STUDIES IN CARBONYLATION REACTION BY HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

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BY

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FORM A

Certified that the work incorporated in this thesis entitled "STUDIES IN CARBONYLATION REACTIONS BY HOMOGENEOUS AND HETEROGENEOUS CATALYSIS ", submitted by Mr. Venkatesh Prasad K. was carried out by him under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

(Dr. R. V. Chaudhari)

[Supervisor]

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Venkatesh Prasad K

DEDICATED TO

MY

MOTHER AND FATHER

SUMMARY AND CONCLUSIONS

Carbon monoxide was found to be attractive as an alternative feedstock, for the production of speciality and bulk chemicals, after the oil crisis of early 1970s. It is abundantly available from resources like natural gas, coal and biomass. The carbonylation reactions are known to be catalyzed by transition metals, in both the homogeneous and heterogeneous phases. Some examples of the commercial processes using carbonylation technology are : the synthesis of liquid hydrocarbons from syn gas, hydroformylation of olefins to alcohols and aldehydes, carbonylation of methanol to acetic acid, carbonylation of methyl acetate to acetic anhydride, carbonylation of methanol to dimethyl carbonate and the synthesis of ethylene glycol from methanol. The developments in carbonylation chemistry, catalysts used, industrial applications and future prospects have been well documented in several monographs and reviews [Sheldon (1983), Keim (1988), Colquhoun et. al. (1991)].

Considering the industrial importance of carbonylation reactions, there is a need for fundamental research to understand the role of promoters, solvents and reactions conditions. The kinetics and mechanism of many carbonylation reactions has also not been studied in detail. Therefore, further research on carbonylation reactions would be most useful in the development of new catalytic systems for important reactions.

The present work was undertaken with the objective of understanding the fun-

damental aspects of transition metal catalyzed carbonylation reactions in both homogeneous and heterogeneous phases. The study was undertaken on the oxidative carbonylation of aniline and the carbonylation of allyl chloride. Catalytic oxidative carbonylation of aniline to ethyl phenyl carbamate is an industrially important reaction (Fukuoka et. al. (1984)). It provides an alternative route to the hazardous and corrosive phosgenation route for the manufacture of methylene diphenyl diisocyanate (MDI). A major advantage of the oxidative carbonylation route is that it gives very high yields with high degree of product purity. This methodology can be extended to oxidative carbonylation of various other amines to form disubstituted ureas and carbamate derivatives, which find extensive applications as insecticides, herbicides, pesticides and monomers for polymerization. Most of the previous work on this reaction is based on palladium catalysts. Rhodium has also been reported to be active, though no detailed studies have been reported. Therefore, the present work was focused on Rh catalyzed oxidative carbonylation of aniline.

The carbonylation of allyl chloride to vinyl acetic acid is a synthetically important reaction. Vinyl acetic acid and its isomer crotonic acid are used in the synthesis of fungicides, polymers and insecticides. An important aspect of the catalytic carbonylation of allylic compounds is that products with high regio and steroselectivity can be obtained which are important in the synthesis of steroids, alkaloids and drugs. The carbonylation of allyl chloride in a biphasic medium is an interesting case of multiphase catalytic reaction, which involves three or four phases. Only a few reports, mainly addressing the synthesis aspects of this reaction, are published. Therefore, the aim of this work was to investigate the role of promoters, solvents and kinetics of Pd catalyzed carbonylation of allyl chloride in a biphasic medium.

In the present thesis, the following specific problems were investigated.

1. Oxidative carbonylation of aniline to ethyl phenyl carbamate using supported rhodium catalysts.
2. Ethanolysis of diphenyl urea to ethyl phenyl carbamate.
3. Carbonylation of allyl chloride to vinyl acetic acid using palladium complex catalysts in a biphasic medium.

The thesis is presented in four chapters, a brief summary of which is given below.

Chapter 1 presents a detailed literature survey on the oxidative carbonylation of aniline, ethanolysis of diphenyl urea to ethyl phenyl carbamate and the carbonylation of allyl chloride.

For the oxidative carbonylation of aniline a variety of catalysts consisting of Rh, Pd, Ru, Co, Cu, Ni, Pt in homogeneous and heterogeneous forms have been proposed. The effect of catalyst precursors, solvents, promoters, co-catalysts, reaction conditions, as well as the kinetics and mechanism for the reaction are reviewed. Supported rhodium catalysts are also reported to give similar activity and selectivity to that of palladium, however, no detailed studies have been reported. Therefore, the present work was undertaken with the aim of investigating the effect of promoters, solvents and reaction conditions on the activity and selectivity of the supported rhodium catalysts.

The oxidative carbonylation of aniline results in the formation of diphenyl urea, which subsequently reacts with ethanol to give ethyl phenyl carbamate and aniline. There are very few published reports (Giannoccaro (1988), Kalkote and Ayyangar (1991)) on the ethanolysis of diphenyl urea. Various homogeneous catalysts like sulfuric acid (conc) and palladium complexes have been reported to give good conversions and selectivities for ethyl phenyl carbamate, but no kinetic studies have been reported on this reaction. For a better understanding of the oxidative carbonylation of aniline, the study of ethanolysis reaction is also necessary and hence the effect of catalysts, solvents and the kinetics of the reaction were investigated.

A review of literature on carbonylation of allyl chloride has been presented which indicated that a variety of catalysts consisting of Pd, Ni, Co or Cu complexes have been suggested, but Pd and Ni catalysts were found to be particularly effective [Tsuji et. al. (1963), Medema et. al. (1969), Chiusoli and Cassar (1967)]. The conversion of allyl chloride to unsaturated carboxylic acid, acid chloride, or esters is in the range of 70-90 %, however, the pressure of carbon monoxide required is high ($\sim$ 100 atms.). Joò and Alper (1985) have reported the phase transfer nickel catalyzed carbonylation of allyl chloride, at ambient reaction conditions (298 K and 1 atm of CO), to 14 % vinyl acetic and 86 % crotonic acids. Similarly, when carbonylation of allyl chloride is carried out in a two phase system using Pd catalyst with aqueous NaOH solution, the reaction occurs at ambient conditions (Kiji et. al. (1988)). This is a significant improvement in the activity of Pd catalysts. However, no detailed reports on the role of solvents, co-catalysts, promoters and the nature of two phase system have been published. Further work on these aspects is most desirable in view of potential importance of this class of reactions in the synthesis of carboxylic acid derivatives.

Chapter 2 presents a detailed study on the oxidative carbonylation of aniline to ethyl phenyl carbamate over supported rhodium catalysts. The stoichiometric reaction is shown below:

$$C_6H_5NH_2 + CO + \frac{1}{2} O_2 + C_2H_5OH \xrightarrow{Rh} C_6H_5NHCOOC_2H_5 + H_2O \qquad (i)$$

The effect of catalyst precursors, supports, promoters, solvents, catalyst loading, aniline concentration, partial pressures of carbon monoxide and oxygen and pretreatment of the catalyst with reactants on the activity and selectivity of the supported rhodium catalyst has been studied. The catalyst prepared with activated carbon as a support, rhodium trichloride as a catalyst precursor and lithium iodide as a promoter was found to give a conversion of aniline of around 96 % and a selectivity to ethyl phenyl carbamate around 97 %. The formation of carbon dioxide, as a side product, has been reported quantitatively and was found to account for more than 55 % of CO:O_2 consumed at high conversions of aniline. Solvents with high polarity like DMF and acetonitrile were found to decrease the formation of ethyl phenyl carbamate (~ 30 %) and high yield of of diphenyl urea (~ 70 %). The conversion of aniline and selectivity to ethyl phenyl carbamate was high in ethanol and ethyl acetate. The activity of Rh/C catalyst was found to decrease with decrease in the Rh metal content, while the formation of carbon dioxide increased. A marginal increase in the initial activity of catalyst was observed when the catalyst was pretreated with hydrogen. Addition of $SnCl_2$, $MnCl_2$ and $CoCl_2$ as co-catalysts was found to marginally increase the activity of the catalyst. The 5 % Rh/C catalyst, could be reused more than seven times without significant loss of activity. The characterization of 5 % Rh/C catalyst before and after the reaction was done by ESCA, TEM and XRD techniques. A change in the morphology of the surface of the catalyst was observed after the reaction. The Rh crystallite size was found to decrease and redispersion over the support was observed. The oxidation state of Rh metal was found to be zero in both the samples.

The intrinsic kinetics of the reaction at 443, K has been reported. The initial rate of the reaction was found to be first order with respect to aniline concentration, partial pressure of carbon monoxide and the catalyst loading. The initial rate was first order with partial pressure of oxygen at lower pressures and independent at higher pressures. The following rate equation has been proposed.

$$R_A = \frac{k\ A\ B\ C\ D}{(1 + K_C\ C)} \qquad \text{(ii)}$$

Where,

R_A is the initial rate of reaction, kmol/m^3/s; A, B and C, the liquid phase concentrations of aniline, carbon monoxide and oxygen respectively, kmol/m^3; k the rate constant, (m^9/kg/kmol^2/s); K_C, the absorption constant for oxygen, m^3/kmol; and D, the concentration of the catalyst, kg/m^3. The rate parameters k, K_C were evaluated and the above rate equation was found to represent the experimental rates within ± 6 % error.

In Chapter 3, the effect of catalysts, solvents, concentration of diphenyl urea, water, ethanol, aniline, ethyl phenyl carbamate, on the ethanolysis of diphenyl urea to ethyl phenyl carbamate is discussed. The reaction proceeds as follows:

$$C_6H_5NHCONHC_6H_5 + C_2H_5OH \longrightarrow C_6H_5NHCOOC_2H_5 + C_6H_5NH_2 \qquad \text{(iii)}$$

The conversion of diphenyl urea and selectivity to ethyl phenyl carbamate was found to be independent ($\sim$ 98 % and 96 % respectively) of the catalyst used (Pd/C, Rh/C, Pd/C-LiI, Rh/C-LiI, $CoCl_2$, $SnCl_2$, $MnCl_2$). Addition of water was found to increase the conversion of diphenyl urea, however, the selectivity to ethyl phenyl carbamate drops significantly due to the formation of aniline as a side product.

The conversion of diphenyl urea decreased (from 96 % to 30 %) with increase in the concentration of aniline and diphenyl urea, however, with increase in ethanol concentration, the conversion of diphenyl urea increased (from 96 % to 100 %).

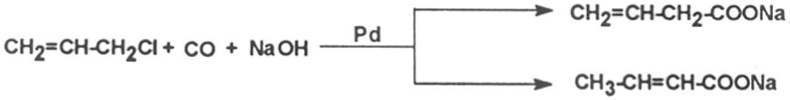
The kinetics of the reaction was studied in a temperature range of 413-433 K. The effect of diphenyl urea, ethanol and aniline concentrations on the initial rate of the reaction was investigated. The initial rate behavior showed linear dependence at lower concentrations of diphenyl urea and ethanol and but was independent at higher concentrations. The rate decreased linearly with increase in the concentration of aniline. Several kinetic models were examined and the following rate equation was found to best fit the observed rates.

$$R_A = \frac{k\ A\ B}{(1 + K_A\ A)\ (1 + K_B\ B)\ (1 + K_C\ C^{2.4})} \qquad \text{(iv)}$$

Where,

R_A = Rate of reaction, kmol/m^3/s; A = Concentration of diphenyl urea, kmol/m^3; B = Concentration of ethanol, kmol/m^3; C = Concentration of aniline, kmol/m^3; k = rate constant of the reaction, m^3/kmol/s; K_A = rate parameter dependent on A, m^3/kmol K_B = rate parameter dependent on B, m^3/kmol; K_C = rate parameter dependent on C, (m^3/kmol)$^{2.4}$. The rate parameters k, K_A, K_B, K_C were evaluated and the energy of activation was calculated as 26.9, kcal/mol.

In Chapter 4, the results on carbonylation of allyl chloride with palladium catalysts in a biphasic medium is presented. The main reaction is shown below and the



$$CH_2{=}CH{-}CH_2Cl + CO + NaOH \xrightarrow{Pd} \begin{cases} CH_2{=}CH{-}CH_2{-}COONa \\ CH_3{-}CH{=}CH{-}COONa \end{cases} \qquad (v)$$

major products are sodium salt of vinyl acetic acid and crotonic acid. This an unique example of a gas-liquid-liquid-solid reaction. The effect of catalyst precursors, ligands, ligand concentration, solvents, organic to aqueous liquid phase hold-up ratio, concentrations of allyl chloride, catalyst and sodium hydroxide, partial pressure of carbon monoxide and temperature on the activity and selectivity of palladium catalysts has been discussed.

It was observed that the reaction is feasible at mild operating conditions (308, K and 2 MPa partial pressure of carbon monoxide) only in a biphasic system comprising of organic phase (water immiscible, eg. toluene) and aqueous phase, with sodium hydroxide. All the palladium catalyst precursors screened were found to be active for the reaction. An interesting observation was that all the palladium complexes decomposed to palladium metal and were found to be present at the interface of the two immiscible liquids. The activity of the catalyst was independent ($\sim 2.7 \times 10^{-4}$ kmol/kg/s) of the different catalyst precursor used. Addition of triphenyl phosphine was found to enhance the activity (from 2.17 to 2.66×10^{-4}

kmol/kg/s) of the Pd metal catalyst upto a molar ratio of 1:1, but a significant decrease in the activity was observed with further increase (from 2.66 to 0.69 × 10^{-4} kmol/kg/s) in the concentration of triphenyl phosphine. The increase in the concentration of sodium hydroxide was found to increase the activity of the catalyst, however, the selectivity to vinyl acetic acid decreased from 88.4 % to 35.4 % and the major product was crotonic acid.

