at mild operating conditions are very significant for many cases. In contrast, heterogeneous catalysts are easy to handle and separate from the reaction mixture. Because of these advantages, the heterogeneous catalysts find a wide spread use in industries. Some of the basic differences between homogeneous and heterogeneous catalysts are shown in Table 1-1. The applications of both the type of catalysts in industry are growing due to a strong need for the development of more economical and environmentally cleaner processes.

Carbon monoxide (CO) is one of the important feedstocks for many industrial catalytic processes. It can be obtained easily from resources like coal, crude oil fraction and natural gas. Much attention has been given to the conversion of chemicals after the oil crisis in early 70's, when a need for alternative sources of raw material for the production of industrial chemicals was realized (Sheldon 1983). Some of the important commercial processes based on CO or synthesis gas as raw materials for the synthesis of liquid hydrocarbons from syngas, oxidative carbonylation of amines, alcohols and olefins, hydroformylation of olefins (OXO-synthesis), carbonylation of methanol to acetic acid and the carbonylation of methyl acetate to acetic anhydride (Wender 1987). Industrial processes which utilize CO as a raw material are summarised in Table 1-2.

TABLE 1.1

HOMOGENEOUS vs HETEROGENEOUS CATALYSIS

	Homogeneous	Heterogeneous
Form	Soluble metal complexes usually mononuclear Liquid	Metals, usually supported or metaloxides
Phase	Liquid	Gas/Solid
Temperature	Low(<523,K)	High (523-1173,K)
Active Centres	All metal atoms	Surface metal atoms
Selectivity	High	Frequently low
Mechanism	Reasonably well understood	Poorly understood
Reproducibilty	Yes	Slow
Concentration	Small	High
Diffusion Problems	Not present	Present
Catalyst separation	Costly	Easy
Modification	High	Small
Applicatiions	Limited	Wide

References :

R. Whyman " Industrial applications of homogeneous catalysis", Reidel Publ. Co. (1988).

Falbe,J. and Bahrman, H., J.Chem. Ed. **61**, 961 (1984).

TABLE 1.2

SOME INDUSTRIAL PROCESSES WHICH UTILIZE CO AS A RAW MATERIAL

Sr No	Process	Catalyst System	Company	References
1	Carbonylation of methanol to acetic acid	Rh/I	Monsanto	Roth et al., (1971)
2	Carbonylation of benzyl chloride to phenyl acetic acid	$Na[Co(CO)_4]$	Montedison S.p.A	Cassar et al., (1969)
3	Hydrocarbonylation of methyl acetate to vinyl acetate	$RhCl_3/MeI$	Halcon	Ehler and Juran (1982)
4	Carbonylation of butadiene to adipic acid	$Co_2(CO)_8/Py$	BASF	Chem. week (1984)
5	Oxidative carbonylation of methanol to dimethyl carbonate	$PdCl_2/CuCl_2$	Assoreni	Ugo et al., (1980)
6	Carbonylation of nitrous acid methyl ester to dimethyl oxalate	Pd	Ube Industries.	Shiomi et al., (1984)
7	Synthesis gas to ethylene glycol	$Ru_3(CO)_{12}$	Union Carbide	Dombek (1986)
8	Homologation of acetic acid to propionic acid	Ru/HI	Texaco	Knifton (1981)
9	Carbonylation of methyl acetate to acetic anhydride	Rh/MeI	Eastman Chemical	Agreda et al., (1992)
10	Hydroformylation of propene to butyraldehyde	Rh/PR_3 (water soluble complex)	Ruhrchemie Rhone - Poulenc	Bach et al., (1984) Jenk et al., (1984)
11	Carbonylation of ethylene to propionic acid	Ni	BASF	Weissermel and Arpe (1978)
12	Carbonylation of acetylene to acrylic acid	$NiBr_2$	BASF	Weissermel and Arpe (1978)

Several reviews are available in the literature dealing with catalysts and their applications for carbonylation reactions (Beller et al., 1995, Gates 1992, Parshall and Ittel 1992, Colqubhoun et al., 1991, Whyman 1988, Keim 1988, Fahey 1987, King and Grate 1985, Falbe and Bahrmann 1984, Sheldon 1983 Masters 1981, and Falbe 1980). The CO conversion processes to useful chemicals have been put into practice and play an important role in industry to demonstrate the feasibility of the utilization of CO. Eventhough, the utilization of CO has already been established, there is a need for further investigations on various aspects such as role of different types of metal complex catalysts, promoters, solvents, and co-catalysts in the activity and selectivity of carbonylation reactions. Such a study would be extremely useful in the development of new catalyst systems and in improving the selectivity to desired products. An important example of carbonylation is the oxidative carbonylation reactions which are important in the synthesis of several industrial chemicals such as alkyl carbonates, carboxylic acids, substitute ureas and carbamic acid esters (Golodov et al., 1979). Some specific examples are:

i Oxidative carbonylation of alcohols to alkyl carbonates.
ii Oxidative carbonylation of olefins to unsaturated carboxylic acids
iii Oxidative carbonylation of amines to Urea derivatives and Carbamates.

The aim of this thesis was to investigate the oxidative carbonylation of amines using Pd metal catalysts. Particularly, the activity of Pd metal and supported Pd catalysts, role of solvents, promoters and reaction conditions on the selectivity behaviour in oxidative carbonylation of methyl amine and n-butyl amine have been investigated. The following sections describe the relevant literature on oxidative carbonylation of aliphatic and aromatic amines alongwith the scope of the present work.

1.2 LITERATURE SURVEY

The oxidative carbonylation of amine leads to alkyl carbamates via dialkyl urea as an intermediate. The stoichiometric reactions are given below:

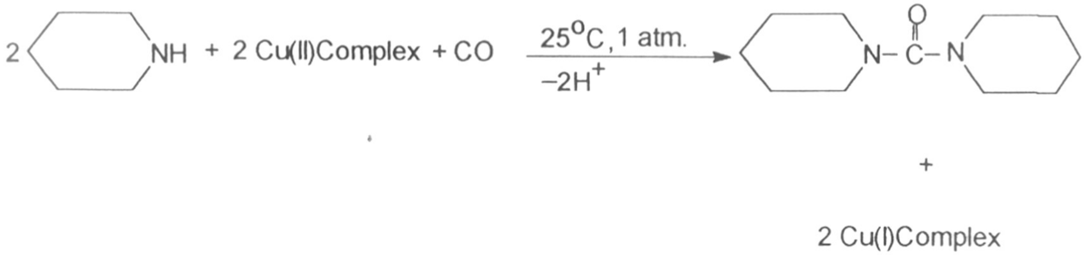
$$RNH_2 + CO + 1/_2 O_2 \xrightarrow{\text{Catalyst}} \underset{\text{Dialkyl urea}}{RNHCONHR} + H_2O \qquad (1.1)$$

$$\underset{\text{Dialkyl urea}}{RNHCONHR} + R'OH \longrightarrow \underset{\text{Dialkyl carbamate}}{RNH\text{-}\overset{\overset{O}{\|}}{C}O\text{-}R'} + RNH_2 \qquad (1.2)$$

This reaction is usually carried out in the presence of a Pd or Rh catalyst in a slurry reactor. A summary of the literature on oxidative carbonylation of various aliphatic and aromatic amines is presented in Tables 1.3 and 1.4 respectively and some important studies are discussed below.

1.2.1 Aliphatic Amines

Brackmann (1968) was the first to report the oxidative carbonylation of piperidine and aliphatic amines of the type, RNH_2 (R = Me, Bu, $PhCH_2$) in the presence of a Cu(II) complex catalyst at 298 K and at 1 atm.



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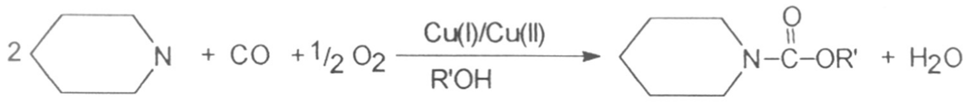


(1.4

TABLE 1.3

SUMMARY OF LITERATURE IN OXIDATIVE CARBONYLATION OF ALIPHATIC AMINES

Sr. No.	Amine	Solvent	Catalyst	Promotor	Temperature (K)	Pressure		Conversion (%)	Product		Reference
						(PCO)	(PO_2)		I	II	
1.	C_5H_{10}-NH (piperidine)	-	Pd(II)	Cu (II)	298	B	B	96	95	-	Brackmann, (1968)
2.	n-C_4H_9-NH_2	THF	Se	-	293	B	B	100	96	-	Sonoda, (1971)
3.	$_3$HC-NH_2	-	Pd(II)	Cu(II)	298	B	B	-	-		Sheludyakov et al.,(1979)
4.	CH_3-NH_2 CH_3-NH_2	dioxane pyridine	Pd (II) Pd(II)	Cu (II) Cu(II)	313 313	B B	B B	5 95	4 94	- -	Golodov et. al.,(1979)
5.	C_4H_9-NH_2	THF	SeCO	-	298	B	B	82	82		
6.	C_5H_{10}-NH (piperidine)	-	Pd(II)	Cu(II)		B	-				Kondo et al., (1979)
7.	C_4H_9-NH_2	ethanol	Pd (OAc)2	$(C_4H_9COO)_2Cu$	298	B		85			Sheludyakov et al., (1984)
8.	1-adamantyl amine	methanol	$Co^{II}(Salen)^a$	-	298	20	2	14	0.3	4.2	Waller F . J. (1986) Cenini et al., (1987)

I = urea derivative; II = carbamate derivative; a = bis (salicylaldehyde) ethynediamine Co (II); B=bubbling

In this reaction, Cu(I) complex formed in-situ accelerated the rate of the reaction indicating autocatalytic behaviour.

Sonoda et al., (1971) and Kondo et al., (1979) have reported the preparation of dibutyl urea from the reaction of n-butylamine with CO and oxygen in the presence of Se as a catalyst. These reports conclude that, 100% conversion of n-butylamine with 95% of selectivity to dibutyl urea was observed. Various amines such as n-octylamine, ethylenediamine, cyclohexylamine benzylamine and piperidine have been screened for the oxidative carbonylation. An intermediate Selenocarbamate salt was isolated in these reactions, which on oxidation led to urea derivatives indicating that the process takes place in two steps:

$$2RNH_2 + Se + CO \longrightarrow (RNH_3)^{+}RNH{-}CO{-}Se)^{-}$$ **(1.5)**

$$(RNH_3)^{+}(RNH{-}CO{-}Se)^{-} + 1/2\,O_2 \longrightarrow (RNH)_2CO + Se + H_2O$$ **(1.6)**

Sheludyakov et al., (1979 and 1984) and Giannoccaro (1987) have studied oxidative carbonylation of amines such as methylamine, diethylamine , n-butylamine etc. in the presence of $PdCl_2$-$CuCl_2$ catalyst.

$$2RNH_2 + CO + 1/2\,O_2 \xrightarrow{Pd^{(II)}/Cu^{(II)}} (RNH)_2CO + H_2O$$ **(1.7)**

It was understood from this work that the reaction proceeds via formation of a Pd(II)-CO complex, which reacts further with amines to form a Pd-carbamoyl complex. The subsequent reaction of Cu(II)-amine complex with Pd-carbamoyl complex gives rise to the urea derivatives. Kinetics of oxidative carbonylation of piperidine to 1,1'-carbonyldipiperidine in the presence of Pd(II)-Cu(II) complex at 413 K was investigated by Sheludyakov et al., (1984). The rate of the reaction was independent of piperidine concentration and first order with CO and Pd(II) concentrations.

Alper and co-workers (1987) have studied the oxidative carbonylation of aliphatic and secondary amines in the presence of $PdCl_2/CuCl_2$ and HCl catalyst system using di-tert.butyl peroxide as a substitute to oxygen. Oxidative carbonylation of secondary amines with the above catalyst system leads to the formation of oxamides along with carbamates. The yield to the carbamate was 67%. Various primary amines have been carbonylated to give carbamates in yields varying from 17 % to 98%. A mechanism has also been proposed (Figure 1.1) by these investigators with chloroalkoxy palladium as an intermediate species.

It was noticed from the literature that only a limited work has been done on oxidative carbonylation of aliphatic amines. There is no detailed report on the effect of reaction conditions, promoters, catalysts, solvents etc. on the activity and selectivity of transition metal catalyzed oxidative carbonylation of amines. Also, the mechanism is not well understood, indicating a need for further investigations.

1.2.2 Aromatic Amines

Oxidative carbonylation of aromatic amines in the presence of transition metal catalyst has been reviewed in this section. Table 1.4 shows a summary of literature on oxidative carbonylation of aromatic amines and some important studies are discussed in details.

Kondo et al., (1972) have reported that diphenylurea can be conveniently synthesized by oxidative carbonylation of aniline in the presence of Se and triethylamine under mild conditions. Substituted aromatic amines such as $X\text{-}C_6H_4NH_2$ (X = H, p-OMe, p-Me, m-Me, o-Me, p-NH_2, p-Cl) were also studied as substrates in which corresponding urea derivatives were formed. In the absence of triethylamine, Se showed no activity for this reactions.

Chono et al., (1983) and Fukuoka et al.,(1984a,b) have reported a new route for the synthesis of methylene diphenyldiisocyanate (MDI) consisting of three steps in which the first step is oxidative carbonylation of aniline to ethyl phenylcarbamate (EPC) using Pd metal as a catalyst and an iodide compound as a promoter. This route is described by the following reactions.

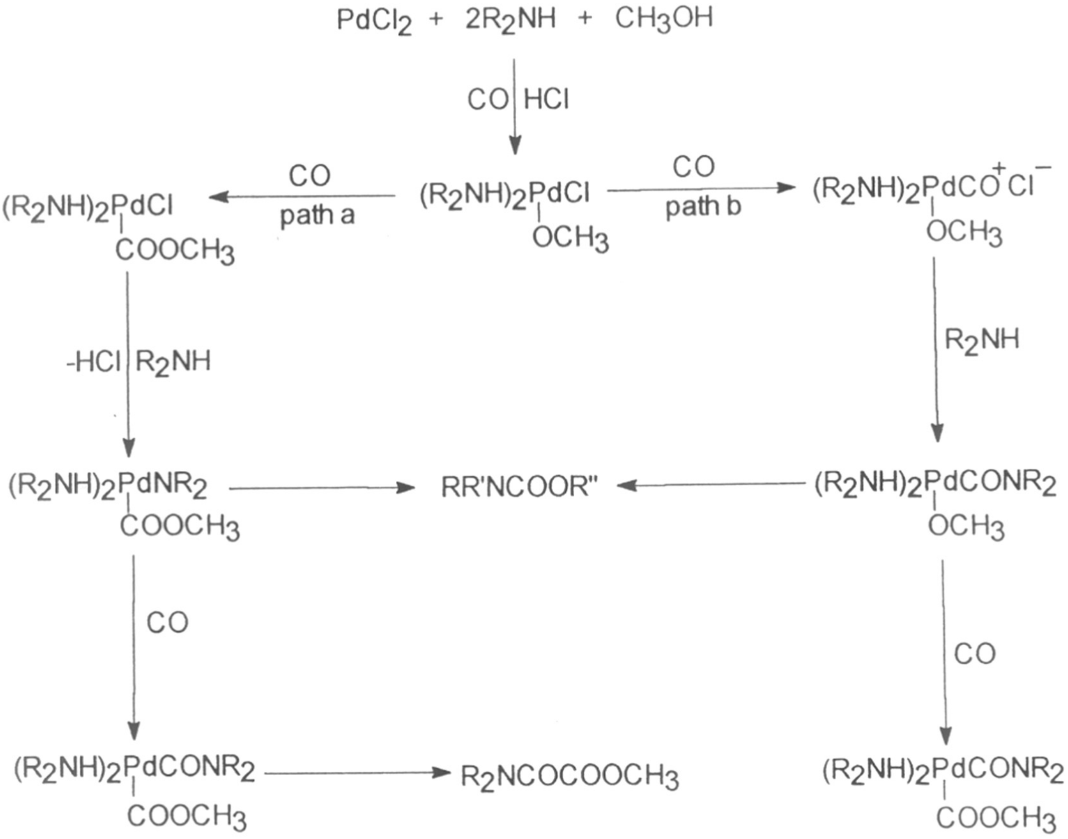


Figure 1.1 **Mechanism of oxidative carbonylation of secondary amine [Alper et al., 1987]**

TABLE 1.4

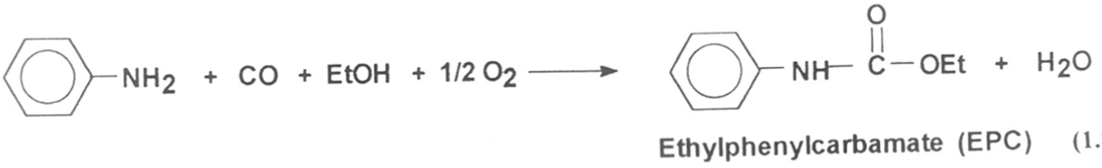
SUMMARY OF LITERATURE IN OXIDATIVE CARBONYLATION OF AROMATIC AMINES

Sr. No.	Amine	Solvent	Catalyst	Promotor	Temperature (K)	Pressure		Conversion (%)	Product		Reference
						(PCO)	(PO_2)		I	II	
1.	C_5H_5-NH (piperidine)	benzene	Se	triethyl amine	353	B	B	26	24	-	Kond et al., (1972)
2.	C_4H_5-NH_2	ethanol	$PdCl_2$	ironoxy chloride	-	B	B	-	-	90	Becker et.al., (1980)
3.	C_6H_5C-NH_2	ethanol	Pd	KIO_3	433	80	6	-		85	Asahi Chem.Ind., (1983)
4.	C_6H_5 C-NH_2	ethanol	Pd	CH_3 I	433	80	6	87	-	85	Fukuoka and Chono. (1984)
5.	C_6H_9-NH_2	ehanol	Pd	NaI	433	80	6	92	1.5	93	Fukuoka et.al.(1984a)
6.	C_6H_5-NH_2	ethanol	Rh/C	NaI		80	6	92	1.5	93	Fukuoka et.al.(1984b)
7.	C_6H_5C-NH_2	methanol	$PdCl_2$	CuCl2/HCl	438	B	B	100	-	99	Alper and Hartstock, (1985)
8.	4-F-C_6H_4-NH_2	methanol	$Co^{II}(Salen)^a$	-	298	10	2	-	25	31	Cenini et.al. (1987)
9.	C_6H_5-NH_2	-	$Pd(PhNH_2)_2Cl_2$	-	353	0.6	0.3	10	10	-	
10.	4-F-C_6H_4-NH_2	methanol	$Co^{II}(Salen)^a$	-	Reflux Temp.	9	1	100	24	27	Benedini et.al. (1986)

TABLE 1.4 contd.

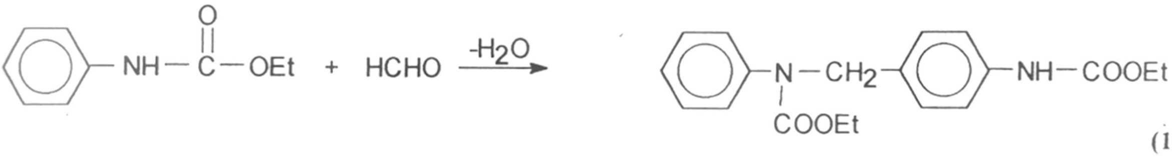
11.	1-adamantyl amine	methanol	$Co^{II}(Salen)^a$	-	333	10	2	80	10	70	Maddinelli et.al., (1987)
12.	C_4H_5-NH_2	methanol	ZP[BPy-Pd] and ZP[BPyPd]	-	403	25	7	60	-	66	Giannaccaro et.al., (1989)
13.	C_6H_5-NH_2	ethanol	Pd/C	NaI	373	34	6.8	120	98	-	Gupte and Chaudhary (1988)
14.	C_6H_5-NH_2	methanol	Pd^{II}-Cu^{II}	NaI	room temp.	B	B		-	67	Alper et.al., (1987)
15.	C_6H_5-NH_2	ethanol	Catalyst screening	NaI	453	38	3	59	23	76	Mulla et al.,(1991)
16.	C_6H_5-NH_2	ethanol	Co(TPP)	NaI	463	14	1	100	-	33	Leung and Dombak (1992)
17.	C_6H_5-NH_2	DMF	Rh/C	NaI	453	2	1	98	-	98	Prasad and Chaudhari (1994)
18.	C_6H_5-NH_2	methanol	Pd/C	NaI	323						Gupte and Chaudhari (1992)
19.	C_6H_5-NH_2	methanol	Co(TPP)	NaI							Li and Peng (1993)
20.	C_6H_5-NH_2	methanol	Pd -Clay	NaI							Valli and Alper (1995)

I = urea derivative; II = carbamate derivative; a = bis (salicylaldehyde) ethylenediamine Co (II); B=bubbling oxidative carbonylation of aniline to ethylphenylcarbamate(EPC)



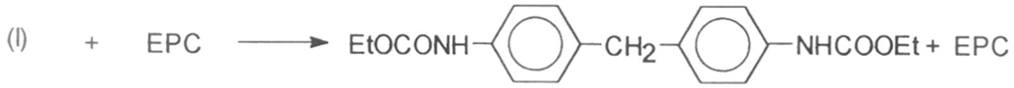
(1.8)

condensation of EPC with formaldehyde and subsequent inter-molecular transfer reaction with EPC to form methylene diphenyldiurethane(MDU)



(1.9)

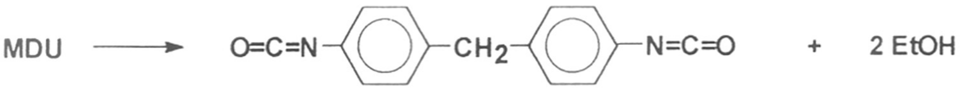
(I)



(1.10)

(MDU)

decomposition of MDU to MDI.



(MDI)

This route has the following advantages (Chono et al., 1983).

i Pd^o/I^- catalyses the oxidative carbonylation of aniline to EPC with a high activity (95 % conversion) and selectivity to EPC(95 %) without producing heavy by-products, which are very difficult to separate.

ii Separation of the catalyst is simple, since, Pd metal settles at the bottom after the reaction.

iii Iodide promoter gives high stability to the catalyst, thereby the catalyst maintains its activity throughout the reaction without decomposition.

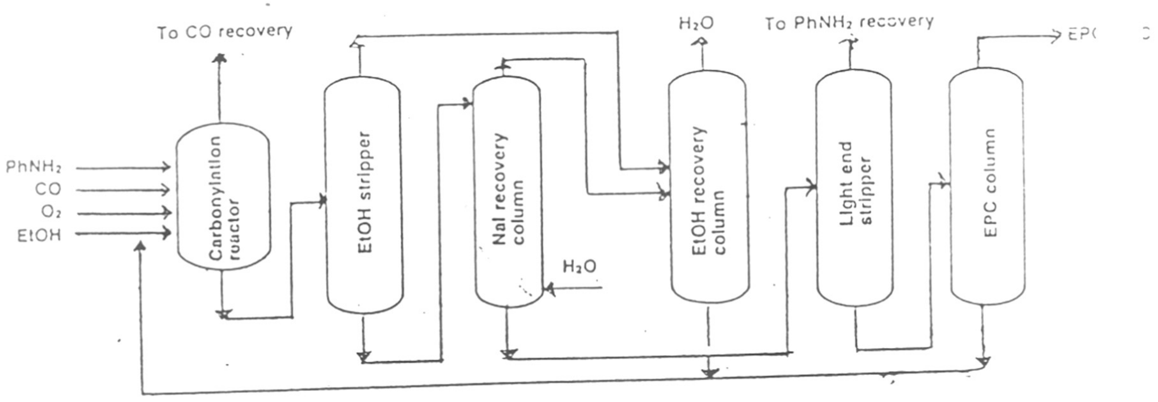
iv These iodide promoter used is less corrosive than the Lewis acids.

A schematic diagram of the MDI process outline is shown in Figure 1.2.

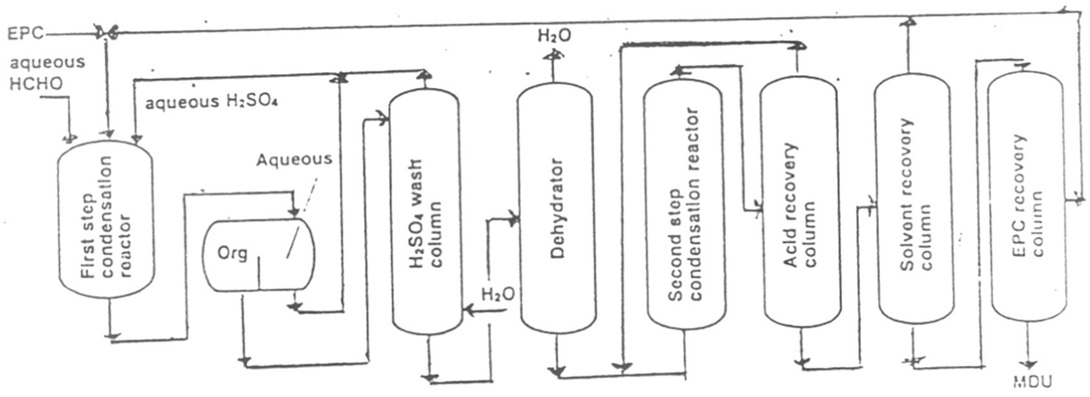
Fukuoka et al., (1984c) have also reported the use of supported transition metal catalysts (2% Pd, 5% Pt, 5% Rh on Carbon or Silica) in oxidative carbonylation of aniline. They found that the activity of the catalyst decreases in the following order Pd>Rh>Ru>Pt>Ir. They have screened several halogen containing promoters and the activity was found to decrease in the order: I>Br>Cl. It was concluded by these investigators that the catalyst system comprising of Pd or Rh with iodide promoter shows highest activity and selectivity for the oxidative carbonylation of aniline. Reaction mechanism for the oxidative carbonylation of aniline was proposed by these investigators (Figure 1.3). However, the mechanism does not explain the role of iodide promoter in enhancing the catalytic reaction.

Alper and Hartstock (1985) have studied the oxidative carbonylation of p-toluidine with methanol as a solvent in the presence of $PdCl_2/CuCl_2$ and HCl under atmospheric conditions to yield 68 % methyl N-p-tolylcarbamate. Various substituted amines (p-methyl, p-chloro, p-methoxy, 2,5-dimethyl, 3,5-dimethyl, 2,6-dimethyl anilines) have been screened. However, the conversion and selectivity of carbamate derivatives decreased with increase in ring substitution.

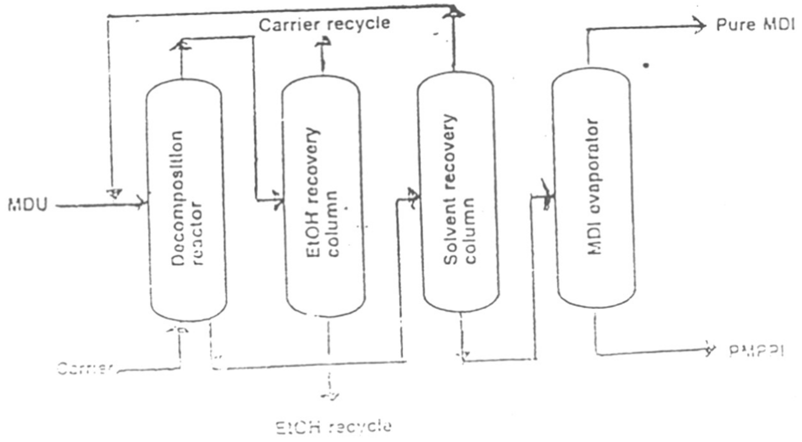
Benidini et al., (1986) and Maddinelli et al., (1987) have studied the oxidative carbonylation of various amines $X\text{-}C_6H_4NH_2$ (X = OMe, Me, OPh, F, Ph) in the presence of Co(II)-Salen catalyst. This system is not selective to carbamates (9-30%) and many side reactions



Condensation



Decomposition



A SCHEMATIC DIAGRAM OF MDI PROCESS (CHONO et al., 1983)

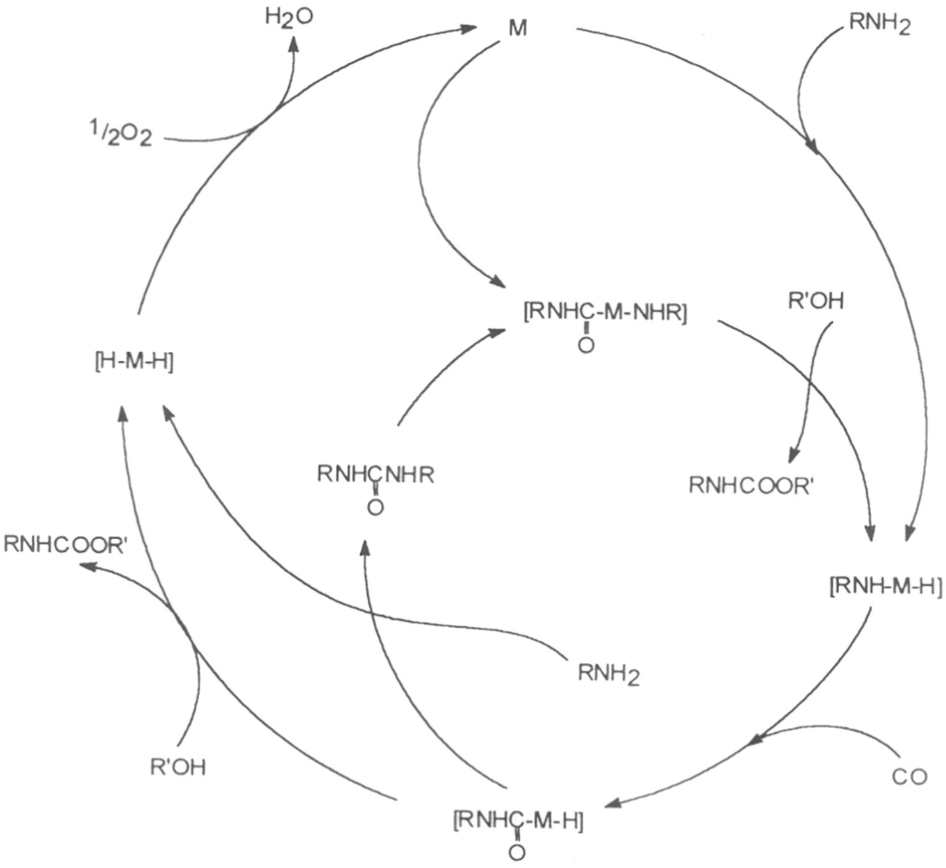


Figure 1.3 : Reaction Mechanism for Carbamate synthesis Fukuoka et al.,(1984c)

occur forming azo derivatives and urea. Amines seem to undergo a Co(II)-Salen catalyzed oxidation reaction followed by insertion of CO. A mechanistic explanation of this fact can be based on the assumption that the oxidative carbonylation reaction could be affected by a superoxo complex of Cobalt(II) known to be formed by co-ordination of dioxygen on the five co-ordinate Schiff base complex (I) derived from the reaction of Co(II) Salen with the amine.

$$\mathrm{ArNH_2(I)} + \mathrm{Co^{II}\,Salen} \rightleftharpoons \underset{\mathrm{(I)}}{\mathrm{Ar\,NH_2 -- Co^{II}\,Salen}} \qquad (1.10)$$

$$\mathrm{(I)} \overset{O_2}{\rightleftharpoons} \mathrm{Ar\,NH_2 -- Co^{III}Salen\,(O_2^{\cdot}-)} \qquad (1.11)$$

The reactivity pattern of amines found by the authors is shown below in a decreasing order (Benidini et al., 1987).

1-adamantylamine > 4-OMe-Ph-NH_2 > 4-Me-Ph-NH_2 > 4-OPh-Ph-NH_2 > 4-Ph-Ph-NH_2 > 4-Cl-Ph-NH_2 (no reaction)

This pattern shows that the electron donating groups present on the aromatic ring increases the reactivity of amines.

Giannoccaro (1987) reported the oxidative carbonylation of aromatic (aniline) and aliphatic (diethylamine) amines in alcohol solution in the presence of Pd (II) complexes at 353 K and 1 atm pressure. Giannoccaro et al., (1989) reported the oxidative carbonylation aniline using Pd(II)-2,2'-bipyridyl complexes and copper(II) complexes intercalated with α-Zirconium phosphate as a catalyst. A low activity is observed in the initial stages with an induction period which can be reduced by pretreating the catalyst with either CO or CO/O_2 mixture at higher temperature.

Gupte and Chaudhari (1988 and 1992) and Gupte (1989) have studied oxidative carbonylation of aniline using 5% Pd/C-NaI catalyst in detail. The role of promoters, solvents and effect of the reaction conditions on activity and selectivity has been reported. Also, the kinetic modeling of oxidative carbonylation of aniline to diphenyl urea in the presence of Pd/C and NaI catalyst system has been reported. A reaction mechanism based on this study has been proposed (Figure 1.4). Main findings of their work are :

i The pretreatment of the catalyst with aniline, CO and oxygen retards the initial activity in oxidative carbonylation reaction.

ii A catalytic cycle, involving Pd-carbamoyl species as intermediate has been proposed incorporating the role of NaI. The activity of the catalyst as a function of promoter(NaI) concentration was found to pass through a maximum.

iii The rate of the reaction was found to be first order with respect to catalyst and 1.6th order with respect to aniline concentration.

Choudhary et al., (1991) have reported oxidative carbonylation of aniline to diphenyl urea. Heterogeneous catalyst system comprising montmorillonite-bipyridine palladium (II) acetate/ copper(II) chloride with di-tert-butyl peroxide has been used. An yield of 89 % diphenyl urea at room temperature and atmospheric pressure was observed.

Guan et al., (1992) have investigated the effect of temperature and carbon monoxide to oxygen ratio on the activity of $CuCl_2$-CuI catalyst system. Only 59 % yield to ethyl phenyl carbamate was observed due to the side reaction leading to the azo products by oxidation of aniline. The selectivity and conversion increases with the increase in temperature, however, the conversion is decreased with the partial pressure of carbon monoxide.

Leung and Dombek (1992) have reported oxidative carbonylation of amines using [Co(TPP)] (TPP = tetraphenyl phorphyrinato dianion) as a catalyst and NaI as a promoter. Various transition metals with porphyrin ligand have been screened for this study. Co, Ru, Rh were found to be the most active catalysts for this reaction.

Prasad and Chaudhari (1994) have studied the activity and selectivity of the Rh catalyzed oxidative carbonylation of aniline to ethyl phenylcarbamate (EPC). The selectivity behaviour with respect to CO and formation of CO_2 (as a side reaction) has been studied in detail. CO_2 formation

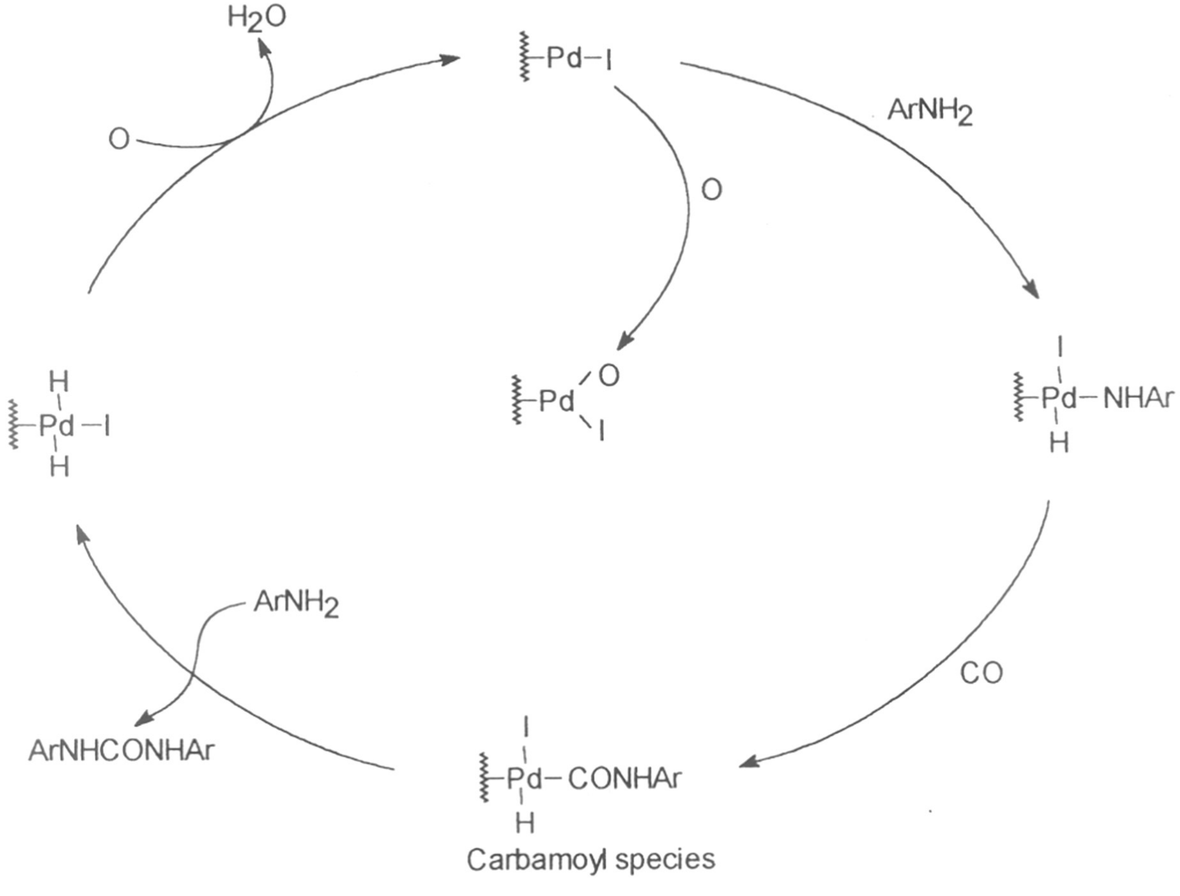
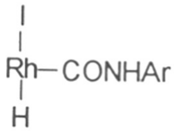


Figure 1.4 Mechanism for oxidative carbonylation of aniline to diphenylurea [Gupte and Chaudhari 1988]

was found to be dependent on the type of support used and the concentration of Rh. A Rh carbamoyl species of the type



$$\overset{|}{\underset{\mathrm{H}}{\overset{|}{\underset{|}{\mathrm{Rh}}}}}-\mathrm{CONHAr}$$

has been proposed as a likely catalytic species

Recently, Valli and Alper (1995) have reported on oxidative carbonylation of aliphatic and aromatic amines in the presence of montmorillonite bipyridyl palladium(II)acetate /NaI catalyst system. Various mono, di and triamines have been oxidatively carbonylated in the presence of montmorillonite-bipyridyl palladium(II)acetate / NaI catalyst system. This catalyst gives high selectivity for the formation of aliphatic and alicyclic carbamates directly by oxidative carbonylation of the corresponding diamines. The activities of other conventional catalysts like $Pd(PPh_3)_4$, $Pd(OAc)_2$, Pd/C were compared with that of Pd-Clay for the oxidative carbonylation of various amines. The activity of Pd-Clay was found to be significantly than other catalysts.