Kinetics of carbonylation of allyl chloride was also studied in a temperature range of 298-318 K. The effect of allyl chloride, catalyst, sodium hydroxide concentrations and partial pressure of carbon monoxide on the rate of carbonylation was studied. The rate was found to increase linearly with increase in partial pressure of carbon monoxide. A maximum in the rate was observed with increase in the concentration of allyl chloride. The rate increased linearly with sodium hydroxide and catalyst concentrations initially but was independent at higher concentrations. Various rate equations were examined and the following rate equation was found to best fit the experimental data.

$$R_A = \frac{k\ A\ B\ C\ D}{(1 + K_A\ A)^{3.2}\ (1 + K_B\ B)\ (1 + K_D\ D)} \qquad \text{(vi)}$$

Where,

A = Concentration of allyl chloride, kmol/m^3; B = Concentration of sodium hydroxide, kmol/m^3; C = Partial pressure of carbon monoxide, MPa; D = Concentra-

tion of catalyst, kg/m^3; k = rate constant of the reaction, m^6/kmol/kg/MPa/s; K_A = rate parameter dependent on A, m^3/kmol; K_B = rate parameter dependent on B, m^3/kmol; K_D = rate parameter dependent on D, m^3/kg.

The rate parameters k, K_A, K_B, K_D have been evaluated and the energy of activation was calculated to be 23.3 kcal/mol. A reaction mechanism based on the observed results has been discussed.

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CHAPTER 1

GENERAL INTRODUCTION AND LITERATURE

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, fertilizers, agrochemicals, pharmaceuticals and fine chemicals [Parshall and Nugent (1988a,b,c), Satterfield (1981)]. The type of catalysts used in industries are generally classified as homogeneous or heterogeneous, depending on the form in which they are used. Heterogeneous catalysis using solid catalysts has been the basis of a large number of chemical processes (Satterfield (1980)), however, homogeneous catalysts used in the liquid phase have also important applications in industry [Nakamura and Tsutsui (1980), Parshall (1980)].

One of the important developments in the field of catalysis has been the use of carbon monoxide and synthesis gas as a chemical feedstock. This subject has become particularly important after the oil crisis in early 1970s, when a need for alternative sources of raw materials for the production of industrial chemicals was realized (Sheldon (1983)).

Carbon monoxide can be obtained at a lower cost from resources like natural gas, biomass and coal which are easily available (Cornils (1987)). Some of the important commercial processes based on carbon monoxide or synthesis gas as raw materials are the synthesis of methanol and liquid hydrocarbons from syngas, hydroformylation of olefins (OXO-synthesis), carbonylation of methanol to acetic acid and the carbonylation of methyl acetate to acetic anhydride (Wender (1987)).

A wide range of carboxylic acids, hydroxy acids, acid anhydrides, lactones, ketones, aldehydes can be obtained via carbonylation [Falbe (1970), Colquhoun et. al. (1991)]. A list of industrially important reactions based on carbon monoxide as one of the raw materials is summarized in Table 1.1. These processes are carried out in the presense of homogeneous or heterogeneous catalysts. The carbonylation chemistry has led to new routes and innovative processes which have potential applications in industry (King et. al. (1981)). These processes have significant advantages with respect to the overall economics as well as environmental problems [Waller (1985), Keim (1989)].

An important development in this regard has been the oxidative carbonylation chemistry (Chiusoli (1980)). The oxidative carbonylation of organic substances such as alcohols, olefins and amines lead to alternative routes for several industrial chemicals. The carbonylation of unsaturated substrates is a synthetically important reaction for the synthesis of natural products and pharmaceuticals. The aim of this thesis was to investigate novel carbonylation reactions which provide alternative routes for important chemicals. The problems chosen for the present work are:

Oxidative carbonylation of aniline using supported rhodium catalysts.

Carbonylation of allyl chloride using palladium catalysts in a biphasic medium.

The oxidative carbonylation of aniline is industrially important in the develop-

Table 1.1

CATALYTIC PROCESSES INVOLVING CARBON MONOXIDE

Sr.No	Process	Catalyst	Industry	Reference
1	Syngas to methanol	Het. $CuO, ZnO, Al_2O_3, Cr_2O_2$	Lurgi	Kung, (1980)
2	Syngas to ethylene glycol	$PdCl_2$-$CuCl_2$	Union Carbide	Chem. Eng. News, (1983)
3	Syngas to liquid hydrocarbons	Fe/Al_2O_3	SASOL	Sheldon, (1983)
4	Syngas and methanol to acetic acid	Rh	Monsanto	Roth, (1971)
5	Methyl acetate to acetic anhydride	Rh complexes	Tennesse Eastman Co.	Chem. Eng. News, (1980)
6	Methyl acetate to vinyl acetate	Rh complexes	Halcon	Ehrler, (1976)
7	Propylene to n-butraldehyde	Rh complexes	Rhone-Poulenc, Ruhrchemie, Union carbide	Jenck, (1984) Cornills, (1980)
8	Butadiene to adipic acid	Co complexes	BASF	Waller, (1985)
9	Methanol to diethyl oxalate	Pd-Cu complexes	Ube industries/ Union carbide	Aquilo, (1983)
10	Methanol to dimethyl carbonate	Pd-Cu complexes	Enichimia	Chem. Eng., (1983, 1988)
11	Dinitrotoluene to toluene diisocyanate	$PdCl_2$, Selenium	ARCO, Mitsui-Toatsu	Zajacek, (1974), Tsumura, (1977)
12	Ethylene to propionic acid	Nickel	BASF	Weissermel (1993)
13	Nitrobenzene to MDI	Ruthenium complex	Catalytica Associates	Chem. Eng., (1987)
14	Syngas to Acetic anhydride	Rh or Ni, I^-	Eastman Kodak	Chem. Eng. Prog., (1984)

ment of a non phosgene process for methylene diphenyl diisocyanate (MDI) (Fukuoka et. al. (1984)c), while the carbonylation of allyl chloride leads to vinyl acetic acid and crotonic acid, which are useful as intermediates in the synthesis of fungicides, polymers, insecticides and synthetic resins [Weisshaar and Kuwana (1984), Kao and Kuwana (1984), Akihisa et. al. (1987), Wegner et. al. (1989), Shirota et. al. (1990)].

Thus the problems chosen here are industrially important, at the same time, the work presented in this thesis on catalysts and kinetics provides basic knowledge on these novel carbonylation reactions. The relevant literature on this subject is summarized in the following sections.

1.1.1 Oxidative carbonylation reactions

The oxidative carbonylation reactions are important in the synthesis of several industrial chemicals like organic carbonates, oxalates, unsaturated and saturated carboxylic acids, substituted ureas and carbamic acid derivatives (Golodov et. al. (1979)). This route provides an alternative route to the processes based on phosgene and hydrocyanic acid. Some important examples of oxidative carbonylation reactions are:

- Oxidative carbonylation of alcohols.

Chemical products like organic carbonates, oxalates, glycols can be obtained via oxidative carbonylation of alcohols [Rivetti and Romano (1979), Romano et. al. (1980)]. The main reactions involved are :

$$2\ \mathrm{ROH} + \mathrm{CO} + \tfrac{1}{2}\,\mathrm{O_2} \longrightarrow \mathrm{ROCOOR} + \mathrm{H_2O} \qquad (1.1)$$

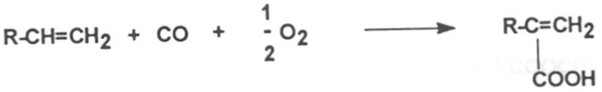
$$2\ \mathrm{ROH} + 2\ \mathrm{CO} + \tfrac{1}{2}\,\mathrm{O_2} \longrightarrow \mathrm{ROCOCOOR} + \mathrm{H_2O} \qquad (1.2)$$

The synthesis of dimethyl carbonate from methanol by catalytic oxidative carbonylation using a homogeneous copper catalyst has been commercialized (Chem. Eng. 1983, 1988). A plant which has a capacity of 3,000 mt/year is proposed to be expanded to 8,000 mt/year. This route is less hazardous and eliminates the corrosion problems associated with the conventional phosgenation route (Buysch et. al. (1979)). Another important example is the synthesis of ethylene glycol from methanol (Nakamura (1990)) using rhodium complex catalysts.

- Oxidative carbonylation of olefins

The synthesis of unsaturated and saturated carboxylic acids can be carried out using the oxidative carbonylation of olefins (Falbe (1970)). The following reactions occur during the oxidative carbonylation of olefins:

$$R\text{-}CH{=}CH_2 + CO + \tfrac{1}{2}\,O_2 \longrightarrow RCH_2\text{-}CH_2\text{-}COOH \qquad (1.3)$$



$$R\text{-}CH{=}CH_2 + CO + \frac{1}{2}O_2 \longrightarrow R\text{-}\underset{\displaystyle COOH}{\underset{|}{C}}{=}CH_2 \qquad (1.4)$$

Oxidative carbonylation of propylene to methyl methacrylate (MMA) can be achieved in single step using homogeneous palladium catalysts [Falbe (1970), Porcelli and Juran (1986), Ganzler et. al. (1977)]. This route appears to be highly promising for future considering the multistep processes involved in the MMA production (Nemec and Kirch (1981)). The oxidative carbonylation of butadiene to adipic and sebacic acids is another industrially important oxidative carbonylation reaction (Kesling (1987)).

- Oxidative carbonylation of amines.

The oxidative carbonylation of amines leads to disubstituted ureas and carbamic acid derivatives. The following reactions represent the oxidative carbonylation of amines:

$$2\,RNH_2 + CO + \tfrac{1}{2}\,O_2 \longrightarrow RNHCONHR + H_2O \qquad (1.5)$$

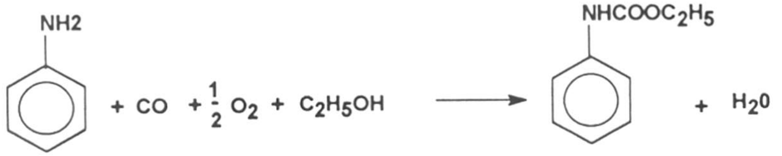
$$RNH_2 + CO + \tfrac{1}{2}\,O_2 + R'OH \longrightarrow RNHCOOR' + H_2O \qquad (1.6)$$

Both aliphatic and aromatic amines may be carbonylated. The oxycarbonylation of methyl amine to N-methyl, methyl carbamate is one of the key steps in the non MIC, non phosgene route for the synthesis of Carbaryl [Chaudhari et. al. (1991), Kelkar et. al. (1992)]. N-methyl, methyl carbamate is further reacted with α-napthol to give carbaryl (Kulkarni et. al. (1991)). The various reactions involved in the synthesis of Carbaryl are given below:

$$CH_3NH_2 + CH_3OH + CO + \frac{1}{2}O_2 \longrightarrow CH_3NHCOOCH_3 + H_20 \qquad (1.7)$$

(1.8)

The oxidative carbonylation of aniline to ethyl phenyl carbamate is the first step in a new process for MDI (Fukuoka et. al. (1984c)). Ethyl phenyl carbamate is further condensed with formaldehyde and subsequent dehydration leads to MDI. A schematic flow sheet of the process is shown in Fig. 1.1. The stoichiometric reactions for MDI synthesis are given below :



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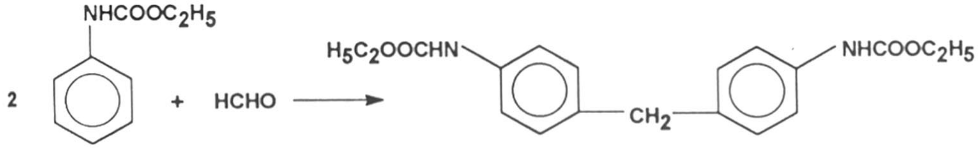

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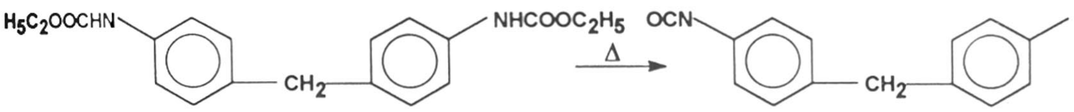
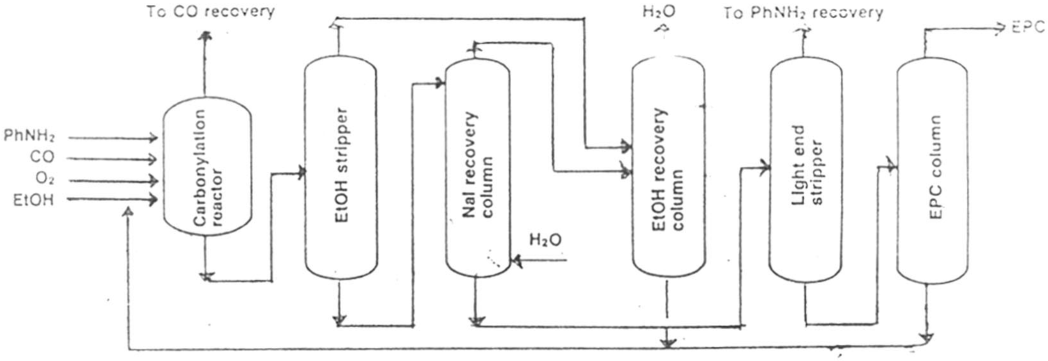
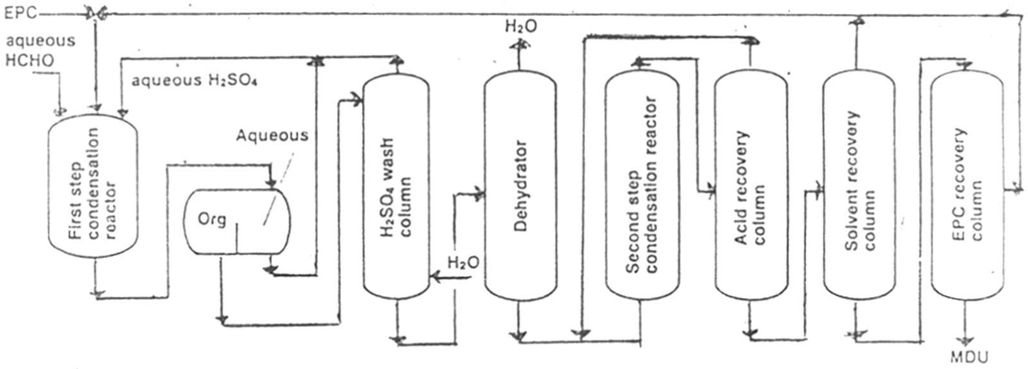