1.3 SCOPE AND OBJECTIVES OF THE PRESENT WORK

The literature review on oxidative carbonylation of amines clearly indicates that for the most of the catalytic system, the role of solvents, promoters catalyst preparation and reaction conditions in the activity and selectivity is not well understood. Considering the practical significants of this reaction, it would be worthwhile investigating the catalysis aspects of the reaction. Particularly, oxidative carbonylation of aliphatic amines using Pd catalyst need further investigation. The scope of the present work is i Oxidative carbonylation of methyl amine to methyl N-methyl carbamate using Pd-NaI catalyst system.

ii Oxidative carbonylation of n-butyl amine to methyl N-butyl carbamate using Pd-NaI catalyst system.

The emphasis of the present study is to investigate the average activity of the Pd-NaI catalyst in these reactions for different promoters, solvents and reaction conditions.

REFERENCES

Agreda V.H., Pond D.M., and Zoller J.R., CHEMTECH, 172 , (1992).

Alper, H. and Hashem, K.H., J. Am. Chem. Soc.,**103**, 6514, (1981).

Alper H.,Vasapollo G., Hartstock F.W., Mlekuz M., Organomet.**6**,239, (1987).

Alper H, and Hartstock F.W, J. Chem. Soc., Chem. Commun.,1141, (1985).

Asahi Chem. Ind. Jap. Pat. 58,146,549 (1983) .

Bach, H., Gick, W., Wiebus, E. and Cornils, B.,Proc.Int. Congress on Catalysis, held in Berlin, 417 (1984).

Becker R., Groling J., and Rasp C., Ger. Offen. 2,908,251 (1980).

Beller M., Cornils B., Frohning C.D. and Kohlpaintner C.W., J. Mol. Catal., **104**, 17, (1995).

Benidini F., Nali M., Rindone B., Tollari S., Cenini S, La Monica G. and Porta F., J. Mol. Catal., **34**, 155, (1986).

Benidini F., Nali M., Rindone B., Tollari S., Cenini S, La Monica G.and PortaF., J. Mol. Catal., **39**, 71, (1987).

Brackmann W., Disc. Faraday Soc., **46**,112, (1968).

Casser L., Foa M., and Chiusoli G.P., Ital. Pat. Appl. A/69 19996 (1969).

Cenini, S., Crotti, C., Pizzotti, M. and Porta, F., J. Org. Chem.,**53**, 1243, (1988).

Chem. Week, July 4, 36 (1984).

Chiusoli G.P., Pure Appl. Chem., **52**, 635, (1980).

Choudhary B.M., Rao K.K., Priozhkov S.D. and Lapidus A.L., Synthetic Communication, **21**, 1923, (1991).

Chono M., Fukuoka S and Kohno M., J. Cellular Plastics, Nov-Dec., 385, (1983).

Cornils, B., in `New Synthesis with Carbon Monoxide', Ed . by Falbe J.,Springer - Verlag, Berlin, Heidelberg, New York (1980).

Dake, S.B.,Kolhe, D.S. and Chaudhari, R.V., J. Mol. Catal., **24**, 99, (1984).

Dombek, B.D., J.Chem.Ed.,**63**, 210, (1986).

Dombek, B.D., J.Chem. Soc., Chem. Commun., 205, (1992).

Ehler J and Juran B., Hydrocarbon Processing, **61**, 109, (1982)

Fahey, D.R., Industrial Chemicals Via C_1, Processes, Ed. ACS Sym. Sr., 328 Am. Chem. Soc., Washington (1987).

Falbe, J., `Carbon monoxide in Organic Synthesis', Springer Verlag, Berlin (1980).

Falbe, J. and Bahrmann, H., J. Chem. Ed., **61**, 961, (1984).

Fukuoka S. and Chono M., European patent 83,096 (1983).

Fukuoka S. and Chono M., J. Chem. Soc. Chem. Commun., 399, (1984)[a].

Fukuoka S. and Chono M. and Kohno M., J. Org. Chem., **49**, (1984)[b].

Fukuoka S., Chono M. and Kohno M., Chemtech., **14,** 670, (1984)[c].

Fukuoka, S., Chono, M. and Kohno, M., Chem. Tech., **14**, 670 (1984).

Gates B.C., Catalytic Chemistry., (1992).

Giannoccaro P., J. Organomet. Chem., **336**, 271 (1987).

Giannoccaro P., Nobile C., Moro G., Ginesrta A.L., Ferragina C., Massucci M.A., and Patrono P., J. Mol. Catal., **53,** 349, (1989).

Golodov V.A., Sheludyakov Yu. L. and Sokolsky D.V., Fundamental Research in Homogeneous Catalysis, 3, 239, Ed. by Tsutsui M., Plenum Press, N.Y. (1979).

Guan S., Huang M., and Jiang Y., Fenzi Cuihua **6**, 168, (1992).

Gupte S.P., and Chaudhari R.V., J. Catl., **114**, 246, (1988).

Gupte S.P., and Chaudhari R.V., Ind. Eng. Chem. Res., **31**, 2069, (1992).

Gupte S.P. Ph.D thesis, University of Pune, April, (1989).

Jenk J.F., and Kuntz E.,187, ACS National meeting, April,St.Louis, M.O.Inde paper 72, (1984).

Keim W., Industrial applications of homogeneous catalysis, Mortreux A and Petit(Eds),335, (1988).

King D.L., and Grate J.H., CHEMTECH., 244, (1985).

Kondo K., Sonoda N. and Tsutsumi S., J. Chem. Soc. Commun., 307 (1972).

Kondo K., Yokoyama S., Miyoshi N., Murai S. and Sonoda N., Angew. Chem. Int. Ed. Engl., 18, 692 (1979).

Knifton J.F., J. Mol. Catal., **11**, 91, (1981).

Leung T.K., and Dombek B.D., J. Che. Soc., Chem. Commum. 205, (1992).

Li K. T and Peng Y.J., J. Catal. **143**, 631, (1993).

Masters. C.`Homogeneous Transition-metal Catalysis', Chapmann and hall (1981).

Maddinelli G., Nali M., Rindone B., and Tollari S., J. Mol. Catal., **39**, 71, (1987).

Mulla S.A.R., Gupte S.P., and Chaudhari R.V., J. Mol. Catal., **67**, L7, (1991).

Nakamura A., and Tsuitsui M., "Principles and applications of homegeneous catalysis" John Wiley and Sons, New York, (1980).

Parshall, G.W., Homogeneous Catalysis' Wiley Interprise Publication, New York, (1980).

Parshall, G.W., Nugent W.A., CHEMTECH., **18**, 184, (1988)^a.

Parshall, G.W., Nugent W.A., CHEMTECH., **18**, 314, (1988)^b.

Parshall, G.W., Nugent W.A., CHEMTECH., **18**, 376, (1988)^c.

Parshall G.W., and Ittel S.D., "Homogeneous Catalysis: The application and Chemistry of catalysis by solible metal complexes" Wiley and Sons, New York., (1992).

Prasad V.K., Ph.D thesis, University of Poona, India, (1994).

Prasad V.K., and Chaudhari R.V., J. Catal., **145**, 204, (1994).

Romano U.,TeseiR.,Mauri M.M. and Rebora R., Ind. Eng. Che. Prod. Res. Dev., **19**, 396,(1980)

Roth, J.F., Craddock J.H., Hershman, A. and Panlic F.E., Chem. Tech.,**1**, 600 (1971).

Satterfield C.N.,"Heterogeneous catalysis in practice" McGraw Hill, New York., (1980).

Satterfield C.N., CHEMTECH, **11**, 618, (1981).

Schiomi Y., Matsuzaki T., Masunoga K(Ube Industries), Eur. Pat.Appl. EP 108 359,(1984).

Schwetlick, K., Unverferth, K. and Tietz, H., Sys. pur Reporter,**19**, 3 (1981).

Sheldon, R.A.,`Chemicals from Syngas' Reidel Publishing Co. (1983).

Sheludyakov Y.L., Golodov V.A. and Sokolskii D.V., Dokl. Akad. Nauk, USSR, 249, 658 (1979).

Sheludyakov Y.L. and Golodov V.A., Bull. Chem. Soc. Japan, **57**, 251 (1984).

Sonoda N., Yasuhara T., Konda K., Ikeda T. and Tsutsumi S., J. Am. Chem. Soc., **93**, 6344 (1971).

Ugo R., Renato T., Marcello M.M. and Plerluigi R., Ind. Eng. Chem. Prod. Res. Dev., **19**, 396, (1980).

Valli V.L.K ., and Alper H., Organometallics **14**, 80, (1995).

Waller F.J., European Patent 195,515 (1986).

Weissermal K and Arpe H.J., "Industialle Organische Chemie", Verlag Chemie Weinheim, (1978).

Wender I., 45, "Chemicals from Coal : New Process" Ed. Payne K.R., John Wiley and Sons, New York, (1987).

Whymann R., Industrial application of homogeneous catalysis Reidel Publ. Co. (1988).

CHAPTER 2

OXIDATIVE CARBONYLATION OF METHYLAMINE TO METHYL-N-METHYLCARBAMATE USING Pd-NaI CATALYST SYSTEM

2.1 INTRODUCTION

Oxidative carbonylation of amines is important as a non-phosgene route for carbamates and isocyanates (Fukuoka et al., 1984a and 1984b). An important example of industrial relevance is the oxidative carbonylation of methylamine which provides an alternative route for a carbamate insecticides such as Carbaryl (1 naphthyl, N-methyl carbamate) and BPMC (2 sec -butyl phenyl methyl carbamate). The relevent literature on this subject is discussed in the previous chapter. This process involves a three phase catalytic reaction with two gas phase reactants and there have been very few attempts to study the activity and selectivity behaviour in oxidative carbonylation of aliphatic amines. Conventionally, the synthesis of carbamate insecticides involves use of phosgene and methyl isocyanate(MIC) as raw materials and leakage of these materials in one such process for the manufacture of Carbaryl, led to Bhopal tragedy in December 1984 in India, in which more than 3000 people died. Since then, the production of aryl, N-methyl carbamate insecticides by MIC route has been prohibited. The phosgene and MIC based processes also have other drawbacks such as corrosion problems and hazards in handling large quantities.

From the point of view of agriculturists, the carbamate insecticides are still important for several applications and hence there is a need for developing an environmentally acceptable and less hazardous process for the preparation of this class of compounds.

The stoichiometric reactions of oxidative carbonylation of methylamine to methyl N-methyl carbamate are given below.

$$2\,CH_3NH_2 + CO + 1/2\,O_2 \xrightarrow{catalyst} CH_3NH\text{-}CO\text{-}NHCH_3 + H_2O \qquad (2.1)$$

n-methylamine

N,N'-dimethylurea (DMU)

$$CH_3NH\text{-}CO\text{-}NHCH_3 + CH_3OH \longrightarrow CH_3NH-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 + CH_3NH_2 \qquad (2.2)$$

N,N'-dimethylurea (DMU)

Methyl N-methylcarbamate(MMC)

In the present work, catalytic activity and selectivity behaviour oxidative carbonylation of methylamine to MMC was investigated. The effect of promoters, methylamine concentration, Pd-NaI ratio catalyst concentration on the conversion of methylamine and selectivity to methyl N-methyl carbamate was studied using Pd-NaI catalyst system. A catalytic cycle describing the role of iodide promoter has been proposed.

2.2 EXPERIMENTAL SECTION

2.2.1 Materials

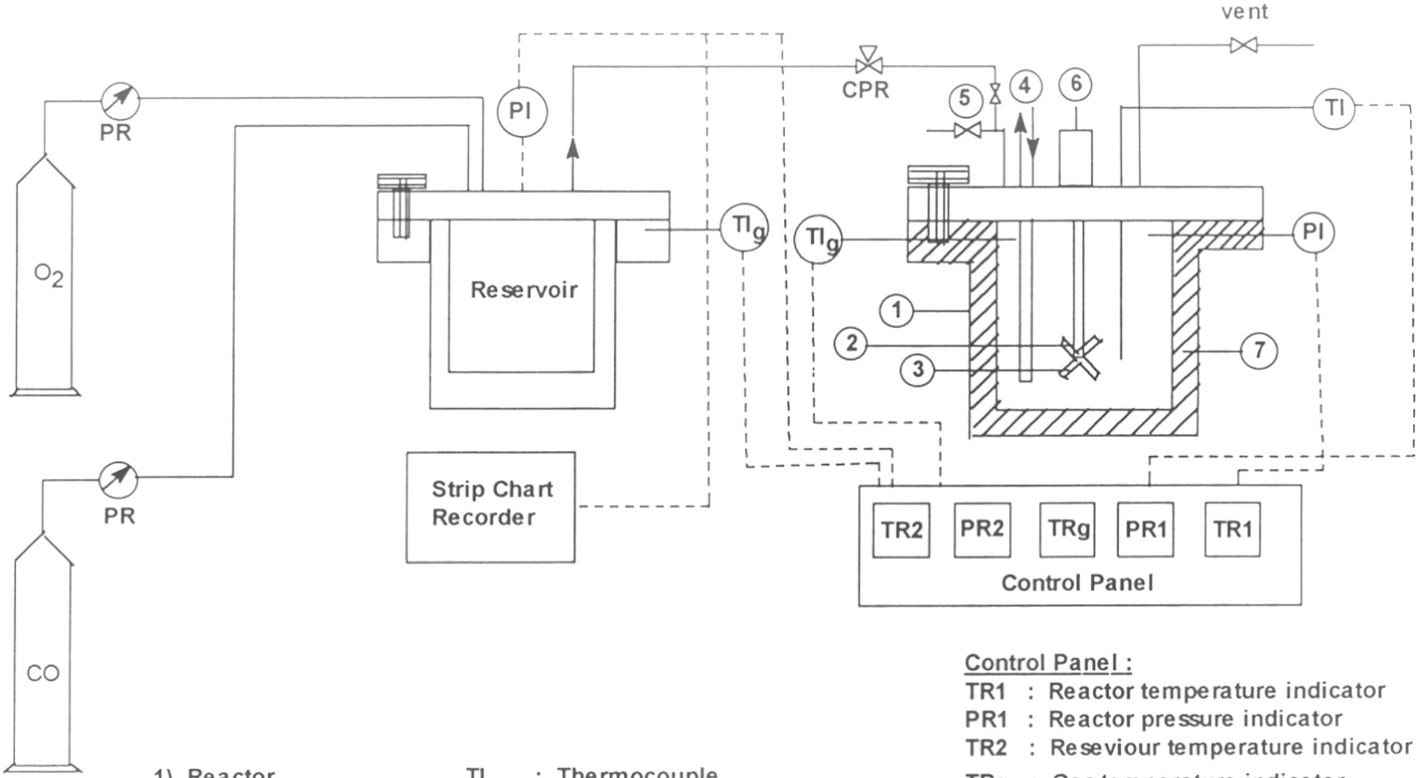
Palladium chloride and Ruthenium chloride trihydrate were purchased from Arrora Mathey, India. Sodium iodide (AR grade) supplied by Loba Chemie was used as received. 5% Rh/C and 5% Ru/C were obtained from Engelhard, USA. Triphenylphosphine, tetrabutyl ammonium iodide and 18-Crown 6 ether were obtained from Aldrich, USA. Methanol was freshly distilled before use. Methylamine supplied by RCF, Bombay was used directly from the cylinder. Carbon monoxide was purchased from Matheson USA and used directly from the cylinder. Oxygen was used directly from the cylinder supplied by Indian Oxygen Ltd., Bombay.

2.2.2 Experimental Set-Up

Oxidative carbonylation experiments were carried out in a 300 cm^3 capacity high pressure stainless steel autoclave supplied by Parr Instrument Co., USA. This reactor was equipped with automatic temperature control and variable speed control. The autoclave was provided with a gas inlet and outlet valves, liquid sampling valve, a rupture disc and a cooling coil. The reactor was designed for a working pressure of 14 MPa and a temperature upto 523 K. Figure 2.1 shows a schematic diagram of the experimental set up used for this study.

2.2.3 Experimental Procedure

In a typical experiment, known quantities of methylamine in methanol, catalyst and iodide promoter were charged to the reactor. The contents were heated to a desired



1) Reactor
2) Stirrer shaft
3) Impeller
4) Cooling water
5) Sampling valve
6) Magnetic Stirrer
7) Electic furnace

TI : Thermocouple
PI : Pressure transducer
Tlg : Thermocouple for gas
O_2 : Oxygen cylinder
CO : Carbon monoxide cylinder
PR : Pressure regulator
CPR : Constant pressure regulator

Control Panel :
TR1 : Reactor temperature indicator
PR1 : Reactor pressure indicator
TR2 : Reseviour temperature indicator
TRg : Gas temperature indicator
PR2 : Reservior pressure indicator

Figure 2.1: A Schematic of the high pressure set up used for oxidative carbonylation reactions

temperature. After attaining the temperature, the autoclave was pressurized with $CO:O_2$ mixture (in a ratio desired for the experiment) up to a required pressure level. The reaction was initiated by switching the stirrer on. The reaction was carried out at a constant pressure by supplying $CO:O_2$ mixture in a ratio of 2:1 from a reservoir as per the stoichiometric requirement. Some reactions were carried out till the completion of absorption of gas. While in some cases the reactions were carried out for a fixed time duration.

The contents were cooled below room temperature and the liquid samples were analysed by Gas Chromatography (GC) using an external standard method. The gas phase containing CO_2, was also analyzed by GC and by ORSAT method. The products were identified by GC-MS analysis. Pure MMC was isolated by fractional distillation and characterized by IR and ^{1}H NMR spectroscopy (Figure 2.2). Methylamine was analyzed by volumetric method reported by Streuli and Averell (1970).

2.2.4 Analytical Conditions

The quantitative analysis of methylamine, dimethyl urea and methyl N-methyl carbamate was carried out using GC as per the details given below:

Liquid Samples	
G.C.	(Hewlett Packard model 5840A)
Column	5 % OV 17, 15 ft
Injector Temperature	523 K
Detector Temperature	523 K
Column Temperature	423 K
Carrier Gas (Nitrogen)	35 ml/min.

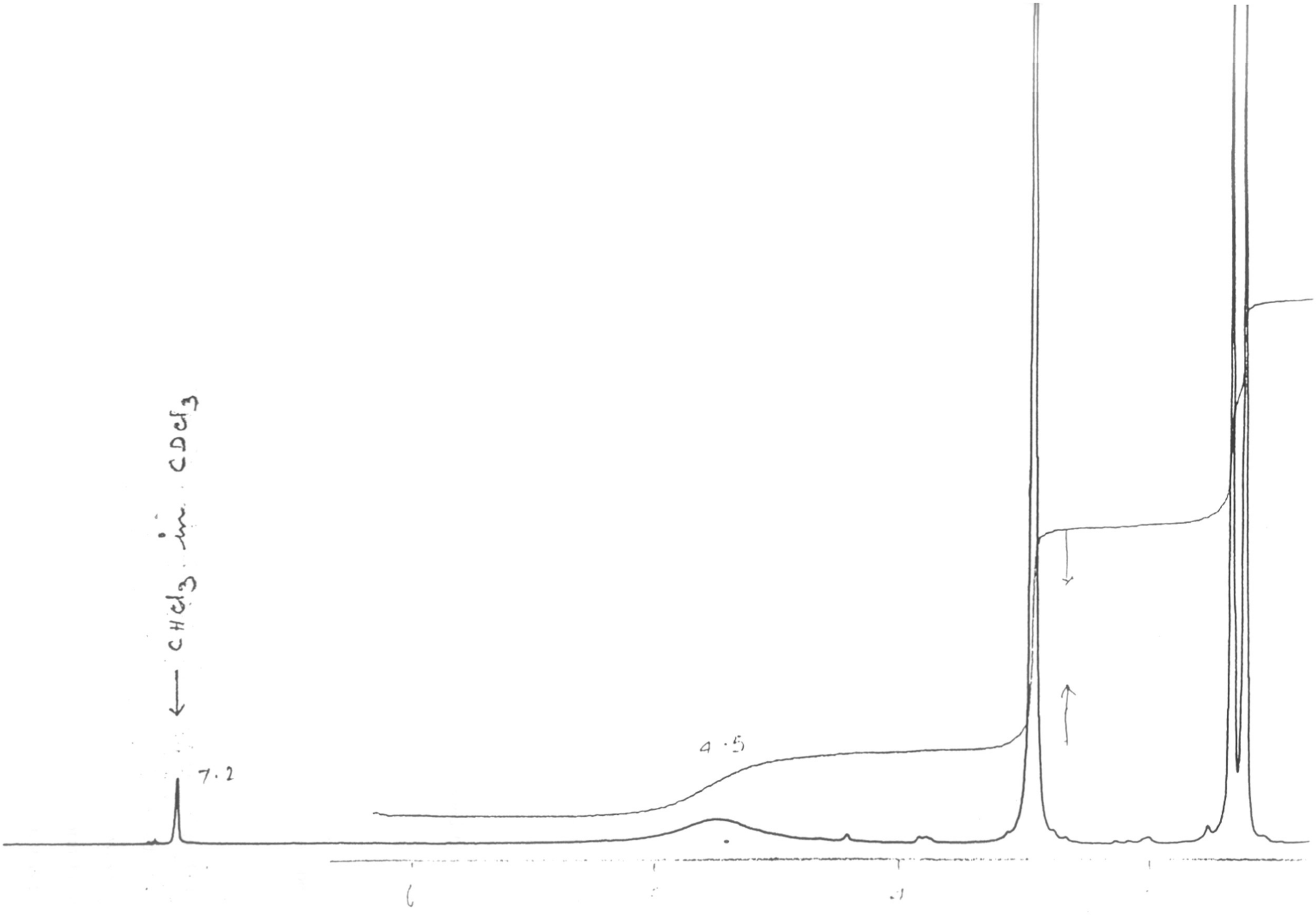


Figure 2.2 1H NMR Spectrum for Methyl N-methylcarbamate (MMC)

The gas phase analysis for CO_2 and CO content was carried out by GC as per the following conditions

CO_2 analysis	
Column	Porapak Q 6 ft
Filament Temperature	433 K
Injector Temperature	323 K
Detector Temperature	383 K
Column Temperature	303 K
Carrier Gas (Hydrogen)	35 ml/min.

2.3 PREPARATION OF CATALYSTS

2.3.1 Preparation of Pd-metal

0.5 g of $PdCl_2$ was dissolved in conc. HCl and to this solution, 500 ml of distilled water was added. The solution was then boiled for 10 min. and cooled to room temperature. To this solution, hydrazine hydrate (99/100 %) was added dropwise till precipitation of the metal was completed. The supernatant solution was decanted after the palladium metal was allowed to settle down. The precipitate was washed thrice with distilled water and dried in vacuum.

2.3.2 Preparation of 5 % Pd/C

The catalyst 5% Pd/C was prepared according to the procedure described by Mozingo (1955). Palladium chloride (16 g) was dissolved in 40 ml concentrated HCl and diluted with 1000 ml of distilled water. The solution was heated on a water bath at 368K under constant stirring. After a few minutes, all $PdCl_2$ was dissolved and a clean dark red solution was obtained. This solution was added to a slurry of 200 g of activated charcoal (acid treated, neutralized and dried) in 1000 ml of distilled water. The mixture was stirred slowly with heating on a water bath at 353 K. At this stage, 16 ml of 37% formaldehyde solution was added slowly to the slurry with constant stirring. The solution was made slightly alkaline (pH = 8) by adding 30% NaOH solution under vigorous stirring. The solution was filtered after stirring it for about 10 minutes. The catalyst was washed with distilled water to remove alkali and then dried under vacuum at 333 K.

2.3.3 Preparation of $Pd(PPh_3)_2Cl_2$

The complex $Pd(PPh_3)_2Cl_2$ was prepared by the procedure described by Itatani, and Bailer, (1967). Accordingly, 8 gm (5.64 mmol) of $PdCl_2$, triphenyl phosphine (17.0 mmol), conc. HCl (two drops), ethanol (150 ml) and H_2O (50 ml) were refluxed for 4 hrs under constant stirring. On cooling the solution to room temperature, a yellow complex precipitated out immediately which was filtered, washed with ethanol (500 ml) and dried under vacuum.

Yield of $Pd(PPh_3)_2Cl_2$: 95 %
Characteristic IR frequencies (cm^{-1}) : 750 s, 690 s,520 s,510 s, 350 s,

2.3.4 Preparation of $Bu_4N[Ru(CO)_3I_3]$

The procedure for the synthesis of $Bu_4N[Ru(CO)_3I_3]$ was followed from the work of Colten and Forthing (1971). $RuCl_3.3H_2O$ (100 mg), conc. HI (4 ml), and formic acid (4 ml) were refluxed for 5 hrs under magnetic stirring. After cooling the solution to 293 K, 200 mg of $(Bu)_4NI$ was slowly added. Shining black crystals developed after keeping for over night, which was washed with petroleum ether and dried in vaccum.

IR analysis shows frequencies for this complex is given below

[CO] (cm^{-1}) : 2115 $_{(s)}$ and 2040 $_{(s)}$

2.3.5 Preparation of 18-crown-6-ether $[Ru(CO)_3I_3]$

18-crown-6-ether $[Ru(CO)_3I_3]$ was prepared according to the procedure described by Colton and Forthing (1971). $RuCl_3.3H_2O$ (100 mg), conc. HI (4 ml) and formic acid (4 ml) were refluxed for 5 hrs under magnetic stirring. After cooling the solution to 293 K, 150 mg of 18-crown-6-ether dissolved in 5.7 ml tetrahydrofuran (THF) was added to the reaction mixture. Brown coloured crystals were developed over night, which were washed with ether and dried in vaccum.

IR spectrum of the complex 18-crown-6-ether $[Ru(CO)_3I_3]$ showed the frequencies for CO and 18-crown-6-ether as given below.

[CO] (cm^{-1}) : $2115_{(s)}$, $2040_{(s)}$, $1350_{(s)}$

18-crown-6-ether (cm^{-1}) : $1100_{(s)}$ $955_{(s)}$ $840_{(s)}$

2.3.6 Preparation of Palladium Iodide (PdI_2)

Palladium iodide was prepared from palladium chloride and potassium iodide by the procedure described by Roolsten (1961).

4 g of $PdCl_2$ was dissolved in 70 ml of conc. HCl and followed by slight warming. KI solution (16 g in 30 ml of water) was added to the mixture. The colour of the solution turned from red brown to black with precipitation. The precipitate was washed with water and dried in vaccum desiccator.

Yield : 7.834 g (~94%). The complex was characterized by IR spectroscopy. The IR frequencies were 720 and 215 cm^{-1} which correspond to the frequencies for Pd-I (Roolsten 1961) .

2.3.7 Preparation of Pd-ZSM-5

Pd-ZSM-5 was prepared by the procedure described by Kulkarni et al., (1982). 0.9 g of $PdCl_2$ was dissolved in 1N HCl. The mixture was heated with constant stirring till clear red solution was obtained. 5 g of ZSM-5(SiO_2:Al_2O_3 = 35) was then added to the solution along with the addition of 10 ml of water. This solution was heated till all the water was completely evaporated. The solid obtained after the evaporation was calcined at 823 K for 12 hrs. The pore size of the catalyst was ~5.5 A°.

2.3.8 Preparation of trans-$[Ru(CO)_2(PPh_3)_2Cl_2]$

The complex trans-$Ru(CO)_2Cl_2(PPh_3)_2$ was prepared by a procedure described by Stephenson and Wilkinson (1965). This complex was prepared starting from $RuCl_2(PPh_3)_3$.

A) Preparation of dichlorotris (triphenyl phosphine) ruthenium (II)

For preparation of $RuCl_2(PPh_3)_3$, ruthenium trichloride trihydrate (0.5 gm) was dissolved in 250 ml of methanol and six fold excess (3 gm) of triphenyl phosphine was added. After vigorous shaking, the solution was filtered and the deep brown solution was refluxed under nitrogen for several hours. The dark brown crystals of the complex obtained were washed with methanol and diethyl ether and dried in vacuum for several hours. Yield of the complex obtained was 70% .

B) Preparation of trans - $Ru(CO)_2Cl_2(PPh_3)_2$

$RuCl_2(PPh_3)_4$ was dissolved in 100 ml acetone under nitrogen atmosphere and then carbon monoxide was bubbled through the solution. The solution immediately turned pale yellow and yellow crystals were deposited. The complex was filtered, washed with methanol and dried. The product, trans-$Ru(CO)_2$ Cl_2 $(PPh_3)_2$ is a microcrystalline pale yellow complex. The infrared spectrum of the complex (in nujol mull) showed a carbonyl absorption at 2005 cm^{-1} . It was observed that some times the complex obtained was containing small quantities of cis isomer, identified by the carbonyl stretching frequencies at 2050 and 1990 cm^{-1}. It is known from the literature (Krassowski et al. 1988) that trans $Ru(CO)_2Cl_2(PPh_3)_2$ complex thermally isomerizes in solution to give cis $Ru(CO)_2$ Cl_2 $(PPh_3)_2$. In order to avoid the mixture of complex the procedure was slightly changed. Acetone solution of $RuCl_2(PPh_3)_4$ was chilled to 273 K and then CO was bubbled through the solution. Complex obtained using this procedure was pure trans complex. The elemental analysis given below confirmed the formation of the above complex.

	Theoretical %	**Experimental %**
C	60.63	60.44
H	4.00	4.52
P	8.24	8.22
Cl	9.44	9.41

2.3.9 Preparation of $Ru(PPh_3)_4Cl_2$

The complex $Ru(PPh_3)_4Cl_2$ was prepared by the procedure described by Stephenson and Wilkinson (1965). Ruthenium trichloride trihydrate (0.5 gm) was dissolved in 250 ml of methanol and seven fold excess of triphenyl phosphine was added.

After vigorous shaking, the solution was filtered and the deep brown solution was refluxed under nitrogen for several hours. The dark brown crystals of the complex obtained were washed with methanol and diethyl ether and dried in vacuum for several hours. Yield of the complex obtained was found to be 70% .

Elemental analysis of the complex is as follows:

	Theoretical %	**Experimental %**
C	67.60	67.80
H	4.70	4.60
P	6.47	6.40
Cl	7.40	7.55

2.4 RESULTS AND DISCUSSION

2.4.1 Preliminary Experiments

Several experiments were carried out on oxidative carbonylation of methylamine, using various catalyst systems at 443 K and total pressure of CO and O_2 was 6 MPa. From the preliminary experiments, it was observed that Methyl N-methyl carbamate (MMC), N,N'-dimethylurea (DMU) and N-methyl formamide (NMF) [under certain conditions] were the main products. Figure 2.3 shows a typical Concentration vs Time profile in a batch reactor. In all the experiments, material balance (based on methylamine charged initially) up to 98% was obtained. From the gas analysis, it was observed that CO_2 was a gaseous product formed by the oxidation of CO .

2.4.2 Promoter Screening :

In order to examine the role of iodine promoter, the reaction was first carried out without using an iodide promoter (NaI). In this experiment, no conversion of methylamine was observed. Similarly, the experiment with only NaI but no Pd catalyst also showed no conversion of methylamine (Table 2.2). This indicates that, both Pd metal

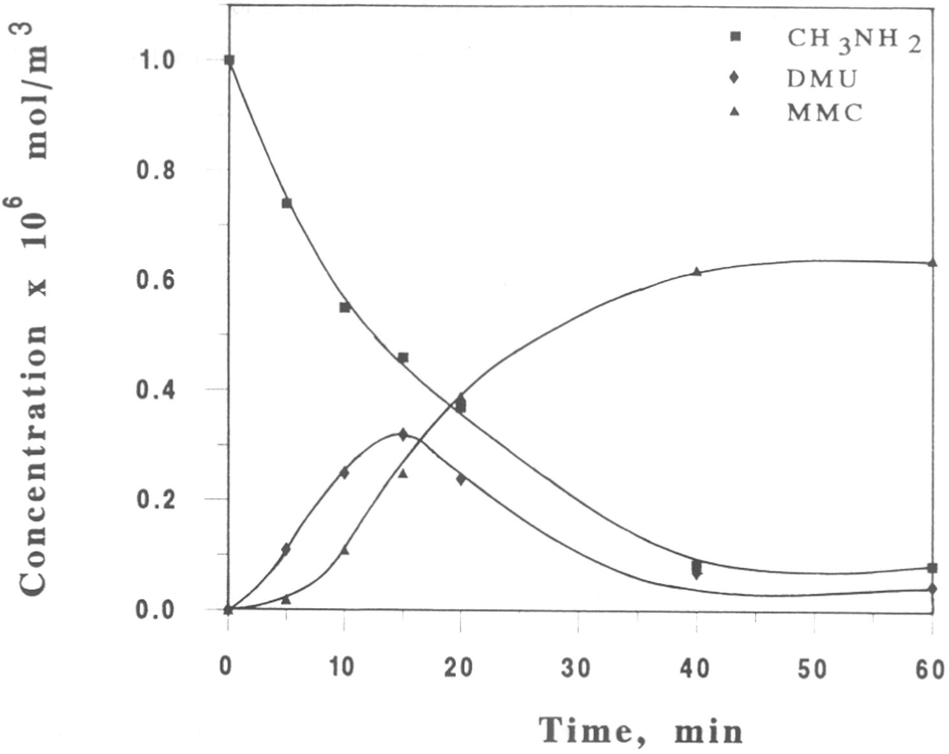


Figure 2.3 A Typical Concentration - Time plot for Oxidative Carbonylation of methylamine.

Reaction Conditions

Promoter (NaI) Concentration : 2.30 X 10^{-6}, mol, cm^3

Catalyst (Pd) Concentration : 2.30 X 10^{-6}, mol, cm^3

Methylamine Concentration : 1 X 10^{-3}, mol, cm^3

Solvent : Methanol

Temperature : 443 K

Total Pressure : 6.1 Mpa

$CO : O_2$: 13 : 1

and NaI are essential for oxidative carbonylation of methylamine. Various alkali metal iodides (LiI, NaI, KI) were tested for their promoting activities and it was observed that LiI and NaI gave comparable performance (Table 2.2). Hence, for further work NaI was chosen as a promoter.

2.4.3 Catalyst Screening

Various homogeneous and heterogeneous catalysts were tested for oxidative carbonylation of methylamine. The results are presented in Table 2.3. For all the supported catalysts studied (Table 2.3) the conversion level of methylamine was lower than that for Pd metal catalyst and the selectivity to dimethyl urea (DMU) was high. Palladium was found to be most active and selective catalyst for MMC formation irrespective of the type of the catalyst precursors used (Pd metal or homogeneous Pd complexes). In all the experiments with Pd precursors, palladium metal was found to be precipitated at the bottom of the reactor. The selectivity of MMC and DMU was dependent on the conversion level in which, at lower conversion of methylamine, DMU selectivity was higher but, at higher conversions, MMC selectivity was higher than that of DMU.

Ruthenium catalysts were found to be less active and selective as compared to the Pd catalysts. With ruthenium precursors such as $RuCl_2(PPh_3)_4$, trans- $Ru(CO)_2Cl_2(PPh_3)_2$ and trans-$Ru(CO)_2Cl_2(Py)_2$, the conversion of methylamine as well as the selectivity to MMC was very low (2.34 to 8.13 %). While with tricarbonyl ruthenium complexes, the conversion of methylamine was higher (81-88 %) and the selectivity to MMC was in a range of 40-50 %. With homogeneous catalysts containing iodide ligands such as PdI_2 and $NBu_4(Ru(CO)_3I_3)$, the activity of the catalysts was not further enhanced by addition of the iodide promoters. This indicates that iodide present in the catalyst is sufficient for the catalytic activity. Thus, of all the catalyst precursors studied, Pd metal was found to be highly active and selective. Therefore, further work was carried out with Pd metal and NaI as a catalyst system.

TABLE 2.2

EFFECT OF PROMOTERS ON OXIDATIVE CARBONYLATION OF METHYLAMINE

Sr. no.	Catalyst	Promoter	Conversion of Methylamine (%)	Selectivity	
				DMU (%)	MMC (%)
1	Pd	–	00.00	00.00	00.00
2	–	NaI	00.00	00.00	00.00
3	Pd	LiI	90.20	14. 08	84.90
4	Pd	NaI	82.82	13.84	85.52
5	Pd	KI	74.32	17.73	81.53

Reaction conditions :

Catalyst(Pd) Concentration : 2.35×10^{-6}, mol/cm^3
NaI Concentration : 2.30×10^{-6}, mol/cm^3
Methylamine Concentration : 1.03×10^{-3}, mol/cm^3
Temperature : 443 K
$CO:O_2$ Ratio : 13:1
Total Pressure : 6.1 MPa
Solvent : Methanol

TABLE 2.3

SCREENING OF CATALYSTS FOR OXIDATIVE CARBONYLATION OF METHYL AMINE

Sr. no.	Catalyst system	Conversion of methylamine (%)	Selectivity	
			DMU (%)	MMC (%)
1	(0.01%)Pd-ZSM5	73.00	88.20	08.98
2	(5%)Pd/C[b]	76.00	27.38	68.55
3	(0.01%)Pd-ZSM5[b]	84.50	43.35	55.62
4	(5%) Pd/C	39.85	85.59	10.78
5	(5%) Ru/C	17.20	97.37	01.69
6	(5%) Rh/C	70.31	93.78	02.30
7	(5%) Pd/C[b]	76.00	27.38	68.55
8	Pd metal	93.22	13.84	85.32
9	PdI_2	85.00	16.15	83.00
10	PdI_2[a]	84.25	14.85	82.45
11	$Bu_4N[Ru(CO)_3I_3]$	90.85	44.40	50.60
12	$BU_4N[Rn(CO)_3I_3]$[a]	81.30	49.42	47.60
13	$[18Brown\text{-}6\text{-}Ether\ Ru(CO)_3I_3]$	88.72	51.89	42.45
14	trans-$[Ru(CO)_2(PPh_3)_2Cl_2]$	45.16	93.15	02.55
15	trans-$[Ru(CO)_2(Py)_2Cl_2]$	55.38	75.34	02.34
16	$RuCl_2(PPh_3)_4$	48.96	88.73	08.13
17	$PdCl_2(PPh_3)_2$	87.47	19.62	79.85

Reaction conditions :

Methylanime Concentration : 1.0×10^{-3}, mol/cm^3
Promoter(NaI) : 2.30×10^{-6}, mol/cm^3
Temperature : 443 K
CO : O_2 : 13 : 1
Total Pressure : 6.1 MPa
Volume of liquid : 100, cm^3
Reaction Time : 120 min.
Solvent : Methanol

[a] Experiment without promoter
[b] reaction time 360 min.

2.4.4 Effect of Reaction Conditions

2.4.4.1 Pd-NaI ratio

The effect of Pd-NaI ratio on the selectivity was studied in a range of 1:0.5 to 1:4 at 443 K and 6 MPa total pressure of CO and O_2. The results are presented in Table 2.4. It was observed that, at a lower ratio of 1:0.5, the conversion of methylamine was found to be 75% and the selectivity to MMC was 83%. With increase in Pd-NaI ratio to 1:1, the conversion was improved considerably. With increasing Pd-NaI ratio (beyond 1:1), selectivity was not affected, while, conversion increased from 93 to 98%. Since selectivity to MMC was not affected and only moderate rise in conversion was observed by a change in ratio of Pd-NaI from 1:1 to 1:4, further experiments were carried out with Pd-NaI ratio of 1:1.

2.4.4.2 Methylamine Concentration

The effect of methylamine concentration on the activity and selectivity of the catalyst was studied in a range of 9.67×10^{-4} to 6.355×10^{-3} mol/cm^3. The results are presented in Table 2.5. It was observed that at higher methylamine concentrations such as 3.23×10^{-3} and 6.355×10^{-3} mol/cm^3, the selectivity to MMC was very poor (10-20 %). Under these conditions DMU was the major product (79 - 89 %). At lower methylamine concentration ($<1.613\times10^{-3}$ mol/cm^3) the selectivity to MMC increased significantly to the level of 75 to 86 % and the formation of DMU was reduced considerably.

2.4.4.3 Catalyst Concentration

The effect of catalyst concentration was studied in a range of 0.94×10^{-6} to 47.0×10^{-6} mol/cm^3 a total pressure 6 MPa and 443 K. The results are shown in Table 2.6. It was observed that the catalyst concentration has only a marginal effect on the selectivity of MMC.

2.4.4.4 Temperature

The effect of temperature on the selectivity was studied in a range of 353-463 K. The results are presented in Table 2.7. At a temperature of 353 K, only DMU was formed with

TABLE 2.4

EFFECT OF Pd-NaI RATIO ON OXIDATIVE CARBONYLATION OF METHYLAMINE

Sr. no.	Pd-NaI ratio	Conversion of methylamine (%)	Selectivity	
			MMC (%)	DMU (%)
1	1:0.5	75.00	83.10	11.53
2	1:1	93.22	85.00	10.97
3	1:2	95.00	86.00	12.46
4	1:4	98.00	86.00	11.67

Reaction conditions :

Catalyst(Pd) Concentration : 2.35×10^{-3}, mol/ cm^3
Methylamine Concentration : 1×10^{-6}, mol/cm^3
Temperature : 443 K
CO : O_2 Ratio : 13:1
Total pressure : 6.1 MPa
Total Volume of liquid : 100 ml
Reaction Time : 120 min.
Solvent : Methanol

TABLE 2.5

EFFECT OF METHYLAMINE CONCENTRATION ON OXIDATIVE CARBONYLATION OF METHYLAMINE

Sr. no.	Methylamine mol/cm^3 x 10^6	Reaction time * min	Selectivity MMC (%)	Selectivity DMU (%)
1	6.355	240	10.35	88.50
2	3.232	180	20.12	79.23
3	1.610	160	75.23	23.45
4	0.967	140	85.67	12.98

Reaction conditions :

Catalyst (Pd) Concentration	:	2.35×10^{-6}, mol/cm^3
Promoter (NaI) Concentration	:	2.30×10^{-6}, mol/cm^3
Temperature	:	443 K
CO:O$_2$ Ratio	:	13:1
Total Pressure	:	6.1 MPa
Solvent	:	Methanol

* Reaction time for complete conversion of methylamine

TABLE 1.

EFFECT OF CATALYST CONCENTRATION ON OXIDATIVE CARBONYLATION OF METHYLAMINE

Sr. no.	Pd Catalyst mol/cm^3 x 10^6	NaI mol/cm^3 x 10^6	Initial DMU (mmol)	Reaction time (min)	Product Distribution		
					DMU (mmol)	MMC(unreacted) (mmol)	Methylami (mmol)
1	–	–	56.18	300	20.39	35.80	34.27
2	–	–	112.40	360	62.34	50.18	47.95
3	2.35	2.30	56.20	300	20.89	35.18	33.93
4	2.35	2.30	112.45	370	62.91	48.33	47.33
5*	–	–	56.18	310	56.05	–	–

Reaction conditions:

Temperature : 443 K
Solvent : Methanol
* Temperature of the reaction : 353 K

TABLE 2.7

EFFECT OF TEMPERATURE ON OXIDATIVE CARBONYLATION OF METHYLAMINE

Sr. no.	Temperature K	Reaction time * (min)	Selectivity	
			MMC (%)	DMU (%)
1	353	120	00.00	98.17
2	413	420	52.95	45.30
3	423	330	65.50	32.80
4	433	200	72.84	26.56
5	443	140	86.67	12.92
6	453	120	86.15	17.75
7	463	100	85.96	12.78

Reaction conditions

Catalyst(Pd) Concentration	:	2.35×10^{-6}, mol/cm^3
Promoter (NaI) Concentration	:	2.30×10^{-6}, mol/cm^3
Methylamine Concentration	:	9.67×10^{-4}, mol/cm^3
$CO:O_2$ Ratio	:	13:1
Total Pressure	:	6.1 MPa
Solvent	:	Methanol

* Reaction time for complete conversion of methylamine

a selectivity as high as 98 % while, MMC was not detectable. However, at higher temperatures (> 413 K) the selectivity to MMC increased, with highest in the temperature range of 443-463 K. At lower temperature (353 K) CO_2 formation was below 1%. Poor selectivity of MMC at lower temperatures indicates that, a certain minimum temperature is required for the non-catalytic conversion of DMU to MMC. Also from the variation in selectivity of MMC with temperature, it appears that the non-catalytic conversion of DMU to MMC is an equilibrium reaction and by raising the temperature (from 413-443 K), selectivity of MMC is improved substantially (53-87%), with further increase in temperature, selectivity to MMC is not improved further. In order to confirm this observation, separate experiments were carried out on the non catalytic conversion of DMU to MMC and the results are presented section 2.4.4.6..

2.4.4.5 $CO:O_2$ ratio

The effect of $CO:O_2$ ratio was studied in the range of 10:1 to 25:1. For safety reasons $CO:O_2$ ratios below 10:1 were not studied. The results are presented in Table 2.8. It was observed that, the selectivity to MMC was highest for $CO:O_2$ ratio in a range of 10:1 to 13:1. However, at $CO:O_2$ ratio of 20:1 and 25:1, the selectivity to MMC decreased drastically and the formation of NMF increased substantially. In a reaction carried out using pure CO, NMF was formed with a selectivity of 86 %. **This is the first report on the preparation of NMF using such a catalyst system.** At higher $CO:O_2$ ratios (20:1 and above), CO_2 formation was below 1%. At higher $CO:O_2$ ratios oxygen concentration is very low and due to oxygen starvation, only carbonylation is favoured resulting in high selectivity to NMF. The reaction 2.3 shows the formation of NMF by the reaction between methylamine and CO.

$$CH_3NH2 + CO \longrightarrow CH_3NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}H \qquad (2.3)$$

TABLE 2.8

EFFECT OF CO : O_2 RATIO ON OXIDATIVE CARBONYLATION OF METHYLAMINE

Sr. no.	CO:O_2 Ratio	Reaction time * (min)	Selectivity		
			MMC (%)	DMU (%)	NMF (%)
1	10 : 1	130	85.82	10.65	02.63
2	13 : 1	140	85 .67	10.95	02.31
3	20 : 1	200	14.00	08.97	75. 21
4	25 : 1	260	08.43	07.21	84.36
5	pure CO	320	–	06.17	92. 61

Reaction conditions :

Catalyst (Pd) Concentration	:	2.30×10^{-6}, mol/cm^3
Promoter (NaI) Concentration	:	2.30×10^{-6}, mol/cm^3
Methylamine Concentration	:	9.67×10^{-4}, mol/cm^3
Temperature	:	443 K
Total Pressure	:	6.1 MPa
Solvent	:	Methanol

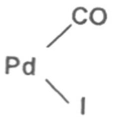
* Reaction time for complete conversion of methylamine

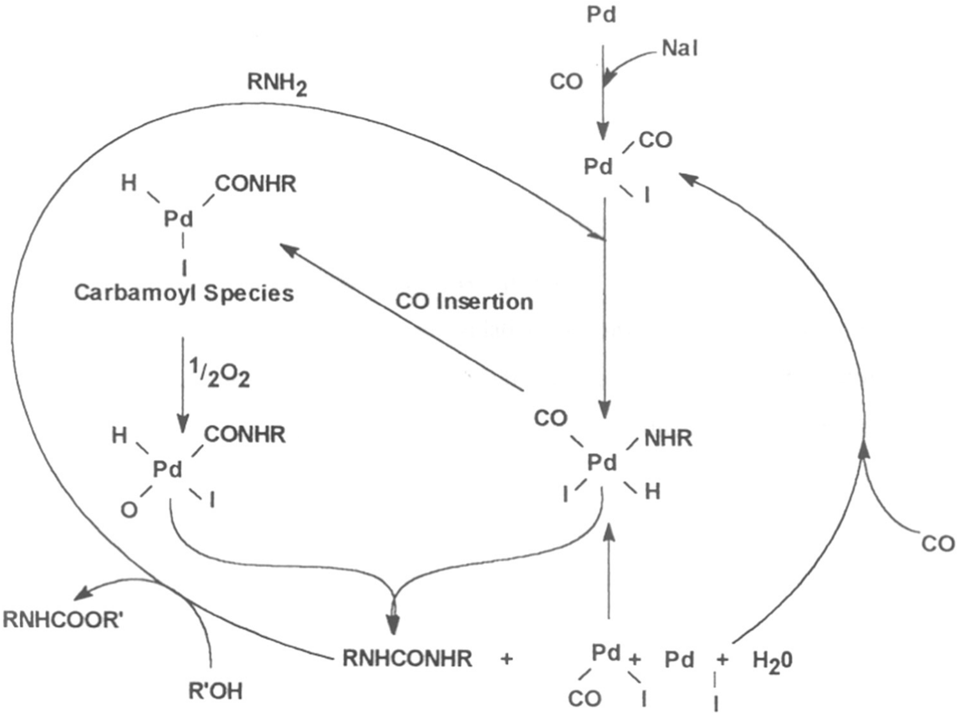
2.4.4.6 Effect of Catalyst on Conversion of DMU to MMC

The effect of various process parameters on oxidative carbonylation of methylamine, clearly indicates that DMU is an intermediate product in MMC synthesis (reactions 2.1 and 2.2). In order to confirm this, reaction (2.2) was studied independently with and without Pd-NaI catalyst. The results are shown in Table 2.9, which indicate that reaction (2.2) is a non-catalytic equilibrium reaction and Pd-NaI catalyst has no influence on this reaction. However, it was observed that reaction (2.2) stops after certain conversion unlike the reaction of diphenyl urea with ethanol,(Gupte and Chaudhari, 1988), in which nearly complete conversion of diphenyl urea was observed. This means that, for the reaction of dimethyl urea with methanol, the equilibrium is favoured more towards left side. This also explains the observations in Table 2.5 wherein, higher DMU selectivity was obtained at higher methylamine concentration as well as the improved MMC selectivity for lower methylamine concentration. At 353 K, the reaction did not proceed and MMC formation was not observed. This explains very high selectivity to DMU in the oxidative carbonylation of methylamine at 353 K.

2.5 REACTION MECHANISM

The mechanism of oxidative carbonylation of amines to carbamates is not well understood. Fukuoka et al., (1984b) have proposed a possible mechanism on the assumption that a Pd-carbamoyl complex (Pd-CONHAr) is formed as an intermediate species. However, this scheme does not explain the role of iodine promoter. In the absence of NaI, reaction does not take place indicating that Pd^0 catalyst, modified in the presence of NaI is an active catalytic system for oxidative carbonylation of alkyl amines. The mechanism of oxidative carbonylation of alkyl amine can be rationalized by assuming the





[R,R' = Alkyl Group]

Table 2.4 **Mechanism of oxidative carbonylation of amines to Carbamate** formation of Pd as an active catalytic species, similar to that proposed earlier for other amines (Gupte, 1989). The reaction scheme is speculated in Fig.2.4. However, further work would be necessary to establish the individual steps in the catalytic cycle and the nature of active species.

2.6 CONCLUSIONS

Oxidative carbonylation of methylamine using Pd metal-NaI catalyst has been shown to give methyl N-methyl carbamate as a product. Product distribution is found to be sensitive to the reaction conditions in oxidative carbonylation of methylamine. DMU was found to be an intermediate product in MMC synthesis. At lower temperature and higher methylamine concentration, DMU was the major product. At higher temperatures and lower methylamine concentration, MMC was the major product while at higher $CO:O_2$ ratios (20:1 and above) NMF was a major product. Thus synthesis of MMC by oxidative carbonylation of methylamine reported here can provide an alternative and safer route (non-phosgene and non-MIC) for carbamates and hence has important implications from synthetic as well as environmental point of view.

REFERENCES

Alper H., and Hartstock F. W., J.Chem. Soc., Chem. Commun., 1141, (1985).

Colton R., Farthing R. H., Aust.J.Chem., **24**, 903, (1971).

Dombek B.D., J.Chem. Soc., Chem. Commun., 205, (1992).

Fukuoka S., Chono M., Kohno M.A., J. Chem. Soc. Chem. Commun., 399, (1984_a).

Fukuoka, S.; Chono M., Kohno M. A., J. Org. Chem., **49**, 1458, (1984_b).

Golodov V.A., Sheludyakov Yu.L., Sokolsky D.V., Fundemental Resin Homogeneous

Catalysis; Tsutsui M., Ed.,; Plenum Press, New York, **3**, 239, (1979).

Gupte S. P., Chaudhari R.V., J.Catal., **114**, 246, (1988).

Gupte S. P. , Ph.D. Dissertation, University of Pune,India, (1989).

Halligudi S.B., Bhatt K.N., and Taqui Khan M.M., J. Mol., Catal., **63**, 261, (1991).

Itatani H., Bailer J.C.Jr., J.Am.Oil.Chem.Soc., **44,** 147, (1967).

Kulkarni S.B., Shiralkar V.P., Kotesthane A.N., Borade R.B., and Ratnasamy P., Zeolites **2**, 313, (1982) .

Mozingo R., `Organic Synthesis' Hornning, E.C. Ed. Wiley London, Collective **3**, p.685, (1955).

Mulla S.A.R., Gupte S.P. and Chaudhari R.V., J. Mol. Catal., L7, (1992).

Roolsten R., ``Iodide metals and metal iodides " John Wiley and sons, New York. (1961).

Sonoda N., Yasuhura T., Konda K., Ikeda T., Tsulsumi S.A., J.Am., Chem., Soc., 93, 6344, (1971).

Stephenson T.A.; Wilkinson G. J., Inorg. Nucl. Chem., **28**,945, (1965).

Streuli C.A., Averell P.R., 'The analytical chemistry of nitrogen and its compounds'Elving P.J. and Kolthoff I.M., Ed. Publisher Wiley-Interscience A division of John Wiley & sons, Inc., New York/London, **28**, p.271, (1970).

CHAPTER 3

OXIDATIVE CARBONYLATION OF N-BUTYL AMINE USING Pd-NaI CATALYST SYSTEM

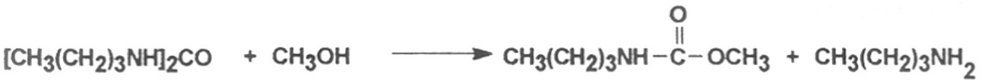
3.1 INTRODUCTION

Oxidative carbonylation of N-butyl amine is important in the synthesis of dibutyl urea and methyl N-methyl carbamate. In continuation with the work on oxidative carbonylation of aliphatic amine, the activity and selectivity of Pd-NaI catalyst system in oxidative carbonylation of n-butyl amine was also investigated. The reaction involved are :

$$2\,CH_3(CH_2)_3NH_2 + CO + 1/2\,O_2 \xrightarrow{\text{catalyst}} [CH_3(CH_2)_3NH]_2CO + H_2O \qquad (3.1)$$

n-butylamine

N,N'-butylurea (DBU)



$$[CH_3(CH_2)_3NH]_2CO + CH_3OH \longrightarrow CH_3(CH_2)_3NH-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 + CH_3(CH_2)_3NH_2$$

(3.2)

N,N'-butylurea (DBU)

Methyl N-butylcarbamate(MBC)

The previous work on this subject relates to oxidative carbonylation of aromatic amines and particularly aniline using different types of catalysts (Fukuoka and Chono, 1984a ; Fukuoka et al., 1984b). Chapter 1 describes the breif literature on this reaction. Most of the reports concern aniline as a substrate and there are only a few studies on alkyl amine as substrates (Alper and Hartstock 1985, Dombek, 1992, Sonoda et al., 1971, Golodove et al., 1979, Halligudi et al., 1991). However, none of these reports cover detailed investigations on the selectivity behaviour of this reaction. The aim of this work was to present results on oxidative carbonylation of n-butyl amine using supported and soluble Pd and Ru based catalysts with respect to activity and selectivity behaviour.

The reaction 3.1 is catalytic while the reaction 3.2 is non-catalytic therefore, it is important to understand the selectivity behaviour of the two products (N,N'-dibutyl urea (DBU) and methyl N-butylcarbamate (MBC)) and its dependence on the type of catalyst used and the reaction conditions used. Results of the effect of solvents, promoters and reaction conditions as well as the product distribution, in a batch reactor are discussed.

3.2 EXPERIMENTAL

The details of the chemicals, analytical methods and experimental set up used for oxidative carbonylation of N-butyl amine have described already in the previous chapter (section 2-2).

3.2.1 Preparation of $Pd(Py)_2X_2$ X = Cl, Br, I

These complexes were prepared by the procedure described by Prasad (1994). Typical procedure for the preparation of $Pd(Py)_2Cl_2$ is given below:

To a solution of palladium chloride (5,64 mmol) in 25 ml of water, 22.5 mmol of pyridine was added. The solution was refluxed for 4.5 hrs. The colour of the solution changed from wine red to yellow after 30 min of reflux. The yellow solution was cooled to 278 K, which resulted in precipitation of the complex. It was filtered and washed repeatedly with petroleum ether. The compound was crystallized from hot methanol giving a yield of 92 %. The elemental analysis of the complex given below.

	Theoretical %	**Experimental %**
C	35.82	35.8
H	2.98	3
N	8.36	8.3
Cl	21.19	21.2
Pd	31.64	31.2

3.2.2 Experimental Procedure

In a typical experiment known quantities of n-butyl amine, catalyst (metallic Pd), promoter (NaI) and solvent (methano)l were charged into the autoclave. The autoclave was flushed with nitrogen prior to heating. It was heated to a desired temperature and then pressurized with CO:O_2 (13:1) to a total pressure of 6.1 MPa. The reaction was carried out for 2 hrs. at 373 to 443 K and at a constant pressure of 6.1 MPa by supplying gas from small reservoir (CO:O_2 = 2:1; proper safety precautions were employed during this work against any explosion hazards). After 2 hrs., the contents were cooled and the liquid and gas samples were analyzed by G.C. The product was identified by NMR and IR. Urea analysis was carried out on HPLC using Bondapak phenyl stainless steel column. The ^{1}H NMR spectrum data of products isolated are presented in Table 3.1.

3.2.3 Analytical Conditions:

Liquid Samples	
G.C.	(Hewlett Packard model 5840A)
Column	5 % OV 17, 15 ft
Injector Temperature	473 K
Detector Temperature	573 K
Column Temperature	393 K
Carrier Gas (Nitrogen)	35 ml/min.

Table 3.1

^{1}H NMR data for Methyl-N-butylcarbamate and N,N'-dibutyl urea

Solvent	δ (ppm) chemical shift reference to TMS
	MBC [$H_3C(CH_2)_3NHCOOCH_3$]
$CDCl_3$	0.86 - 0.91 (t, 3 H, CH_3); 1.29 - 1.54 (m, 4 H, -CH_2-CH_2-CH_3); 3.05 - 3.17 (q, 2 H, -CH_2-NH-); 3.48 - 3.60 (s, 3 H, -OCH_3); 6.21 - 6.34 (s, 1 H, NH)
	DBU [$H_3C(CH_2)_3NHCONH(CH_2)_3CH3$]
CD_3COCD_3	0.89 - 0.91 (t, 6 H, CH_3); 1.31 - 1.41 (m, 4 H, -CH_2-CH_2-); 1.50 - 1.62 (m, 4 H, -CH_2-CH_2-); 3.21 - 3.30 (q, 4 H, -NH-CH_3); 7.96 - 8.12 (s, 2 H, NH)

Abbreviations : s, singlet; t, triplet, q, quartet; m, multiplet

CO_2 analysis	
Column	Porapak Q 6 ft
Filament Temperature	433 K
Injector Temperature	323 K
Detector Temperature	383 K
Column Temperature	303 K
Carrier Gas (Hydrogen)	35 ml/min.

N-butylamine was analyzed by volumetric method described by Streuli (1970).

3.3 RESULTS AND DISCUSSION

The aim of this work was to study the activity and selectivity of different types of Ru and Pd catalysts for oxidative carbonylation of n-butylamine. For this purpose several experiments were carried out in which reactant/product concentration vs time data were obtained. The average activity and selectivity for a fixed time duration were calculated. The results on screening of catalysts and effect of solvents, promoters and temperature are discussed in this chapter.

3.3.1 Screening of Catalysts

Several Ru and Pd catalysts were tested for their activity and selectivity in oxidative carbonylation of n-butylamine at 443 K and a total pressure of 6.1 MPa (CO : O_2 ratio = 13 : 1). These experiments were carried out in methanol as a solvent, which also is a reactant in the formation of carbamate. The results are presented in Table 3.2. In all the cases two major products namely N,N' -dibutylurea and methyl N-butyl carbamate were formed. These products were separated by column chromatography and identified by MS, IR, ^{1}H NMR and elemental analysis.

The activity of Pd based catalysts was found to be significantly higher compared to those of Ru catalysts. Both homogeneous and supported Pd catalysts were studied; however, for

TABLE 3.2

SCREENING OF CATALYSTS FOR OXIDATIVE CARBONYLATION OF N-BUTYLAMINE

Sr. no.	Catalyst system	Conversion (%)	Selectivity	
			BMC (%)	DBU (%)
1	(0.01%) Pd-ZSM5	84.27	75.28	20.14
2	(1%) Pd/Al_2O_3	15.84	74.58	22.70
2	(5%) Pd/C[b]	76.00	27.38	68.55
3	Pd-ZSM5[b]	84.50	43.35	55.62
4	Pd metal	84.27	75.28	20.14
5	(10%) Pd/C	52.27	92.15	O2.87
6	(5%) Pd/C	71.90	89.32	07.98
7	(1%) Pd/C	76.86	70.75	22.80
8	Pd metal [a]	78.15	73.20	21.28
9	PdI_2	78.25	72.81	23.14
10	$Pd(Py)_2Cl_2$	44.66	21.78(19.73)[b]	76.42(79.32)[b]
11	$Pd(Py)_2Br_2$	54.01	28.63(23.91)[b]	70.42(75.23)[b]
12	$Pd(Py)_2I_2$	79.23	32.64(29.7)[b]	65.78(69.32)[b]
13	(1%) Ru/C	41.05	29.43	69.42
14	PdI_2[a]	84.25	14.85	82.45
15	cis$[Ru(CO)_3Cl_3PPh_3]_2$	37.45	28.37	69.42
16	trans$[Ru(CO)_2Cl_2PPh_3]_2$	41.25	19.82	72.65
17	$Bu_4N[Ru(CO)_3I_3]$	58.61	10.21	80.76
18	[18Brown-6-Ether $Ru(CO)_3I_3$]	45.43	16.58	81.05
19	$RuCl_2(PPh_3)_3$	50.81	15.41	79.74
20	$PdCl_2(PPh_3)_2$	51.13	12.78	81.47
21	$RuCl_2(CO)_2(Py)_2$	47.91	10.83	84.10

Reaction conditions :

Methylanime Concentration : 1.0×10^{-3}, mol/cm^3
Promoter (NaI) Concentration : 2.30×10^{-6}, mol/cm^3
Temperature : 443 K
CO : O_2 : 13 : 1
Total Pressure : 6.1 MPa
Volume of Liquid : 100 cm^3
Reaction Time : 120 min
Solvent : Methanol

[a] Experiment without promoter
[b] Reaction time 360 min

homogeneous catalysts precursors the Pd metal precipitation was observed at the end of the reaction. The effect of Pd content in Pd/C catalysts showed that 1% Pd/C catalysts gives higher average activity compared to 10% Pd/C. However, the selectivity of methyl N-butyl carbamate increased with increase in Pd content in the catalysts. The type of support used also showed a significant effect on the catalyst activity. Pd-ZSM5 catalyst with 0.01% Pd showed remarkably higher activity compared to Pd/C and Pd/γ-Al_2O_3 catalysts (Table 3.2). This effect is primarily due to the better dispersion of Pd metal on the surface of the ZSM5 support. This unusual higher activity observed for 0.01% Pd-ZSM5 catalysts deserves some comments. It is known that the activity of the transition metals exchanged zeolites depends on the type of zeolites and the amount and location of metal site in the zeolite structure (Ghosh and Kevan, 1990). Decrease in the activity with increase in Pd content (> 1%) arises not only due to under utilization of densely occupied Pd sites but also due to pore blockage due to adsorbed Pd complex on the mouth of the pore. The possibility of such blockage increases with increase in Pd content in the catalyst. The pore blockage renders the Pd sites located in the inner cage inaccessible to the reactants, thus decreasing the catalyst activity. For 0.01% Pd containing catalyst such type of blockage may be minimum resulting in higher activity of the catalyst. The effect of 0.01 % Pd/ZSM-5 on oxidative carbonylation of aromatic amines such as aniline was also studied (Kanagasabapathy et al., 1994).

Some blank experiments were carried out without the catalyst and promoters. It was observed, neither catalyst nor promoter alone catalyze the reaction but both are essential components. For the case of Pd-I_2 catalysts, however the activity was significant even in the absence of NaI. The activity of the Pd catalysts containing Cl ligands increases remarkably when NaI promoter is added to the system. However, the activity of complexes containing iodide ligands increases only slightly upon addition of NaI. This indicates that iodide promoter plays an important role in the oxidative carbonylation of n-butylamine (Table 3. 2).

The homogeneous Ru complex catalysts were also found to be active in the oxidative carbonylation of n-butylamine, though the average activity was lower compared to Pd catalysts. The selectivity for N,N'-dibutylurea was higher than that for methyl N-butylcarbamate (Table 3.2).

Since the highest activity and selectivity for carbamate were obtained using Pd/NaI catalysts, the product distribution and the role of promoters, solvents, reaction conditions, catalyst reusability were studied using this system. Several experiments were carried out to identify the role of Pd/NaI catalyst system in the synthesis of methyl N-butyl carbamate. Figure 3.1c shows a typical concentration profile which indicates that 80% conversion of n-butylamine is possible and methyl N-butyl carbamate and N,N'-dibutylurea are the products. Figure 3.1c also indicates > 96% material balance of products (carbamate and urea) formed based on n-butylamine converted. In order to ensure that the activity of the catalyst was constant during a run, catalyst recycle experiments were carried out using Pd/NaI system, which indicated constancy of the catalyst activity even after 4 recycles (Table 3.3)

From these studies it was concluded that Pd catalysts are more selective for carbamate synthesis. The effect of solvents, promoter and temperature for Pd/NaI catalyst system was studied. The conversion and catalyst behaviour in a batch reactor was also studied at different temperatures. The results are discussed below.

3.3.2 Effect of Solvents

The effect of different solvents on the activity and selectivity of Pd metal catalyst with NaI as a promoter was investigated at 443 K and total pressure of 6 MPa. The results are presented in Table 3.4. Methanol, ethanol, propanol, p-xylene, and toluene were used to study the role of solvents for this reaction . These results indicate that the activity of the catalyst was very poor in non-polar solvents like p-xylene and toluene. Whereas the activity of the catalyst was found to be significantly higher for polar solvents such as methanol, ethanol and propanol. However, the selectivity to methyl N-butylcarbamate was found to decrease with increase in the carbon number of the polar solvents (alcohols), while that of dibutylurea increases with the increase in the carbon number of the alcohol. It was also noticed from the solvent effect that the activity and selectivity of the catalyst has increased with increase in the dielectric constant of the solvents. Among the solvents screened for this study, methanol was found to be the better solvent for oxidative carbonylation of n-butylamine. Therefore methanol was chosen as a solvent for further work.

3.3.3 Effect of Promoter

It was already explained in the preliminary studies that for the oxidative carbonylation of n-butylamine to methyl N-butylcarbamate, promoters containing iodide are essential in the catalyst system. Therefore, the effect of different types of promoters containing iodides on the activity

TABLE 3.3

EFFECT OF CATALYST REUSABILITY ON OXIDATIVE CARBONYLATION OF N-BUTYLAMINE

Sr. no.	Number of recycles	Conversion (%)
1	0	61.25
2	1	68.25
3	2	84.27
4	3	80.68
5	4	78.12

Reaction conditions :

Catalyst (Pd) Concentration : 2.35×10^{-6}, mol/cm^3
Promoter (NaI) Concentration : 2.30×10^{-6}, mol/cm^3
N-butylamine Concentration : 4.11×10^{-4}, mol/cm^3
Temperature : 443 K
CO:O$_2$ Ratio : 13:1
Total Pressure : 6.1 MPa
Reaction Time : 120 min.
Total volume : 100 cm^3
Catalyst / Promoter Ratio : 1 : 1
Solvent : Methanol

TABLE 3.4

EFFECT OF SOLVENT ON OXIDATIVE CARBONYLATION OF N-BUTYLAMINE

Sr. no.	Solvent	dielectric constant (e) 293 K	Conversion of N-butylamine	Selectivity (%)	
				BMC	DBU
1	p-xylene	02.3	18.6	–	100
2	toluene	02.4	19.5	–	100
3	methanol	32.7	84.4	88.6	04.8
4	ethanol	24.6	80.3	73.8	25.8
5	1-propanol	20.5	67.7	43.9	54.9

Reaction conditions :

Catalyst (Pd) Concentration	:	2.35×10^{-6},mol.cm^3
Promoter (NaI) Concentration	:	2.30×10^{-6}, mol/cm^3
N-butylamine Concentration	:	4.11×10^{-4}, mol/cm^3
Temperature	:	443 K
CO:O$_2$ Ratio	:	13:1
Total Pressure	:	6.1 MPa

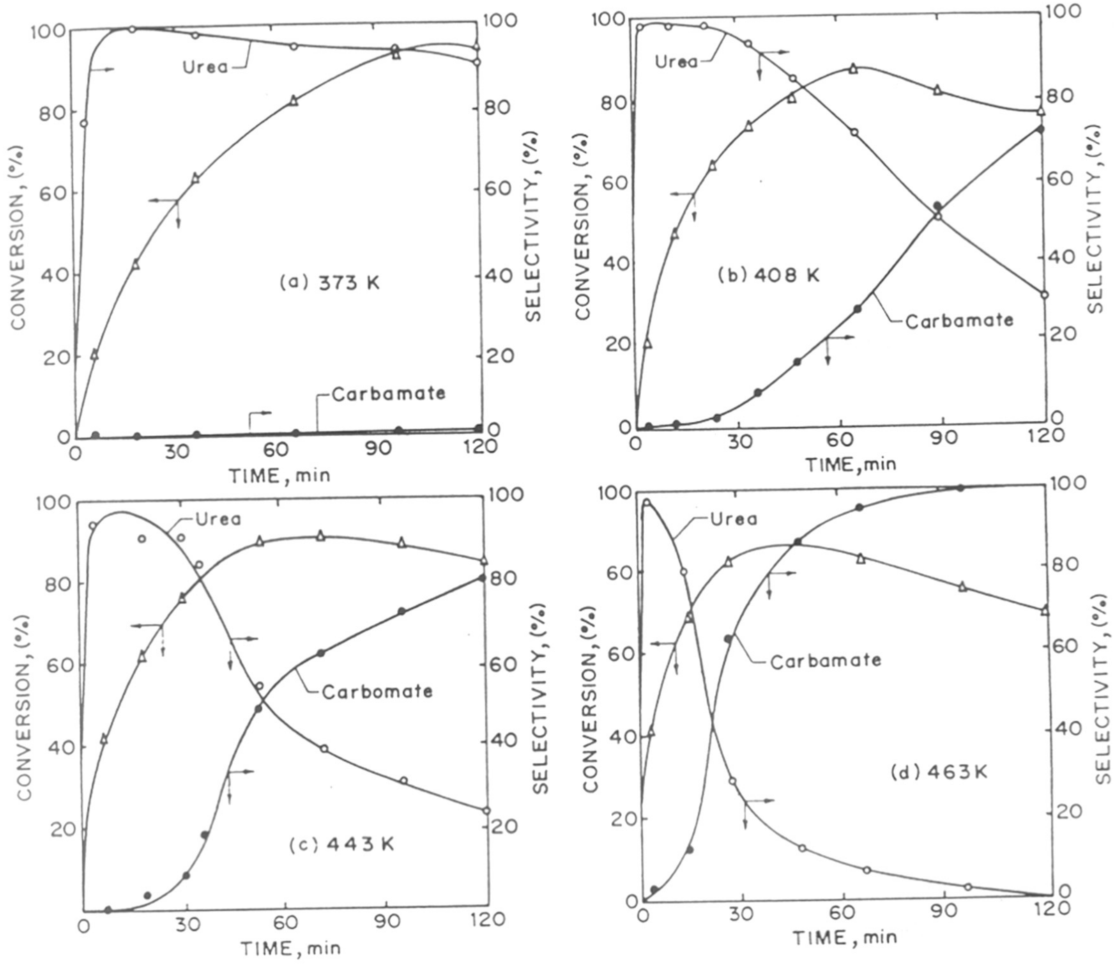


Figure 3.1 Concentration vs Time profile for oxidative carbonylation of n-butylamine

and selectivity of the palladium catalyst was investigated. The results are presented in Table 3.5. It was observed from this study that the activity of the catalyst was decreased in the following order.

$$NaI > CH_3I > C_2H_5I > LiI = HI > NH_4I > I_2 > KI > SnI_2$$

It was very much interesting to note that with SnI_2, the activity of the catalyst was very low but the selectivity for methyl N-butylcarbamate was higher than other promoters screened. It was also observed from the previous study that the halide promoters play an important role in governing the activity of the catalyst and are believed to stabilize the Pd-carbamoyl species formed during the reaction. This species is likely to play a key role in deciding the activity and selectivity of the catalyst. Gupte and Chaudhari (1988) proposed a mechanism for the role of iodide promoter for oxidative carbonylation of aniline. At the end of this chapter the mechanism on oxidative carbonylation of alkylamine was proposed and role of iodide promoter during the reaction was also explained in detail. In other carbonylation reactions such as carbonylation and hydrocarbonylation of alcohols, a similar trend in activity behavior for iodide promoter is observed (Lafeye et al., 1982). In these reactions the activity of the catalyst generally depends upon the ease with which iodide is liberated by the promoter. The activity trend observed from oxidative carbonylation reaction also agrees with this reasoning.