(1.11)

Carbonylation



Condensation



Decomposition

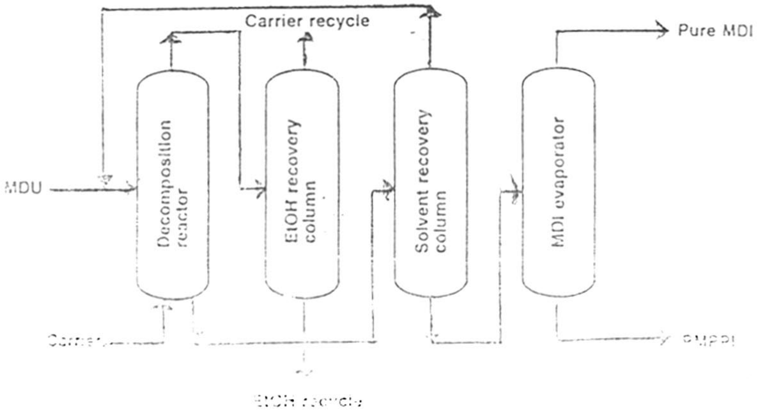


FIGURE 1.1 FLOW DIAGRAM OF NEW MDI PROCESS (Fukuoka (1984)c)

1.1.2 Carbonylation of allylic substrates

The carbonylation of allylic substrates finds applications in a variety of synthetic reactions (Tsuji (1982, 1985)). Some of the important uses of these reactions are in the synthesis of steroids, alkaloids and vitamins (Trost and Verhoeven, (1982)), unsaturated aldehydes (Baillargeon and Stille (1986)), bi-allylic ketone, egomaketone, (Sheffy et. al. (1984), Merrifield et. al. (1984)), unsaturated cyclic ketones (Larock et. al. (1986), Amari et. al. (1985)), unsaturated acids (Kiji et. al. (1988), Joó and Alper (1985)), unsaturated esters (Milstein (1982), Soderberg et. al. (1988)), unsaturated amides (Murahashi et. al. (1988)), α-methylene-γ lactone (Martin and Stile (1982)), lactones (Alper and Leonard (1985)) and pyrrolidinones (Knifton (1980), Falbe and Korte (1965)).

The catalysts for the carbonylation reactions usually consist of transition metal complexes. Of these, palladium and nickel catalyzed reactions are well known [Jolly (1982), Trost and Verhoeven (1982)]. The active catalytic species for these reactions are believed to be the π allyl metal complexes (Trost and Verhoeven (1982)). Palladium π-allyl complexes are easy to prepare and are very labile. They undergo a variety of exchange reactions with nucleophiles and ligands under very mild reaction conditions [Maitlis (1971), and Hegedus (1991)].

1.2 OXIDATIVE CARBONYLATION OF ANILINE

The oxidative carbonylation of aniline to ethyl phenyl carbamate is catalyzed by different catalyst systems. A majority of the catalyst systems comprise of platinum group metals and palladium in particular. It has been shown by Fukuoka et. al. (1984a,b) and Gupte and Chaudhari (1988), that palladium alone cannot catalyze the reaction,but, the presence of a promoter consisting of a metal halide is necessary for the catalytic cycle to proceed. A summary of the literature on catalysts and promoters used for oxidative carbonylation of aniline is given in Table 1.2 and the salient features are discussed below.

1.2.1 Palladium Based Catalyst Systems

Becker et. al. (1980), Merger et. al. (1980) and Ashai Chemical Ind. (1983g), have reported the use of iron chlorides and iron oxychlorides as the promoters for palladium catalyzed oxidative carbonylation of aniline to ethyl phenyl carbamate. The selectivity of the reaction to ethyl phenyl carbamate is reported to be in the range of 65 to 90 %. Air, oxygen or nitro compounds have been used as oxidizing agents.

Fukuoka and Chono (1983) have used alkali metal iodide as a promoter with palladium metal as the catalyst. A conversion of 85% of aniline and a selectivity of 98% to ethyl phenyl carbamate, is reported with Pd-CsI catalyst system at 433,

TABLE 1.2
A SUMMARY OF LITERATURE ON THE OXIDATIVE CARBONYLATION OF ANILINE

Sr.No	Catalyst system	Temperature	Pressure		Conversion	Selectivity		Reference
			CO	O_2		1	2	
		K	atm	atm	%	%	%	
1	2	3	4	5	6	7	8	9
	Palladium based							
1	$PdCl_2$, Fe oxychloride	-	-	-	-	-	91	Becker (1980)
2	$PdCl_2$, $FeCl_3$	373-463	-	-	70	-	82.4	Merger (1980)
3	Pd black, $KBiI_4$	433	80	6	-	-	70	Ashai Ltd. (1982a)
4	$PdCl_2$, $FeCl_3$, Mol. sieves	433	80	85	-	-	86	Ashai Ltd. (1982b)
5	$PdCl_2$, $FeCl_3$, Mg silicate	433	80	85	97	-	91	Ashai Ltd. (1982c)
6	Pd black CHI_3	433	80	6	-	-	41	Ashai Ltd (1983a)
7	Pd black, KIO_4	433	80	6	-	-	85	Ashai Ltd (1983e)
8	Pd-$FeCl_3$/graphite	433	80	5	-	-	66	Ashai Ltd (1983g)
9	Pd^o, I^-	423-453	50-80	-	> 95	-	> 95	Fukuoka (1984b)
10	Pd black, NaI	433-443	80	6	95	0.5	98	Fukuoka (1984c)
11	$PdCl_2$, $CuCl_2$ di-tert butyl peroxide	RT	B	-	60	-	-	Alper (1985a)
12	Pd/SiO_2, NaI	433-443	80	-	-	-	99	Fukuoka (1985a)
13	Pd metal, CsI	433	80	6	85	-	98	Fukuoka (1985b)
14	Pd acetate, Cu acetate, Conc. HCl	RT	B	B	-	-	91	Alper (1986a)
15	$PdCl_2CuCl_2$, molecular sieves	-	-	-	-	-	88	Alper (1986b)
16	$PdCl_2$, $CuCl_2$, HCl	RT	B	B	-	-	64	Alper (1987)
17	Pd (II) complexes	353	B	B	low	low	low	Giannoccaro (1987)
18	Pd, NaI	373	40	8	97	97.8	-	Gupte (1988)
19	$PdCl_2$, CuCl	443	10	-	-	-	-	Yamada (1988a)
20	$PdCl_2$, CuCl, Sulfolane	443	20	-	-	-	85	Yamada (1988b)
21	Pd/support, $CuCl_2$	433	24.75	9.9	-	-	-	Dong (1989)
22	α Zirconium phosphorous Intercalated Pd and Cu complex	403	25	7	56	-	40	Giannoccaro (1989)

TABLE 1.2 (continued)

1	2	3	4	5	6	7	8	9
23	$PdCl_2$, CuCl, Sulfolane	443	10	-	-	-	-	Murakami (1988)
24	Pd/C, KI	433	-	-	56	100	94**	Ikariya (1990)
25	Pd acetate, Cu(II) tosylate 1,10 phenanthroline	403	-	-	-	-	-	Goodall (1990)
26	Pd acetate, K_2CO_3, I_2	368	2.7	-	46	-	-	Ilan Pri-Bar (1990)
27	Pd acetate, $CuCl_2$ montomorrilonite bipyridine complex	RT	B	B	-	-	-	Choudary (1991)
28	$Pd(C_6H_7N)_2I_2$	443	38	3	65	-	100	Mulla (1991)
	Other metals							
29	Sulfur, triethyl amine	403	34	-	86.2	-	-	Franz (1961)
30	Mercury acetate, $PdCl_2$	363	B	77	-	63.8	-	Nefedov (1976)
31	KI	363	40	40	-	45	-	Mizorogi (1979)
32	Pt black, NaI, 2,2 bipyridyl	433-443	100	-	99	-	99	Fukuoka (1983)
33	Rh/C, CsI	433-443	80	6	92	1.5	94	Fukuoka (1984a)
34	$Co(CO)_8$	423	-	-	-	-	-	Moy (1981)
35	Co salen complexes	333	10	2	60	-	37	Bassoli (1990)
36	Cu carboxylate	ambient	B	B	-	-	-	Waller (1985)
37	CuI_2	431	110	-	-	-	92.3	Okawa (1989)
38	$CuCl_2$, CuI	-	-	-	-	-	> 50	Guan (1992)

RT : Room Temperature, 1 : Diphenyl urea, 2 : Ethyl phenyl Carbamate,
B : Bubbling, ** : Conversion of separated diphenyl urea.

K and 86 bar pressure (CO:O_2 ratio 13 : 1). Fukuoka and Chono (1985b) further reported 99 % selectivity to ethyl phenyl carbamate when molecular sieves are used along with Pd-CsI catalyst system.

The oxidative carbonylation of various amines (aniline, butylamine, cyclohexylamine, hexamethylenediamine), to the respective carbamate derivatives using palladium metal catalyst and various iodide as promoters has been reported by Fukuoka et. al. (1984b). The catalyst consisting of palladium black and sodium iodide could be reused at least twenty times without significant loss of activity.

Alper and Hartstock (1985a) have reported that oxidative carbonylation of aniline using palladium chloride and copper(II) chloride with hydrochloric acid as a catalyst, gives 99% yield for methyl phenyl carbamate and 64% for ethyl phenyl carbamate. The substituted amines (p-methyl, p-chloro, p-methoxy, 2,5 dimethyl, 3,5 dimethyl and 2,6 dimethyl anilines) as precursors were also studied, however, the conversion and selectivity of carbamate derivatives decreased with increase in ring substitution.

Yamada et. al. (1988a,b), have suggested a catalyst consisting of palladium chloride - cuprous chloride with complexing ligands such as benzonitrile and sulfolane for the oxidative carbonylation of aniline. The catalyst and reactant aniline are first reacted with oxygen to form oxygen complex which is further reacted with carbon monoxide to give ethyl phenyl carbamate with a selectivity of 85 %.

Other promoters like, potassium iodide, KIO_4, CHI_3, $KBiI_4$, mercury acetate and additives like mol. sieves and Mg sulfate have been found to give reasonably good selectivity for ethyl phenyl carbamate [Goodall et. al. (1990), Ikariya et. al. (1990), Mizorogi (1980), Ashai Chemical Ind. (1982a,b,c, 1983a,e), Nefedov et. al. (1976)].

Giannoccaro (1987) has reported the oxidative carbonylation of aliphatic and aromatic amines under ambient conditions with palladium complexes and quarternary ammonium salts as a catalyst system. Giannoccaro et. al. (1989) reported the oxidative carbonylation of aniline to diphenyl urea and the carbamate ester derivative using palladium 2,2$'$ bipyridyl complexes and copper (II) complexes intercalated in α zirconium phosphate layers. A low activity is observed for the catalyst in the initial stages and an induction period is reported. This induction period can be reduced by pretreating the catalyst with either carbon monoxide or carbon monoxide/oxygen mixture at higher temperature.

Choudary et. al. (1991) have reported a heterogeneous catalyst system comprising of montmorillonite-bipyridine palladium (II) acetate/ copper (II) chloride with di-tert-butyl peroxide to give 89 % diphenyl urea from aniline at room temperature and carbon monoxide atmosphere.

Mulla et. al. (1991) have reported alkoxycarbonylation of aniline to diphenyl urea and methyl phenyl carbamate using homogeneous palladium, ruthenium and rhodium catalysts. The activity and selectivity of different complexes has been discussed.

1.2.2 Other Catalyst Systems

A variety of catalyst systems for the oxidative carbonylation of aniline, using other metals as catalysts have been reported by many investigators. However, the activity of these is very low compared to that of palladium. Copper based catalysts, such as copper carboxylate with Lewis base promoter (Waller (1986)) and copper iodide (Okawa et. al. (1989)) have been reported to give selectivity for ethyl phenyl carbamate in the range of 85-95 %. Guan et. al. (1992) have investigated the effect of temperature and carbon monoxide and oxygen ratio on the activity of $CuCl_2$-CuI catalyst system. The yield of ethyl phenyl carbamate was 59%, due to side reactions leading to azo products by oxidation of aniline. Selectivity as well as the conversion increases with increase in temperature, however, with increase in partial pressure of carbon monoxide the conversion of aniline decreased.

Sulfur with tertiary amines, (Franz et. al. (1961)), cobalt carbonyl (Moy (1981)) and N N bis (salicylidene) ethylenediaminecobalt(II) (Bassoli et. al. (1990)) catalysts have also been reported for the oxidative carbonylation of aniline, however, the conversion and selectivity to diphenyl urea was low.

Kuo-Tseng Li and Yuang-Ju Peng (1993), have studied $MnBr_2$ $4H_2O$ catalyzed oxidative carbonylation of aniline. The effect of reaction conditions on the conversion of aniline and selectivity to diphenyl urea and ethyl phenyl carbamate has been investigated. Addition of ligands, like α benzoinoxim, was found to improve the activity of the catalyst. The conversion of aniline and selectivity to ethyl phenyl carbamate increased with increase in the reaction temperature, time of reaction, catalyst loading and the P_{O_2} to P_{CO} molar ratio. Loh et. al. (1992) reported 98 % conversion of aniline and 97 % selectivity to ethyl phenyl carbamate, using a catalyst consisting of cerium oxide and cesium iodide.

1.2.3 Reaction Kinetics and Mechanism

Fukuoka et. al. (1984a) have reported catalyst systems based on platinum group metals and with alkali metal halides as promoters. Alkali metal iodides as promoters showed the highest activity. Of the different platinum group metals (Pd, Pt, Ir, Ru, Rh) palladium and rhodium were found to have the highest activity when used along with an alkali metal iodide promoter. A mechanism of the reaction has been proposed, (Fig 1.2), based on the formation of a Pd-carbamoyl species, however, the role of alkali metal halide in the catalytic cycle has not been clarified.

Alper et. al. (1987) have used di-tert-butyl peroxide in place of oxygen for the carbonylation of aniline to methyl phenyl carbamate using a catalyst system consisting of palladium chloride, cupric chloride and hydrochloric acid. The carbonylation

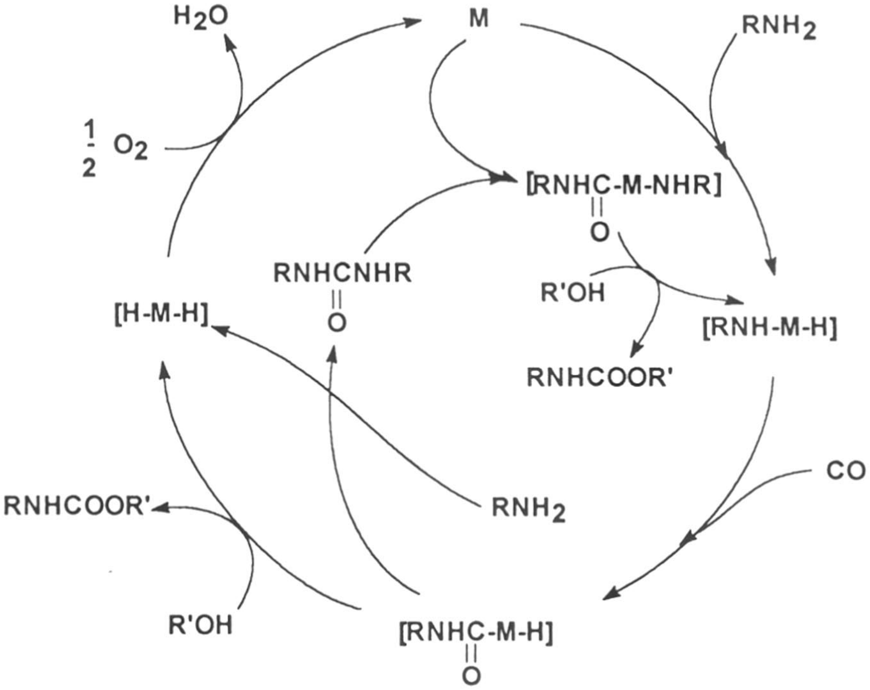


FIGURE 1.2 PROPOSED MECHANISM FOR PALLADIUM CATALYZED OXIDATIVE CARBONYLATION OF ANILINE (Fukuoka (1984)b)

of secondary amines with the above catalyst system leads to the formation of oxamides along with carbamates. A reaction mechanism (Fig 1.3) has been proposed, involving formation of a chloro alkoxy palladium intermediate species. A catalyst consisting of palladium acetate, potassium carbonate with iodine promoter was reported by Ilan Pri-Bar and Alper (1990), for the oxidative carbonylation of amines. This catalyst gives lower activity for aniline carbonylation (46% conversion, at 368, K and 2.5 atms of carbon monoxide), however, it is more active for the carbonylation of primary and secondary aliphatic amines. A mechanism for the carbonylation of secondary amines to oxamides and carbamate derivatives has been proposed (Fig 1.4), which involves the formation of a palladium dicarbonyl diiodide intermediate species.

Gupte and Chaudhari (1988) have studied the oxidative carbonylation of aniline to diphenyl urea using 5 % Pd/C-NaI catalyst. The effect of reaction temperature, partial pressures of carbon monoxide and oxygen, agitation speed, solvent, promoter to metal ratio on the activity of the catalyst has been reported. Pretreatment of the catalyst with reactants oxygen, carbon monoxide and aniline was found to give lower initial activity of catalyst. A catalytic cycle, involving Pd-carbamoyl species as the intermediate, has been proposed (Fig 1.5) incorporating the role of NaI. Gupte and Chaudhari (1992) have also reported the kinetics of oxidative carbonylation of aniline to diphenyl urea using 5 % Pd/C - NaI catalyst system. The rate was found to be first order with respect to catalyst loading and 1.6th order with respect

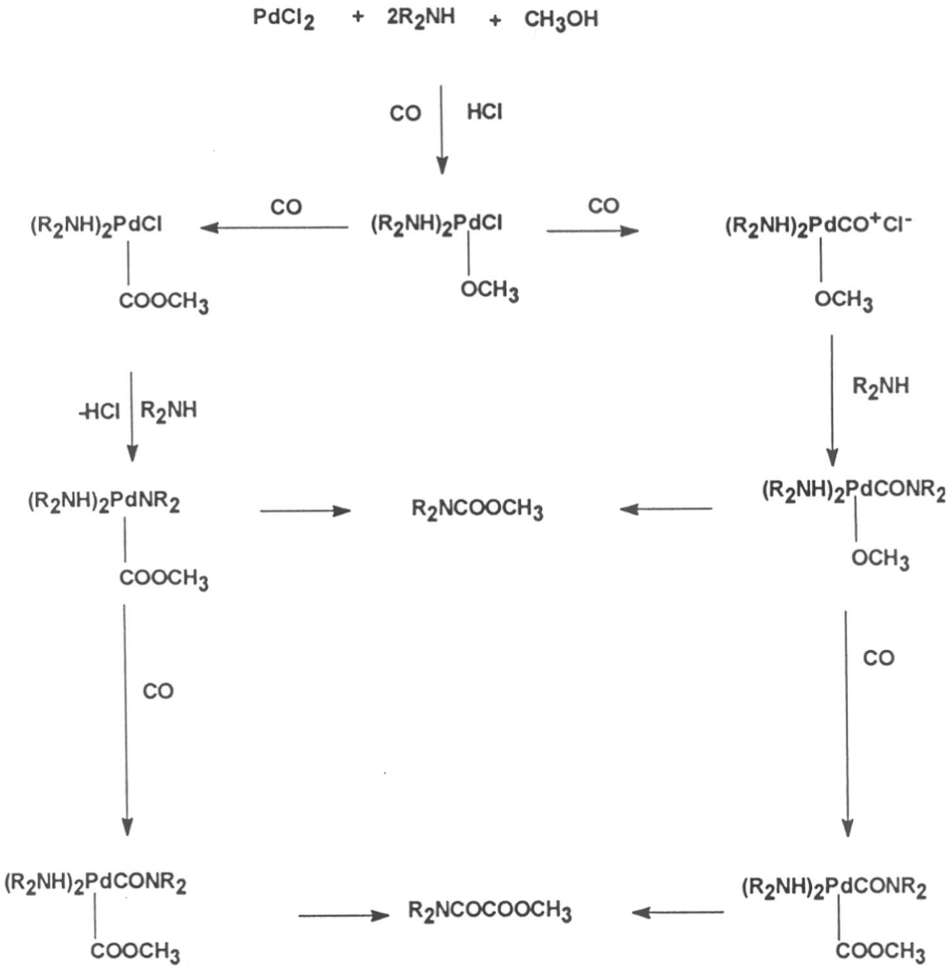


FIGURE 1.3 PROPOSED MECHANISM FOR PALLADIUM CATALYZED OXIDATIVE CARBONYLATION OF SECONDARY AMINES (Alper (1987))

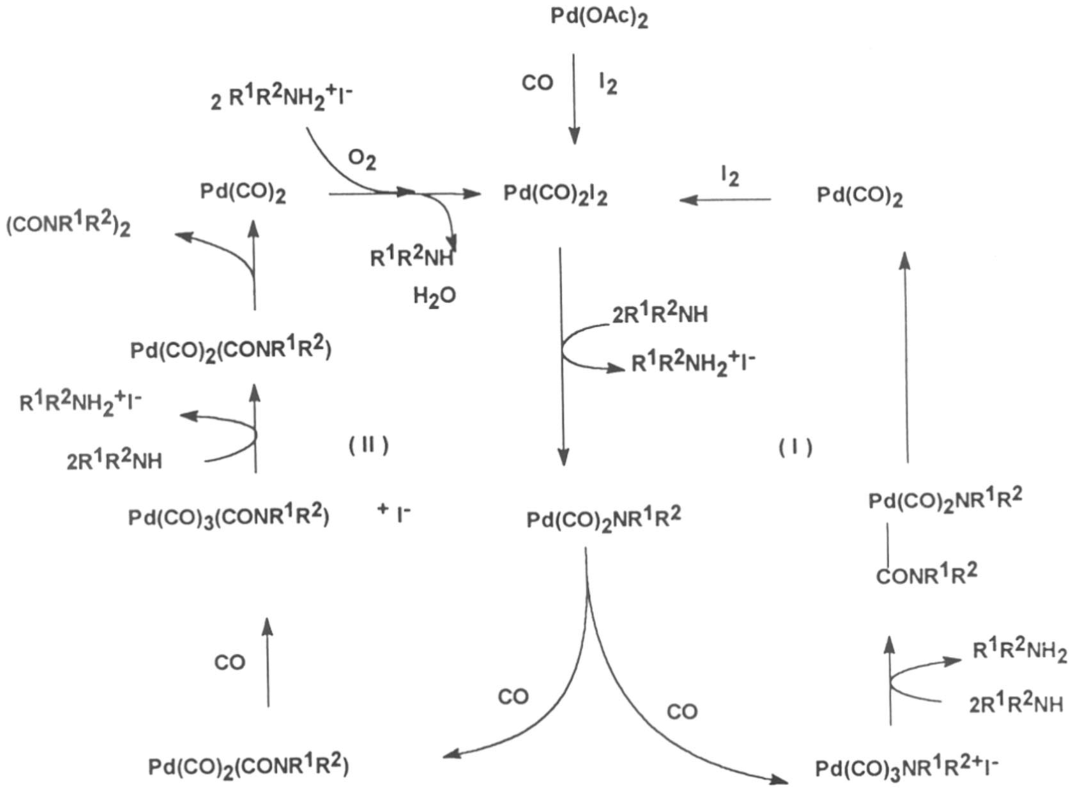


FIGURE 1.4 PROPOSED MECHANISM FOR PALLADIUM CATALYZED OXIDATIVE CARBONYLATION OF SECONDARY AMINES (Ilan Pri-Bar (1990))

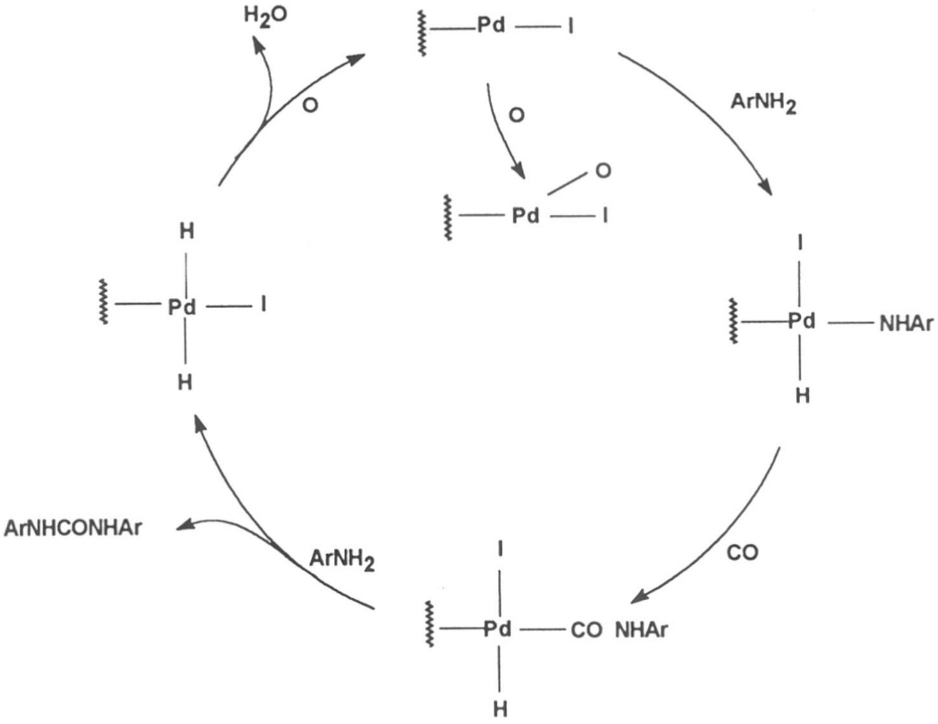


FIGURE 1.5 PROPOSED MECHANISM FOR PALLADIUM CATALYZED OXIDATIVE CARBONYLATION OF ANILINE (Gupte (1988))

to aniline concentration. The rate was found to increase linearly with increase in partial pressure of carbon monoxide upto 45 atm., beyond which the rate was found to be independent of carbon monoxide pressure. With increase in partial pressure of oxygen, the rate of reaction passed through a maxima. The following rate equation was proposed:

$$R_A = \frac{k\ w\ C_A^2\ C_B\ C_C}{(1 + K_A C_A + K_B C_B + K_C C_C)^2} \qquad (1.12)$$

Where

R_A = Reaction rate of aniline, mol/cm^3/sec, k = reaction rate constant, (cm^3)^4/mol^3/gm/sec, w = catalyst concentration, gm/cm^3, C_A, C_B, C_C =Concentrations of aniline, carbon monoxide, and oxygen respectively, mol/cm^3, K_A, K_B, K_C = Adsorption rate constants, cm^3/mol.

and the energy of activation was found to be 82.7 kJ/mol.