3.3.4 Effect of Temperature

The effect of temperature on the activity and selectivity of Pd/NaI catalyst system for the oxidative carbonylation of N-butylamine was investigated between 373 K to 463 K and at 60 atm. The results are presented in Table 3.6. It has been shown in the earlier study that the oxidative carbonylation of amine to produce urea is a catalytic step (reaction 3.1), while the further interaction of urea with alcohol to produce carbamate is non-catalytic reaction (reaction 3.2) (Gupte and Chaudhari (1988). The non-catalytic reaction is known to proceed only at higher temperatures (>423 K). Therefore, it was thought important to investigate the influence of temperature on the activity and selectivity of Pd catalyst. For this purpose, several experiments have been carried out at different temperatures (between 373 to 463 K). The results are shown in Figure 3.2 as concentration - time plots. It was observed that at 373 K and 408 K, concentration of n-butylamine decreases with time with formation of dibutylurea and

TABLE 3.5

EFFECT OF PROMOTERS ON OXIDATIVE CARBONYLATION OF N-BUTYLAMINE

Sr. no.	Promoter	Conversion of N-butylamine(%)	Selectivity(%)	
			BMC	DBU
1	NaI	84.27	75.28	20.14
2	CH_3I	71.84	57.62	41.34
3	EtI	68.73	70.42	21.35
4	LiI	62.21	27.85	65.42
5	HI	62.62	72.28	22.42
6	NH_4I	59.24	65.16	29.81
7	I_2	50.53	76.73	18.84
8	KI	38.68	78.23	20.54
9	SnI_2	20.13	89.25	05.21

Reaction conditions :

Catalyst (Pd) Concentration : 2.35×10^{-6}, mol/cm^3
Promoter (NaI) Concentration : 2.30×10^{-6}, mol/cm^3
N-butylamine Concentration : 4.11×10^{-4}, mol/cm^3
Temperature : 443 K
$CO:O_2$ Ratio : 13 : 1
Total Pressure : 6.1 MPa
Solvent : Methanol

* Reaction time for complete conversion of N-butylamine

TABLE 3.6

EFFECT OF TEMPERATURE ON OXIDATIVE CARBONYLATION OF N-BUTYLAMINE

Sr. no.	Temperature K	Conversion of N-butylamine (%)	Selectivity BMC (%)	Selectivity DBU (%)
1	353	62.40	03.90	91.32
2	363	64.75	09.47	84.34
3	373	66.16	14.70	82.91
4	398	68.37	27.78	59.41
5	423	78.00	65.54	22.89
6	443	84.63	75.11	19.95

Reaction conditions :

Catalyst (Pd) Concentration : 2.35×10^{-6}, mol/cm^3
Promoter (NaI) Concentration : 2.30×10^{-6}, mol/cm^3
N-butylamine Concentration : 4.11×10^{-4}, mol/cm^3
CO:O_2 Ratio : 13:1
Total Pressure : 6.1 MPa
Solvent : Methanol

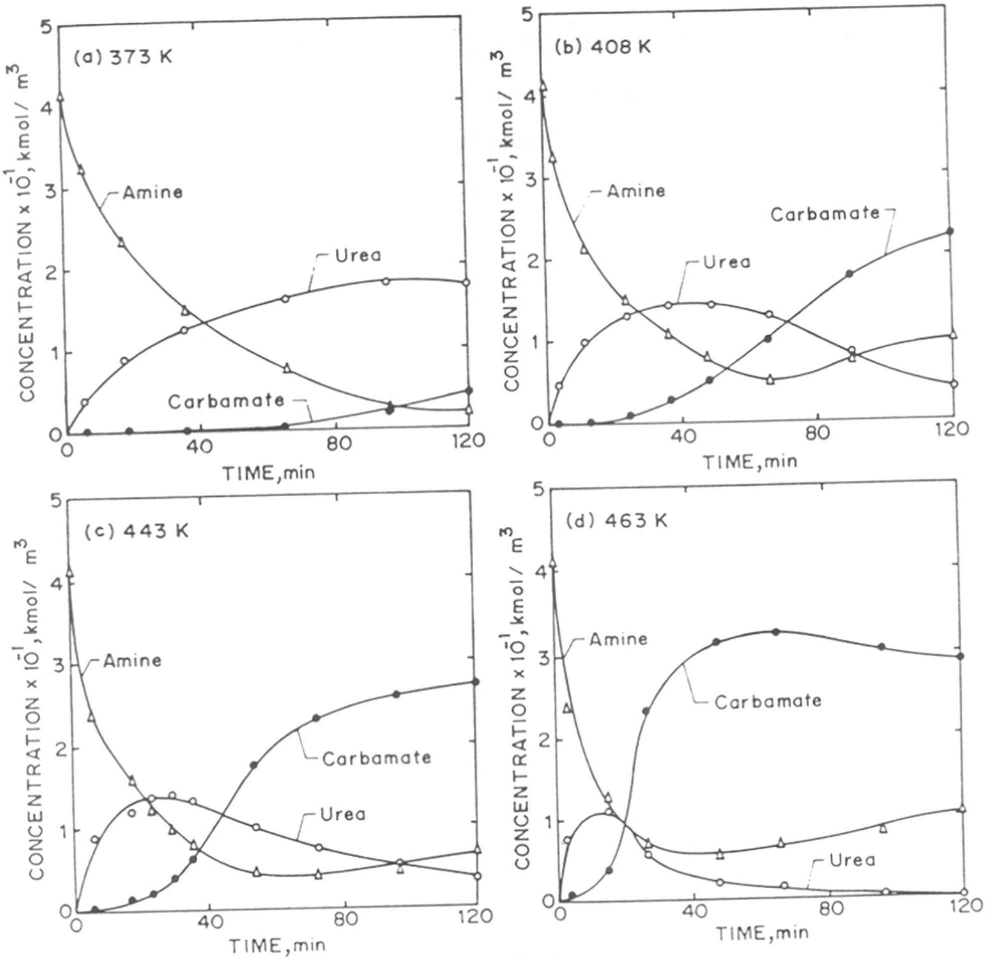


Table 2 for reaction conditions)

Figure 3.2 Effect of temperature on oxidative carbonylation of n-butylamine corresponding carbamate derivatives as major products. The concentration of N,N'-dibutylurea goes through maximum and then decreases, while the concentration of methyl N-butylcarbamate increases with time (Figs. 3.2 b and 3.2 c) . Between 408 and 443 K, the concentration-time profile (Figs. 3.2 b and 3.2 c) shows a complex behavior in the n-butylamine concentration where it decreases first and then increases with time.

In the initial period of the reaction (about 30 min.), conversion of n-butylamine to N,N'-dibutylurea is predominant. As the concentration of N,N'-dibutylurea increased, non-catalytic reaction between N,N'-dibutylurea and alcohol picks up and methyl N-butylcarbamate and n-butylamine are produced according to the reaction 3.2. This explains the formation of n-butylamine at an intermediate stage of the reaction (Fig. 3.2 b,c). Therefore, the concentration profiles shown in Fig. 3.2 at different temperatures indicate that the catalytic reaction (conversion of n-butylamine to N,N'-dibutylurea) is fast even at lower temperatures (373-408 K) while the non-catalytic reaction takes place at higher temperatures (above 408 K). At very high temperatures (463 K) methyl-N-butylcarbamate concentration attains an optimum value in about 60 min. and then decreases while that of butylamine increases (Fig. 3.2 d). It was well known that the carbamates are known to be thermally unstable at higher temperatures (Arnold, 1957). Therefore, it is believed that at higher temperatures like 463 K, methyl N-butylcarbamate is likely to decompose to butylisocyanate and methanol. The isocyanate, being highly reactive toward compounds containing active hydrogen atoms, would react immediately with water present in the reaction mixture as a co-product to give n-butylamine and CO_2 (reactions 3.3 and 3.4).

$$CH_3(CH_2)_3NH-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 \rightleftharpoons \underset{\text{butyl isocyanate}}{CH_3(CH_2)_3NCO} + CH_3OH \qquad (3.3)$$

$$CH_3(CH_2)_3NCO + H_2O \longrightarrow CH_3(CH_2)_3NH_2 + CO_2 \qquad (3.4)$$

It can be concluded from this discussion that the yield of methyl N-butylcarbamate decreases at temperatures above 463 K.

The results on selectivity to methyl N-butylcarbamate and N,N'-dibutylurea vs time and conversion of n-butylamine vs time are shown in Fig. 3.2. These data show some very interesting trends in the selectivity pattern. The unusual shape of these plots can be understood from the concentration - time plots discussed above. At low temperature (< 373 K), selectivity for urea is nearly 100 % (Fig. 3.2a) and very little methyl-N-butylcarbamate is formed. At temperatures > 373 K but < 443 K, the selectivity for N,N'-dibutylurea passes through maximum and then drops, while that of carbamate increase with increase in conversion of n-butylamine (Fig. 3.2 b,c). At higher conversion of n-butylamine (> 80 %), selectivity to methyl-N-butylcarbamate increases sharply with very little increase in the conversion of n-butylamine. This is because at higher concentration of N,N'-dibutylurea, the rate of the urea condensation with alcohol to produce carbamate (reaction 3.2) is much more than the rate of the oxidative carbonylation reaction (reaction 3.1), resulting in generation of n-butylamine. This effect is clearly shown by a decrease in conversion of n-butylamine with increase in selectivity to methyl N-butylcarbamate. At temperatures above 463 K, conversion-selectivity plot is similar in shape (Fig. 3.2 d), but the conversion decreases due to the production of n-butylamine by decomposition of methyl N-butylcarbamate (reactions 3.3 and 3.4). Thus, a judicious manipulation of reaction parameters is necessary for optimum yield of methyl N-butylcarbamate and higher conversion of n-butylamine.

3.3.5 Effect of Stirrer Speed

To ensure the catalytic activity observed is under conditions of negligible gas-liquid mass transfer resistance, several experiments were carried out to know the effect of agitation speed. The results are shown in the Table 3.7. It was observed that, the activity of the catalyst is slightly coming down when the agitation speed was above 600 rpm. So, the mass transfer effect is not important beyond 600 rpm. All the experiments were carried out at a stirrer speed of 600 rpm for oxidative carbonylation of n-butylamine.

TABLE 3.7

EFFECT OF AGITATION SPEED ON OXIDATIVE CARBONYLATION OF N-BUTYLAMINE

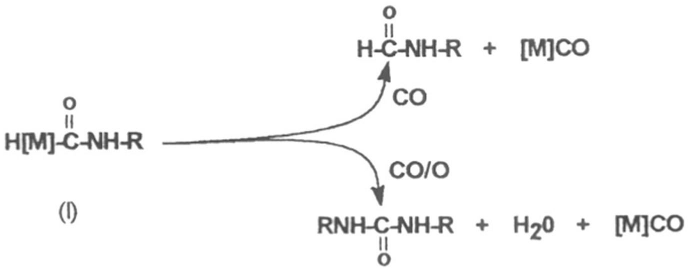
Sr. no.	Agitation Speed in rpm	Conversion of N-butylamine(%)
1	200	61.25
2	400	68.25
3	600	84.27
4	700	80.68
5	800	78.12

Reaction conditions :

Catalyst (Pd) Concentration : 2.35×10^{-6}, mol/cm^3
Promoter (NaI) Concentration : 2.30×10^{-6}, mol/cm^3
N-butylamine Concentration : 4.11×10^{-4}, mol/cm^3
Temperature : 443 K
$CO:O_2$ Ratio : 13:1
Total Pressure : 6.1 MPa
Reaction Time : 120 min
Total volume : 100 cm^3
Catalyst / Promoter Ratio : 1 : 1
Solvent : Methanol

3.3.6 Reaction Mechanism

The mechanism of oxidative carbonylation of amines to carbamates is not well understood. Fukuoka et al.(1984_b) have proposed a possible mechanism for oxidative carbonylation on aniline. It was assumed by the investigators that a Pd-carbamoyl complex (Pd-CONHAr) is formed as an intermediate species. However, this scheme does not explain the role of iodide promoter. In the mechanism it was explained that carbamoyl and aminocarbonyl species have been believed to form. These intermediates were earlier identified for carbonylation of amines giving formamides and ureas (Tsuji et al., 1986). Therefore oxidative carbonylation of amines is likely to proceed through formation of amides as intermediate species. However it was not possible to detect any formamides even at the beginning of the reaction. A similar observation was made earlier(Stern and Spector, 1966) wherein the carbonylation of n-butylamine catalyzed by $PdCl_2$ produced isocyanate without the formation of formamide as an intermediate.



(I)

Therefore, it can be assumed that in the presence of oxygen, the hydridocarbamoyl species (I) is forming during the reaction. Upon reaction with oxygen to give urea and water as proposed earlier by Gupte and Chaudhari (1988), rather than formamides. The possibility of the formation of isocyanate as an intermediate may also be ruled out, since for formation of isocyanate, a nitrene intermediate is necessary (Williams et al 1987) and is not likely to be present under the reaction conditions employed in this work.

3.4 CONCLUSION

Oxidative carbonylation of n-butylamine using Pd/NaI catalyst system has been shown to give N,N'-dibutylurea and methyl N-butylcarbamate as products. Selectivity of urea and carbamate is influenced by the type of catalysts used and process parameters employed. Palladium based catalysts give higher selectivity for carbamates, whereas higher yield of urea are obtained when ruthenium catalyst are used. Higher activity of the catalyst was observed in polar solvents such as methanol and ethanol. From the promoter study, NaI was found to be the best promoter for this system. At temperatures below 373 K, urea is obtained as a main product, while above 423 K, carbamate is selectively produced. A possible reaction mechanism is discussed which shows that the oxidative carbonylation of amines to carbamate does not proceed via the formamide and isocyanate intermediates.

REFERENCES

Alper H, and Hartstock F.W, J. Chem. Soc., Chem. Commun.,1141,(1985).

Arnold R.G., Nelson J.A., and Verbanc J.J., Chem. Rev., **57**, 47, (1957).

Dombek, B.D., J.Chem. Soc., Chem. Commun., 205, (1992).

Fukuoka S. and Chono M., European patent 83,096 (1983).

Fukuoka S. and Chono M., J. Chem. Soc. Commun., 399, (1984)[a].

Fukuoka S. and Chono M. and Kohno M., J. Org. Chem., **49**, (1984)[b].

Fukuoka S., Chono M. and Kohno M., Chemtech., **14,** 670, (1984)[c].

Ghosh A.K., and Keven L., J. Phys. Chem., **94**, 1953, (1990).

Golodov V.A., Sheludyakov Yu. L. and Sokolsky D.V., Fundamental Research in Homogeneous Catalysis, 3, 239, Ed. by Tsutsui M., Plenum Press, N.Y. (1979).

Gupte S.P., and Chaudhari R.V., J. Catl., **114**, 246, (1988).

Gupte S.P., and Chaudhari R.V., Ind.Eng.Chem.Res.,**31**, 2069, (1992).

Gupte S.P. Ph.D thesis, University of Pune, April, (1989).

Halligudi S.B., Bhatt K.N., and Taqui Khan M.M., J.Mol. Catal., **63**, 261, (1991).

Kanagasabapathy S., Thangaraj A., Gupte S. P. and Chaudhari R. V., Cat. Lett., **25**, 361, (1994).

Lefeye J.G., Perron R., and Colleuille Y., J.Mol. Catal., **17**, 339, (1982).

Prasad V.K. and Chaudhari R.V., J. Catal., **145**, 204, (1994)

Sonoda N., Yashuhara T., Konda K., Ikeda T., and Tsulsumi S.A., J.Am.Chem.Soc., **93**, 6344, (1971).

Streuli C.A., and Averell P.R., 'The analytical chemistry of nitrogen and its compounds', Elving P.J. and Kolthoff I.M., Ed. Publisher Wiley-Interscience A division of John Wiley & sons Inc., New York/London, **28**, p.271, (1970).

Tsuji Y., Ohsum T., Kondo T., and Watanabe T J. Organomet. Chem., **309**, 333, (1986).

Williams G.D., Whittle R.R ., Geoffroy R.R., Reheingold A.L., J.Am.Chem.Soc., **109**, 3936, (1987).

PART II

HYDROFORMYLATION OF OLEFINS USING HOMOGENEOUS AND BIPHASIC CATALYSIS

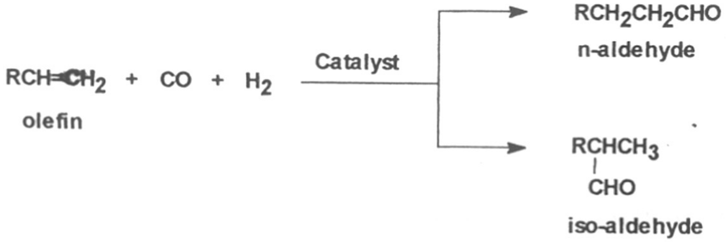
CHAPTER 4

HYDROFORMYLATION OF OLEFINS

A LITERATURE SURVEY

4.1 INTRODUCTION

Hydroformylation of olefin involves reaction of carbon monoxide and hydrogen with olefin in the presence of a metal complex catalyst to give a mixture of linear and branched aldehydes. The reaction stoichiometry is :



(4.1)

This reaction discovered in 1938 by Roelen at Ruhrchemie in Germany, has developed into an important industrial process and has been the most intensively studied of all reactions involving carbon monoxide (Pruett 1979). More than 5 million tonnes of aldehydes are produced every year by this route. The products obtained by olefin hydroformylation find various applications as intermediates for plasticizers, solvents, surfactants, lubricants, perfumery ingredients, as well as raw materials for detergents. A summary of the commercial hydroformylation processes and their applications is given in Table 4.1. 1-butanol (solvent) and 2-ethyl hexanol (plasticizer intermediate) derived by the hydroformylation of propene to butyraldehyde find major commercial uses. A major drawback of homogeneous catalysts has been the difficulties in separation of the catalysts and products. Particularly for higher olefins as reactants, this problem is severe due to non-volatility of the products. An important development in this context in recent years has been the use of water soluble catalysts in a two phase systems. This involves two immiscible liquid phases, one containing the catalyst and the other phase containing reactants and products. The subject of the biphasic catalysis has been reviewed by Kalck and Monteil (1992), Herrmann and Kohlpaintner (1993) and Beller et al., (1995). The synthesis of water soluble ligands and the role of co-solvents and additives in activity and selectivity of hydroformylation of olefins are important issues. Also, the kinetics and mechanism of biphasic hydroformylation has not been well understood. Therefore the aim

TABLE 4.1

MAJOR COMMERCIAL OXO PRODUCTS AND THEIR APPLICATIONS

(Kirschenbaum et al 1977: Stewart 1982/83)

Sr. No	Starting material	Aldehyde/ Oxo product	End product	Application
1	Ethylene	Propionaldehyde	Propionic acid	Grain Preservative and agricultural chemical, solvent
2	Propylene	Butyraldehyde	Butyraldehyde Butanol 2 ethyl hexanol	Solvent Solvent Plasticizer
3	Butene	Pentaldehyde	Pentanol decanol	Lubricant, oil additive, metal extractive agent Plasticizer
4	Pentene	Hexaldehyde	Hexanol	Oil additive and Plasticizer
5	Hexene	Heptaldehyde	Heptanol	Solvent, Fragrance
6	C_{7-11} olefins	C_{8-12} aldehyde	C_{8-12} alcohol	Plasticizer
7	Octenes	Nonanal and isononanal	Isononyl alcohol	heat resistant. electrical insulator, Plasticizer
8	C_{12-19} olefins	C_{13-20} aldehydes	C_{13-20} alcohols	Detergents

of this thesis was to study the role of different types of water soluble ligands in hydroformylation of olefins such as 1-Hexene, 1-tetradecene and styrene. It was also the purpose of this work to investigate the kinetics of hydroformylation of ethylene using water soluble rhodium complexes.

In this chapter a brief review of literature on the catalysts used, the reaction mechanism, and the kinetics of hydroformylation of olefins has been presented.

4.2 CATALYSTS FOR HYDROFORMYLATION REACTIONS

Hydroformylation of olefins has been extensively studied using a variety of transition metal complexes as catalysts. The role of different types of catalysts, ligands, solvents as well as reaction conditions has been studied in detail for a variety of olefinic substrates. The subject has been reviewed by Falbe (1980) and Parshall (1980). Table 4.2 gives a summary of the catalyst system screened for hydroformylation reactions. In the following section only important development have been summarised.

4.2.1 Cobalt Catalyst

The first catalyst studied for this reaction was the soluble $Co_2(CO)_8$ complex which led to the first industrial hydroformylation process (for hydroformylation of propylene). The reaction requires relatively drastic conditions (20 to 40 MPa pressure of syngas and 423 to 473 K), since, the cobalt complexes are stable only at higher pressures of CO. At lower CO partial pressures, the complex decomposes to metallic cobalt (Falbe 1980). In addition, the following side reactions also occur during the hydroformylation reaction.

i Hydrogenation of olefins and aldehydes to alkanes and alcohols respectively.

ii Isomerization of olefins

iii Condensation of aldehydes into acetals and aldols

iv Formate formation.

Due to these side reactions, the selectivity to the linear aldehydes (desired product) is lower for cobalt based catalysts.

Brown and Cotten (1982) modified the conventional Co catalyst by the addition of donor ligands such as triarylphosphines to obtain more efficient catalysts for the hydroformylation

TABLE 4.2

ASUMMERY OF CATALYST SCREENED FOR THE HYDROFORMYLATION REACTION

Sr. No.	Catalyst system	Olefin	Range of Condition Temp. K	Range of Condition Press MPa	Remarks	Reference
1.	Co/SiO_2+ alkaline earth oxide	Ethylene	463	1.1	Effect of alkaline earth oxide on selectivity	Takeuchi et. al. (1991)
2	$Co_2(CO)_8$	1- hexene	373	10.1	Reaction mechanism and influence of polar solvents on rate	Guertler et. al. (1993)
3	$Rh(CO)_3(PPh_3)_2BPh_4$	1-hexene	353	9.12	n/i = 3	Monsanto Co. (1974)
4	$Rh(PPh_3)_2NO$	allyl acetate	373	4.05	-	Hayashi et. al. (1978)
5	Rh carbonyl complexes	Ethylene	308	8.07	Catalyst intermediates using IR	King et.al. (1979)
6	$HRh(PPh_3)_4$	Styrene	443	6.28	-	Hayashi (1981)
	$[Rh(CO)_2Cl]_2$	styrene	403	6.28	-	
7	$[Rh(CO)_2Cl]_2$/PEG 1600	hexene	413	10.13	$CO/H_2 = 0.5$, 97.9% n- alcohol	Jap. Patent (1981)

TABLE 4.2
(cont.)

Sr. No.	Catalyst system	Olefin	Range of Condition		Remarks	Reference
			Temp. K	Press MPa		
8	$[Rh(pz)(COD)]_2$ $[Rh(pz)(PPh_3)CO]_2$	heptene, hexene	353	5.07	76% selectivity	Uson (1982)
9	$Rh(AA)(CO)(PPh_3)$ AA=β-biketone or 8-hydroxyquinoline	1- hexene	358	12.8	Effect of ligand on activity and selectivity	Janecko et. al (1984)
10	$HRh(CO)(PPh_3)_3$ & $Rh_6(CO)_{16}$	1- hexene	323-398	2.07	Regeoselectivity as a function of conversion	Hanson & Davis (1987)
11	$HRh(CO)(PPh_3)_3/SiO_2$	Propylene	363 -393	-0.71	Influence of ligand structure on activity & selectivity	Hjortkjaer et. al

reaction. The process using the catalyst $[HCo(CO)_3PBu_3]$ is also known as the Shell process. This process operates at lower pressures of CO and H_2 (4.5 to 5.0 MPa), but requires higher temperature (453 to 473 K). The modified cobalt catalyst directly gives the oxo alcohols which is an advantage, since, the aldehydes are hydrogenated to alcohols simultaneously. However this catalyst system also suffers from the disadvantage that it hydrogenates olefins significantly (Weissermal and Arpe 1978 and Cornils 1980), thus reducing the selectivity to hydroformylation products.

4.2.2 Rhodium Catalyst (Low Pressure Oxo Process)

A major breakthrough in hydroformylation technology was the development of Rh complexes which give high activity and selectivity at mild operating conditions (333 to 393 K and 0.1 to 2.0 MPa) as compared with Co based process. Baird et al., (1968) developed triphenylphosphine(TPP) modified rhodium carbonyls like $HRh(CO)(TPP)_3$ which catalyze the hydroformylation reaction at ambient conditions (0.1 MPa and 298 K). The modified rhodium complex, $HRhCO(TPP)_3$ also shows excellent selectivity (>94%) towards linear aldehydes for hydroformylation of linear olefins (Pruett and Smith 1969). Based on this catalytic system, Union Carbide, Johnson Matthey and Davy McKee jointly developed a low pressure oxo process operating at 2 MPa and 393 K which was commercialized in 1976. Followed by this commercial success, 11 more plants have been constructed worldwide to convert propene to butanol (Falbe 1980). This was considered a remarkable improvement over the conventional cobalt catalysed process which requires severe operating conditions. Some key features of this catalyst are i) high activity and selectivity ii) high n/iso ratio, iii) mild operating conditions.

Eventhough the low pressure oxo process leads to high selectivity to desired products, besides catalyst stability, it has some disadvantages regarding product isolation, catalyst separation and recycle, which are more evident for higher olefins/aldehydes. The low pressure oxo-process is thus useful only for butyraldehyde manufacture from propene. Table 4.3 shows a comparison of cobalt and rhodium based processes.

Table 4.3

COMPARISON OF THE VARIOUS OXO PROCESSES (Bahrmann and Bach 1991)

Catalyst	$[HRh(CO)(PR_3)_3]$		$[HRh(CO)_4]$	$[HCo(CO)_3(PBu_3)]$	$[HCo(CO)_4]$
	$R=C_6H_5$	$R=m\text{-}C_6H_4SO_3Na$			
Hydroformylation conditions					
Pressure, atm	15-20	10-100	200-300	50-100	200-350
Temperature, C	75-115	50-130	100-140	160-200	110-180
Results					
Selectivity for aldehydes	high	high	high	low	medium
n/iso ratio	92:8	95:5	50:50	88:12	80:20
Hydrogenation	low	low	low	high	medium

4.2.3 Other Transition Metals as Hydroformylation Catalyst

Although, the cobalt and rhodium catalyst systems have been studied extensively for hydroformylation reactions, other transition metals such as Ru (Taqui Khan et al., 1988a, 1988b), Fe (Tsuji and Moro(1969), Pd (Tsuji et al., 1965). Kalck and co-workers (1991) reviewed the use of Ru complexes as catalysts for hydroformylation reactions. Exclusive formation of linear aldehyde was observed in hydroformylation of 1-hexene using aqueous Ru^{III}/EDTA catalyst system(Taqui Khan and co-workers 1988). Phosphine modified Pt-tin complexes $[PtH(SnCl_3)(CO)(TPP)_2]$ also gave 99% selectivity to linear products for hydroformylation of alkenes. The relative activity of the transition metals in the hydroformylation reaction is given in Table 4.4 (Russel 1988). But none of these metals has met the requirement for industrial applications (Cornils 1980).

4.3 WATER SOLUBLE CATALYSTS

Homogeneously catalyzed hydroformylation processes give excellent performance and operate under mild conditions. In spite of these attractive features of the homogeneous catalysts, their applications in industry are limited due to the difficulties in separation of catalysts from reactants/products. To overcome the difficulties in recovery/recycle of homogeneous catalysis several attempts were made to heterogenize these catalysts by a) Anchoring of metal complex catalysts to polymeric or mineral supports b) supported liquid phase catalysts and c) biphasic catalysis involving two immiscible solvents. Of these, the polymer bound and supported liquid phase catalysts have yet to be proven on a commercial scale due to problems such as leaching of the metal, deactivation of catalysts and low activity. The development of biphasic catalysis involving two immiscible liquid phases has been a major advancement in this context (Kuntz (1987), Haggin (1994)). This concept involves selection of two liquid phases such that the catalyst is soluble only in one phase, while the product exists in the other phase. It is essential that the solubility of the catalyst in the other phase is almost negligible. The substrate, while being immiscible with catalyst phase should have a finite solubility in the catalyst phase so as to obtain reasonable reaction rates. Some important applications of biphasic reactions are summarized in Table 4.5.

Table 4.4 : Relative activity of transition metals in hydroformylation reactions (Russel 1988).

Metal	Relative Activity
Rhodium	$10^3 - 10^4$
Cobalt	1
Ruthenium, Platinum	10^{-2}
Manganese	10^{-4}
Iron	10^{-6}
Chromium, Molybdinum Nickel	0

Table 4-5

Applications of Biphasic Catalysis

Sr. No	Reaction	Catalyst	Catalyst Type	Reference
1	Hydroformylation of			
	i Propylene to Butyraldehyde	Rh-TPPTS	Water soluble	Kuntz (1987)
		Rh-BISBIS	Water soluble	Herrmann et al., (1992)
	ii 1-hexene to Heptaldehyde	Rh-BISBIS	Water soluble	Herrmann et al., (1992)
2	Hydrogenation of α-β unsaturated aldehyde	Rh-TPPTS Ru-TPPTS	Water soluble	Grosselin et al., (1991)
3	Oligomerization of			
	i Ethylene to α olefin (SHOP Process)	$Ni(C_6H_5)_2PCH_2$-COOH	Organic phase	Bauer et al., (1972) Mason (1973)
	ii Terminal alkynes	Rh-water soluble phosphines	water phase	Baidossi et al., (1993)
4	Carbonylation of			
	i Iso-butyl phenyl ethyl alcohol to ibuprufen (Boots-Hoechst Process)	$Pd(PPh_3)2Cl_2$ -aq-HCl	Organic phase	Elango et al., (1990)
	ii Benzyl chloride to phenyl acetic acid	$NaCo(CO)_4$/ PTC	Phase transfer catalysis	Cassar and Foa (1977)
	iii Allyl chloride to vinyl acetic acid/crotonic acid	Pd/PPh_3/aq-NaOH	Solid	Venkatesh Prasad (1994)

Biphasic catalysis offers the following advantages over conventional homogeneous systems:

- i The most important advantage of catalysts used in biphasic media is the easy separation of catalysts and products by simple phase separation. This has direct impact on recycle/recovery of catalysts and their economic utilization.
- ii Contamination of catalysts with products is minimized and helps in preventing deactivation in some cases.
- iii For substrate inhibited kinetics, higher activity is achievable in such systems as the concentration of reactants in the catalyst phase can be controlled taking advantage of the solubility limitations. In certain cases, desired selectivity can also be obtained.

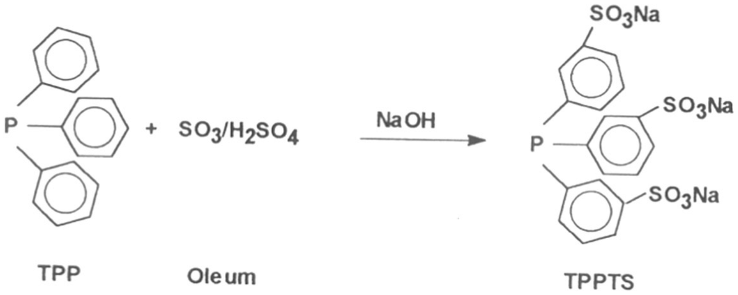
Generally biphasic catalytic reactions are classified as a) Water soluble metal complex catalysis b) Organic soluble metal complex catalysis c) organometallic phase transfer catalyst catalysis and d) catalysis by colloidal metal particles. In most industrial processes, reactants and products are water immiscible and hence, the concept of water soluble catalysis provides an important tool for separation of homogeneous catalysts and products.

In recent years biphasic catalysis using water soluble catalysts has been extensively studied to develop new routes and efficient processes for a variety of products and the subject has been reviewed by Kalck and Monteil (1992), Herrmann and Kohlpaintner (1993) and Beller et al., (1995). These catalysts have been applied in a variety of reactions such as hydrogenation, hydroformylation, carbonylation, telomerizations, oxidation etc. A very easy separation of catalysts from the organic reactants and products by simple phase separation is one of the major advantage of water soluble catalysis. In addition, catalysis in aqueous media could decrease the toxicity inherent to organic solvents. Thus offering environment friendly processes (Dartt and Davis (1994)). This approach involves synthesis of catalytic complexes such that they are highly soluble in water and insoluble in organic phase.

4.3.1 Preparation of water soluble phosphines and their complexes

Numerous complexes of the transition metals in low oxidation state are stabilized by phosphorous containing ligands (Kalck and Monteil (1992)) and hence, a majority of the water soluble ligands have been developed based on phosphorous containing ligands. Generally, water soluble phosphines are synthesized by introducing hydrophilic functional groups such as carboxylic, amino, hydroxy and sulfonate in the conventional phosphine ligands. The solubility of water soluble phosphines depends on the nature and number of hydrophilic substituents.

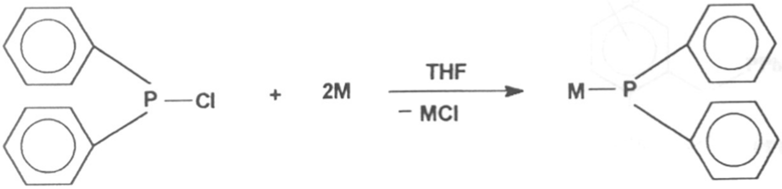
Transition metal complexes with sulfonated phosphines are widely used in water soluble catalysis mainly due to the very high solubility of sulfonated phosphines in water (e.g. triphenylphosphine trisulfonate- sodium salt, (TPPTS) has a solubility of 1.12 kg/l in water (Kuntz (1987)). These ligands are commonly sythesized by direct sulfonation of phosphines.



(4.2)

The first ligand of this type triphenylphosphine monosulfonate (TPPMS) was prepared (Ahrland et al., (1958)) by direct sulfonation of triphenylphosphine at 298 K and 20% oleum followed by neutralization with sodium hydroxide. Kuntz (1987) showed that selective synthesis of TPPTS was possible by careful control of reaction conditions, since, several side products such as oxides and sulfides are also formed in reasonable quantities. It has been shown that the amount of mono and disulfonated phosphines can be minimized by increasing SO_3 concentration (Jenck and Morel (1987)). A decrease in the reaction temperature reduces the amount of oxide formed (Morel (1983)). After sulfonation quenching of excess SO_3 and neutralization of the reaction mixture are key points, since, large quantities of the oxide and sulfide derivatives are produced at these stages. Separation of sulfuric acid from the TPPTS by liquid-liquid extraction was shown to be a further improvement in the synthesis of TPPTS (Sabot (1982)).

Many other phosphines are sulfonated to give corresponding water soluble derivatives. Some important water soluble phosphines used for hydroformylation reaction are shown in Fig. 4.1. Paetzold et al.,(1987, 1989) prepared water soluble sulphonated phosphine ligand by the reaction of chlorodiphenyl phosphine with sultone.



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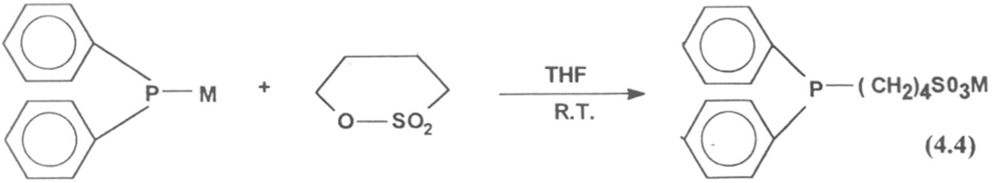
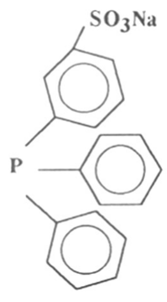


(4.4)

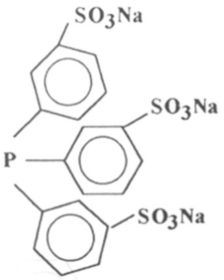
Alkaly metal salt of butane sulphonated diphenyl phosphine [MBSDPP]

M = Li / Na

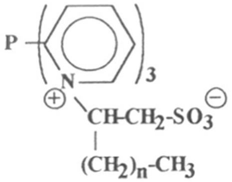
Fell and Papadogianakis (1991) have proposed a novel method by extending the above work to bind sulphonated groups to a phosphine [tris(2-pyridyl)phosphine] with sultones.



[TPPMS] (1)

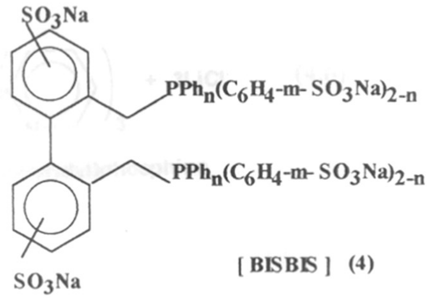


[TPPTS] (2)

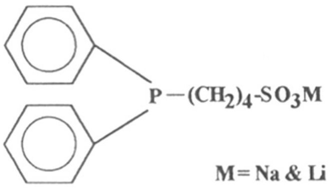


n = 3,5,7,9

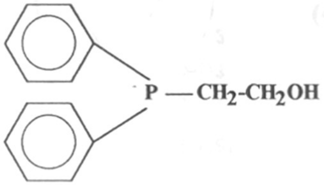
[TPyPTS] (3)



[BISBIS] (4)



[NaBSDPP & LiBSDPP] (5)



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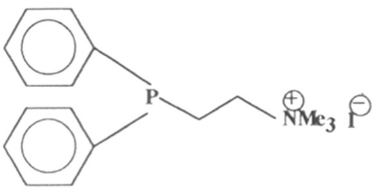
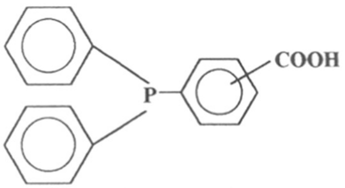
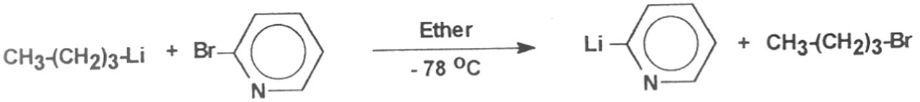


[AMPHOS] (7)

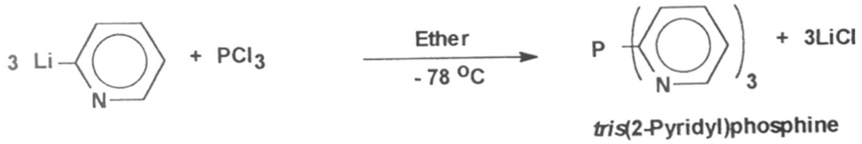


(8)

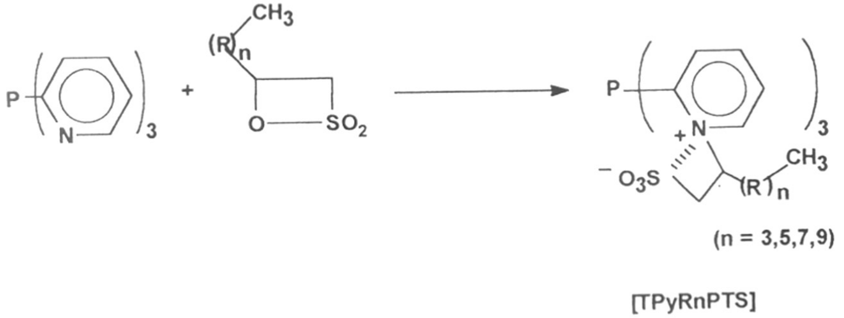
Figure 4.1 Water soluble phosphine ligands used for hydroformylation reactions



(4.5)



(4.6)



(4.7)

Herrmann et al., (1992) have prepared 2,2'-bis (diphenyl phosphinomethyl)-1-1'biphenyl sodium salt (BISBIS) by sulfonation of the BISBI. The solubility of BISBIS-Na in water is higher than that of TPPTS i.e. 1.5 kg/l.

(4.8)

BISBI

BISBIS

The introduction of a sulfonated group by reaction with oleum is not limited to arylphosphines. It can also be carried out with the tris (ω-phenyl alkyl phosphanes), $P[(CH_2)_nC_6H_5]_3$ (n = 1,2,3 and 6) (Bartik et al., (1994)). As expected, the sulfonate groups occupy the para position and to a lesser extent to ortho positions. Many surface active phosphine ligands are synthesized wherein sulfonate group is introduced as a hydrophilic component.