1.3 ALCOHOLYSIS OF DIPHENYL UREA

The oxidative carbonylation of aniline to ethyl phenyl carbamate is known to proceed through the formation of diphenyl urea which subsequently reacts with ethanol to give ethyl phenyl carbamate (Gupte and Chaudhari (1988), Giannoccaro (1988)). A summary of the various investigations on the reaction of diphenyl urea with alcohols to form carbamate derivatives is presented in Table 1.3 and their salient features are

TABLE 1.3

A SUMMARY OF LITERATURE ON ETHANOLYSIS OF DIPHENYL UREA

Sr.No	Catalyst system	Temperature	Pressure		Conversion	Selectivity	Reference
			CO	O_2			
		K	atm	atm	%	%	
	Palladium based						
1	Pd metal, KBI_4	433	80	6	-	90	Ashai Ltd. (1983b)
2	Pd metal, KIO_4	433	80	6	-	90	Ashai Ltd. (1983c)
3	Pd metal, CHI_3	433	80	6	-	90	Ashai Ltd. (1983d)
4	Pd metal, I_2	433	80	6	-	90	Ashai Ltd. (1983f)
5	Pd black, NaI, 2,2$'$ bipridyl	433-443	15*	5*	99	98	Fukuoka (1985c)
6	Pd/SiO_2, NaI,	433-443	60	20	100	99	Fukuoka (1985d)
7	Pd acetate, Cu acetate 2,3 dichloronapthaquinone	453	100	25	-	73	Stammann (1983)
8	Pd$(C_6H_7N)_2I_2$, Cu (II) complexes	403	20	10	90	90	Giannoccaro (1988)
	Other catalysts						
9	-	443	-	-	97.3	97.3	Miyazawa (1990)
10	Conc. H_2SO_4	423	-	-	-	89	Kalkote (1991)

* : Total pressure : 100 atms, ($CO:O_2:N_2$ :: 15:5:80)

discussed below.

Csuros et. al. (1971) have reported thermal dissociation of diphenyl urea in glacial acetic acid and cyclohexanol to acetanilide and cyclohexyl phenyl carbamate respectively. The effect of ring substituents on the dissociation rate of diphenyl urea has also been investigated. Electron donating substituents like methyl group decrease the reaction rate while electron withdrawing groups like chlorine increase the reaction rate. The kinetics of the reaction in glacial acetic acid has been reported at different temperatures (373 to 381 K). The energy of activation was found to be 26.4 kcal/mol. In cyclohexanol medium, the kinetics of the reaction has been reported at 393, 395, 398, 403 and 416 K. A rate equation has been proposed and the energy of activation has been estimated at 27.5 Kcal/mol.

Miyazawa et. al. (1990) have reported the synthesis of ethyl phenyl carbamate by heating diphenyl urea at 443, K in the presence of ethanol, giving a selectivity of 97.5%.

Stammann et. al. (1983) have used a catalyst system comprising of palladium acetate, copper acetate and 2,3 dichloronapthaquinone to get a yield of 73% of ethyl phenyl carbamate from diphenyl urea at 453, K, under a pressure of 125 bar (carbon monoxide : oxygen :: 5:1).

Giannoccaro (1988) has reported $Pd(PhNH_2)_2Cl_2$ and $Cu(PhNH_2)_2Cl_2$ catalysts for getting more than 90% selectivity to ethyl phenyl carbamate at 423 K, and under a pressure of 30 atmospheres (carbon monoxide : oxygen :: 2:1).

Kalkote and Ayyangar (1991) have used concentrated sulfuric acid as the catalyst for alcoholysis of various substituted ureas to carbamate derivatives at 423 K, to get more than 85% yields.

1.4 CARBONYLATION OF ALLYL CHLORIDE

The carbonylation of allyl chloride results in the formation of two isomeric unsaturated acids as shown below:

$$\begin{aligned} &CH_2{=}CH\text{-}CH_2Cl \;+\; CO \;\longrightarrow \\ &\qquad CH_2{=}CH\text{-}CH_2\text{-}COOH \;+\; CH_3\text{-}CH{=}CH\text{-}COOH \end{aligned} \tag{1.13}$$

The main products are crotonic and vinyl acetic acid. Crotonic acid is an industrially important chemical and is used as an intermediate for the synthesis of synthetic resins, fungicides, surface coatings, hot melt adhesives and in paper industry (Baxter (1979), Baltes (1987)). Vinyl acetic acid is also used as a monomer and intermediate for pesticide synthesis. The isomerization of vinyl acetic acid to crotonic acid is feasible with both acid and base catalysts. In the following sections, the relevant literature on the carbonylation of allyl chloride with different catalysts and reaction conditions is presented. A summary of literature on catalysts used for the carbonylation of allyl chloride is presented in Table 1.4.

TABLE 1.4

A SUMMARY OF LITERATURE ON CARBONYLATION OF ALLYL CHLORIDE

Sr.No	Catalyst system / Solvent	Temperature K	Pressure atms	Product	Conversion %	Selectivity %	Reference
	Palladium based						
1	$PdCl_2$	423	500	1	-	-	Imperial Industries (1965)
2	Pd (π allyl)$_2Cl_2$	373	50-60	1	-	-	Shell (1965)
3	$PdCl_2$	368	81	1	77	-	National Distillers (1965)
4	5% Pd/C	398	204	2	-	27	Closson (1967)
	5% Pd/C	423	204	3	-	51	Closson (1967)
5	3 % Pd/C	346-388	-	1	-	-	Mador (1969)
6	o-(N-phenylformimidoyl)phenyl $PdCl_2$	368	100	1	67	-	Scheben (1969)
7	$Pd(PPh_3)_2Cl_2$, $SnCl_2$ / Benzene, methanol	368	136	4	83	-	Knifton (1976)
8	Amberlyst A (7.71% Pd)	393	81.6	1	-	-	Haag (1978)
9	Pd (π allyl)$_2Cl_2$ / ethanol	343	100	1	-	58	Tsuji (1963)
10	Pd (π allyl)$_2Cl_2$	383	500	3	-	96	Dent (1964)
11	Pd (π allyl)$_2Cl_2$	323	200	3	-	65	Long (1964)
12	$PdCl_2$, / ethanol	393	100	2	-	47	Tsuji (1964)
13	Pd (π allyl)$_2Cl_2$ / dimethoxyethane	363	85	3	90	95	Medema (1969)
14	$PdCl_2$	-	-	-	-	-	Volger (1970)
15	Pd (π allyl)$_2Cl_2$ / benzene	-	-	-	-	-	Yoshida (1974)
16	$PdCl_2$	368	90	3	85	85	Scheben (1976)
17	$Pd(PPh_3)_2Cl_2$, $SnCl_2$ / Benzene, methanol	353	204	4	-	75	Knifton (1980)
18	$Pd(PPh_3)_2Cl_2$, NaOH/ Benzene	303	A	2	-	90	Kiji (1988)
	Nickel based						
19	$Ni(CO)_4$ / alcohol	RT	A	1	-	-	Chiusoli (1959a)
20	$Ni(CO)_4$	-	-	-	-	-	Chiusoli (1960)
21	$Ni(CO)_4$	373	50	2	-	-	Chiusoli (1962)
22	$Ni(CO)_4$	-	-	-	-	-	Heck (1963)
23	$Ni(CO)_4$	-	-	-	-	-	Chiusoli (1971)
24	$Ni(CO)_4$, $(CH_3)_4N)^+$	-	-	-	-	-	Foa (1979)
25	$Ni(CN)_2$, tetrabutyl ammonium hydrogen sulfate, NaOH	RT	A	2	-	14	Joó (1985)
	Cobalt based						
26	$Co_2(CO)_8$, Na_2CO_3 / Methanol	-	-	-	-	-	Terekhova (1991)
27	$Co_2(CO)_8$, n-$(C_4H_9)_4NI$, $NaOC_2H_5$/ benzene	298	A	1	-	45	Kantam (1990)

A : Atmosphere, RT : Room temperature, 1 : Ethyl but-3-enoate, 2 : Vinyl acetic acid, 3 : But-3-enoyl chloride, 4 : Methyl but-3-enoate 1 : But-3-enoyl Chloride, 2 : Vinyl acetic acid,
3 : Crotonic acid, 4 : Methyl but-3-eonate

1.4.1 Palladium Based Catalysts

The carbonylation of allyl chloride to but-3-enoyl chloride with Pd(π allyl)$_2$Cl$_2$ complex catalysts has been investigated by Dent et. al. (1964) (96 % yield at 500 atms. of CO and 383 K), Long and Whitfield (1964) (200 atms. of CO and 333 K) and Shell Internationale Research Maatschappi N V (1965) (53% yield at 373 K and under 50-60 atms. of CO).

Palladium chloride as a catalyst was reported for the carbonylation of allyl chloride by Tsuji et. al. (1964) (47 % yield of ethyl but-3-enoate at 393 K, under a pressure of 100 atms. of carbon monoxide), Imperial Chemical Industries Ltd. (1965) (to but-3-enoyl chloride and crotonyl chloride under pressure of 500 atms. of carbon monoxide at 423 K) and National Distillers and Chemical Corp. (1965) (at 77 % conversion of allyl chloride to but-3-enoyl chloride and at 368 K, under a pressure of 81 atms. of carbon monoxide).

Closson et. al. (1967) have investigated heterogeneous catalysts such as 5 % Pd/C, Rh/C, PdCl$_2$ and RhCl$_3$ for the carbonylation of allyl chloride to vinyl acetic and crotonic acids. A yield of 27% of vinyl acetic acid and 15% of crotonic acid was observed with 5 % Pd/C catalysts under a pressure of carbon monoxide at 398 K. Increase in the reaction temperature to 423 K led to the formation of crotonic acid exclusively, due to the increase of the isomerization rate with temperature. Mador and Scheben (1969) reported vapour phase carbonylation of allyl chloride over a catalyst bed comprising of 3% palladium on sintered alumina at 346-388 K, to but-3-enoyl chloride. Haag and Whitehurst (1978) have used a 7.71 % palladium catalyst prepared from Amberlyst A, tetrachloro potassium palladate and potassium chloride.

1.4.2 Nickel Based Catalysts

Most of the nickel based catalysts reported consists of nickel tetracarbonyl complex or derivative. These catalysts are less active than the palladium based catalysts. Chiusoli and Merzoni (1962) have reported the carbonylation of allyl chloride to the methyl but-3-enoate using nickel tetracarbonyl as a catalyst at 373 K, and 50 atm of carbon monoxide. Isomerization of the ester to methyl but-2-enoate has also been observed.

Other nickel based catalysts are nickel metal (Chiusoli and Cassar (1967)), tetracarbonyl nickel (Chiusoli (1959)a,b, (1960), Chiusoli and Merzoni (1971), Heck (1963)) for the carbonylation of allyl chloride to but-3-enoyl chloride.

1.4.3 Cobalt Based Catalysts

Kantam et. al. (1990) report the formation of 45 % ethyl but-3-enoate and 40% ethyl but-2-enoate at room temperature and carbon monoxide atmosphere under solid-liquid phase transfer conditions with cobalt octacarbonyl catalyst. A reaction scheme for the reaction has been proposed. Terekhova et. al. (1991) have reported that addition of bases like sodium carbonate, potassium carbonate, calcium carbonate, calcium oxide and calcium hydroxide to the cobalt octacarbonyl catalyst improves the yield.

1.4.4 Kinetics and Mechanism

Palladium Catalysts

Tsuji et. al. (1963) have reported the carbonylation of allyl chloride to 58 % ethyl but-3-enoate, under a pressure of 100 atmospheres of carbon monoxide at 343 K, in ethanol using $(Pd(\pi\text{-allyl})Cl)_2$ as the catalyst. Isomerization of the product to ethyl but-2-enoate was also observed. In benzene, but-3-enoyl chloride was formed under similar conditions. Other catalyst systems with noble metals such as palladium, platinum and rhodium were also found active for the reaction. Palladium carbonyl species has been postulated to be the active catalytic species. The ester is formed from but-3-enoyl chloride, by reaction with an alcohol.

Medema et. al. (1969) have studied the kinetics and the mechanisms of carbonylation of allyl chloride to but-3-enoyl chloride using $(Pd(\pi\text{-allyl})Cl)_2$ complex catalyst at 85 atms. of carbon monoxide and 363 K. Other complexes such as $(\pi\text{-allyl}\ RhCl_2)_n$ and $(\pi\text{-allylRhCl})_2$ were also studied. The reaction was found to be first order with respect to the concentrations of catalyst and allyl chloride and the second order with carbon monoxide. The reaction rate was found to be affected by the basicity of the solvent used and was found to vary in the following order:

Dimethoxyethane > benzene > carbon tetrachloride

Other complexes of palladium such as palladium benzonitrile, palladium chloride and palladium metal showed lower rates and an induction period was observed. Addition of triphenyl phosphine to the system increased the rate of the reaction. This increase was observed upto the molar ratio of palladium to triphenyl phosphine of 1:0.5. Beyond this the rates decreased and above 1:4 the rates were severely inhibitted. Based on the above observations, a mechanism of the reaction in the absence and presence of triphenyl phosphine (Figs 1.6 and 1.7 respectively), has been proposed. The active catalytic species is a chloride bridged π-allyl palladium complex. Characterization of the catalytic species by infrared and elemental analysis has been attempted. The effect of substituent on the allyl fragment has also been studied and it has been observed that the rates decrease with these substituents.