Recently, Herrmann et. al. (1995) have developed new types of sulfonated ligands such as NORBOS (tris trisulfonatophenyl dimethyl phosphanonorboran-adiene and BINAS (bis disulfonato diphenylphosphinomethyl tetrasulfonato binaphthene). BINAS molecules are very bulky complexes as compared with TPPTS. Despite this, the central atom is fully accessible during the catalyst cycle. BINAS gives highest activity and selectivity performance in hydroformylation of olefins (Cornils and Wiebus (1995)).

Water soluble phosphines can also be prepared by quaternization of nitrogen atom of amino alkyl and aminoaryl phosphines. However, the phosphorous center has to be protected either by oxidation or by complexation with the metal (prior to alkylation of nitrogen atom). Subsequently reduction or decomplexation yields a desired derivative of the amphos ligand. The most important example of this class is "amphos- iodide" (Smith and Baird (1981), (1982)).

Alkyl phosphines with carboxylic groups are some of the earliest investigated water soluble ligands. Mann and Miller (1952) have prepared carboxyethyl phosphine by cyanoethylation of diphenyl phosphane with subsequent nitrile saponification. Finally, many water soluble phosphines having different groups such as hydroxy, polyether etc. are known and these are reviewed by Kalck and Monteil (1992) as well as by Herrmann and Kohlpaintner (1993) in detail.

Water soluble complexes are prepared by two different approaches (Borowski et al., (1978)). 1) The transition metal complex is dissolved in the organic solvent and then brought into contact with an aqueous solution of the water soluble phosphine. The exchanged complex is extracted into the aqueous phase and may be reprecipitated. 2) Transition metal complex and the water soluble ligand are allowed to react either at room temperature or reflux in a solvent in which both are soluble. The exchanged product crystallizes on cooling or on addition of a nonpolar solvent.

4.3.2 Hydroformylation using water soluble catalysts:

Ruhrchemie/Rhone-Poulenc have developed a process for the manufacture of n-butyraldehyde using water soluble Rh-TPPTS catalyst. The catalyst is prepared by exchange of $[Rh(COD)Cl]_2$ with TPPTS. Conversion of 99% and selectivity of 95% towards n-butyraldehyde is obtained (Kuntz (1987)) at 353 K and 4 MPa pressure. Various approaches for the catalyst separation in hydroformylation reaction are shown in Fig. 4.2.

Hermann et al., (1992) have reported hydroformylation of propylene using Rh-BISBIS catalyst system in a continuous reactor. The activity of this catalyst is (45.5 mol/g/min) was three times higher than Rh-TPPTS catalyst (15 mol/g/min). The n/i ratio also improved from 94:6 (TPPTS) to 97:3 (BISBIS).

Most reports on hydroformylation of liquid olefins deal with 1-hexene as the substrate due to its higher solubility in water phase compared to other liquid olefins (Monteil et al., (1994)). Borowski et al., (1978) used water soluble $HRh(CO)(TPPMS)_3$ complex catalyst for the hydroformylation of 1-hexene. The catalyst was found to be active at 343 K. However, at the end of the catalytic runs, the organic layer was found to be orange colored due to the presence of some soluble rhodium species. Hydroformylation of 1-hexene using Rh/amphos

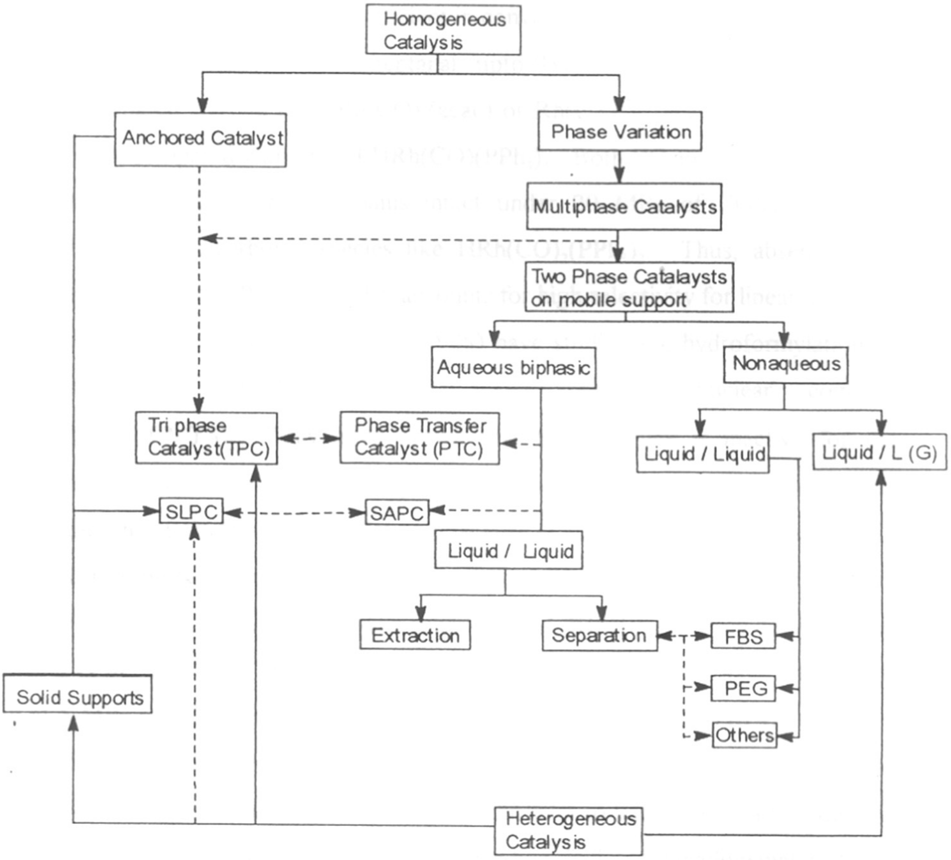


Figure 4.2 Different approaches for the catalyst separation in hydroformylation reactions (Beller et al., 1995).

catalyst system (amphos: $Ph_2PCH_2CH_2NMe_3^+$) has been studied by Smith (1983). The catalyst generated by the addition of six equivalents of amphos to $RhCl(NBD)_2$ (NBD = Norbornadiene), catalyze the hydroformylation of 1-hexene at 4 MPa and 363 K with a n/i ratio of about 4. They have also observed the n/i ratio to be solvent dependent. The complex of the type $HRh(CO)(TPPTS)_3$ is highly efficient in converting 1-hexene to heptanal at 0.5 MPa and 353 K with a selectivity for n-heptanal upto 93% (Thorez (1985)). The same complex was prepared starting from $Rh(CO)_2(acac)$ or $Rh(C_2H_4)_2$ (acac) and its catalytic behavior has been compared with that of $HRh(CO)(PPh_3)_3$. Both ^{13}C and ^{31}P NMR studies indicate that $HRh(CO)(TPPTS)_3$ remains intact under 20 MPa of CO/H_2, whereas $HRh(CO)(PPh_3)_3$ gives dicarbonyl species like $HRh(CO)_2(PPh_3)_2$. Thus, absence of a dicarbonyl species in case of TPPTS complex accounts for high selectivity for linear aldehyde products. Horvath (1990) and Kalck et al., (1988) have studied the hydroformylation of 1-hexene in biphasic media using a water soluble dinuclear complex $[Rh_2(\mu SBu)_2(CO)_2(TPPTS)_2]$. They have shown that this complex is inactive for the hydrogenation of alkene and provides a complete selectivity towards aldehydes. Moreover, linearities higher than 97% have been achieved. Escaffre et al., (1987) have used water as a solvent as well as a source of hydrogen in hydroformylation of 1-hexene at 353 K and 0.8 MPa using Rh-TPPTS catalyst. Application of water soluble ligand, BISBIS has been demonstrated by Hermann et al., (1992) in the hydroformylation of 1-hexene. They have studied the reaction at 5 MPa of CO/H_2 pressure and in the temperature range of 396 to 428 K. They have observed that the activity increases from 0.73 to 10.73 when the temperature was raised from 396 to 428K whereas the n/i ratio decreased from 97:3 to 94:6. They have tested the catalyst stability after 16 hrs of continuous hydroformylation. Fell and Papadogianakis (1991) achieved the micellar biphasic hydroformylation of higher olefins using sulfonated tri (2-pyridyl)phosphane as a ligand. The properties of these interfacially active compounds (n= 0,3,5,7,9,11) can be tuned. By suitable choice of carbon number (n) they acquire surfactant properties. For example, 1-tetradecene can be hydroformylated with a 79% yield of aldehyde. For n > 5, stable emulsions are formed and phase separation becomes a problem. Ding et al., (1994) studied the hydroformylation of 1-octene using a biphasic system using surface active ligands such as $P[C_6H_4(CH_2)_nC_6H_4\text{-}pSO_3Na]_3$. These ligands give improved activity and selectivity (n/i = 8.0 to 9.5). The hydroformylation of 1-octene with dinuclear $[Rh_2(u\text{-}SR)_2(CO)_2(TPPTS)_2]$ and $HRh(CO)(TPPTS)_3$ complex catalysts have been investigated by Monteil et al., (1994). The rate of reaction is controlled by solubility of 1-octene in the aqueous catalyst phase. To increase the reaction rate various co-solvents were employed and ethanol was found to be the best co-solvent. The selectivity to normal aldehyde was found to be proportional to the amount of ethanol in the aqueous phase. Recently, Purwanto and Delmas (1995) have reported the kinetics of hydroformylation of 1-octene using $[Rh(COD)Cl]_2$-TPPTS catalyst, in the presence of ethanol as a cosolvent. An empirical rate equation has been proposed.

The recent development of Supported Aqueous Phase Catalysis (SAPC) opened the way to hydroformylate hydrophobic alkenes such as oleyl alcohol, octene etc, (Arhancet et al., (1989), (1990)). SAPC involves disolving an aqueous phase $HRh(CO)(TPPTS)_3$ complex in a thin layer of water adhering to a silica surface. Such a catalyst shows significantly high activity for hydroformylation. For classical liquid-liquid systems, the rate of hydroformylation decreases in the order 1-hexene > 1-octene > 1-decene. However, with SAP catalysts these alkenes react virtually with the same rate and the solubility of the alkene in the aqueous phase is no longer the rate determining factor (Horvath et al., (1989)). The low n/i ratio of 2.8 in all three cases is due to coordinatively unsaturated complexes such as $HRh(CO)_2(TPPTS)$, which are known for their poor selectivities.

Horvath and Rabai (1994) recently described a flourous biphasic system, in which the aqueous phase is replaced by fluorohydrocarbons. These fluorohydrocarbons are immiscible with the organic phases at temperatures typical for hydroformylation. This type of a system might be attractive for processes that are water sensitive or those in which the reactants or the desired catalysts have an unacceptably low solubility in water.

Another interesting and fast developing area in hydroformylation chemistry is the synthesis of chiral aldehydes and alcohols using chiral complex catalyst. In contrast to the conventional hydroformylation reaction, in this reaction the desired product is the branched compound with an asymmetric carbon atom as a carrier of chirality. These products are valuable precursors for the pharmaceutical and agrochemical industry. Several water soluble chiral ligands have been effectively used for asymmetric hydroformylation reactions. Several reviews have appeared on asymmetric hydroformylation (Botteghi et al., (1991).

4.4 KINETICS OF HYDROFORMYLATION REACTIONS

Knowledge of intrinsic kinetics of catalytic reaction is necessary to understand the reaction mechanism and optimisation of a particular process. Kinetics of hydroformylation of olefins has been studied by several investigators and rate equations have been proposed. The relevant literature is summarized in Table 4.6. The details of few important catalyst systems are summarised below.

The kinetics of hydroformylation of methyl oleate was first reported by Natta and Beati (1945) using $Co_2(CO)_8$ catalyst. The rate of reaction was found to be independent of the total pressure when $CO:H_2$ ratio was 1. This was mainly due to the opposing effects of CO and H_2 partial pressures on the rate of hydroformylation.

The kinetics of hydroformylation of propylene using $Co_2(CO)_8$ catalyst with toluene as a solvent has been reported in the temperature range 383-423 K (Gholap et al., 1992a). The rate increases with increase in the concentration of catalyst, propylene and hydrogen while it was inhibited at higher partial pressures of carbon monoxide. An empirical rate equation has been developed based on the observed trends (Table 4.6). In a subsequent report these authors have investigated the kinetics of formation of normal and branched butyraldehyde. The rate equations for formation of each aldehyde isomer has also been proposed (Gholap et al., 1992b) (Table 4.6).

The kinetics of hydroformylation of 1-hexene using $HRh(CO)(PPh_3)_3$ complex catalyst in benzene has been reported in the temperature range of 290-305 K (Brown and Wilkinson 1970). It is observed that the rate varies linearly with catalyst concentration and partial pressure of hydrogen. The rate was inhibited at higher partial pressures of CO due to the formation of catalytically inactive species. With 1-hexene concentration, the rate of reaction increases linearly at lower concentration of 1-hexene and showed zero order at higher concentration.

The kinetics of hydroformylation of 1-hexene using $HRh(CO)(PPh_3)_3$ complex catalyst

TABLE 4. 6

A SUMMARY OF STUDIES ON THE KINETICS OF HYDROFORMYLATION REACTIONS

Not : A = P_{H2}; B = P_{CO} ; C = Concentration of catalyst;
D = Concentration of olefin; P = TPP; R = Rate of reaction; k = Rate constant

Sr. No	Catalyst	Olefin	Range of condition		Remarks	Rate model	Reference
			Temp. K	Press. MPa			
1	$Co_2(CO)_8$	Methyl oleate	383-403	7.1-21.3	R independent of (A+B)	-	Natta and Beati (1945)
2	$Co_2(CO)_8$	Propene	383-393	12-33	R α C,D R independent of (A+B)	$R = \frac{kACD}{B}$	Natta and Ercoli (1952)
3	$Co_2(CO)_8$	Cyclohexene	383-393	12-38	R α C,D R independent of (A+B)	$R = \frac{kACD}{B}$	Natta et. al (1954)
4	$Co_2(CO)_8$	Propylene	383-423	3.5-10	empirical rate model	$R = \frac{kA^{0.6}BC^{0.8}D}{(1+K_B B)^2}$	Gholap et al (1992)

Sl. No	Catalyst	Olefin	Range of condition		Remarks	Rate model	Reference
			Temp K	Press. MPa			
5	$Co_2(CO)_8$	Propylene	383-423	3.5-10	R_N, R_{ISO} are the rates of formation of n- and iso-aldehyde	$R_N = \frac{kA^{0.6}BC^{0.75}D^{0.87}}{(1+K_{NB}B)^2}$ $R_{ISOB} = \frac{kA^{0.32}BC^{0.62}D}{(1+K_{ISOB}B)^2}$	Gholap et. al.(1992b)
6	Rh/active carbon	Ethylene	393			R= kABD	Takahashi et. al. (1992)
7	$HRh(CO)(TPP)_3$	Cyclo-dodecene	373		R α A,B,D		Ushakov et. al. (1979)
8	$HRh(CO)(TPP)_3$	1- Hexene	298	0.65	R α A,B,D R α 1/B	$R = \frac{kACD}{B}$	Brown and Wilkinson (1970)
9	$HRh(CO)(TPP)_3$	1- Hexene	363		R α A,B,D R α 1/B	$R = \frac{kACD}{B}$	Strohmeier and Michel (1981)
10	$HRh(CO)(TPP)_3$	1- Hexene	303-323	2.2	Critical conc. of catalyst is needed	$R = \frac{kAB(C_o - C_c)D}{(1+K_BB)^{2.5}.(1+K_DD)^2}$	Deshpande and Chaudhari (1988)

Sl. No	Catalyst	Olefin	Range of condition		Remarks	Rate model	References
			Temp K	Press. MPa			
11	$HRh(CO)(TPP)_3$	Allyl alcohol	363-383	5.4	R α $A^{1.5}$,C,D Rα1/B	$R = \frac{kA^{1.5}BCD}{(1+K_BB)^3.(1+K_DD)^2}$	Deshpande and Chaudhari (1989a)
12	$Rh(CO)_2Cl_2$	Vinyl acetate	353			$R = \frac{kABCD}{(1+K_CC+K_DD^2)}$	Deshpande and Chaudhari (1989b)
13	$[RhCl(1.5\text{-}COD)]_2$/TPPTS	1-Octene	333-343			$R = \frac{kABCD}{(1+K_BB)^2.(1+K_AA)}$	Purwanto and Delmas (1994)

in ethanol has been reported in the temperature range 303-323 K (Deshpande and Chaudhari 1988). The most striking observation is that the rate is inhibited at higher concentration of 1-hexene and a critical concentration of the catalyst is required to initiate the reaction. An empirical rate equation has also been proposed (Table 4.6).

The kinetics of hydroformylation of allyl alcohol using $HRh(CO)(PPh_3)_3$ complex catalyst in ethanol has been reported in the temperature range 333-353 K (Deshpande and Chaudhari 1989). The effect of various process parameters on the rate of reaction is investigated and a rate equation has been proposed based on these observed trends (Table 4.6). The important observation in the study was that the rate varies as 1.5th order with respect to hydrogen.

The kinetics of hydroformylation of vinyl acetate using $[Rh(CO)_2Cl]_2$ complex catalyst in ethanol has been reported at 353 K (Deshpande and Chaudhari 1989). The effect of various process parameters on the rate of reaction is investigated and a rate equation has been proposed based on these observed trends (Table 4.6).

Recently, Divekar (1995) has studied the intrinsic kinetics on hydroformylation of ethylene using $HRh(CO)(TPP)_3$ complex catalyst in the temperature range 333 to 373 K. The reaction was found to be 1.5th order with respect to the partial pressure of hydrogen and negative order for partial pressure of ethylene. The rate of the reaction varies linearly with catalyst concentration. The rate equation proposed based on this data is given below.

$$R = \frac{k\,(A)^{1.5}\,(B)\,(E)}{(1+K_B B)^2\ \ (1+K_E E)^2}$$

For the hydroformylation of olefins using newly developed water soluble catalysts, only few reports on the kinetic modeling are published (Puruwanto 1994). Considering the future potential of water soluble catalysis, there is a need for further work on kinetics and mechanism.

4.5 MECHANISM OF HYDROFORMYLATION REACTIONS

4.5.1 Cobalt Catalyst

The mechanism for hydroformylation reaction using cobalt carbonyl catalyst was first proposed by Heck and Breslow (1961) and is illustrated in Fig 4.3. From the mechanism it can be seen that the reaction is initiated by the formation of intermediate complexe, $HCo(CO)_4$ (step i) from the reaction between $Co_2(CO)_8$ and hydrogen, which further dissociates into $HCo(CO)_3$ (step ii). The reaction of $HCo(CO)_3$ with the olefin form a π complex which rearranges to an alkyl cobalt carbonyl complex (step iii). An acyl complex (step v) results via insertion of CO between the carbon atom of the alkyl group and the cobalt atom. The aldehyde formation occurs by a reaction either with hydrogen or with $HCo(CO)_4$ (step vii and viii). Therefore, it is believed that both the complexes $HCo(CO)_4$ and $HCo(CO)_3$ are present in the catalytic cycle and contribution of each would depend upon the reaction conditions. It is also reported that the nature of the active species plays an important role in deciding the selectivity pattern of product aldehydes (Taylor and Orchin 1971 and Bianchi and Piacenti 1977).

4.5.2 Rhodium Catalyst

Schiller (1956) was the first to report the use of rhodium carbonyls as catalysts in hydroformylation reactions. The mechanism of hydroformylation using $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ was first studied by Heil and Marko (1968). The active catalytic species is proposed to be $HRh(CO)_3$, which is in equilibrium with the rhodium carbonyl cluster under reaction conditions. The activity and selectivity of this catalyst was found to be 10^3 to 10^4 times higher than Co catalyst and requires milder conditions. The rhodium carbonyl catalysts however show less selectivity to the desired products, giving higher isomerization of olefins (Cornils 1980). The potential importance of Rh catalyst was realized only after the discovery of $HRh(CO)(TPP)_3$ complex catalyst by Evans et al., (1968a ,b).

It was suggested that the species, $HRh(CO)_2(TPP)_2$ is a key intermediate even though several species might exist in solution in equilibrium [Pruett and Smith (1969)]. It has been shown from NMR studies that out of $HRh(CO)(TPP)_2$ and $HRh(CO)_2(TPP)_2$ only the latter reacts with ethylene at 298 K and at 0.1 MPa. Two different pathways have been proposed involving associative and dissociative mechanisms. In the dissociative mechanism, as shown in Fig. 4.4, dissociation of a phosphine ligand from the bis(phosphine) complex (2) is followed by the addition of olefin to the co-ordinatively unsaturated square planar complex (3). The addition of olefin via π complex gives sigma alkyl complex (5). Alkyl migration or CO

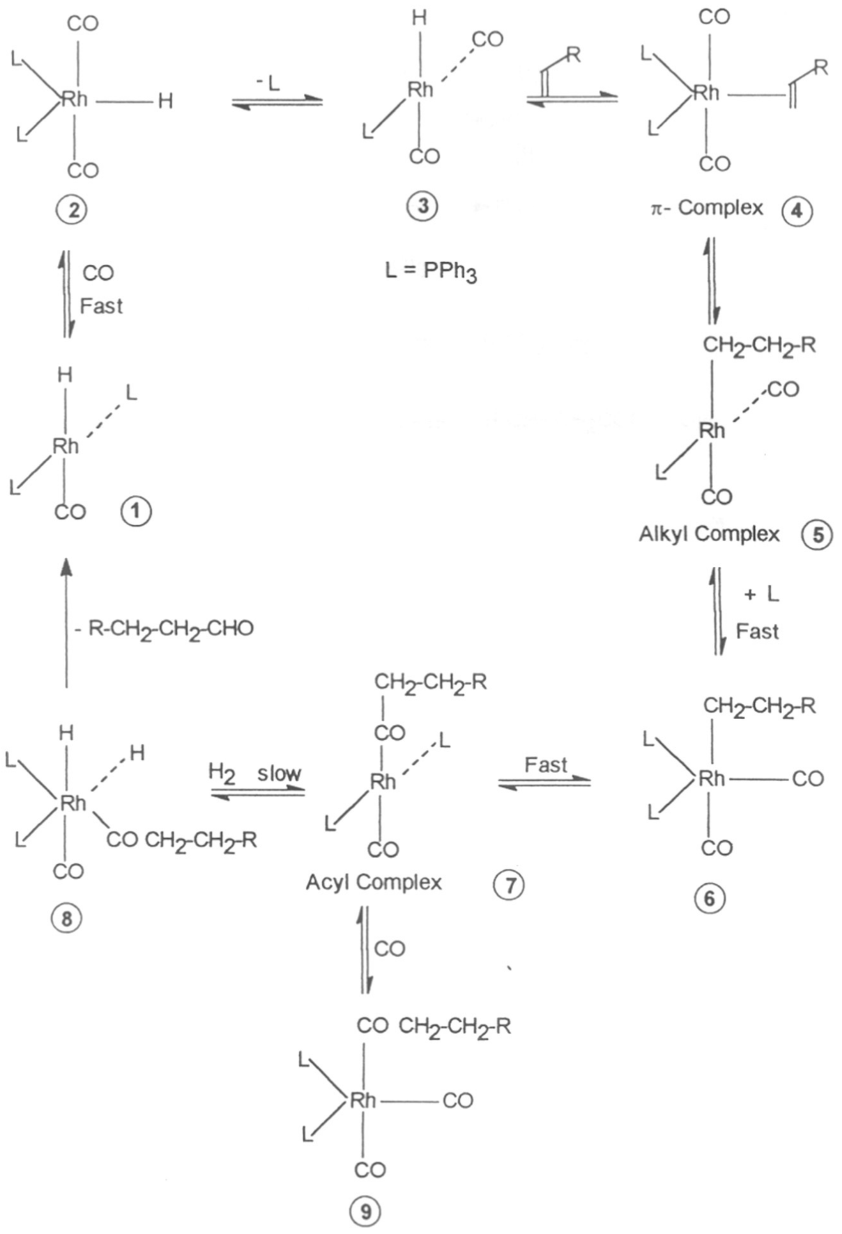


Figure 4.3 **Dissociative mechanism of hydroformylation of olefin using $HRh(CO)(TPP)_3$ complex catalyst [Bahrmann (1991)].**

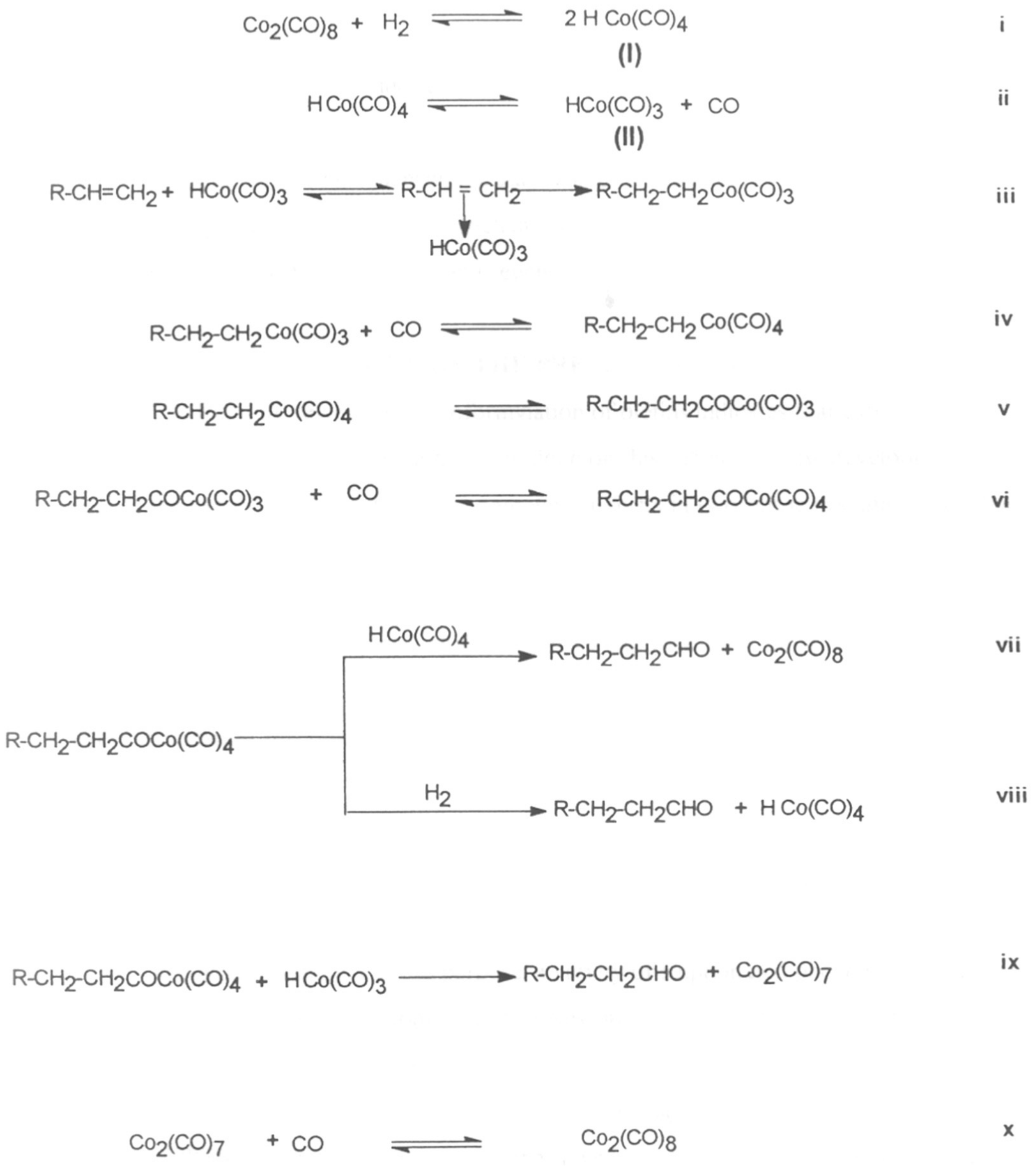


Figure 4.4 **Mechanism of cobalt carbonyl catalysed hydroformylation of olefins [Heck and Breslow (1961)].**

insertion leads to the formation of acyl complex (7) which on oxidative addition of hydrogen gives rise to the dihydride complex (8). This is reported to be the rate controlling step in the mechanism. Finally, the dihydride complex reductively eliminates the product and the catalyst (1) is regenerated.

In the associative mechanism the alkyl complex is formed by the addition of olefin to the bis(phosphine) complex. The mechanistic cycle again operates through the above mentioned steps giving the product and regenerating the catalyst.

4.6 SCOPE AND OBJECTIVE OF THE PRESENT WORK

The literature review on hydroformylation of olefins indicates that extensive work on catalysis and the kinetic modeling has been done on this subject. A new development in this area is the use of water soluble metal complex catalysts in two phase systems, which has a major advantages in separation of the catalyst and the products. The role of different types of water soluble rhodium ligands and kinetics and mechanism of the biphasic hydroformylation reactions has not been very well studied. Such a information is most essential in order to develop new catalyst systems and improved processes for industrially relevant hydroformylation reactions. The aim of this work was to investigate the following specific problems.

i Hydroformylation of olefins such as 1-hexene, 1-tetradecene and styrene using water soluble rhodium complexes was studied to understanding the role of different ligands in biphasic medium. For this purpose, a variety of sulphonated phosphine ligands were synthesised and the rhodium complexes prepared from them were evaluvated for hydroformylation reactions.

ii Kinetics of hydroformylation of ethylene was studied in detail using water soluble Rh-TPPTS catalysts. In this case the kinetics of a complex reaction involving simultaneous absorbtion of three gaseous components (H_2, CO and C_2H_4) followed by a catalytic reaction has been studied.

REFERENCES

Abatjoglou A.G. and Bryant D.R., The Arabian J. Sci. Eng., **10**(4), 427, (1985)

Ahrland S., Chatt J., Davies N.R. and Williams A.A., J. Chem. Soc. 276, (1958).

Arhancet J.P., Davis M.E., Merola J.S. and Hanson B.E., Nature, **339,** 454, (1989).

Arhancet J.P., Davis M.E., Merola J.S. and Hanson B.E., J. Cat., **121,** 327, (1990).

Bartik T., Bartik B. and Hanson B.E., J. Mol. Cat. 88, 43 (1994).

Bahrmann H., Bach H., Ullmann's Encyclopedia ofIndustrial Chemistry, Elvers B., Hawkins S. and Schulz G., (Eds.) fifth edition (VCH, Weinheim) **A18**, 321, (1991).

Baidossi W., Goren N. Blum J., Schumann H. and Hemling H., J. Mol. Cat., **85,** 153 (1993).

Baird M.C., Whyman C.J. and Wilkinson G., J. Chem. Soc. A, 348 (1968).

Bauer R.S., Chung H., Glockner P.W. and Keim W., US Patent 3644563, (1972).

Beller M., Cornils B., Frohning C.D. and Kholpaintner C.W., J. Mol. Catal., **104**, 17 (1995)

Bianchi M. and Piacenti F., J. Organomet. Chem, **135,** 387, (1977).

Borowski A.F., Cole-Hamilton D.J. and Wilkinson G., Nouv. J. Chem., **2,** 137, (1978).

Botteghi C., Gladiali S., Bellagamba V., Ercoli R. and Gamba A., Chem. Ind.
(Milan) 63, 29 (1991).

Brown C.K. and Wilkinson G., J. Chem. Soc. A, 2753, (1970).

Cassar L. and Foa M., J. Organomet. Chem., **134** , C15 (1977).

Cornils B., New Synthesis with carbon monoxide edited by Falbe J., Springer-Verlag, Berlin, Heidelberg, New York (1980).

Dartt C. B. and Davis M.E., Ind. Eng. Chem. Res., 33, 2887 (1994).

Ding H., Hanson B.E., Bartik T. and Bartik B., Organometallics, **13**, 3761 (1994).

Deshpande R.M. and Chaudhari R.V., Ind. Engg. Chem. Res., **27** 1996, (1988).

Deshpande R.M. and Chaudhari R.V., J. Catal., **115**, 326, (1989a).

Deshpande R.M. and Chaudhari R.V., J. Mol. Catal., **57**, 177,(1989b).

Deshpande R.M., S.S. Divekar, Bhanage B.M. and Chaudhari R.V., J. Mol. Cat. **75** L19 (1992).

Divekar S.S., Deshpande R.M. and Chaudhari R.V., Cat. Lett., **21,** 191 (1993).

Divekar S.S., Ph.D. Thesis, University of Poona. (1995).

Ding H., Hanson B.E., Bartik T. and Bartik B., Organometallics, **13**, 3761 (1994).

Elango V., Davenport K. G., Murphy M. A., Mott G. N., Zey E. G., Smith B. L. and Moss G. L., European Patent 40089283, (1990).

Escaffre P., Thorez A. and Kalck P., J. Chem. Soc. Chem. Comm., 146 (1987).

Evans D., Yagupski and Wilkinson G., J. Chem. Soc. A, 2660, (1968a).

Evans D., Osborn J.A. and Wilkinson G., J. Chem. Soc. A, 3133, (1968b).

Falbe J., New Synthesis with carbon monoxide, Springer-Verlag, Berlin, Heidelberg, New York (1980)

Fell B. and Papadogianakis G., J. Mol. Cat., **66**, 143, (1991).

Gholap R. V., Kut O. M. and Bourne J. R., Ind. Engg. Chem. Res., **31**(7), 1597, (1992a).

Gholap R. V., Kut O. M. and Bourne J. R., Ind. Engg. Chem. Res., **31**(11), 2446, (1992b).

Grosselin J.M., Mercier C., Allmand G. and Grass F., Organometallics, **10**, 2126 (1991).

Guertler O., Silberg C., Laarz W., Saus. A., Chem. Ing. Tech., **65**(5), 575, (1993).

Haggin J., Chem. and Engg. News, Oct. 10, 28, (1994).

Hanson B.E. and Davis M.E., J. Chem. Edu., 64, 928, (1987)

Hayashi T., Tanaka M. and Saeki K., Jap. Pat., JP 7831614, (1978).

Hayashi T., J. Mol. Catal., **13**, 323, (1981).

Heck R.F. and Breslow D.S., J. Am. Chem. Soc., **83**, 4023, (1961).

Heil B. and Marko L., Chem. Ber., **101,** 2209, (1968).

Herrmann W.A., Kohlpaintner C.W., Bahrmann H. and Konkol W., J. Mol. Cat., **73,** 191, (1992).

Herrmann W.A. and Kohlpaintner C.W., Angew. Chem. Int. Ed. Engl., **32,** 1524, (1993).

Herrmann W.A., Albanese G., Manetsberger R., Balamann H., and Lappe P., Angew. Chem. Int. Ed. Engl., **34**, 891, (1995).

Hjortkjaer J., Heinrich B. and Capka M., Applied Organomet. Chem., **4**, 369, (1990).

Horvath I.T., Kastrup R. V., Oswald A. A. and Mozeleski E. J., Cat. Lett., **2,** 85, (1989).

Horvath I.T., Cat. Lett., **6,** 43, (1990).

Horvath I.T. and Rabai J., Science, **266**, 72, (1994).

Janecko H., Trzeciak A.M. and Ziolkowski J.J., J. Mol. Catal., **26,** 355, (1984)

Jap. Pat. 8155323, (1981).

Jenck J.F. and Morel D., US Patent US 4,688,824 (1987).

Kalck P. and Monteil F., Adv. in Organomet. Chem., **34,** 219, (1992).

Kirschenbaum I. and Inchalik E.J., Encyclopedia of Chemical Technology edited by Krik Othmer, 3rdEdition (John Wiley & Sons, New York), **16,** 637, (1977).

Kuntz E., CHEMTECH, **17,** 570, (1987).

Mann F.G., and Millar I.T., J. Chem. Soc., 3039(1952).

Mason R.F., US Patent 3737475, (1973).

Monteil F., Queau R. and Kalck P., J. Organomet. Chem., **480,** 177, (1994).

Morel D. and Jenck J., Fr. Patent 2550202, (1983).

Monsanto C., Neth. Pat. 7500745, (1974).

Natta G.and Beati E., Chem. Ind. (Milan), **27**, 84, (1945).

Natta G. and Ercoli R., Chem. Ind. (Milan), **34**, 503, (1952).

Natta G., Ercoli R., Castellano S. and Barberi F. H., J. Am. Chem. Soc., **76**, 4049, (1954).

Parshall G.W., Homogeneous Catalysis (Wiley Interscience, New York), 1, (1980).

Paetzold E., Kinting A. and Oehme G., J.Prakt.Chemie. **329**, 725, (1987).

Paetzold E. and Oehme G., Z.Chem., **29**, 447, (1989).

Pruett R. L. and Smith J. A., J. Org. Chem. **34**, 327, (1969).

Pruett R.L., Adv. in Organomet. Chem., **17**, 1, (1979).

Purwanto P. and Delmas H., Eur. Symp. Catalysis in Mutiphase Reactors, Lyon, France, C IV-2, Dec. (1994).

Purwanto and Delmas H., Catalysis Today, **24,** 134 (1995).

Roelen O., German Patent 849558, (1938).

Roth J.F., Craddock J.H., Hershmann A. and Paulik F.E., CHEMTECH, **1**, 600, (1971).

Russel M. J. H., Platinum Met. Rev., **32**(4), 179, (1988).

Sabot J.L., European Patent 0104967 (1982).

Schiller G., German Patent 953605, (1956).

Smith R.T. and Baird M.C., Transition Met. Chem. London, **6**, 197, (1981)

Smith R.T. and Baird M.C., Inorg. Chim.Acta., **62**, 135 (1982).

Smith R.T., Ungar R.K., Sanderson L.J. and Baird M.C., Organometallics, **2,** 1138 (1983).

Stewart J.L., Indications (The international Journal of Davy Mckee), 20, Winter (1982/1983).

Strohmeier W. and Michel M., Z. Phy-Chem. Wiesbaden, **124**(1), 23, (1981).

Takeuchi K., Hanaoka T., Matsuzuki T. and Sugi Y., Applied Catalysis, **73**, 281, (1991).

Taqui Khan M.M., Halligudi S.B. and Abdi S.H.R., J. Mol. Cat., **45,** 215, (1988a).

Taqui Khan M.M., Halligudi S.B. and Abdi S.H.R., J. Mol. Cat., **48,** 313, (1988b).

Taylor P. and Orchin M. J. Am. Chem. Soc. **93**, 6504, (1971).

Thorez A., Ph. D. Thesis, E.N.S.I.G.C., Toulouse, (1985).

Tsuji J., Iwamoto N and Morikawa M., Buul. Vhem. Soc. Jap., **38**, 2613, (1965).

Tsuji J., and Moro Y., Bull. Chem.Soc. Jap., **42**, 527, (1969).

Uson R., J. Mol. Catal., 14, 375, (1982).

Ushakov V. M., Kazarnovskaya D. B., Klinova L. L. and Malygina N. M., Neftekhimia **19**(1), 62, (1979).

Venkataesh Prasad V.K., Ph.D Thesis, University of Poona India, (1994).

CHAPTER 5

HYDROFORMYLATION OF 1-HEXENE , 1-TETRADECENE AND STYRENE USING WATER SOLUBLE RHODIUM COMPLEX CATALYSTS

5.1: INTRODUCTION

Hydroformylation of olefins has wide range of applications in the chemical industry for the manufacture of detergents, lubricants, perfumes and solvents. The relevant literature on the various aspects of this reaction has been presented in Chapter 4. A variety of catalysts have been investigated for the hydroformylation of olefins in homogeneous and biphasic systems (Chapter 4). Particularly, extensive work has been done using homogeneous non-aqueous systems for hydroformylation of olefins due to their technological importance (Cornils 1980). The major problem associated with this system was the separation of the catalyst from the products. This was successfully overcome by the catalysis carried out in a biphasic medium using metal complexes containing water soluble ligands. Such ligands keep the catalyst in the aqueous phase and the substrate and products in the other (organic) phase. The first hydroformylation process using water soluble [(HRhCO(TPPTS)$_3$] catalyst was developed for the commercial production of butyraldehyde by Rhone-Poulenc/Ruhrchemie (Kuntz 1987). The subject of rhodium catalyzed hydroformylation of olefins in biphasic systems has been reviewed by Kalck and Monteil (1992), Herrmann and Kohlpaintner (1993) and Beller et al., (1995). Only a few reports describe detailed investigations on catalytic aspects of water soluble rhodium complex catalyzed hydroformylation of olefins (see Table 5.1). This chapter presents an experimental study on the role of different types of water soluble ligands and reaction conditions in hydroformylation of 1-hexene, 1-tetradecene and styrene.

Sinou (1987) reported the hydroformylation of 1-hexene using HRhCO(TPPTS)$_3$ system at 363 K and 4 MPa total pressure of CO and H$_2$. pH of the solution strongly influenced the conversion as well selectivity. 96 % conversion of 1-hexene was observed at 5.8 pH with negligible hydrogenation of 1-hexene (< 1 %). But, at 5.0 pH, the conversion of 1-hexene was found to be less 76 % and the hydrogenation of 1-hexene was predominant (16 %).

Fell and Papadogianakis (1991) studied the hydroformylation of 1-hexene and 1-tetradecene using Rh$_4$(CO)$_{12}$ with a novel water soluble phosphine ligand, tris-2[1-(2-pyridinium alkyl sulphonated]phosphine, (TPyR$_n$PTS) for different ratios of P/Rh, and observed that the conversion of 1-tetradecene decreased from 33% to 0.4 % when, P/Rh ratio increased from 10 to 80. They also compared the results with Rh$_4$CO$_{12}$/NaTPPTS system

Table 5.1

A SUMMARY OF STUDIES ON HYDROFORMYLATION OF 1-HEXENE, 1-TETRADECENE AND STYRENE USING WATER SOLUBLE Rh COMPLEX IN BIPHASIC SYSTEM.

S.No	Olefins	Catalyst	Reaction conditions (T) °C	(P) atm	References
1.	1-Hexene	$Rh/Ph_2P(CH_2)_2N^+Me_3I^-$	90	40	D.Sinou (1987)
2.	1-Hexene	$Rh/4\text{-}PPh_2C_6H_4COOH$ with surfactant	80	5.5	M.J.H.Russell (1988)
3.	1-Hexene	Rh/TPyRnPTS	120	50	G.Papadogianakis Ph.D Thesis (1989)
4.	1-Hexene	Rh/NaTPPTS	125	6	G.Papadogianakis Ph.D Thesis (1989)
5.	1-Hexene	$HRh(CO)(TPPTS)_3$	120	20	Ding et al., (1995)
6.	1-Tetradecene	Rh/TPyRnPTS	120	75	Fell and Papadogianakis (1989)
7.	1-Tetradecene	Rh/SAPC	100	68	J.P.Arhancet etal., (1989)
8.	Styrene	Rh/NaTPPTS	118	22	T.Bartik et al., (1995)
9.	Styrene	Rh/P(Menthyl)alkyl phenylphosphine	120	14	T.Bartik (1995).

for the hydroformylation of 1-tetradecene and reported two fold higher conversion for Rh-TPyR$_n$PTS compared to Rh-NaTPPTS.

Arhancet et al., (1989 and 1991) reported a novel Supported Aqueous-Phase Catalyst (SAPC) for the hydroformylation of 1-tetradecene. This catalyst enables the efficient use of a water soluble rhodium complexes [HRhCO(TPPTS)$_3$] to promote the reaction of higher olefins such as 1-tetradecene which is soluble only in the organic phase.

Herrmann and Kholpaintner (1992) reported a new water soluble ligand [sodium salts of 2,2'-bis(diphenylphosphino methyl) 1,1'-biphenyl (BISBIS)] for the hydroformylation of 1-hexene in a continuous process. The activity of the catalyst was increased from 0.7 to 10.7 when the temperature was raised from 393 K to 425 K, whereas, the n/iso decreased from 97:3 to 94:6. The stability of the catalyst was unaffected even at higher temperatures as well as higher reaction times (more than 16 hrs).

The studies on different water soluble ligands for the Rh catalyzed hydroformylation of 1-hexene, 1-tetradecene and styrene in biphasic systems are very limited and also no detailed studies on the effect of reaction conditions such as temperature, pressure, catalyst and ligand concentration and pH etc. on the rate of hydroformylation of these olefins has been reported. It was the aim of this work to investigate the activity and selectivity behaviour of various water soluble Rh catalysts in the hydroformylation of olefins. The ligands such as TPyR$_n$PTS (n= 3,5,7,9), NaBSDPP and LiBSDPP were synthezised and their role in hydroformylation of 1-hexene, 1-tetradecene and styrene has been investigated .

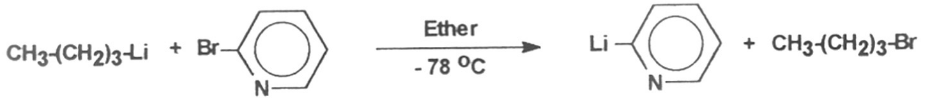
5.2 SYNTHESIS OF LIGANDS AND CATALYSTS

5.2.1 Tris-2[1-(2- Prydinium)alkyl) sulfonated] Phosphine(TPyR$_n$PTS)

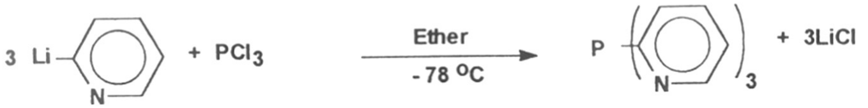
TPyR$_n$PTS was prepared by the procedure described by Fell and Papadogianakis (1991). It's preparation involves two steps .

Step 1: Tris(2-Pyridyl)Phosphine):

To a very cold (-78°C) solution of 159 ml (254 mmol) of butyl lithium in 225 ml of ether placed in a one litre 3 necked round bottom flask, 40 gm.(254 mmol) of 2-bromopyridine in 95 ml ether (previously cooled to -30°C) was added dropwise during 1 hr . The colour of the solution was changed from black to dark red at the end of the addition. The mixture was stirred for 4 hrs at -78°C. After four hours, a solution of 11.77 gm (85 mmol) of PCl_3 in 160 ml of ether (kept at -30°C) was added into the mixture during $2^1/_2$ hrs. The reaction mixture was stirred for 2 hrs at -78°C and slowly brought to room temperature under stirring overnight. The mixture was then added to 320 ml 2M H_2SO_4 and then treated with NaOH solution (pH=13). A white solid was separated at pH 13. The solid was filtered and washed with oxygen free water. The yield of the compound was 55% . The melting point of the compound (114 °C) was consistent with the literature report (113 to 114 °C). Figures 5.1 and 5.2 show ^{31}P and ^{1}H NMR of Tris(2-Pyridyl)Phosphine ligand. The stoichiometric reactions involved in the synthesis are :



(5.1)

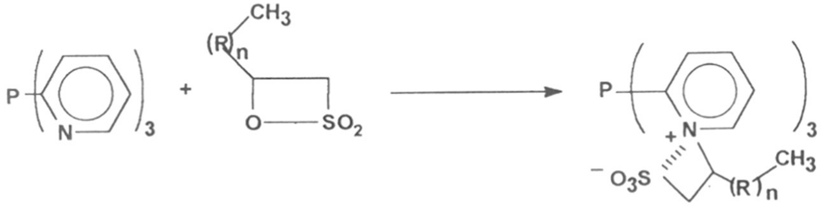


tris(2-Pyridyl)phosphine

(5.2)

Step 2: Tris-2[1-(2- prydinium)alkyl) sulfonated] phosphine(TPyRnPTS) from tris(2-Pyridyl)Phosphine)

To an ice cold solution of tris (2-pyridyl)phosphine in 1,2- dichloroethane, ice cold solution of propane sultone was added dropwise during 1 hr. The mixture was stirred for eight hrs at 0°C and slowly brought to room temperature. This mixture was poured slowly into dry n-hexane and the solid product was separated out. It was further washed with n-hexene and the highly hygroscopic solid was filtered under nitrogen and dried under vacuum. This solid was identified as Tris-2[1-(2- Prydinium)alkyl) sulfonated] Phosphine by ^{1}H and ^{31}P NMR. The synthesis step is described as :



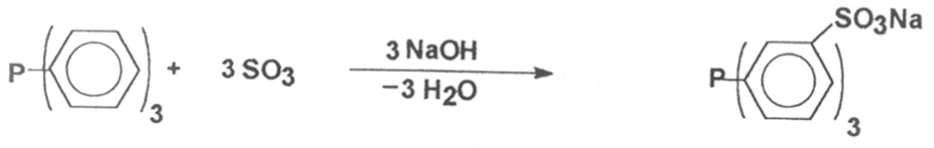
[TPyRnPTS] (n = 3,5,7,9)

(5.3)

5.2.2 Sodium salt of triphenyl phosphine trisulphonate (NaTPPTS)

Oleum (65%) was placed in an ice cold 3 necked round bottomed flask under argon. 40 gm of triphenyl phasphine (TPP) was added to this with constant stirring of the mixture (3gm in every 5 minutes time interval). After complete addition of TPP, the solution was stirred at room temperature for 48 hrs. The solution was chilled and the temperature was brought to -20°C. This mixture was then added to a cold 950 ml of oxygen free water for hydrolysis. The mixture was stirred after hydrolysis for three hrs at -5°C.

155 gm of Triisooctylamine in 700 ml of toluene was added to the hydrolysed mixture and the contents stirred for one hour. 5% NaOH solution was added into the quarternary ammonium salt solution. The addition of NaOH was stopped when the pH came to 4.2. The aqueous layer was separated and discarded. More NaOH solution was added to the quaternary ammonium salt solution till the pH of the solution was 6.8. The aqueous layer was separated and distilled under high vacuum. The white solid obtained was characterized by ^{31}P nmr. The synthesis step is :



NaTPPTS

(5.4)

5.2.3 Lithium and Sodium salts of butylsulphonated diphenylphosphine (LiBSDPP and NaBSDPP)

These ligands were prepared based on a procedure given by Peatzold (1989). 7.3ml (40 mmol) of diphenyl chlorophosphine in 80 ml THF was stirred with (86 mmol) of lithium

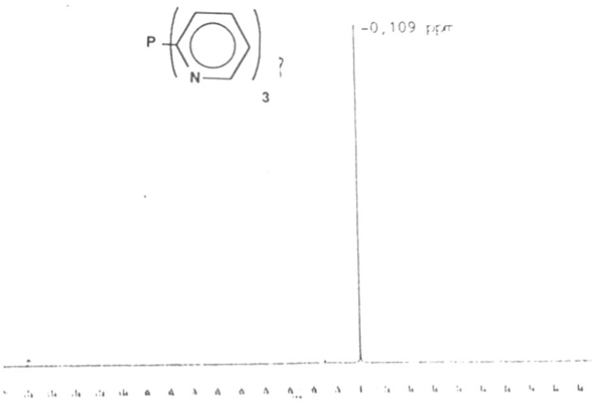


Figure 5.1 : ^{31}P NMR spectrum of tris-(2-pyridyl)phosphine

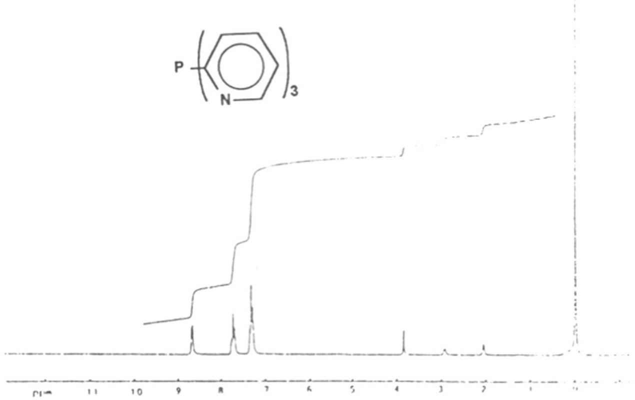


Figure 5.2 : ^{1}H NMR spectrum of tris-(2-pyridyl)phosphine

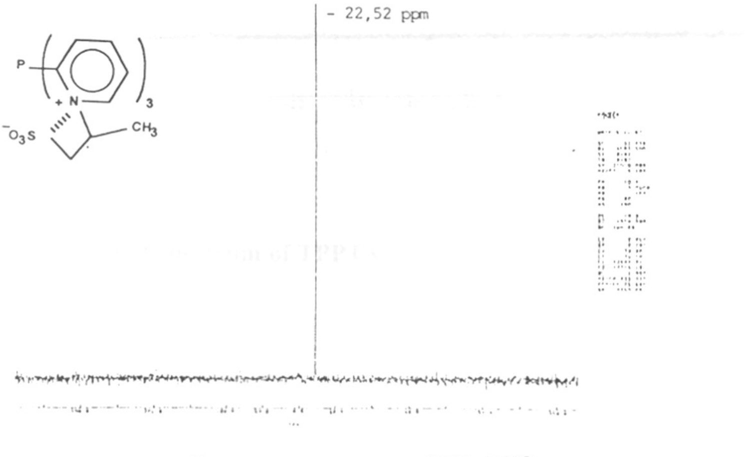


Figure 5.3 : ^{31}P NMR spectrum of TPyPTS

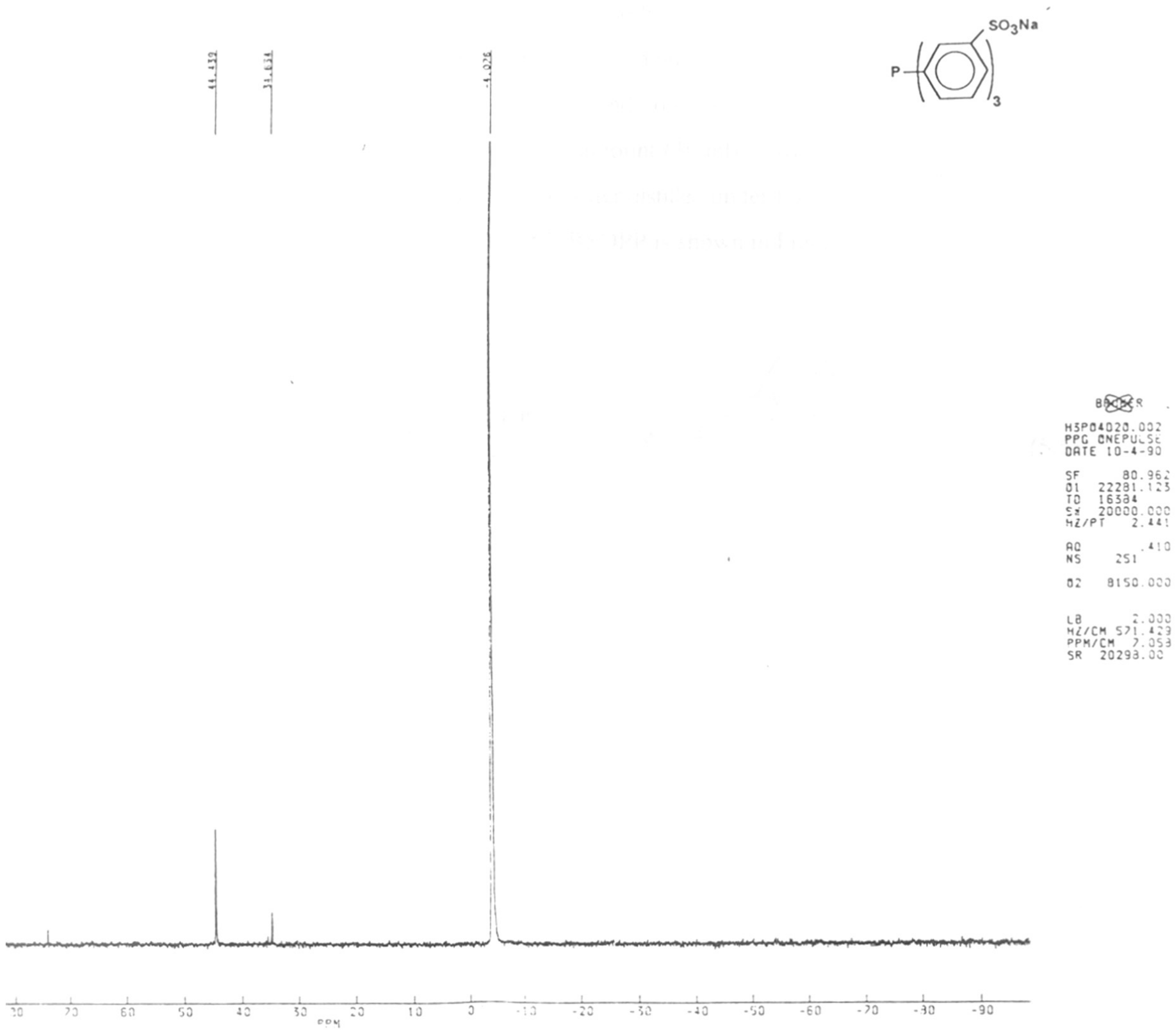
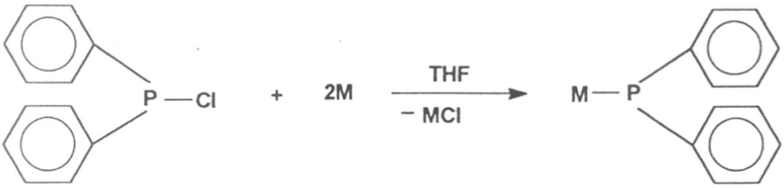
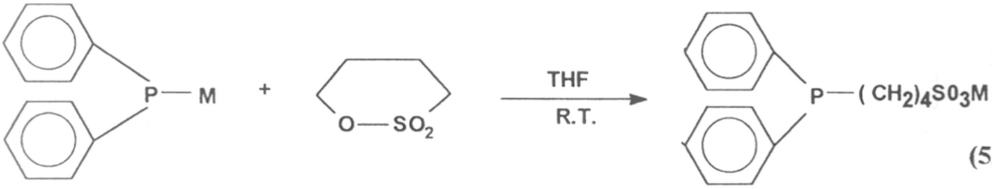


Figure 5.4 : ^{31}P NMR spectrum of TPPTS

or sodium chips in a two necked flask for 5 hrs at room temperature. The colour of the mixture became deep red. After filteration of excess lithium or sodium, 4.2ml (40 mmol) of 1,4-butane sultone was added dropwise to the deep red mixture which on warming up and became yellow. The solvent was evoparated under vaccum and the residue was extracted with chloroform-ether mixture in the presence of a small amount (10 ml) of water. The water phase containing Li or NaBSDPP was separated and the water distilled under high vaccum. The yield of the compound was 50%. The 31P NMR of LiBSDPP is shown in Figure 5.5.



(5.5)



(5.6)

Alkaly metal salt of butane sulphonated diphenyl phosphine [MBSDPP]

M = Li / Na

5.2.4 $HRh(CO)[Ph_2P\text{-}(CH_2)_4SO_3Li]_3$

0.176gm of $HRh(CO)(TPP)_3$ and 0.3 gm of $Ph_2P\text{-}(CH_2)_4SO_3Li]$ were dissolved in 15 ml of THF and stirred for 30 min under argon. This solution was evaporated to 10 ml. and aproximatly 10 ml of toluene added to it. A yellow solid, $[HRh(CO)[Ph_2P\text{-}(CH_2)_4SO_3Li]_3]$, precipitated out as soon as toluene was added. The solid was washed with toluene after

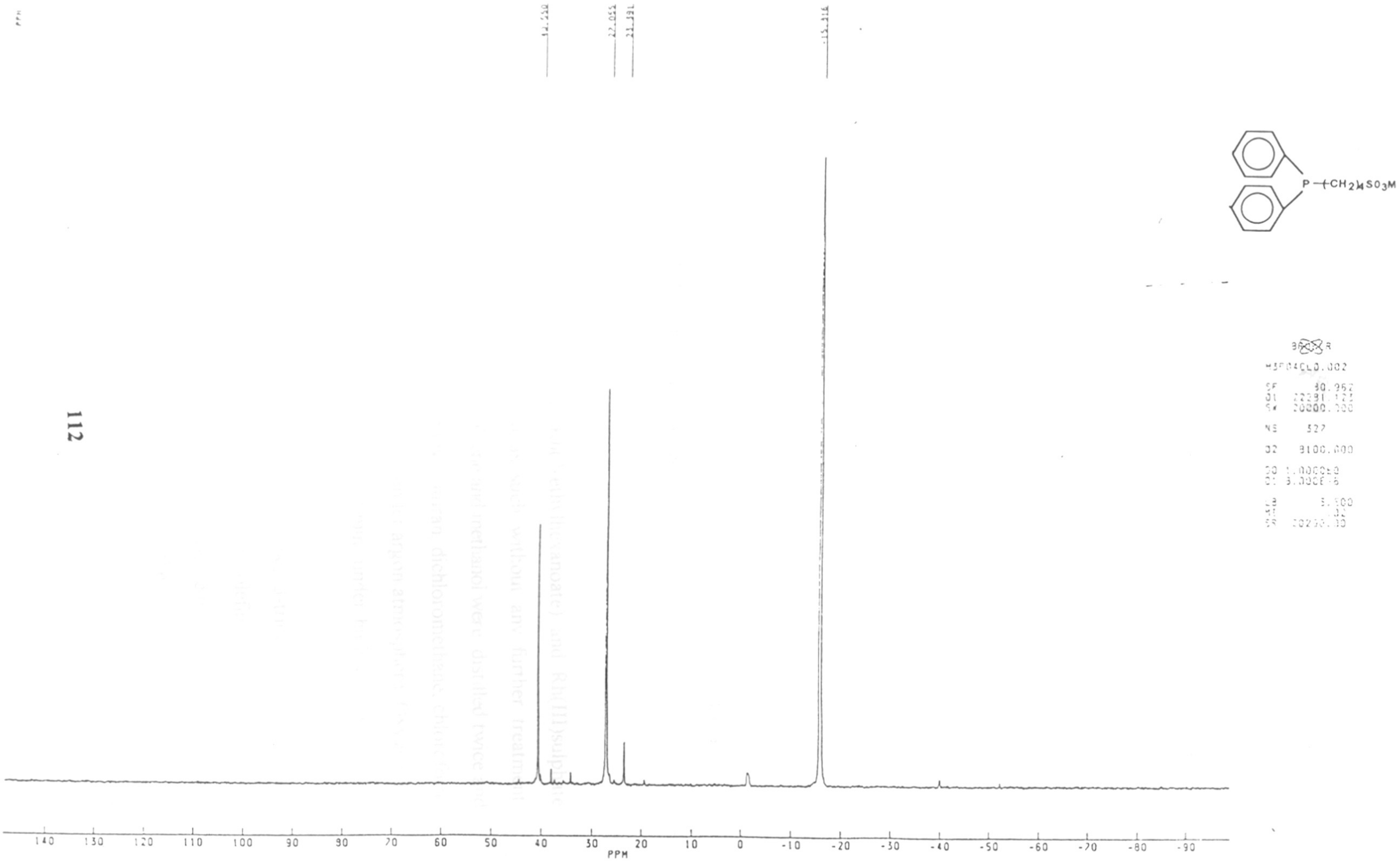
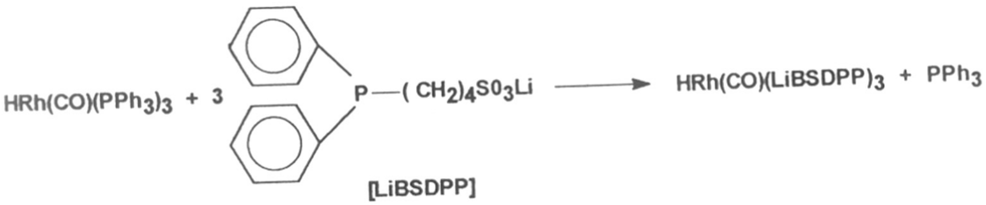


Figure 5.5 : ^{31}P NMR spectrum of LiBSDPP

filtration and dried in vacuum. The complex was characterized by NMR and IR spectroscopy. Figure 5.6 shows the IR spectrum for $HRh(CO)[Ph_2P\text{-}(CH_2)_4SO_3Li]_3$. The stoichiometric synthesis is described by :



[LiBSDPP]

(5.7)

5.3 HYDROFORMYLATION OF 1-HEXENE AND 1-TETRADECENE IN A TWO PHASE SYSTEM USING Rh-TPyR$_n$PTS (n=3,5,7,9) CATALYST

5.3.1 Experimental

5.3.1.1 Materials

Transition metal salts such as Rh(2-ethylhexanoate) and Rh(III)sulphate procured from Degussa, Germany, were used as such without any further treatment. $RhCl_3.3H_2O$ was purchased from Aldrich USA. Toluene and methanol were distilled twice and dried prior to use. The other solvents such as tetrahydrofuran, dichloromethane, chloroform, ethanol and isopropanol were freshly distilled and kept under argon atmosphere. Oxygen free water was obtained by passing ultrasonic waves for 30 min. under high vaccum through distilled water.

1-Hexene, 1-tetradecene, 1-hexadecene, 1-octadecene, 3-tridecene, styrene and p-methylstyrene were obtained from Fluka. The purity of all the olefins were cheked by GC and was greater than 95%. Carbon monoxide and hydrogen mixture in a ratio of 1:1 (syngas) was purchased from BASF, Germany and used directly from the cylinder.

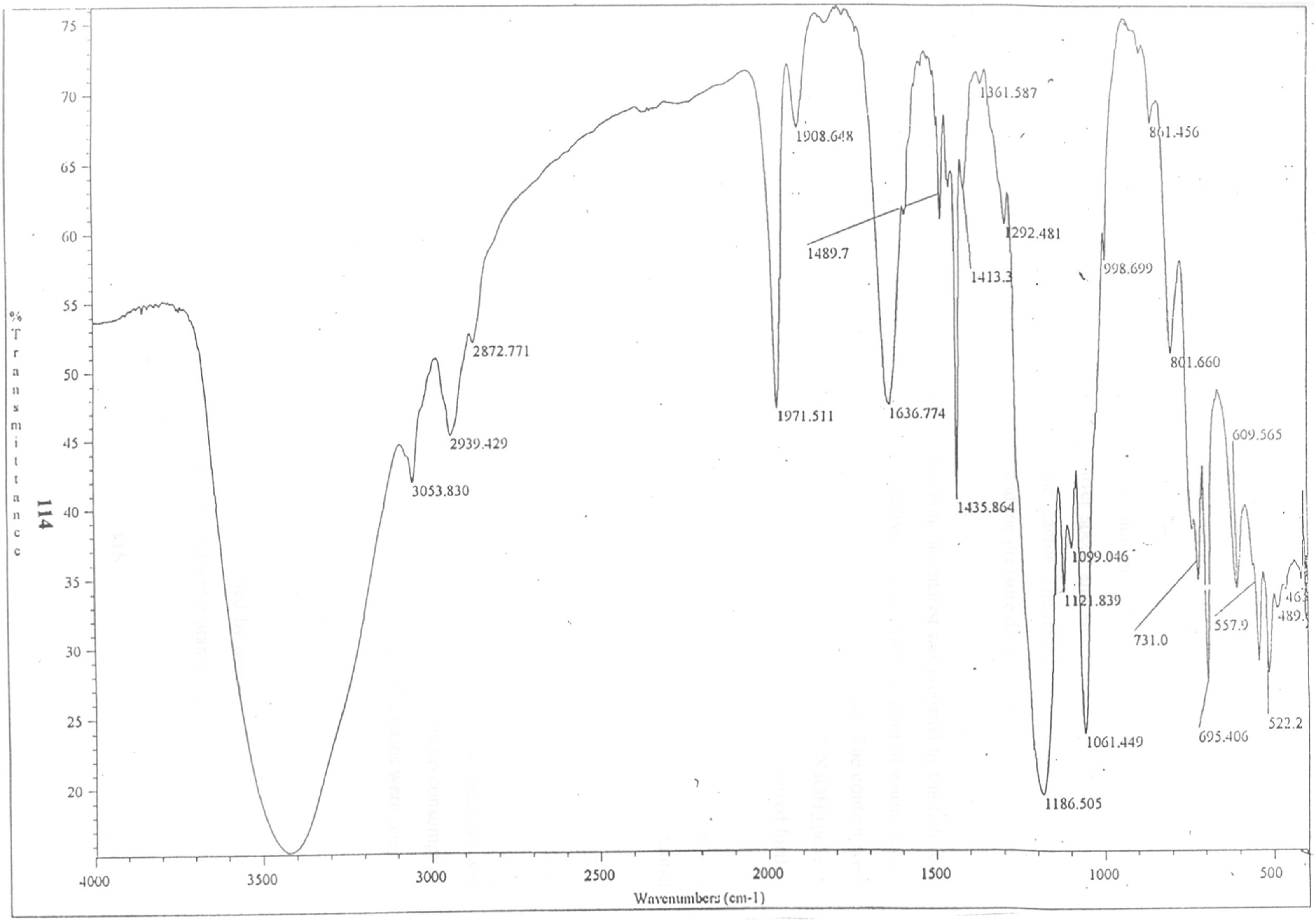


Figure 5.6 : IR spectrum of HRh(CO)[$Ph_2P-(CH_2)_4SO_3Li$]$_3$

5.3.1.2 Experimental procedure

Hydroformylation of olefins was carried out in a 200 ml autoclave, designed in the Institute for Technical Chemistry and Petrochemistry, RWTH Aachen, Germany. The autoclave was provided with arrangement for sampling of liquid and gaseous components, automatic temperature control, variable stirrer speed and addition funnel with a pressure equalizer. A safety rupture disc was fitted to the reactor. The temperature and pressure of the reaction was controlled through a transducer and the pressure drop was monitored using strip chart recorder.

For each biphasic hydroformylation reaction, the catalyst was prepared by the following procedure. A known amount of ligand was dissolved in a measured amount of warm oxygen free water. A known amount of rhodium salt was added to this solution. The content were stirred for 30 min. to obtain a rhodium complex with the water soluble ligand. NaOH (pellets) was added to the mixture for keeping the pH between 9 to 10. The mixture was stirred further for another 30 min.

The autoclave was evacuated twice and kept under argon. The catalyst solution was transferred into the autoclave under argon atmosphere. Olefin was placed in the addition funnel attached to the autoclave. The contents were flushed twice with nitrogen and syngas. The syngas (CO/H_2 =1:1) was introduced to the autoclave up to the required pressure. The stirrer was switched on and the autoclave heated to the desired temperature. The reaction was initiated by adding olefin into the autoclave from the addition funnel. The reaction was continued till the complete conversion of olefins was observed as indicated by no consumption of CO/H_2. The autoclave contents were cooled to room temperature, the gases were released and the liquid products analyzed by GC and GC-MS.

5.3.1.3 Analytical procedure

The products formed in the reactions were identified by using GC-MS. Quantitative analysis was done by GC by comparison with authentic standards under the following conditions.

G.C.	Sichromat 3
Column	FS-WG11 (50 m length)
Column Temperature	50-200°C
Detector	Flame Ionization Detector (FID)
Temperature Programme	5 min. iso, 8°C/min.
Carrier Gas	N_2
Integrator	HP 3359 LAS

Typical gas chromotograms of hydroformylation of 1-hexene, 1-tetradecene are shown in figures (5.7) and (5.8)

The conversion, yield, selectivity, and n/iso ratio were calculated as follows:

$$\text{Conversion (\%)} = \frac{(\text{moles of Olefin})_{\text{initial}} - (\text{moles of Olefin})_{\text{final}}}{(\text{moles of Olefin})_{\text{initial}}} \times 100$$

$$\text{Selectivity to aldehyde (\%)} = \frac{\text{moles of aldehyde formed}}{\text{moles of olefin consumed}} \times 100$$

$$\text{n/iso ratio} = \frac{\text{moles of n-aldehyde formed}}{\text{moles of iso-aldehyde formed}}$$

5.3.2 Results and Discussion

The hydroformylation of 1-hexene and 1-tetradecene to their corresponding aldehydes using Rh-TPyR$_n$PTS complex as a water soluble catalyst in a two phase system was investigated with the objective of screening of rhodium salts and understanding the role of other parameters such as ligands, temperature, pressure, and substrates on the activity and selectivity of the process. The stoichiometric hydroformylation of 1-hexene and 1-tetradecene

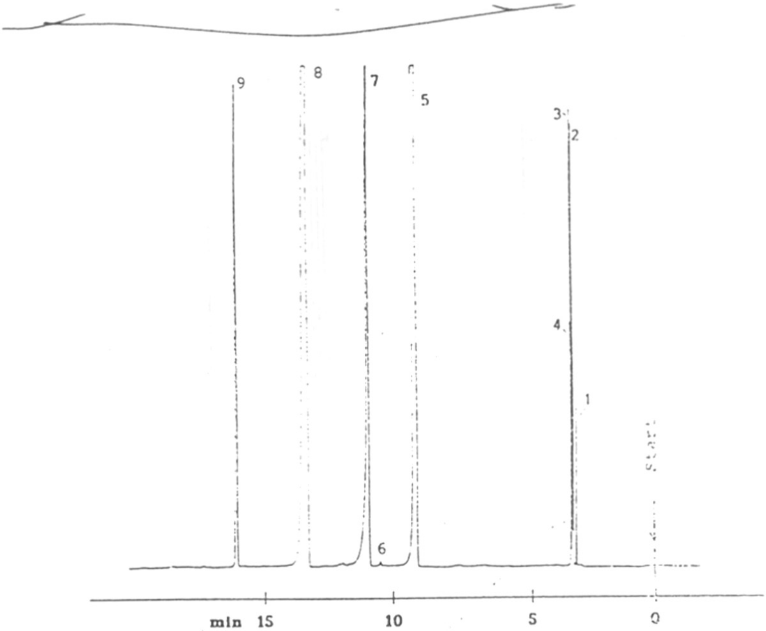


Figure 5.7 : Typical gas chromatogram for 1-Hexene hydroformylation

1) n-Hexane
2) 1-Hexene
3) 2-Hexene
4) 3-Hexene
5) Toluene(solvent)
6) 2-Ethylhexanal
7) 2-Methylhexanal
8) n-Heptanal
9) Tridecene (GC standard)

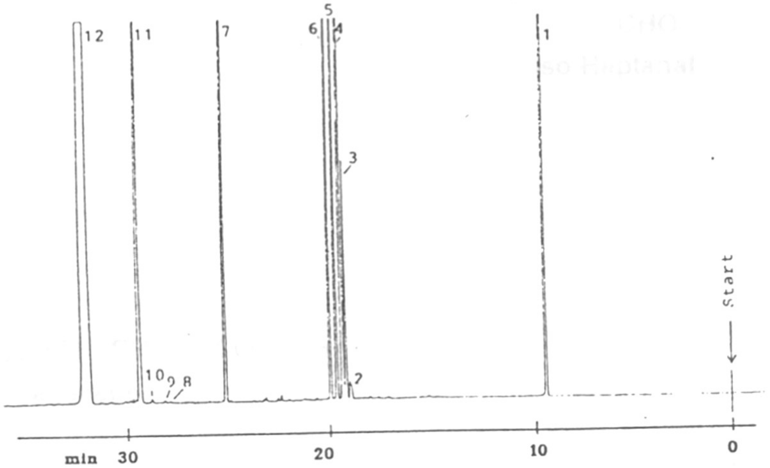


Figure 5.8: Typical gas chromatogram for 1-Tetradecene hydroformylation

1) Toluene(solvent)

2,3,5,6) Tetradecene isomers

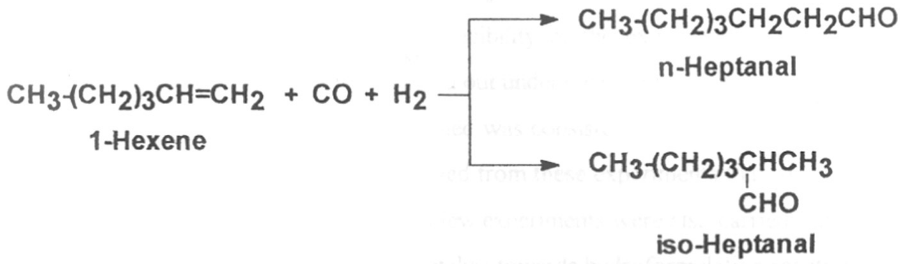
4) 1-tetradecene

7) Octylbenzene(GC standard)

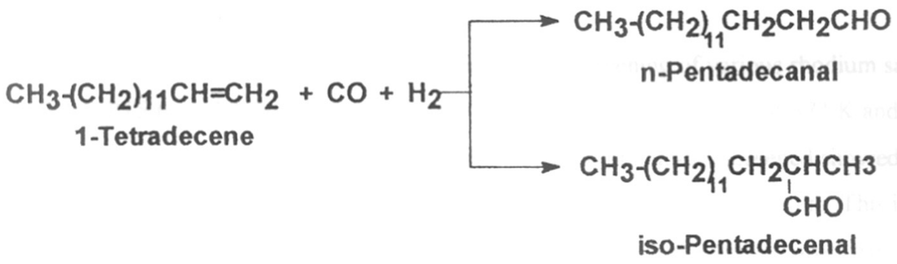
11) 2-Methyltetradecanal

12) n-Pentadecanal

are represented below.