Yoshida et. al. (1974) have suggested a reaction mechanism for $Pd(\pi\ allyl)_2Cl_2$ complex catalyzed carbonylation of allyl chloride to but-3-enoyl chloride in benzene.

Volger et. al. (1970) have investigated the effect of various phosphorous ligands like PPh_3, $P(OPh)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, $PPh_2(C_2H_5)$, $PPh(C_2H_5)_2$, $P(p\text{-}Cl\ Ph)_3$, $PPh_2(p\text{-}Br\ Ph)$ on the palladium catalyzed carbonylation of allyl chloride to but-3-enoyl chloride. The above screening indicated that the enhancement of ac-

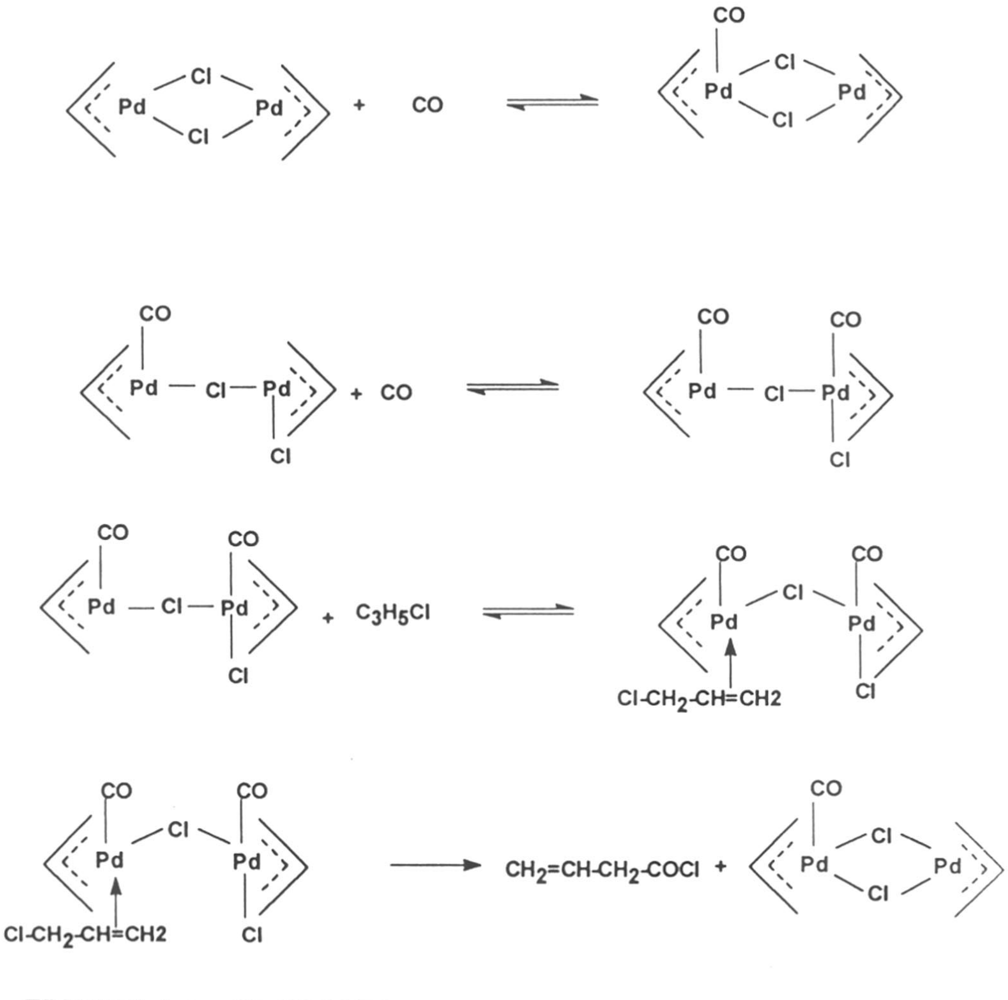


FIGURE 1.6 PROPOSED MECHANISM FOR PALLADIUM CATALYZED CARBONYLATION OF ALLYL CHLORIDE IN ABSENCE OF TRIPHENYL PHOSPHINE (Medema (1969))

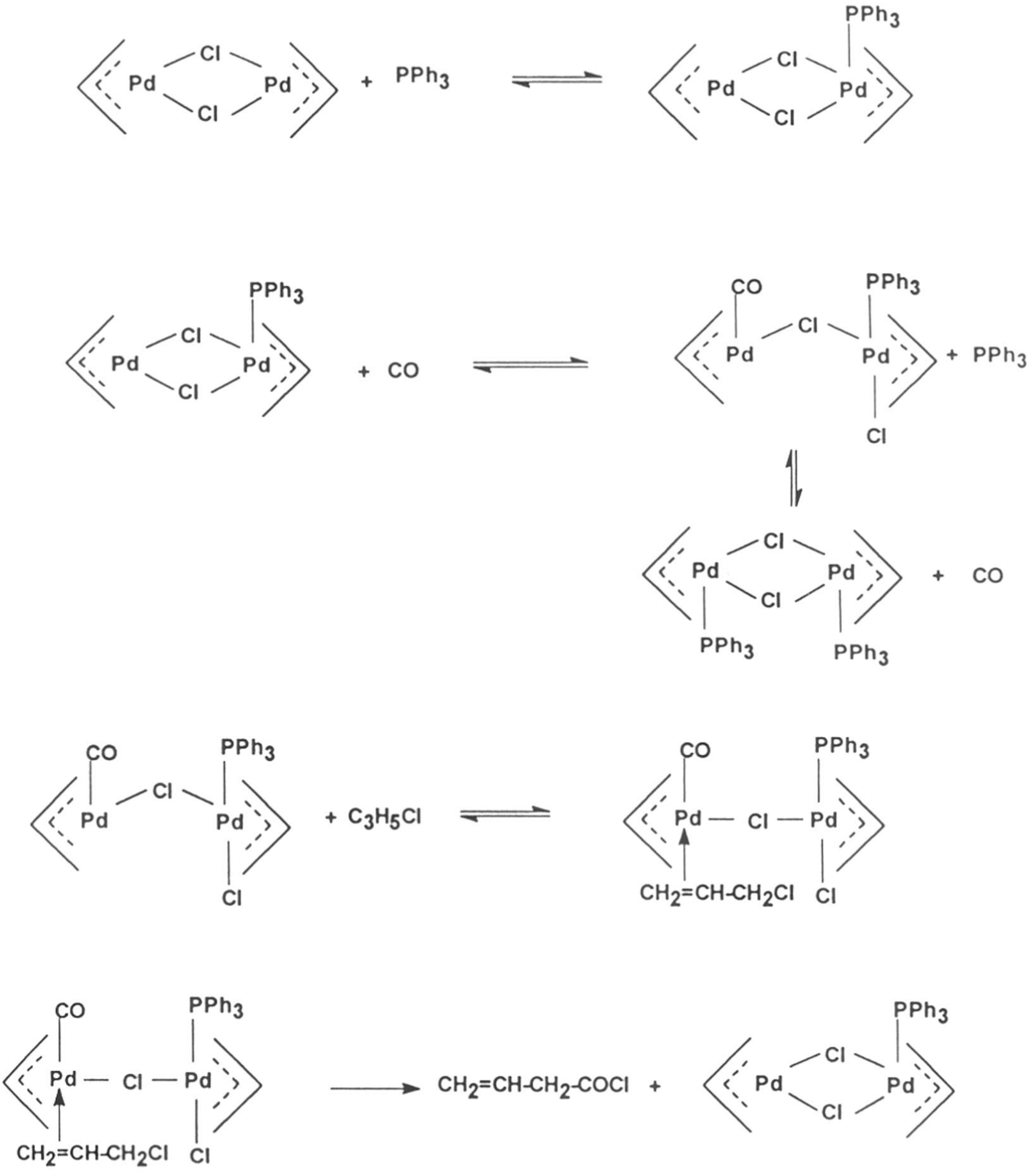


FIGURE 1.7 PROPOSED MECHANISM FOR PALLADIUM CATALYZED CARBONYLATION OF ALLYL CHLORIDE IN PRESENCE OF TRIPHENYL PHOSPHINE (Medema (1969))

tivity of catalyst was observed when the metal to ligand ratio was 1:0.5, however, no significant enhancement in activity was observed due to the change in the ligands. A mechanism for the reaction has been proposed (Fig 1.8), with an intermediate trinuclear palladium species as the active catalytic species.

Scheben and Mador (1976) have reported palladium chloride catalyzed carbonylation of allyl chloride to but-3-enoyl chloride at 85% conversion and a selectivity of 96% at 368 K, under 90 atms. of carbon monoxide. Increase in pressure was found to increase the conversion of allyl chloride, while increase in temperature resulted in increase of the isomerization reaction. The increase in catalyst concentration increases the conversion of allyl chloride marginally . This has been explained on the basis of solubility limitation of palladium chloride in the reaction medium, which thus decreases the rate of of formation of active catalytic species. In inert solvents the rate of reaction is lower compared to that when allyl chloride was used as a solvent.

Knifton (1980) has reported the carbonylation of allyl chloride to methyl but-3-enoate with, $Pd(PPh_3)_2Cl_2$ or platinum chloride, and tin chloride as the catalyst giving 99 % and 95 % conversion of allyl chloride with 75 % and 70 % selectivity to methyl but-3-enoate respectively at 353 K. A reaction scheme has been discussed.

Biphasic and palladium complex catalyzed carbonylation of allyl chloride to ethyl but-3-enoate with a conversion of 90 % and a selectivity of 80 % at 303 K

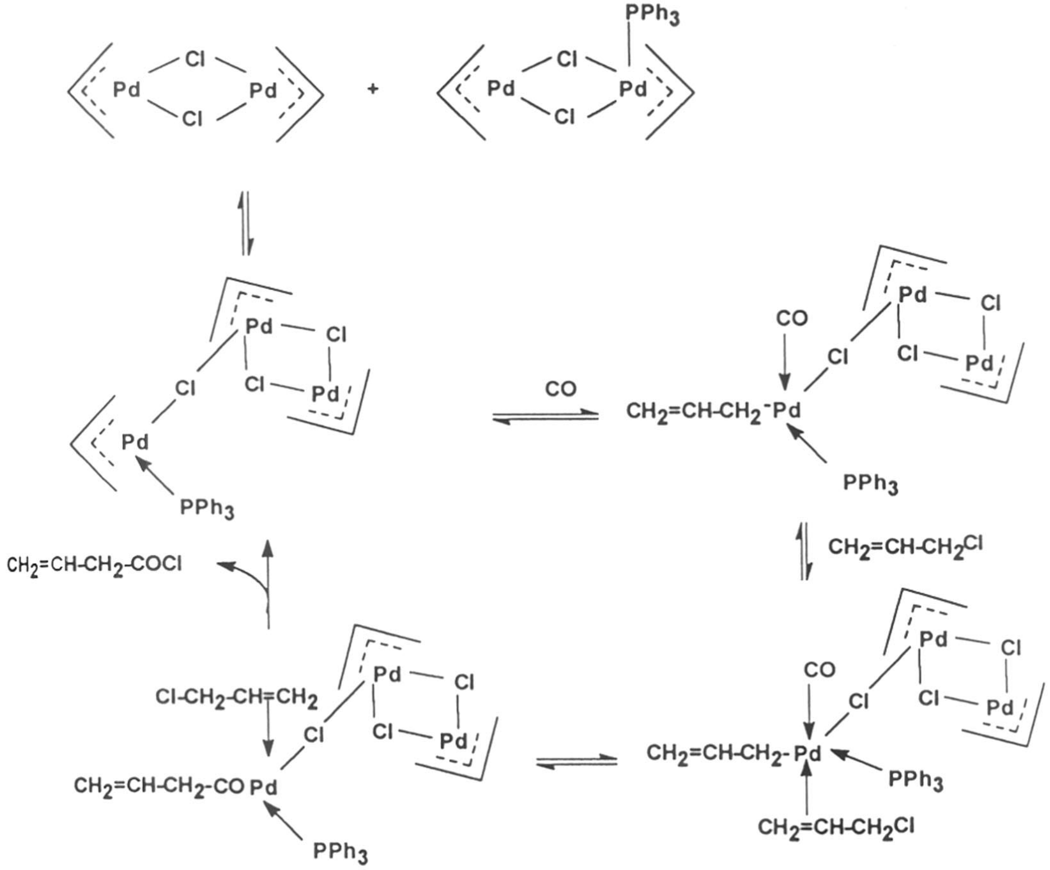


FIGURE 1.8 PROPOSED MECHANISM FOR PALLADIUM CATALYZED CARBONYLATION OF ALLYL CHLORIDE (Volger (1970))

is reported by Kiji et. al. (1988). The reaction is feasible under an atmosphere of carbon monoxide atmosphere only in the presense of aqueous sodium hydroxide. Triphenyl phosphine has been used as a promoter. Carbonylation of methallyl, geranyl and cinnamyl chlorides under similar reaction conditions to the respective unsaturated acids has also been reported.

Nickel Catalysts

Joó and Alper (1985) have reported the atmospheric pressure phase transfer carbonylation of allyl chloride to sodium salt of 2-butenoic acid in a reaction medium of aqueous sodium hydroxide and 4-methyl 2-pentanone at room temperature using cyanonickel(II) complex as the catalyst. The conversion of allyl chloride was more than 86% with a selectivity of 14 % to vinyl acetic acid and 86 % to crotonic acid was observed. A reaction mechanism has been proposed (Fig 1.9) involving a cyanotricarbonylnickel anion as the active catalytic intermediate. This species has been isolated and characterized as bis(triphenylphosphine) nitrogen(1^+) salt.

1.5 OBJECTIVES AND SCOPE OF THE PRESENT WORK

The present work was undertaken to investigate the following problems in detail:

- Oxidative carbonylation of aniline over rhodium catalysts
- Carbonylation of allyl chloride over palladium catalysts

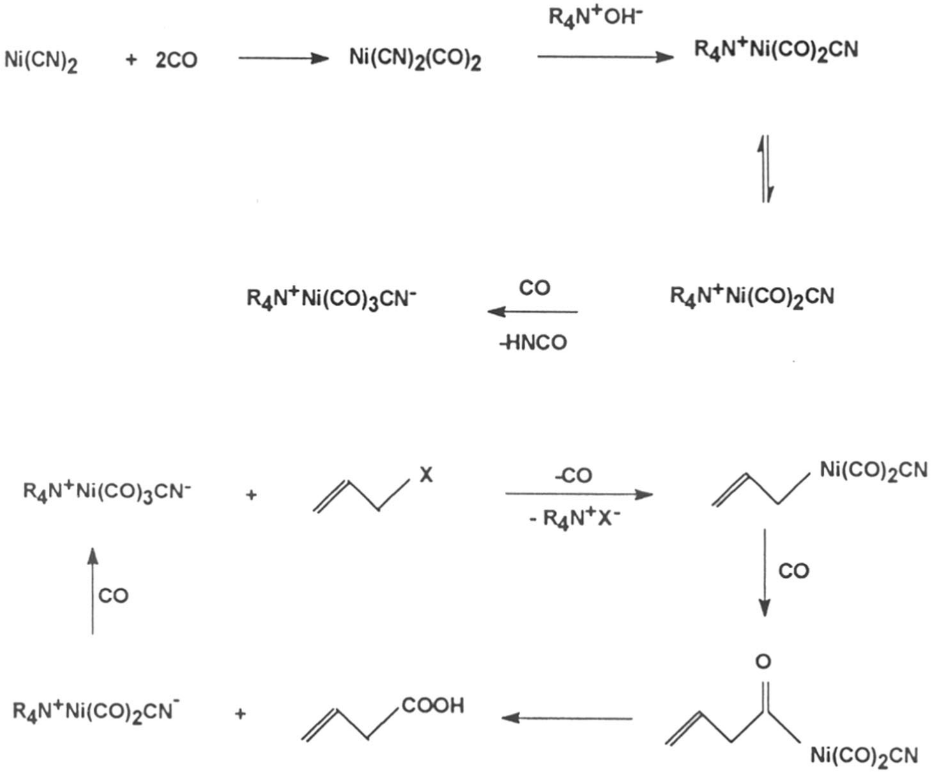


FIGURE 1.9 PROPOSED MECHANISM FOR NICKEL CATALYZED CARBONYLATION OF ALLYL CHLORIDE UNDER PHASE TRANSFER CONDITIONS (Joó (1985))

The oxidative carbonylation of amines is an industrially important reaction for the synthesis of carbamates and substituted ureas. The oxidative carbonylation of aniline to ethyl phenyl carbamate is the first step in the new synthesis of MDI (Fukuoka et. al. (1984c). Palladium has been used as a catalyst metal by most of the investigators and there has been very few reports with other metals. The aim of the present work was to investigate the oxidative carbonylation of aniline with rhodium catalysts and the following problems were investigated:

- Role of catalyst precursors, solvents, promoters, co-catalysts, and reaction conditions on the activity and selectivity of Rh catalysts.
- The intrinsic kinetics of the reaction.
- The screening of catalysts, solvents and effect of reaction conditions on the ethanolysis of diphenyl urea to ethyl phenyl carbamate. The intrinsic kinetics of the reaction.

The kinetics of ethanolysis reaction will be useful in developing a kinetic model for the oxidative carbonylation as a whole.

The carbonylation of allylic substrates is an important synthetic tool to produce regio and stereoselective products by C-C bond formation. For the present investigation, allyl chloride was chosen as the substrate. A major part of the published literature deals with the homogeneously palladium or nickel catalyzed carbonylation of allyl chloride to unsaturated acid chlorides. Recently, Kiji et. al. (1988), have shown the biphasic carbonylation of allyl chloride with palladium catalysts, however, there has been no detailed report on the biphasic carbonylation of allyl chloride. Hence the present work was undertaken to investigate the following problems.

- Screening of various catalyst precursors, solvents, ligand and reaction conditions on palladium catalyzed carbonylation of allyl chloride.
- The intrinsic kinetics of the reaction.

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CHAPTER 2

OXIDATIVE CARBONYLATION OF ANILINE OVER SUPPORTED RHODIUM CATALYSTS

2.1 INTRODUCTION

Catalytic oxidative carbonylation of amines is important in the synthesis of carbamates and urea derivatives (Fukuoka et. al. (1984a)). An important example of practical interest is the conversion of aniline to ethyl phenyl carbamate (EPC), which provides a non-phosgene route for methylene diphenyl diisocyante (MDI) (Fukuoka et. al. (1984c)). The stoichiometric reactions are:

$$2RNH_2 + CO + \frac{1}{2}\,O_2 \longrightarrow RNHCONHR + H_2O \qquad (2.1)$$

Where R represents an alkyl or aryl group.

$$RNHCONHR + R'OH \longrightarrow RNHCOOR' + RNH_2 \qquad (2.2)$$

Where R′ is any alkyl group.

A variety of catalysts, consisting of supported noble metals along with alkali halide promoters, have been proposed for oxidative carbonylation of amines (Fukuoka et. al. (1984b)). Of these Pd catalyzed oxidative carbonylation of amines is extensively studied [Alper et. al. (1987), Giannoccaro (1987, 1988), Gupte and Chaudhari (1988, 1992)]. Fukuoka et. al (1984a) reported Pd/C-NaI catalyzed synthesis of ethyl phenyl carbamate with 90% conversion of aniline and 95% selectivity. The role of promoters, solvents and catalyst pretreatment effects have been studied in detail by Gupte and Chaudhari (1988) for Pd/C-NaI catalyst system. They have shown that the catalytic oxidative carbonylation of aniline gives N,N′ diphenyl urea

(DPU) as a product, which in presence of an alcohol is converted to the carbamate ester by a non-catalytic reaction. Other catalysts consisting of Rh, Ru and Pt have also been reported (Fukuoka et. al. (1984b)), however, there have been no detailed investigations on the behavior of these catalysts, with respect to the role of promoters, reaction conditions in activity and selectivity. An important aspect overlooked in all the previous studies on oxidative carbonylation is the selectivity with respect to CO consumed. This is important, since, with most of the catalysts proposed, oxidation of CO to CO_2 occurs in significant yields.

Hence, in the present work rhodium catalyzed oxidative carbonylation of aniline was investigated. The effect of promoters, solvents, co-catalysts, catalyst preparation methods and supports, on the activity and selectivity of the catalyst has been studied. The catalyst reusability and pretreatment by reactants has also been investigated. Carbon monoxide oxidation during the oxidative carbonylation reaction has been investigated quantitatively. The intrinsic kinetics of the reaction has been studied at 443, K. An empirical rate model has been proposed and rate constants determined.

A brief summary of literature on the oxidative carbonylation of aniline is presented in Section 1.2, Chapter 1.

2.2 EXPERIMENTAL

2.2.1 Reactants

The reactants aniline and ethanol were obtained from SD Fine Chemicals Ltd., India and were freshly distilled before use. The purity was monitored by gas chromatography. The solvents benzene, toluene, chlorobenzene, p-xylene, dimethyl formamide, methyl acetate, ethyl acetate, methanol and acetonitrile were procured from BDH Chemicals, India.

Rhodium chloride trihydrate was procured from Arrora Mathey, Calcutta. Cobalt (III) chloride, copper (II) chloride, manganese (II) chloride, nickel (II) chloride, tin (II) chloride, copper (II) iodide, tin (II) iodide, nickel (II) iodide, lithium iodide, sodium iodide, potassium iodide, sodium chloride, lithium bromide, lithium chloride, triphenyl phosphine, pyridine and acetyl acetonate were all of analytical grade and obtained from SD Fine Chemicals Ltd., India.

The support materials, activated carbon, silica, ZSM-5, titanium dioxide, calcium carbonate, alumina were procured from SD Fine Chemicals Ltd., India. All supports were dried by heating under vacuum before use.

The gases, oxygen, carbon dioxide, hydrogen, nitrogen were procured from Indian Oxygen Limited, Bombay. Carbon monoxide used was of $> 99.8\%$ purity.

2.2.2 Preparation of Rhodium Complexes

Different complexes of rhodium were prepared from rhodium trichloride and these were used as catalysts and precursors for preparation of supported rhodium catalysts. The following complexes were prepared :

a. **Acetylacetonatodicarbonylrhodium (I), [Rh(CO)$_2$(acac)]**

Rh(CO)$_2$(acac) was prepared by a method used by Varshavskii and Cherkasova (1967). To a solution of 3 gms of rhodium chloride in 60 ml dimethyl formamide, 12 ml acetyl acetonate was added with stirring. The solution was refluxed for thirty minutes and then cooled. It was diluted to twice the volume with distilled water. Addition of water resulted in a voluminous crimson precipitate. The precipitate was filtered and washed with alcohol and ether. The complex was recrystallized from hexane solution. The needle shaped red-green crystals were obtained by slow cooling of the hexane solution. The yield was about 68 %. The complex was confirmed from its elemental analysis, which is given below:

	Theoretical (%)	Experimental (%)
C	23.25	23.28
H	2.71	2.69

b. Trans chloro carbonyl bis(triphenylphosphine) rhodium (I), [RhClCO(PPh$_3$)

This complex was synthesized using the method of Evans et. al. (1968). A solution of 2 gms of rhodium chloride in hot ethanol (about 70 ml) was added to a solution of freshly crystallized triphenyl phosphine (about 7.2 gms) in 350 ml of ethanol. To this solution about 10 to 20 ml of 37% formaldehyde solution was added. The red solution turned to pale yellow with the precipitation of yellow crystals. The solution was cooled to room temperature and the yellow crystals were filtered and washed with degassed ethanol and ether. The complex was dried under vacuum. The yield of complex was around 85%. The IR spectrum of the complex in nujol mull, showed a strong absorption band for carbonyl in the region of 1960 cm^{-1} which is characteristic of this complex (Evans et. al. (1968)). The elemental analysis of the complex is given below.

	Theoretical (%)	Experimental (%)
C	64.39	64.11
H	4.35	4.33
Cl	5.15	5.16
P	8.99	8.97

c. Hydridocarbonyl tris(triphenylphosphine) rhodium (I), [HRh(CO)(PPh$_3$)$_3$]

This complex was also synthesized by the method of Evans et. al. (1968). To a solution of 1 gm of trans- chlorocarbonylbis(triphenylphosphine) rhodium (I) in ethanol, 1.5 gms of triphenyl phosphine was added. The solution was refluxed with stirring and about 0.5 gms of sodium borohydride in 60 ml of ethanol was added slowly. After complete addition, the solution was further refluxed for two hours. The complex was filtered hot from the solution and washed with ethanol and dried under vacuum. The yield of the complex was around 75 %. The complex was confirmed from its elemental analysis.

	Theoretical (%)	Experimental (%)
C	71.9	71.91
H	5.01	5.14
P	10.13	10.11

d. **Tris (pyridine) rhodium trichloride, [Rh(py)$_3$Cl$_3$]**

The complex was prepared by the method as described by Gupte and Chaudhari (1984). Rhodium chloride (1gm) was refluxed with 2 gms of pyridine (six fold excess of rhodium chloride) in 100 ml of o-dichlorobenzene for 16 hours. The orange coloured crystals were separated after cooling and washed with ether and dried under vacuum. The yield was around 65 %. The elemental analysis of the complex confirmed the complex and is given below:

	Theoretical (%)	Experimental (%)
C	40.31	40.33
H	3.36	3.41
Cl	23.85	23.84
N	9.41	9.39

2.2.3 Preparation of supported rhodium catalysts

The catalysts were prepared by impregnating the support with Rh compounds in acetone. Catalysts with different metal loadings were also prepared. The Rh compounds on the supports were reduced using different reducing agents. The different reducing agents used were:

a. **Reduction by Sodium Borohydride**

The procedure used was similar to that used by Polyanszyky et. al. (1980). To a slurry of impregnated support in distilled water at 333, K, 10 % sodium borohydride solution was added slowly with stirring. The total time of addition of sodium borohydride solution was over a period of half an hour. The solution was further stirred for two hours at the same temperature. It was then cooled and allowed to settle. The catalyst was filtered and washed with distilled water several times. It was dried in a vacuum desicator at 298, K.

b. **Reduction by methanol**

The reduction procedure was similar to that used by Hidefumi et. al. (1979). The impregnated support was refluxed in methanol for two hours. The solution was cooled and allowed to settle. The catalyst was filtered out and washed with distilled methanol and later with water before drying in a vacuum desicator at 298, K.

c. Reduction by hydrazine hydrate

The reduction was done using a procedure followed by Gorokhov et. al. (1979). An aqueous solution of 10 % hydrazine hydrate (30 ml) was added to a slurry of impregnated support in dilute hydrochloric acid. The addition was carried out with stirring and was completed in one hour. The catalyst was filtered and washed with distilled water several times. It was dried in a vacuum desicator at 298, K.

d. Reduction by formaldehyde and potassium hydroxide

The method followed was similar to that used by Hrusovosky and Vojtko (1974). The reduction was carried out at 313, K. Alkaline formaldehyde solution was added to the slurry of impregnated support in distilled water with stirring. The stirring was continued for two hours after complete addition. The catalyst was filtered out and washed with distilled water till the filtrate showed no traces of the alkali. It was dried under vacuum at 298, K.

e. Reduction by hydrogen (Liquid phase)

The reduction was carried out by the procedure of Zeliger (1967). The metal salt on support was reduced by bubbling hydrogen gas through a slurry of impregnated support in distilled water for three hours. The catalyst was filtered from the solution and after several washings with distilled water, dried at 298, K in a vacuum desicator.