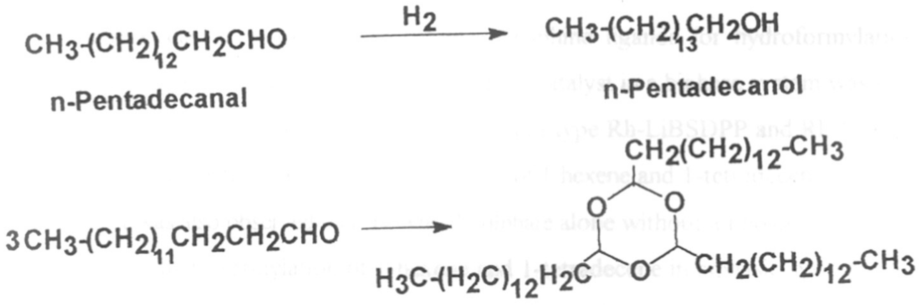


(5.8)



(5.9)

However, the formation of the side products such as alcohols (by the hydrogenation of corresponding aldehydes) and the trimerization of aldehydes to 1,3,5 trioxanes (Scheme 2) is also possible.



(5.10)

In view of the problems mentioned above, it is of interest to check the selectivity of Rh catalyst for new ligands such as TPyR$_n$PTS (n=3,5,7,9), NaBSDPP and LiBSDPP. For ensuring the material balance, reproducibility of the experiments and reusability of the catalysts, a few experiments were carried out under constant reaction conditions. The material balance of CO+H_2 and olefins consumed was consistent with the amount of aldehydes and cyclic ethers formed. It was also observed from these experiments that the results are highly reproducible (>98%reproducibility). A few experiments were also carried out with recovered catalysts, to check the activity of the catalyst towards hydroformylation reactions. The results are shown in Table 5.2. The activity of the catalyst was found to decrease gradually on recycle.

5.3.2.1 Screening of catalyst precursors

Several experiments were carried out for the screening of various rhodium salts with TPyR$_n$PTS (n=5,7,9) ligands for the hydroformylation of 1-Tetradecene at 373 K and 8 MPa. The results are presented in Table 5.3. All the catalyst precursors screened showed similar catalytic activity for the hydroformylation of 1-tetradecene in a biphasic system. This indicates that the same type of species may be forming from all the catalyst precursors. Since, Rh(III)sulphate is easy to prepare and known to form the active species very easily as compared to other rhodium salts, further reactions were carried out using Rh(III) sulphate as a catalyst precursor.

5.3.2.2 Effect of ligands

The effect of various water soluble phosphine ligands for hydroformylation of 1-hexene and 1-tetradecene using Rh(III) sulphate catalyst in a biphase system was studied at 373 K and 8.0 MPa (Table 5.4). The catalysts of type Rh-LiBSDPP and Rh-NaBSDPP were found to be inactive for the hydroformylation of 1-hexene and 1-tetradecene under these condition. It was also observed that the Rh(III)sulphate alone without a phosphine ligand was less active for hydroformylation of 1-hexene and 1-tetradecene in biphasic systems. This is because the ligands such as phosphines, possess the steric and electronic character which

Table 5.2

RECYCLE OF THE CATALYST ON HYDROFORMYLATION OF TETRADECENE-1 IN BIPHASIC SYSTEM:

Number of recycle	Conversion %	Selectivity (%)		n/iso
		Aldehyde	Trimer	
0	98	89	10	76:24
1	96	89	10	76:24
2	93	90	8.4	75:25
3	87	88	3	76:24
4	80	84	4	78:22

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm).
P/Rh ratio : 40
Water/olefin = 2/1
Temperature : 373 K
pH of the catalyst solution = 9.7 -10.8 (with NaOH).
Pressure = 8 MPa(CO:H_2 = 1:1)
Reaction time = 8 hrs
Solvent used = Water/ Toluene

Table 5.3

SCREENING OF THE CATALYST FOR HYDROFORMYLATION OF 1-TETRADECENE in BIPHASIC SYSTEM:

S No.	Ligand	Conversion %	Selectivity (%)		n/iso
			Aldehyde	Alcohol	
Rh-2-ethylhexenoate					
1	TPyRnPTS(n=5)	81	90	8	74:26
2	TPyRnPTS(n=7)	98	89	10.2	76:24
3	TPyRnPTS(n=9)	92	90	9.4	75:25
Rh(III)Sulphate					
4	TPyRnPTS(n=5)	82	87	12	72:28
5	TPyRnPTS(n=7)	94	90	10	76:24
6	TPyRnPTS(n=9)	90	88	12	72:28
$RhCl_3.H_2O$					
7	TPyRnPTS(n=7)	95	89	10	75:25

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm).
P/Rh ratio : 40
Water/olefin = 2/1
Temperature = 373 K
pH of the catalyst solution = 9.7 -10.8 (with NaOH).
Pressure = 8 MPa($CO:H_2$ = 1:1)
Reaction time = 8 hrs
Solvent used = Water/ Toluene

TABLE 5.4

EFFECT OF LIGAND ON HYDROFORMYLATION OF 1-TETRADECENE BIPHASIC SYSTEM:

S No.	Ligand	conversion %	Selectivity (%)		n/iso
			Aldehyde	Trimer	
1	$TPyR_nPTS$ (n=5)	81	90	8	74:26
2	$TPyR_nPTS$(n=7)	98	89	10.2	76:24
3	$TPyR_nPTS$(n=9)	92	90	8.04	75:25
4	TPPTS	--	--	--	--
5	LiBSDPP	--	--	--	--
6	NaBSDPP	--	--	--	--
7	NO ligand	--	--	--	--

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm.)

P/Rh ratio : 40

Water/olefin = 2/1

pH of the catalyst solution = 9.7 -10.8 (with NaOH).

Pressure = 8 MPa ($CO:H_2 = 1:1$)

Reaction time = 8 hrs

Temperature = 373 K

causes the equilibrium of the following reaction to

$$HRh(CO)_4 + PR_3 \rightleftharpoons HRh(CO)_3PR_3 + CO$$

shift towards right hand side. The $HRh(CO)_3PR_3$ is assumed to be the active rhodium species during hydroformylation reactions (Cornils 1980). Therefore this may be explained by the fact that the in-situ formation of such an active Rh(I) species is not possible in the absence of a ligand and hence the activity towards hydroformylation reactions is reduced drastically. It is also well known that the rhodium hydridocarbonyl complex will form in-situ under CO/H_2 atm. with Rh(III)sulphate, but it requires higher reaction conditions (373 to 413 K and 20 to 30 MPa. pressure of CO/H_2, (Cornils 1980). Therefore, the ligands of electron donating phosphine such as TPyRnPTS which have surfactant properties were used to modify the catalyst. These catalysts form a micellar complex with olefin in a biphasic medium which initiate the hydroformylation of higher olefins.

It was also noticed that the conversion of olefins increased with increase in the number of methyl groups of the ligand(being hydrophobic in nature) and decreased with further increase in the alkyl chain (n = >7) (Table 5.4, S.No. 1,2,3). It may be noticed that the side product, such as trimerization of aldehydes (1 - 10 % depending on the ligand used) has occurred during hydroformylation of 1-tetradecene. The proportion of the trimer is higher in the case of TPyR$_n$PTS (n=7) as a ligand than in the case of TPyR$_n$PTS (n=3). Surprisingly, there was no trimerized product observed in the case of ligands such as NaBSDPP and LiBSDPP. It is noted from this study that the ligand TPyR$_n$PTS (n= 7) gives better activity compared to other ligands studied for hydroformylation of olefins.

5.3.2.3 Effect of temperature

The effect of temperature on hydroformylation of 1-tetradecene was studied using Rh-TPyR$_n$PTS catalyst in a temperature range of 348 to 383 K. The results are presented in Table 5.5. It was observed that the conversion of olefin increased with increase in temperature. Higher conversion (98.%) was observed when TPyR$_n$PTS (n=7) was used as a ligand. A higher temperature (383 K), the trimerization of aldehydes was found to be lower. This can

Table 5.5

EFFECT OF TEMPERATURE ON HYDROFORMYLATION OF TETRADECENE-1 BIPHASIC SYSTEM:

S No.	Temp. K	Ligand	Conversion %	Selectivity (%) Aldehyde	Selectivity (%) Trimer	n/iso
1	348	TPyPTS(n=7)	82	89	10	74:26
2	348	TPyPTS(n=9)	86	90	10	72:28
3	368	TPyPTS(n=7)	98	89	10	76:24
4	368	TPyPTS(n=9)	92	90	8.4	75:25
5	383	TPyPTS(n=3)	74	88	3	76:24
6	383	TPyPTS(n=5)	89	91	4	78:22
7	383	TPyPTS(n=7)	98.5	90	3	76:24
8	383	PyPTS(n=9)	92	88	2	74:26

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm).
P/Rh ratio : 40
Water/olefin = 2/1
pH of the catalyst solution = 9.7 -10.8 (with NaOH).
Pressure = 8 MPa($CO:H_2$ = 1:1)
Reaction time = 8 hrs
Solvent used = Water/ Toluene

be explained by the fact that at higher temperatures , 1,3,5-trioxanes are known to undergo cleavage to form the deprotected aldehydes. At 383 K, the conversion of 1-tetradecene was 74 % , 89 %, 98.5 % and 92 % for the ligands of type TPyR$_n$PTS (n = 3, 5, 7, 9) respectively. This indicates that at a particular temperature, the activity of the catalyst was increased by increase in the alkyl chain of the ligand (Table-5.5, S.No 5,6,7,8).

5.3.2.4 Effect of olefin type

The effect of various olefinic substrates for hydroformylations using Rh(III)sulphate/TPyR$_n$PTS (n=3,5,7,9) was studied at temperature 373 K and pressure 8 MPa. The results are presented in Table 5.6. The olefins studied are 1-hexene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 7-tetradecene. It was observed that the activity of the catalyst was increased by increase in the alkyl chain of the olefins and then it decreased. The side reactions such as trimerization of aldehydes were not observed for lower olefins due to the lower stability associated with the corresponding cyclic ethers, whereas the trimerized product (10 %)was observed for all the higher olefins. However no appreciable formation of cyclic ether was formed with the further increase in the alkyl chain.

5.3.2.5 Effect of surfactant

As seen in section 5.3.2.2, the catalysts of the type Rh-NaBSDPP and Rh-LiBSDPP alone have no activity for the hydroformylation reaction. These catalysts are active only when surfactants were used. Therefore, the effect of the ligand with added surfactants on hydroformylation of 1-hexene and 1-tetradecene was investigated. The results are presented in Table 5.7 and 5.8 for 1-hexene and 1-tetradecene respectively. In all the experiments, the ratio of the catalyst to the surfactant was kept constant. It was observed that the conversion of olefins varied significantly depending on the nature of the surfactants used. This may be due to the formation of a quarternary ammonium cation (Fig. 5. 9), which transports the active catalyst to the interfacial layer where the reaction is believed to take place. The nature of surfactant plays an important role in determining the activity of the catalyst. Tetramethylammonium bromide and ethyl trimethylammonium bromide show poor activity (2 to 3%), whereas tetradecyl-trimethylammonium bromide shows the highest activity in

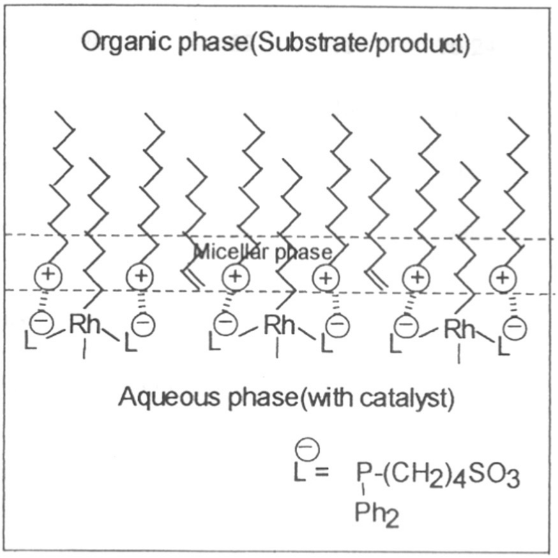


Figure 5.9 : **The role of surfactant on the formation of micellar phase during hydroformylation Reactions.**

TABLE 5.6

EFFECT OF OLEFINS ON BIPHASIC HYDROFORMYLATION REACTION SYSTEM

S No.	Olefins	Conversion %	Selectivity (%) Aldehyde	Alcohol	n/iso	Trimer
1	Hexene-1	76	93	05	73:27	--
2	Dodecene	92	66	40	75:25	09.7
3	1-Tetradecene	98	89	11	76:24	10.2
5	1-Hexadecene	78	77	20	71:29	08.5
7	1-Octadecene	70	71	25	70:30	09.3
8	3-Tridecene	89	83	13	more side products	

Reaction conditions:

Catalyst : Rh(III)sulphate (rhodium concn. 200 ppm.
P/Rh ratio : 40
Water/olefin = 2/1
pH of the catalyst solution = 9.7 -10.8 (with NaOH).
Temperature = 100°
Pressure = 80 atm.($CO:H_2$ = 1:1)
Reaction time = 8 hrs
Solvent used = Water/ Toluene

Table 5.7

EFFECT OF SURFACTANT ON HYDROFORMYLATION OF 1-HEXENE IN BIPHASIC MEDIUM

S. No.	Ligand	Surfactant	Conversion %	Selectivity (%)		n/iso
				Aldehyde	Alcohol	
1.	LiBSDPP	$CH_3(CH_2)_3NCH_3Br$	4	95.0	05	72.38
2	LiBSDPP	$CH_3(CH_2)_6NCH_3Br$	23	92.0	04	77:23
3	LiBSDPP	$CH_3(CH_2)_{12}NCH_3Br$	98	44	54	76:24
4	NaBSDPP	$CH_3(CH_2)_{13}NCH_3Br$	95	79	16	68:30
5	LiBSDPP	$CH_3(CH_2)_{15}NCH_3Br$	03	89	10	83:17
6	LiBSDPP	$C_2H_5NCH_3)_3Br$	03	94	05	71:29
7	LiBSDPP	$(C_6H_5)_4NBr$	02	95	02	75:25

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm).
P/Rh ratio : 40
Water/olefin = 2/1
pH of the catalyst solution = 9.7 -10.8 (with NaOH).
Pressure = 8 MPa ($CO:H_2 = 1:1$)
Temperature = 373 K
Reaction time = 3 hrs
Solvent used = Toluene/Water

Table 5.8

EFFECT OF SURFACTANT ON HYDROFORMYLATION OF 1-TETRADECENE IN BIPHASIC MEDIUM

S. No.	Ligand	Surfactant	Conversion %	Selectivity (%)		n/iso
				Aldehyde	Alcohol	
1.	LiBSDPP	$CH_3(CH_2)_{11}NCH_3Br$	67.3	73	26	73:27
2	NaBSDPP	$CH_3(CH_2)_{11}NCH_3Br$	64.6	72	26	72:28
3	LiBSDPP	$(C_2H_5)_4NBr$	18.7	70	29	70:30
4	LiBSDPP	$(CH_3)_4NBr$	10.5	78	20	78:22
5	LiBSDPP	$CH_3(CH_2)_{15}NCH_3Br$	7.3	82	16	82:18
6	NaBSDPP	$CH_3(CH_2)_{15}NCH_3Br$	3.8	78	19	78:22
7	LiBSDPP	$CH_3(CH_2)_{13}NCH_3Br$	65.7	76	23	76:24
8	LiBSDPP	$CH_3(CH_2)_{11}NCH_3Br$	18.6	78	21	82:18
9	LIBSDPP	$(C_2H_5)_4NBr$	26.4	70	28	73:27
10	LiBSDPP	without surfactant	5.7	81	17	79:21

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm).
P/Rh ratio : 40
Water/olefin = 2/1
pH of the catalyst solution = 9.7 -10.8 (with NaOH).
Pressure = 8 MPa ($CO:H_2$ = 1:1)
Temperature = 373 K
Reaction time = 3 hrs
Solvent used = Toluene/Water

hydroformylation of 1-hexene (98 %) as well as 1-tetradecene (67%). The activity of the catalyst decreased (<3%) when hexadecylammonium bromide was used as a surfactant. This means that the activity of the catalyst initially increases with increase in the alkyl chain of the surfactant and with further increase in the alkyl chain the activity decreases. This trend may be due to the saturation of the formation of micellar phase which reaches the maximum by increase in the alkyl chain of the surfactant and further increase in the alkyl chain of the surfactant may inhibit the reaction rate.

5.4 HYDROFORMYLATION OF 1-HEXENE, 1-TETRADECENE AND STYRENE IN A HOMOGENEOUS SYSTEM

5.4.1 Experimental

The details of the materials, experimental procedure are given in the section 5. 3.1.

5.4.2 Results and Discussion

The aim of this part of the work was to study the effect of the catalyst with ligands such as alkalimetal salts of sulphobutyl diphenylphosphine (NaBSDPP and LiBSDPP) for the hydroformylation of 1-hexene, 1-tetradecene and styrene. There is no literature on the application of these ligands for hydroformylation reactions. Therefore, it was thought worthwhile to evaluate LiBSDPP in Rh catalyzed hydroformylation of various olefins. The catalyst prepared using these ligands (NaBSDPP and LiBSDPP) possess many advantages compared to the conventional hydroformylation catalysts such as $HRh(CO)(PPh_3)_3$(homogeneous) and $HRh(CO)(TPPTS)_3$(biphasic) as can be seen from the following discussion.

The catalyst prepared from these ligands are soluble in methanol at higher temperatures (>60°C) and are insoluble in methanol at room temperature. Thereby, facilitating the separation of products from the catalyst just by filtration. Moreover, the loss of the metal often experienced under homogeneous conditions, does not occur under this conditions.

It is remarkable that even higher olefins can be hydroformylated under mild reaction conditions using Rh-NaBSDPP and Rh-LiBSDPP catalysts which is difficult with conventional water soluble catalysts (HRh(CO)(TPPTS)$_3$). Hence, for all studies, homogeneous system was used with methanol as a solvent and the separation of the catalyst was achieved by simple filtration of the chilled reaction mixture. The effect of various parameters such as temperature, pressure on the rate of hydroformylation of 1-hexene, 1-tetradecene and styrene using NaBSDPP and LiBSDPP in homogeneous systems are discussed below.

5.4.2.1 Olefin type

Hydroformylation activity for olefins such as 1-hexene, 1-tetradecene 1-hexadecene, 1-octadecene, 3-tridecene and styrene using homogeneous Rh-NaBSDPP and Rh-LiBSDPP system was studied, The results are presented in Table 5. 9. It was observed that there was no considerable change in the activity pattern of the catalyst for different olefins.

5.4.2.2 Effect of pH

The effect of pH on the rate of hydroformylation of 1-tetradecene in homogeneous system using Rh-NaBSDPP catalyst was studied at 353 K and 2 MPa (Table 5.10). At a pH of 2.3, lower reaction rates were observed, however the selectivity to alcohol was more 46 % at pH of 2.3. The active Rh species may decompose under the acidic medium, which leads to lower conversion at lower pH. As can be seen from the Table, the rate of the reaction remains almost constant till it reaches the pH 6. After pH 6, the rate increases rapidly up to a pH of 11, giving complete conversion to the product. indicating that an optimum pH of 10 -11 is necessary for an excellent rate and yield of the reaction. Hence, strong basic medium (pH 10-11) was used for all further hydroformylation studies.

5.4.2.3 Effect of temperature

Hydroformylation of 1-tetradecene and styrene using Rh-LiBSDPP and Rh-NaBSDPP ligands in homogeneous system were carried out at temperatures of 323 to 383 K at 2 MPa. pressure (Table 5.11). In the case of 1-tetradecene as a substrate, the change in the temperature does not influence the rate of the reaction . However, the selectivity towards aldehyde formation was increased with increase in temperature. Moreover, the selectivity

Table 5.9

EFFECT OF OLEFINS ON HOMOGENEOUS HYDROFORMYLATION SYSTEM

S No.	Olefins	Ligand	conversion %	Selectivity (%) Aldehyde	Alcohol	n/iso
1	1-Hexene	LiBSDPP	75.2	98	02	71:29
2	1-Hexene	NaBSDPP	98.0	98	02	72:28
3	1-Tetra-decene	LiBSDPP	96.4	89	11	71:29
4	1-Tetra-decene	NaBSDPP	97.9	89	11	67:33
5	1-Hexa-decene	LiBSDPP	99.5	97	03	69:31
6	1-Octa-decene	NaBSDPP	99.5	98	02	71:29
7	Styrene	LiBSDPP	91.6	92	08	12:88
8	Styrene	NaBSDPP	98.2	100	-	09:91

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm).
P/Rh ratio : 40
Water/olefin = 2/1
pH of the catalyst solution = 9.7 -10.8 (with NaOH).
Temperature = 1373 K
Pressure = 80 atm.(CO:H_2 = 1:1)
Reaction time = 3 hrs
Solvent used = Methanol

Table 5.10

EFFECT OF pH ON HOMOGENEOUS HYDROFORMYLATION OF 1-TETRADECENE SYSTEM

S No.	pH	Conversion %	Selectivity (%) Aldehyde	Alcohol	n/iso
1	2.3	07.07	54	46	77:23
2	6	13.6	64	36	78:22
3	9	87	96	04	71:29
4	10	98.5	96	04	71:29
5	12	98.8	36	64	55:45

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm).
P/Rh ratio : 40
Water/olefin = 2/1
Pressure = 8 MPa (Co : H_2 = 1:1)
Temperature = 373 K
Reaction time = 3 hrs
Solvent used = Methanol
Ligand used = $Ph_2P-(CH_2)_4SO_3Li$

Table 5.11

EFFECT OF TEMPERATURE ON HYDROFORMYLATION OF 1-TETRADECENE AND STYRENE IN HOMOGENEOUS MEDIUM

S	Temp.	Ligand	Conversion %	Selectivity (%)		n/iso
				Aldehyde	Alcohol	
1	50	LiBSDPP	17	98.4	-	60:40
2	50	NaBSDPP	75	88	10	66:34
3*	50	NaBSDPP	95	98	03	07:93
4	80	LiBSDPP	98.5	96	04	71:29
5	80	NaBSDPP	97.9	89	11	67:33
6*	80	NaBSDPP	98.3	100	-	09:91
7	100	LiBSDPP	99.4	82	18	61:39
8	100	NaBSDPP	98.6	85	45	69:31
9.	100	NaBSDPP	99.6	98	02	08:92

* Styrene was used as substrate.

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm).
P/Rh ratio : 40
Water/olefin = 2/1
pH of the catalyst solution = 9.7 -10.8 (with NaOH).
Pressure = 80 atm.($CO:H_2 = 1:1$)
Reaction time = 3 hrs
Solvent used = Methanol

towards aldehyde formation was better in case of NaBSDPP than in the case of LiBSDPP. In the case of styrene, the activity of the catalyst increased by increase in the temperature although the selectivity was not affected.

5.4.2.4 Effect of pressure

The effect of total pressure of CO and H_2 on the rate of hydroformylation of 1-tetradecene and styrene using Rh-NaBSDPP catalyst was studied at 353 K. The results are presented in Table 5. 12 and 5.13 for 1-tetradecene and styrene respectively. It was observed that by increase in total pressure for hydroformylation of 1-tetradecene, only a marginal increase in the activity occured . However, a reverse trend was observed in the selectivity to aldehydes. In all the cases, selectivity of the aldehyde decreased with increase in the total pressure of CO and H_2 This is due to higher hydrogen content in the gas phase leading to hydrogenated products. In the case of hydroformylation of styrene, the conversion of styrene was increased by increase in the total pressure (Table 5.13).

5.4.2.5 Effect of ligands

The effect of different ligands on the activity and selectivity of Rh(III)sulphate catalyst for the hydroformylation of styrene in a homogeneous medium was investigated (Table 5.14). The ligands LiBSDPP and NaBSDPP show almost similar activity (>98% conversion) and selectivity (>98%) to aldehyde. In the absence of either ligand or catalyst no reaction took place .

5.5 CONCLUSIONS

ii Hydroformylation of 1-hexene, 1-tetradecene and styrene in homogeneous and biphasic systems using Rh-TPyR$_n$PTS (n-5,7,9), Rh-NaBSDPP and Rh-LiBSDPP was studied with Rh(III)sulphate as a catalyst precursor. The important observations made are summarized below:

iii Rh-TPyR$_n$PTS alone was active for hydroformylation of higher olefins without any binding ligands. It has been established that the activity of the ligand was due to

Table 5.12

EFFECT OF PRESSURE ON HOMOGENEOUS HYDROFORMYLATION OF 1-TETRADECENE SYSTEM

S No.	PCO/H_2 atm.	Conversion %	Selectivity (%) Aldehyde	Selectivity (%) Alcohol	n/iso
1	20	98.1	98	02	70:30
2	50	98.4	95	05	68:32
3	80	98.6	93	07	66:34

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm).
P/Rh ratio : 40
Water/olefin = 2/1
pH of the catalyst solution = 9.7 -10.8 (with NaOH).
Temperature = 373 K
Reaction time = 3 hrs
Solvent used = Methanol
Ligand used = $Ph_2P-(CH_2)_4SO_3Li$

Table 5. 13

EFFECT OF PRESSURE ON HOMOGENEOUS CATALYZED HYDROFORMYLATION OF STYRENE

S. No.	Total Pressure MPa	Conversion %	Selectivity (%)		n/iso
			Aldehyde	Alcohol	
1	1.5	75.2	98	02	07:93
2	2.5	89.6	98	02	08:92
3	3.5	91.4	98	02	12:88
4	4.5	93.5	94	06	10:90
5	6.5	96.1	92	07	09:91
6	8.0	98.2	90	10	09:91

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm).
P/Rh ratio : 40
Water/olefin = 2/1
pH of the catalyst solution = 9.7 -10.8 (with NaOH).
Temperature = 373 K
Reaction time = 3 hrs
Solvent used = Methanol
Ligand used = $Ph_2P-(CH_2)_4SO_3Li$

Table 5.14

EFFECT OF LIGAND ON HOMOGENEOUS CATALYZED HYDROFORMYLATION OF STYRENE

S No.	Ligand	Conversion %	Selectivity (%)		n/iso
			Aldehyde	Alcohol	
1.	LiBSDPP	98.2	100	-	09:91
2	NaBSDPP	98.1	98	02	10:90
3	TPP	98.4	99	01	08:9
4	without ligand	-	-	-	-
5	without catalyst	-	-	-	-

Reaction conditions:

Catalyst: Rh(III)sulphate (rhodium concn. 200 ppm).
P/Rh ratio : 40
Water/olefin = 2/1
pH of the catalyst solution = 9.7 -10.8 (with NaOH).
Pressure = 8 MPa ($CO:H_2$ = 1:1)
Temperature = 373 K
Reaction time = 3 hrs
Solvent used = Methanol

the surfactant properties of the ligand.

iv Side reaction such as trimerization of aldehydes to cyclic ether (1,3,5-trioxane) was observed using $TPyR_nPTS$ as a ligand during Rh catalyzed hydroformylation reactions.

v Various cationic surfactants such as C_2H_5-$N(CH_3)_3Br$, $(C_6H_5)_4$-NBr, $CH_3(CH_2)_n$-$N(CH_3)_3Br$ have been studied for the hydroformylation of 1-tetradecene in biphasic system. The activity of the catalyst was varied significantly depending on the nature of the surfactants used. The surfactant forms a quarternary ammonium cation which transports the active catalyst to the interfacial layer. No activity was observed for the hydroformylation of 1-tetradecene in the absence of a surfactant.

vi The catalysts of type Rh-NaBSDPP and Rh-LiBSDPP catalysts were found to be very efficient for the hydroformylation of styrene in a homogeneous medium. Complete separation of the catalyst in this system was achieved and it could be reused several times without losing its activity.

vii pH of the reaction medium plays an important role in conversion of olefin. Low conversion (7%) was observed for the pH 2. Under acidic medium, the active Rh species decomposes into inactive form which causes the lower conversion

viii Recovery of Rh complex catalyst is possible in homogeneous medium by heterogenization of homogeneous (methanolic solution) phase by adding water.

REFERENCES

Arhancet J.P., Davis M.E., Merola J.S. and Hanson B.E., Nature, **339,** 454, (1989).

Arhancet J.P., Davis M.E., Merola J.S. and Hanson B.E., J. Cat., **121,** 327, (1990).

Beller M., Cornils B., Frohning C.D. and Kohlpaintner C.W., J. Mol. Catal., **104**, 17, (1995).

Cornils B., New Synthesis with carbon monoxide edited by Falbe J., Springer-Verlag, Berlin, Heidelberg, New York (1980).

Ding H., Hanson B.E., Glass T.E., Inorg. Chem. Acta., **229**, 329, (1995)

Fell B. and Papadogianakis G., J. Mol. Cat., **66**, 143, (1991).

Herrmann W.A. and Kohlpaintner C.W., Angew. Chem. Int. Ed. Engl., **32,** 1524, (1993).

Kalck P. and Monteil F., Adv. in Organomet. Chem., **34,** 219, (1992).

Kuntz E., CHEMTECH, **17,** 570, (1987).

Papadokianokis G., Ph.D Thesis, RWTH, Aachen, Germany (1989).

Paetzold E., Kinting A. and Oehme G., J.Prakt.Chemie. **329**, 725, (1987).

Paetzold E. and Oehme G., Z.Chem., **29**, 447, (1989).

Russel M. J. H., Platinum Met. Rev., **32**(4), 179, (1988).

Sinou D., Bull Soc. Chim. Fr., 480, (1987)

CHAPTER 6

KINETICS OF HYDROFORMYLATION OF ETHYLENE USING WATER SOLUBLE Rh-TPPTS CATALYST

6.1 INTRODUCTION

Biphasic catalysts find extensive use in a variety of reactions such as hydroformylation, hydrogenation, hydrocyanation etc. The development of water soluble metal complex catalysts and ligands are considered as a major development in hydroformylation catalysis, because they can be easily separated from the products. In recent years, the hydroformylation of olefins (oxo-process) using water soluble metal complex catalysts has gained considerable attention by many researchers. This system involves selection of two immiscible liquid phases, such that the catalyst is soluble in one phase, while the product exists in the other phase. The commercial importance of this system was realised after the pioneering work on synthesis and applications of triphenyl phosphine trisulphonate (TPPTS) ligand Kuntz (1975).

Even though, several other water soluble ligands and catalysts have been studied for hydroformylation reactions, Rh-TPPTS is the most suitable and commercially proven catalyst system for biphasic hydroformylation reactions. Since, catalysis in aqueous media is also likely to modify the kinetics and selectivity behaviour, further studies on catalysis and kinetic modelling of Rh-TPPTS catalysed hydroformylation would be most desirable. Hydroformylation of ethylene is one such system leading to propionaldehyde. The stoichiometric reaction is

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + CO + H_2 \xrightarrow{\text{Catalyst}} \underset{\text{Propionaldehyde}}{CH_3CH_2CHO} \qquad (6.1)$$

Propionaldehyde can be further hydrogenated to n-propanol. These two products have a significant market as solvents as well as intermediates in the manufacture of pharmaceuticals, pesticides and perfumery products. Also, propionaldehyde is an intermediate in new process for methyl methacrylate without using HCN. This reaction involves simultaneous absorption of three gaseous reactants (ethylene, CO and hydrogen) with reaction in a liquid phase to produce a liquid product. It is important to understand the rate behaviour, kinetics and mechanism of such a complex multiphase reaction. Such a study is not only useful for optimization of the process and improvement of the catalytic system but also provides the basic information for the design and scale up of suitable reactors. Thus the problem chosen is important from both the academic and industrial points of view.

The hydroformylation of ethylene is catalyzed by variety of metal complexes consisting of Co, Rh, Fe and Ni and some of the important studies on the type of catalysts used have been summerised in table 6.1. The kinetics of hydroformylation of olefins using homogeneous Rh-complex catalysts has been studied earlier by many investigators. More recently, Divekar (1995) has reported the kinetics of hydroformylation of ethylene using homogeneous $HRh(CO)(TPP)_3$ (TPP = triphenylphosphine) catalyst system. However, on hydrofomylation of ethylene using water soluble Rh-TPPTS catalyst system, there is practically no published information in the literature. Therefore, the present work was undertaken with the specific objective of studying the intrinsic kinetics of homogeneous catalytic hydroformylation of ethylenein aqueous phase. In this work, the experimental rate data were obtained at various reaction conditions such as effect of partial pressures of ethylene, CO and hydrogen, catalyst concentration, temperature etc. using a stirred high pressure gas-liquid reactor to understand the dependence of the rate on the concentrations of reactants. The rate data were interpreted and different forms of rate equations including both empirical as well as mechanistic rate models were tested. Finally, a rate equation has been proposed and the kinetic parameters are evaluated.

6.2 EXPERIMENTAL :

6.2.1 Materials

Rhodium trichloride ($RhCl_3.3H_2O$) was obtained from Arora Mathey Ltd. Triphenylphosphine (TPP) was procured from LOBA Chemie, Switzerland. 1,5 cyclooctadiene(COD) was procured from Aldrich Chemicals, USA. Solvents like toluene, and ethanol were freshly distilled prior to their use and degassed. Hydrogen gas supplied by Indian

TABLE 6.1

A SUMMARY OF CATALYSTS SYSTEMS USED FOR THE HYDROFORMYLATION OF ETHYLENE

Sr. No.	Catalysts system	Range of condition		Solvent	Remarks	Reference
		Temp. K	Press. MPa			
1	Rh catalyst solution				effect of pressure, temperature, composition on the reaction studied	Eidus and Lapidus (1967).
2	aq. solution of $Rh(NO_3)_3$	373	24	ethanol	100% conversion	Mitsuo and Takeshi (1969).
3	$Rh_4(CO)_{12}$	573	13	butanol	—	Anthony and Thigpen (1972).
4	$HRh(CO)(TPP)_3$			dibutyl pthalate	lean gas from oil cracking is used	Kummer and Platz (1975).
5	$RhCl(CO)(TPP)_2$ + excess $P(PhO)_3$	411	0.81	dioctyl pthalate		Iwamoto et. al. (1977)
6	$RhH_2(allyl)(CO)$- -$(TPP)_2$				kinetics of the reaction, studied	Tjan and Scholten (1977)
7	Rh complexes	308	5-10	n-tetradecane	mechanistic studies with IR spectroscopy	King et. al. (1979).
8	$Rh_4(CO)_{12}$				intermediates involved in the reaction studied	King et. al. (1980).

TABLE 6.1 (contd.)

Serial No.	Catalytic system	Range of condition		solvent	Remarks	Reference
		Temp. K	Press. MPa			
9	$Rh(CO)Cl(TPP)_2$	303-403	5	toluene	reaction first order in ethylene and rate passed through maxima	Polievka et. al. (1980).
10	Rh/SiO_2				the effect of various metal oxide promoters is studied	Ichikawa et. al. (1982).
11	Rh/SiO_2				the specific activity for EtCHO increased with metal dispersion	Huang et. al. (1992).
12	Rh/C prepared with various precursors				the effect of various reaction parameters on the 3-pentanone formation is studied	Takahashi et. al. (1992).
13	$Rh\text{-}ZrO_2$ modified with Se	453	0.04		effect of pretreatment on activity and selectivity for hydroformylation	Izumi et. al. (1988).
14	Rh/SiO_2 +Zn				role of Zn in the mechanism for the formation of oxygenated product is studied	Shriver (1987)
15	$HRh(CO)(TPP)_3$/ TPP/α Al_2O_3				activity of the catalyst depends on the type of support and catalyst deactivates due to formation of aldol	Hermann et. al. (1987).
16	Rh/SiO_2	513	0.1		C_2 oxygenates, reaction mechanism studied	Balakos et. al. (1993).

Oxygen Ltd., Bombay and Carbon Monoxide (> 99.9% pure) supplied by Matheson, USA were used directly from the cylinders. The syngas with 1:1 ratio of H_2:CO was prepared by mixing H_2 and CO in a cylinder. Water used as the solvent was degassed prior to use.

6.2.1.1 Preparation of $[RhCl(COD)]_2$

$[RhCl(COD)]_2$ was prepared by the method described by Chatt and Venanzi (1957). Accordingly, 1.0 x 10^{-3} kg of rhodium trichloride trihydrate was added into a round bottemed flask which contains 2.0 x 10^{-6}, m^3 COD in ethanol (3.0 x 10^{-5}, m^3). The mixture was refluxed for 3, hrs. Orange crystals were found at the bottom of the flask while refluxing. The solution was cooled and the orange solid was filtered off, washed with ethanol, dried, and recrystallised from acetic acid (yield 60%, m.p. 529 K).

The elemental analysis of the complex showed the following results

	Theoretical (%)	Observed (%)
C	39.5	39
H	5	4.9
Cl	14.4	14.4

The IR spectrum of the above complex showed the following characteristic frequencies: (cm^{-1}) : 1325 (s) , 1301(s), 1227(m), 1210(m), 1172(s), 1153(s), 1076 (w), 993, 961(s), 878(w), 866(s), 831(w), 817(s), 795(m), 771(s).

which agree with the reported values (Chatt and Venanzi 1957).

6.2.1.2 Preparation of TPPTS

TPPTS was prepared as reported in the literature (Jenck and Morel (1987)) by the addition of 0.05 kg of triphenyl phosphine (1.91 x 10^{-4} kmol) into 0.28 kg of 65% oleum (SO_3 content: 2.275 x 10^{-3} kmol) dissolved in 0.02 kg conc. sulfuric acid (98%). The temperature of the mixture was maitaned at 288 K for 76 hrs. The sulphonated mixture was hydrolysed by adding 0.05 kg of degassed water. The sulphonic acid obtained after hydrolysis was neutralised with NaOH (50% w/w). Neutralization was carried out to a point where the solution was slightly acidic. This solution was filtered and the residue comprising of only sodium sulfate. The filtrate was evaporated under reduced pressure and the solid obtained was stored as an aqueous solution.

6.2.1.3 Preparation of water soluble (Rh/TPPTS) catalyst

The water soluble catalyst Rh/TPPTS catalyst was prepared by exchange of COD with TPPTS in $[RhCl(COD)]_2$ complex. A known quantity of $[RhCl(COD)]_2$ was dissolved in toluene and extracted with water containing the dissolved ligand (TPPTS). The complete exchange of the organic phase catalyst can be seen from the color change of the aqueous phase (from colorless to yellow orange). This aqueous phase can then be used as the aqueous phase catalyst.

6.2.2 Apparatus

The hydroformylation experiments were carried out in a batch mode in a microclave of 5.0×10^{-5} m^3 capacity and made of Hastelloy C material (Autoclave Engineers, USA). This reactor was equipped with automatic temperature control facilities for variable agitation speed and withdrawal of liquid samples. The agitator used was a gas-induced type, which is efficient for gas-liquid mass transfer. An outlet valve was provided for taking gas samples as well as releasing the pressure when necessary. A safety rupture disc was also fitted to the reactor. The reactor was designed for a working pressure of 27.56 MPa. In order to maintain a constant pressure in the reactor CO, H_2 and ethylene were supplied (1:1:1 ratio) to the reactor through a constant pressure regulator from a gas reservior (2.5×10^{-5} m^3 capacity at 298 K). Fig 2.1 shows a schematic diagram of the experimental set-up used in this study.

6.2.3 Experimental Procedure for Kinetic Studies

For the purpose of kinetic study, the microclave was charged with a required amount of aqueous phase catalyst (Rh-TPPTS complex) without any additional solvent. The microclave was first flushed with nitrogen and then with CO/H_2. The reactor was heated to a desired temperature under slow stirring. The gaseous mixture of CO and H_2 was first charged to the reactor and then ethylene was charged upto a desired pressure. The reaction was started by switching on the stirrer at a required agitation speed. The progress of the reaction was followed by observation of the pressure drop in the reservior as the function of time. The pressure drop in the reservior vessel was observed with a pressure tranducer-recorder system as the function of time. The experiments were carried out for a fixed duration of 1 hr.

6.2.4 Analytical Procedure

The gas and liquid samples were analysed by Varian (3600) gas chromatography using a TC detector. The conditions for the analysis of liquid and gaseous samples are given in Tables 6.2 and 6.3.

6.3 RESULTS AND DISCUSSION

The aim of this work was to investigate the kinetics of hydroformylation of ethylene using $[Rh(Cl)(COD)]_2$/TPPTS complex catalyst in homogeneous (water) medium. Therefore, it was important to ensure the material balance and the reproducibility of the experiments. For this purpose, several experiments were carried and it was observed that the amount of propionaldeheyde formed and the gaseous reactants consumed were consistance with stoichiometry. During the preliminary experiments it was observed that propionaldehyde was the only reaction product. Hence, it was decided to follow the kinetics by observing the consumption of CO, H_2 and ethylene in a 1:1:1 ratio in a reservoir vessel. The range of reaction conditions used for the kinetic study on hydroformylation of ethylene are given in Table 6.4 and the results are discussed below.

6.3.1 Calculation of Initial Rates

TABLE 6.2

ANALYTICAL CONDITIONS FOR THE LIQUID PHASE ANALYSIS

Column	UCW-982, 2′ × 1/8″ Chromosorb 80-100 mesh
Injection Temparature (K)	373
Thermal Conductivity Detector	
Temperature (K)	423
Oven Temperature (K)	323
Carrier Gas (hydrogen) Flow (m^3/hr)	5.0 x 10^{-7}

TABLE 6.3

ANALYTICAL CONDITIONS FOR THE GAS PHASE ANALYSIS

Column	Poropak Q, 10' × 1/8 " 100-200 mesh
Injection Temparature (K)	373
Thermal Conductivity Detector	
Temperature (K)	423
Oven Temperature (K)	313
Carrier Gas (hydrogen) Flow (m^3/hr)	5.0×10^{-7}

TABLE 6.4

RANGE OF CONDITIONS INVESTIGATED FOR THE KINETIC STUDY

Concentration of Catalyst (kmol m $^{-3}$)	0.5 to 4.0 $\times$ 10 $^{-3}$
Partial pressure of Ethylene (MPa)	0.414 to 2.756
Partial pressure of Hydrogen (MPa)	0.414 to 2.756
Partial pressure of CO (MPa)	0.414 to 2.756
Temperature (K)	333 to 373
Reaction Volume (m^3)	2.0 x 10^{-5}

Initial rates of consumption of CO, H_2 and ethylene in the liquid phase were calculated from the pressure drop in the reservoir vs time. The amount of gaseous reactants consumed were calculated using the following equation

$$n = \frac{[(1-P/P_o)P_o]\ V_G}{3ZRT} \qquad (1)$$

where

n = CO or H_2 or ethylene consumed (kmol)

V_G = volume of the gaseous space in the reactor (m^3)

Z = compressibility factor

R = gas constant (MPa m^3 $kmol^{-1}$ K^{-1})

T = temperature of the gas in the reactor (K)

P = total pressure in the reactor (Mpa)

P_0 = initial pressure in the reactor (MPa)

$$R = \frac{n}{t\ V_L} \qquad (2)$$

The rate of reaction (R) was calculated (kmol/m^3/sec) as where

t = time (sec)

V_L = liquid volume in the reactor (m^3)

6.3.2 Effect of Agitation Speed

In order to check the significance of gas-liquid mass transfer resistance, it is essential to study the effect agitation speed on the rate of hydroformylation. For this a few experiments were carried out at different agitation speeds in the range of 900 to 1500 rpm at 303 to 323 K. It was observed that the rate of the reaction was independent of agitation speed below 303 K but is linearly dependent on the agitation speed beyond 303K.

6.3.3 Effect of Partial Pressure of Carbon Monoxide (Pco)

The effect of partial pressure of CO on hydroformylation of ethylene was studied keeping the partial pressure of H_2 and ethylene constant for temperatures 303 to 323 K in a pressure range of 0.413 to 2.087 MPa. The results are shown in Fig. 6.1. It was observed that the initial rates of the reaction decreases with increase in partial pressure of CO (P_{CO}). It is a general observation in kinetics of hydroformylation that the rate varis inversely proportional to P_{CO} (Deshpande and Chaudhari 1988,1989, Divekar et al.,1993, Divekar 1995, Bhanage 1995). It is also reported that the rate of this reaction is very sensitive to slight changes in the P_{CO} in certain ranges and that the sensitivity is more pronounced with increase in temperature. Evans et al.,1968 and Brown and Wilkinson 1970 proposed a mechanism which explains the rate inhibition (Fig. 6.2).

It can be seen from the Fig 6.2 that the inhibition in the rate with increase in P_{CO} is due to the side reactions leading to the formation of inactive species $RCORh(CO)_2(TPP)_2$ and $RCORh(CO)_3(TPP)$ thereby reducing the availability of active rhodium species ($RCORh(CO)(TPP)_2$) and hence reduces the rate of the reaction. The equilibrium reaction (Step 13) leading to the formation of inactive di- and tri carbonyl rhodium species will be more pronounced at higher concentration of CO causing a sharp decrease in the rate of the reaction as observed in this study.

6.3.4 Effect of Partial Pressure of Hydrogen (P_{H2})

The effect of partial pressure of hydrogen on the rate of the hydroformylation of ethylene was investigated keeping partial pressure of CO and ethylene constant in a pressure range of 0.413 to 2.087 MPa and a catalyst concentration 0.5 x 10^{-3} kmol m^3 in the temperature range of 303 to 323K. The results are shown in Fig. 6.3. It was observed from the study that the rate of the hydroformylation of ethylene was linearly dependent on the partial pressure of hydrogen. It is well known from the literature that the oxidative addition of H_2 into acyl rhodium species is the rate limiting step, thus the rate of the reaction is first order with respect to P_{H2}.

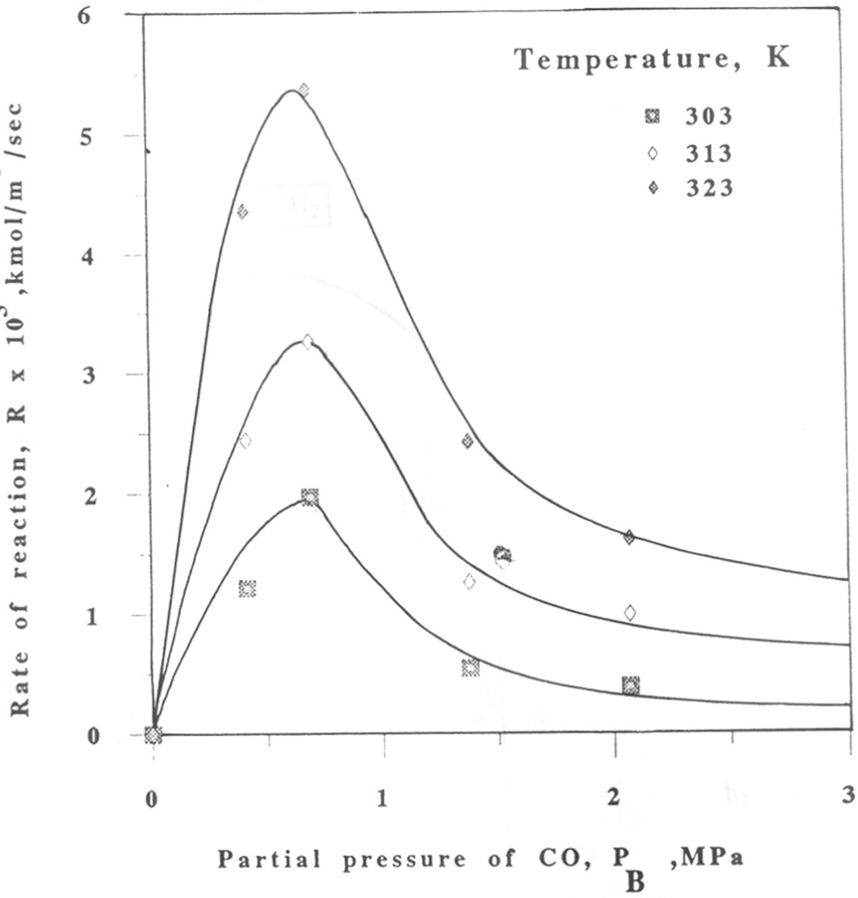


Figure 6.1 Effect of partial pressure of CO in hydroformylation of ethylene

Reaction Conditions

Concentration of the Catalyst : 0.5×10^{-3} kmol/m^3
Partial Pressure of H_2 and ethylene (1:1) : 0.689 MPa
Catalyst : TPPTS ratio : 1:6
Reaction Volume : 25 cc

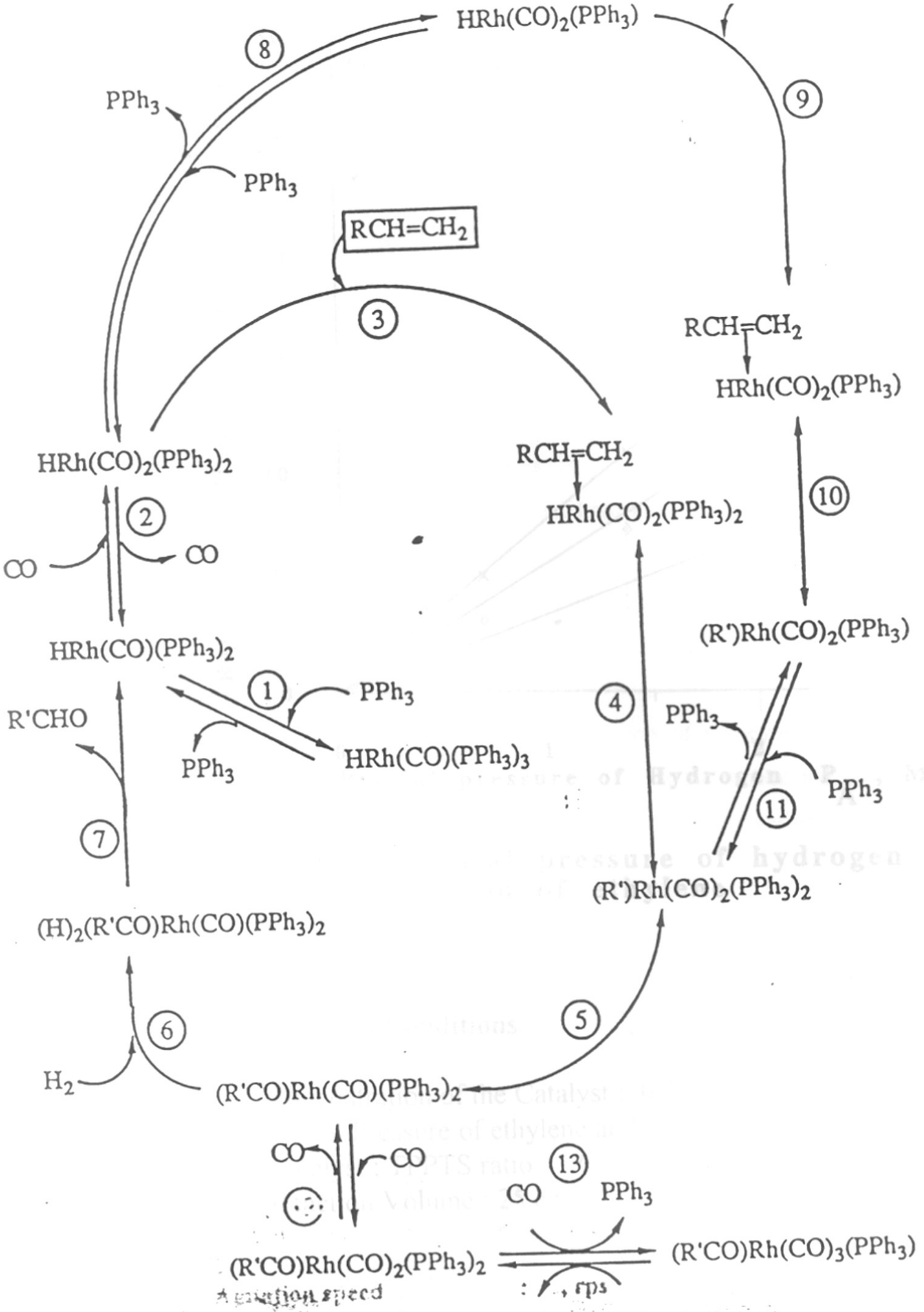


Figure 6.2 A PROPOSED MECHANISM FOR THE HYDROFORMYLATION OF OLEFINS

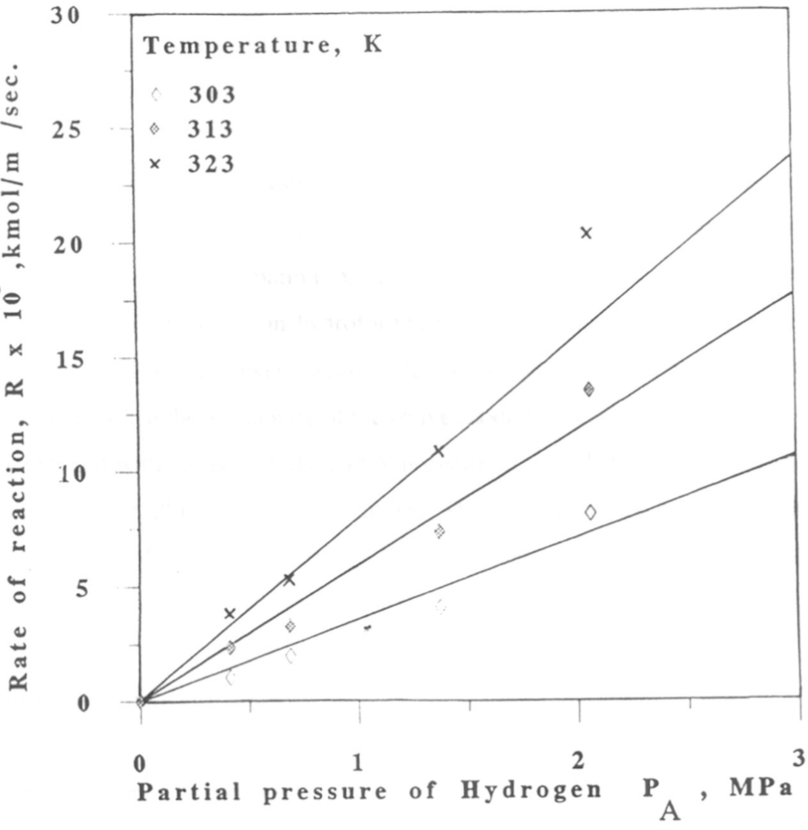


Figure 6.3

Effect of partial pressure of hydrogen in hydroformylation of ethylene

Reaction Conditions

Concentration of the Catalyst : 0.5×10^{-3} kmol/m^3
Partial Pressure of ethylene and CO (1:1) : 0.689 MPa
Catalyst : TPPTS ratio : 1:6
Reaction Volume : 25 cc

6.3.5 Effect of Partial Pressure of Ethylene

The effect of partial pressure of ethylene on the rate of hydroformylation was investigated at a constant partial pressure of CO and H_2 in the range of 0.413 to 2.087 MPa and in the temperature range of 303 to 323K. The results are given in Fig. 6.4. The rate of the reaction was inhibited at higher partial pressures of ethylene. King et al., (1980) reported that at higher concentration of ethylene, the formation of inactive alkyl olefinic complex of type $C_2H_4Rh(CO)_3C_2H_4$ is likely to occur in hydroformylation of ethylene using Rh carbonyl catalyst. Such a species will lead to lower reaction rates. Therefore it is probable that similar species may form and reduce the availability of the active rhodium species, hence the rate of the reaction is reduced with increase in the partial pressure of the ethylene. This substrate inhibition was observed at all the temperature studied. This results are also consistent with the reported literature on hydroformylation of 1-hexene (Deshpande and Chaudhari, 1988, Divekar et al., 1993, Divekar 1995, Bhanage 1995).

6.3.6 Effect of catalyst concentration

Fig. 6.5 shows the the effect of concentration of the catalyst on the rate of hydroformylation of ethylene at a concentration range of 0.5 x 10^{-3} mol/cc and 2 x 10^{-3} mol/cc at 303, 313 and 323 K. It was observed that the rate of the reaction varied with a first order with respect to catalyst concentration.

6.4 Rate model :

In order to develop a suitable rate equation representing the intrinsic kinetics of hydroformylation of ethylene, it is essential to make sure that the rate obtained is in kinetic regime. For this purpose initial rates of hydroformylation of ethylene (consumption of ethylene, CO and H_2 with respect to time) were obtained under different reaction conditions. Initially the rate of the reaction was compared with the maximum rates of mass transfer of the three gases under respective conditions. For this purpose, the factors α_1, α_2 and α_3 were calculated defined as follows.

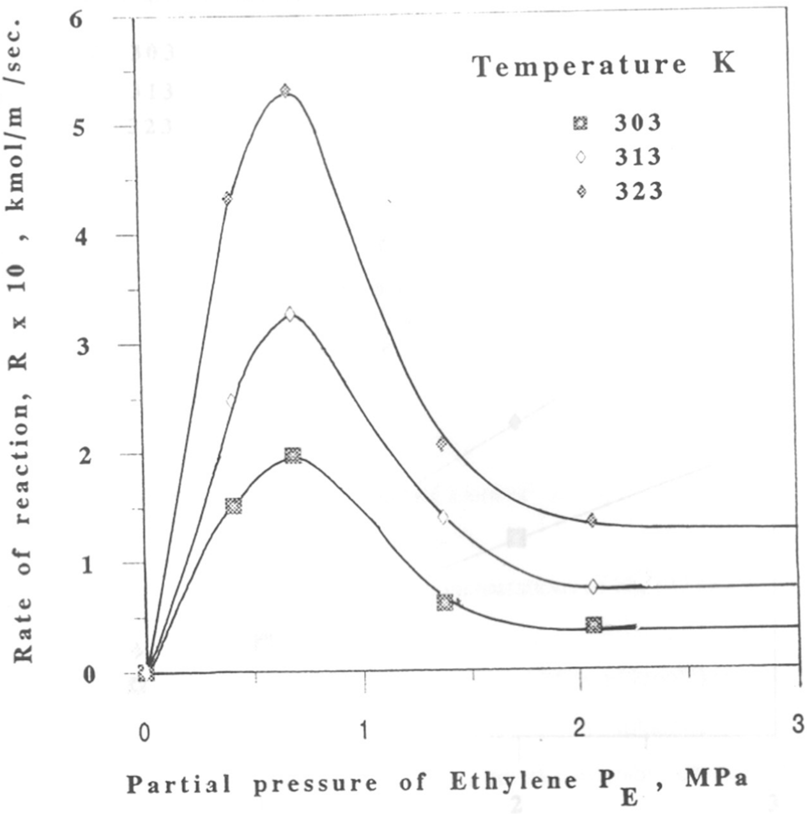


Figure 6.4 Effect of $P_{ethylene}$ on rate of hydroformylation of ethylene

Reaction Conditions

Concentration of the Catalyst : 0.5×10^{-3} kmol/m^3
Partial Pressure of H_2 and CO (1:1) : 0.689 MPa
Catalyst : TPPTS ratio : 1:6
Reaction Volume : 25 cc

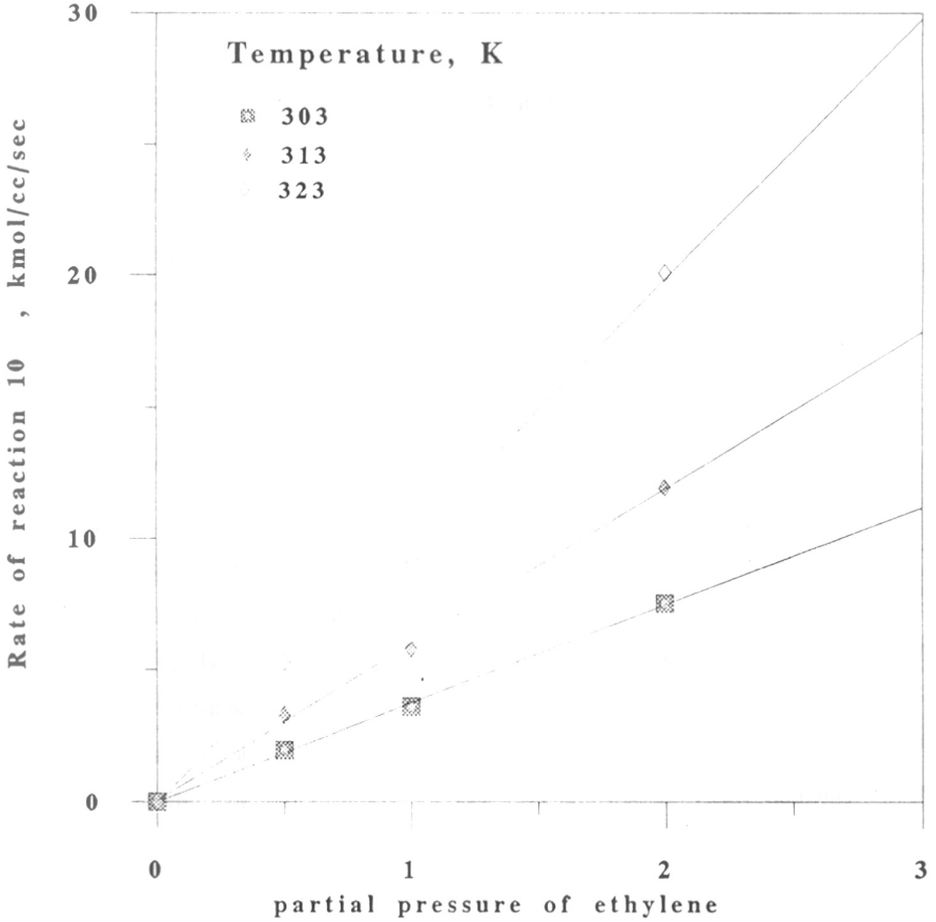


Figure 6.5 Effect of catalyst concentration in hydroformylation of ethylene

Reaction Conditions

Partial Pressure of ethylene, H_2 and CO (1:1:1) : 0.689 MPa
Catalyst : TPPTS ratio : 1:6
Reaction Volume : 25 cc
Temperature : 303 K.

$$\propto_1 = \frac{R}{k_L \, a \, A^*} \tag{3}$$

$$\propto_2 = \frac{R}{k_L \, a \, B^*} \tag{4}$$

$$\propto_3 = \frac{R}{k_L \, a \, E^*} \tag{5}$$

Where

R represents the initial rate of hydroformylation (kmol m^3 sec^{-1})

$k_L a$ is the volumetric mass transfer coefficient (sec^{-1})

$A^* = P_A/H_A$, $B^* = P_B/H_B$ and $E^* = P_E/H_E$ are the concentrations of H_2, CO and ethylene (kmol m^3) respectively at the gas liquid interface.

H_A, H_B and H_E are the solubility of H_2, CO and ethylene (MPa m^3 $kmol^{-1}$) respectively.

For the calculation of α_1, α_2 and α_3 a knowledge of the solubility of the gases involved in the reaction medium is essential. The data for the solubility of H_2, CO and ethylene in water were determined by experimental methods (Table 6. 5) .

Various forms of rate equations were selected based on the trends observed for a variety of conditions. Table 6.6 shows the several rate equations derived from the experimental rate data. For the evaluation of rate parameters k, K_B and K_E (Table 6.7) an optimization program based on Marquardt's method was used. This requires a knowledge of initial guess values under conditions where only one parameter is varied. For example, with P_B/H_B as a variable, at constant P_E/H_E as equation 6. simplifies to

$$R = \frac{k \, A \, B \, E}{(1 + K_B B)^3 \, (1 + K_E E)} \tag{6}$$

TABLE 6.5

SOLUBILITY OF ETHYLENE, H_2 AND CO IN WATER

Sr. No.	Temperature K	Solubility MPa m^3 $kmol^{-1}$		
		Ethylene	H_2	CO
1	303	26.18	159.74	114.81
2	313	39.81	208.33	188.61
3	323	49.75	286.61	275.42

TABLE 6.6

MODELS EXAMINED TO FIT THE DATA ON ETHYLENE HYDROFORMYLATION

Sr. No.	Rate Model	Temperature K	k	K_B	K_E	ϕ_{min}
1	$\frac{k(A^*)^{B^*}E^*}{(1+K_B B^*)^3(1+K_E E^*)^3}$	303	8.47 x 10^3	77.6	11.52	1.89 x 10^{-10}
		313	4.68 x 10^4	1.16 x 10^2	1.162	6.09 x 10^{-10}
		323	5.48 x 10^4	83.9	15.10	1.16 x 10^{-9}
2	$\frac{k(A^*)B^*E^*}{(1+K_B B^*)^2(1+K_E E^*)^2}$	303	2.19 x 10^3	264.7	42.32	3.01 x 10^{-10}
		313	9.08 x 10^3	248.28	71.62	6.82 x 10^{-10}
		323	4.02 x 10^3	231.43	40.82	1.14 x 10^{-9}
3	$\frac{k(A^*)^{1.5}B^*E^*}{(1+K_B B^*)^3(1+K_E E^*)3}$	303	8.97 x 10^3	165.2	27.27	1.897 x 10^{-10}
		313	1.19 x 10^4	176.8	24.39	6.21 x 10^{-10}
		323	3.08 x 10^6	2072.4	29.75	1.14 x 10^{-9}
4	$\frac{k(A^*)^{1.5}B^*E^*}{(1+K_B B^*)^2(1+K_E E^*)^2}$	303	1.24 x 10^4	679.2	441.87	3.72 x 10^{-10}
		313	6.59 x 10^2	331.1	78.15	6.82 x 10^{-10}
		323	4.05 x 10^2	195.0	69.63	1.14 x 10^{-8}
5	$\frac{k(A^*)B^*E^*}{(1+K_B(B^*)^3)(1+K_E E^*)^2}$	303	1.71 x 10^4	142.0	21.14	2.63 x 10^{-10}
		313	2.64 x 10^4	158.8	14.28	2.54 x 10^{-10}
		323	4.85 x 10^4	186.9	9.75	6.95 x 10^{-9}
6	$\frac{k(A^*)B^*E^*}{(1+K_B(B^*)^2)(1+K_E E^*)^3}$	303	9.42 x 10^3	179.9	21.01	2.46 x 10^{-10}
		313	7.37 x 10^3	295.6	7.93	6.28 x 10^{-10}
		323	4.65 x 10^3	541.7	6.74	9.89 x 10^{-10}

ϕ_{min} is minimized sum of the squares of the difference between observed and predicted rates
A^* ($= P_A/H_B$), B^* ($= P_B/H_B$) and E^* ($= P_E/H_E$) are the concentrations in kmol m^{-3} of hydrogen, CO and ethylene respectively.

Table 6.7

RATE PARAMETERS

Temperature K	k (m^3 $kmol^{-1}$ S^{-1})	K_B (m^3 $kmol^{-1}$)	K_E (m^3 $kmol^{-1}$)
303	17162	142.4	121.1
313	26410	158.6	14.3
323	48537	186.9	9.8

$$R = \frac{k' B}{(1 + K_B B)^3} \quad where \quad k' = \frac{k A E}{(1 + K_B E)} \qquad (11)$$

$$\frac{1}{R} = \frac{(1 + K_B B)^3}{k' B} \qquad (7)$$

$$\frac{B}{R} = \frac{(1 + K_B B)^3}{k'} \qquad (8)$$

$$(\frac{B}{R})^{1/3} = \frac{1 + K_B B}{(k')^{1/3}} \qquad (9)$$

$$(\frac{B}{R})^{1/3} = \frac{1}{(k')^{1/3}} + \frac{K_B}{(k')^{1/3}} B \qquad (10)$$

A plot of $(B/R)^{1/3}$ vs B gives slope and intercept of $K_B/(k')^{1/3}$ and $1/(k)^{1/3}$. From this plot, approximate K_B value was obtained. Similarly, K_E can also be calculated and used as the initial guess value. Using these guess values in the optimization routine precise parameter values were determined for different rate models. These are summarised in Table 6.**6** The optimization criterion ϕ_{min} is defined as

$$\phi_{\mathbf{min}} = \Sigma (R_{exp} - R_{theo})^2$$

where R_{exp} is the experimental rate and R_{theo} is the rate predicted from the models which was chosen as an object function to be minimised. The rate models (2), (3) and (4) were discriminated based on the values of ϕ_{min} obtained and the trends observed for the rate and equilibrium parameters at different temperatures.

Rate expression given in model (5) represented the kinetics of hydroformylation of ethylene at different initial conditions unlike model (1) eventhough the values of Φ_{min} are comarative. Thus model (5) was selected to represent the kinetic data satisfactory.

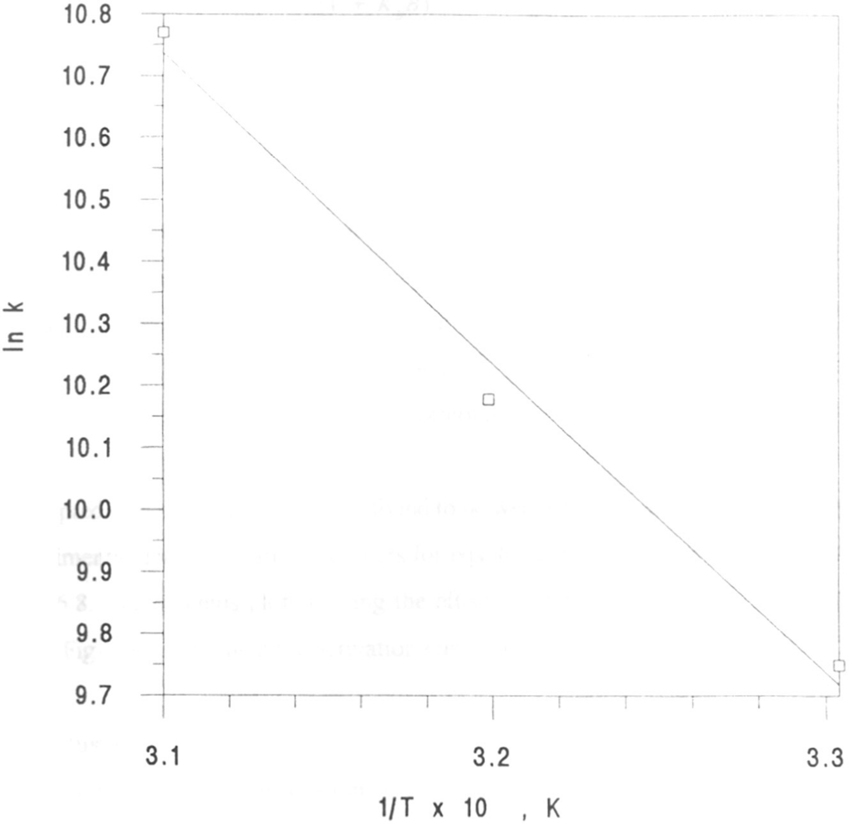


Figure 6.6 Arrhenius plot of ln k vs 1/T

$$R = \frac{k\,A\,B\,E}{(1 + K_B B)^3\,(1 + K_E E)^2} \qquad (12)$$

Where

R = rate of the reaction (kmol m^{-3} sec^{-1})
k = reaction rate constant
A = concentration of H_2 (kmol,m^{-3})
B = concentration of CO (kmol,m^{-3})
E = concentration of ethylene (kmol,m^{-3})

The rates predicted using eqs. 6-12 were found to be well within the error limit and agree with the experimental data. The rate parameters for eqs. 6-12 for various temperatures are given in Table 6.8. The arhenius plot showing the effect of temperature on the rate constants is shown in Fig 6.6 from which the activation energy was calculated as 9.8 Kcal/mol.

6.5 Conclusion

The kinetics of hydroformylation of ethylene using $HRh(CO)(TPPTS)_3$ catalyst in a homogeneous medium has been studied in the temperature range of 303 to 323 K. The reaction was first order with respect to P_{H2} and catalyst concentration. A negative order dependence was observed with respect to $P_{Ethylene}$ and P_{CO}. Based on these data, the following rate equation has been proposed to represent the kinetics and the activation energy of hydroformylation of ethylene (9.8 Kcal/mol).

$$R = \frac{k\,A\,B\,E}{(1 + K_B B)^3\,(1 + K_E E)^2} \qquad (13)$$

REFERENCES

Anthony W. and Thigpen H. H., Ger Offen 2145427, (1972).

Balakos M. W., Chuang S. S. S. Srinivas G., J. Catal. **140**(1), 281, (1993).

Balakos M. W., Pien S. I. Chuang S. S. C., Stud. Surf. Sci. Catal. **68**, 549, (1991).

Bhanage B.M. Ph.D Thesis, University of Pune (1995).

Brit. Patent 614 010, (1948). to E. I. du Pont Nemours and Co.

Chatt J. , Venanzi L.M. , J. Chem . Soc. , 4735 (1957).

Deshpande R. M. and Chaudhari R. V., Ind. Eng. Chem. Res. **27**, 1996, (1988).

Deshpande R. M.and Chaudhari R. V., J. Catal. **115**, 326, (1989).

Divekar S.S., Deshpande R.M. and Chaudhari R.V., Cat. Lett., **21,** 191 (1993).

Divekar S.S., Ph.D. Thesis, University of Poona. (1995).

Eidus Y. T. and Lapidus A. L., Neftekhimiya **57**(1), 51, (1967).

Evans, D., Yagupsky, G., and Wilkinson, G., J. Chem. Soc. A, 2660, (1968a).

Evans, D., Osborne, J., and Wilkinson, G., J. Chem. Soc. A, 3133, (1968b).

Evans J. Jingxing G. Leach H. and Street A. C. J. Organomet. Chem. **372** (1), 61, (1989).

Gresham W. F. and Brooks R. E., US 2,497,303, (1950).

Hagemeyer H.J. Jr. and Hull D. C., US 2694734, (1954).

Hans H. and Werner H., Ger 975502, (1961).

Huang L., Guo W. G., Liu A. M., Li D. M. and Xu Y. D., Chin Chem. Lett. **3**(5), 401, (1992).

Ichikawa M. and Kido Y., Japan Kokai Tokkyo Koho 7941293, (1979).

Ichikawa M., Shikakura K. and Kawai M., China-Jpn-US Symp. Heter. Catal. Relat. Energy Probl. AO8J (1982).

Iwamoto E., Saito T. and Arai S., Japan Kokai 77 105 590, (1977).

Izumi Y., Asakura K. and Iwasawa Y., J. Chem. Soc. Chem. Commun. **19**, 1327, (1988).

Jenck J.F. and Morel D., US Patent US 4,688,824 (1987).

Jiro T., Nobuo I. and Masanobu M., Bull. Chem. Soc. Japan **38**(12), 2213, (1965).

King R. B., King A. D. Jr., Iqbal M. Z., J. Am. Chem. Soc. **101**(17), 4893, (1979).

King R. B., King A. D. Jr., Iqbal M. Z. and Tanaka K., Ann. N.Y. Acad. Sci **333**, 74, (1980).

Kozo K., Hajime I., Reiji A. and Tozo A., Nehryo Kyokaishi **41**(10), 860, (1962).

Kummer R. and Platz R., Ger Offen 2 354 217, (1975).

Mitsuo Y. and Takeshi O., Japn 69,02683, (1969).

Neth. Appl. 6 412 249, (1965) to Lonza Ltd.

Polievka M. Uhlar L. and Macho V., Petrochemia **20**(2), 33, (1980).

Shriver D.F., Report DOE/ER 13/04-2, (1987).

Takahashi N., Takeyama T., Yanagibashi T., Takada Y., J. Catal. **136** (2), 531, (1992).

Takeuchi K., Hanaoka T., Matsuzaki T., Sugi Y., Asaga H., Abe Y. and Misono T., Nippon Kagaku Kaishi **7**, 901, (1993).

Takeuchi K., Hanaoka T., Matsuzaki T.,Reinikainen M. and Sugi Y., Catal Lett. **8**(2-4), 253, (1991).

Tjan P. W. H. L. and Scholten J. J. F., Proc. Int. Cogr. Catal. 6th, 1976 pub. **1**, 488, (1977).

Vannice M. A., Hyun S. H., Kalpakci B. and Liauch W. C., J. Catal. **56** 358 (1979).

Weissermel K. and Arpe H.-J., "Industrial Organic Chemistry", Verlag Chemie Weinheim New York, pg. 118, (1978).