The complete reduction of rhodium compounds to rhodium metal was confirmed, in each of the above preparations, by ESCA technique.

2.2.4 Experimental Setup

The oxidative carbonylation experiments were carried out in a 300 ml stirred autoclave made of SS-316 (supplied by Parr Instrument Co, USA). The reactor was provided with automatic temperature control, a cooling coil, variable agitation speeds and devices for sampling of gas and liquids. The gases were filled into the reactor from a reservoir vessel via a constant pressure regulator. The progress of the reaction was monitored by observing the depletion of pressure in the reservoir vessel. A schematic diagram of the experimental setup is shown in Fig 2.1.

2.2.5 Experimental Procedure

- **Activity and Selectivity Studies**

  In a typical experiment, 0.548, kmol/m^3 of aniline, 1.73, kmol/m^3 of ethanol, 0.4, kg/m^3 of 5% Rh/C catalyst, 8.73×10^{-3}, kmol/m^3 of LiI and solvent ethyl acetate were charged to the reactor and made up to 1×10^{-4}, m^3 volume. The contents were flushed with nitrogen and heated to 443, K. After the desired temperature was attained, a mixture of carbon monoxide and oxygen in a ratio of 14:1 was introduced into the reactor to a desired pressure (proper

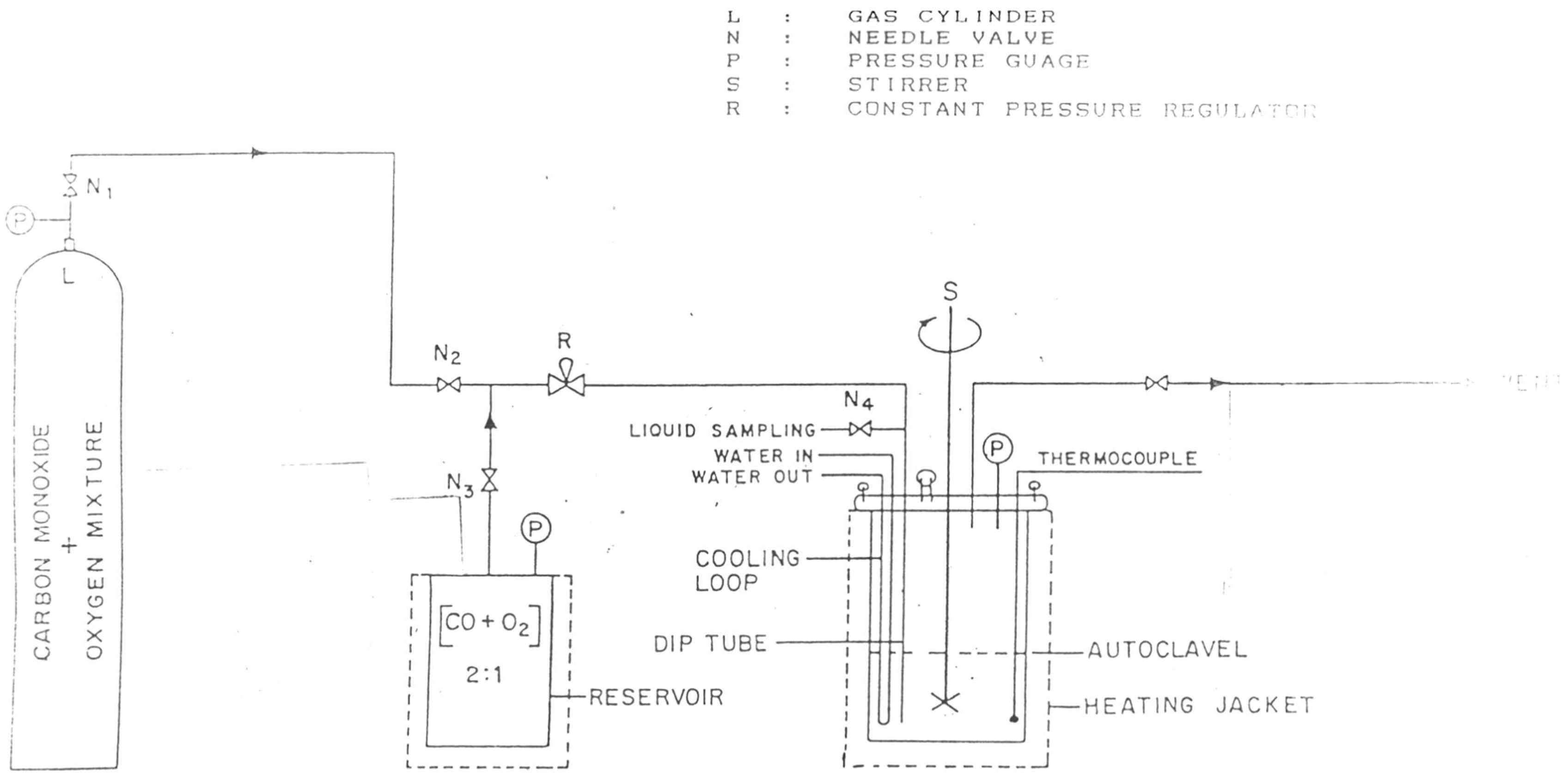


FIGURE 2.1 SCHEMATIC OF EXPERIMENTAL SET UP FOR THE OXIDATIVE CARBONYLATION REACTIONS

safety precautions were taken against explosion hazards in handling carbon monoxide and oxygen mixtures). During an experiment, the pressure in the reactor was maintained constant by supplying carbon monoxide and oxygen in a stoichiometric ratio from a reservoir vessel. Most reactions were carried out for a period of 2 hours. At the end of the reaction, both gas and liquid samples were analyzed. In order to account for carbon monoxide and oxygen consumed, the gas content in the reactor was transferred to a receiver at atmospheric pressure and the volume recorded. This gas was analyzed for carbon monoxide, oxygen and carbon dioxide by gas chromatography.

- **Recycle Experiments**

For the purpose of catalyst recycle studies, the catalyst from a fresh experiment was separated from reaction mixture by filtration. It was washed with solvent, ethyl acetate and then with acetone. The catalyst was dried and then weighed. This catalyst was reused for the next reaction. For the whole set of experiments the loss in weight in transferring and handling was less than 5-6%.

- **Kinetic Runs**

The kinetic runs were carried out by charging known quantities of catalyst, 5 % Rh/C, promoter, LiI, reactants, aniline and ethanol, and solvent ethyl acetate into the autoclave making a total volume of 1×10^{-4} m^3. The reactor was flushed with nitrogen and was heated to the required temperature. After the reaction temperature was attained, a gas mixture of carbon monoxide and oxygen in the ratio of 7:1 was introduced into the reactor to the desired pressure. The pressure in the reactor was kept constant with the help of a constant pressure regulator and a reservoir vessel with gas mixture of carbon monoxide and oxygen in the ratio of 2:1. The reaction was monitored by measuring pressure drop in the reservoir vessel. At the end of the reaction the analysis of gas and liquid components was carried out. The material balance of liquid phase components was estimated by analyzing the initial and final samples. The reactions wherein the material balance was more than 95% were only used for the kinetic study.

2.2.6 Analytical Methods

- **Gas Chromatography**

The liquid and gaseous components of the reaction were analyzed using a Varian 3600 Gas Chromatograph. The liquid phase components, aniline, ethanol and ethyl phenyl carbamate, were analyzed using a 12%, SE-30 on chromosorb W, column of 6 feet in length. A flame ionization detector was for the analysis. The other conditions used for analysis are presented in Table 2.1. The analysis of gaseous components, carbon monoxide, oxygen and carbon dioxide, was done on two separate columns. For carbon monoxide and oxygen, 5A-molecular sieves column of six feet length was used, while for carbon monoxide and carbon dioxide Porapak-Q column of six feet length was used. A

TABLE 2.1

GAS CHROMATOGRAPHY CONDITIONS FOR ANALYSIS OF LIQUID COMPONENTS

Sr.No.		Conditions
1.	Column	6', 12% SE-30 on Chromosrb W
2.	Carrier gas	Nitrogen, 20 ml/min.
3.	Injector temperature	533 K
4.	Oven Temperature	
	Initial	373 K for 4 mins
	Final	433 K for 8 mins
	Rate of heating	30 K/min
5.	FID Temperature	553 K

thermal conductivity detector was used for gas analysis. The other conditions used for analysis are presented in Table 2.2.

- **High Performance Liquid Chromatography**

  High performance liquid chromatography analysis of diphenyl urea was done using a Hewlet Packard HPLC with a UV detector. The column used was a ν-Bondopak column, with a mobile phase comprising of 62%, methanol in 0.1, M aqueous sodium acetate solution and the wavelength of the detection was 254 nm.

2.3 RESULTS AND DISCUSSIONS

2.3.1 Activity and Selectivity of Rhodium Catalysts

Several experiments were carried out to investigate the role of catalyst and reaction conditions on the average activity and selectivity of Rh catalyzed oxidative carbonylation of aniline. The average activity of the catalyst was defined as:

$$\text{Average activity} = \left[\frac{\text{Amount of aniline reacted}}{(\text{ Weight of catalyst})\ (\text{ Time of reaction})} \right], \ \frac{\text{kmol}}{\text{kg hr}} \qquad (2.3)$$

The selectivity of the oxidative carbonylation reaction of aniline was defined with respect to the consumption of aniline and carbon monoxide as follows:

Selectivity with respect to aniline consumed.

TABLE 2.2

GAS CHROMATOGRAPHY CONDITIONS FOR ANALYSIS OF GASEOUS COMPONENTS

Sr.No.		CO and CO_2	CO and O_2
1.	Column	12' Molecular sieves	Porapak Q
2.	Carrier Gas	Hydrogen	Hydrogen
	Flow	20, ml/min	20, ml/min
3.	Injection Temperature	323 K	323 K
4.	Oven Temperature	303 K	303 K
5.	TCD Temperature	383 K	383 K
6.	Filament Temperature	433 K	433 K

$$\text{Selectivity}_{\text{EPC}}\ (\%) = \frac{\text{EPC formed}}{\text{aniline reacted}} \times 100, \left(\frac{\text{kmol}}{\text{kmol}}\right) \tag{2.4}$$

$$\text{Selectivity}_{\text{DPU}}\ (\%) = \frac{\text{DPU formed}}{\text{2 aniline reacted}} \times 100, \frac{\text{kmol}}{\text{kmol}} \tag{2.5}$$

Selectivity with respect to carbon monoxide consumed.

$$\text{Selectivity}_{\text{EPC}}\ (\%) = \frac{\text{EPC formed}}{\text{CO reacted}} \times 100, \frac{\text{kmol}}{\text{kmol}} \tag{2.6}$$

$$\text{Selectivity}_{\text{DPU}}\ (\%) = \frac{\text{DPU formed}}{\text{CO reacted}} \times 100, \frac{\text{kmol}}{\text{kmol}} \tag{2.7}$$

$$\text{Selectivity}_{\text{CO}_2}\ (\%) = \frac{\text{CO}_2\text{ formed}}{\text{CO reacted}} \times 100, \frac{\text{kmol}}{\text{kmol}} \tag{2.8}$$

2.3.2 Preliminary Reactions

The feasibility of rhodium catalysts for oxidative carbonylation of aniline was investigated at 443, K and the main observations summarized are below.

- The oxidative carbonylation of aniline with rhodium catalysts alone proceeds with very low rates but addition of sodium iodide, as a promoter, enhances the rate and conversion of aniline significantly.

- Sodium iodide alone has no catalytic activity.

Various homogenous and heterogeneous catalysts were screened with sodium iodide as the promoter and the results are presented in Table 2.3. The catalysts screened were $RhCOCl(PPh_3)_2$, $HRhCO(PPh_3)_3$, $Rh(CO)_2(acac)$, $Rh(py)_3Cl_3$ and 5 % Rh/C. It was observed that the activity of 5 % Rh/C catalyst (0.5 kmol/kg/hr), was higher than the activity of all the homogenous catalysts screened (between 0.053 to 0.263 kmol/kg/hr) and the selectivity to ethyl phenyl carbamate was also lower with homogeneous catalysts (< 75 %) compared to 96.7 % for heterogeneous 5 % Rh/C catalyst. Hence, for further investigations were carried out using heterogeneous Rh catalyst.

A concentration time profile of a typical experiment is shown in Fig 2.2. The results indicate the following:

- Nearly 100% conversion of aniline is achievable.
- The main products are diphenyl urea, ethyl phenyl carbamate and carbon dioxide.
- The formation of diphenyl urea is very high in the initial stages of the reaction and decreases with time, with the formation ethyl phenyl carbamate.
- The formation of carbon dioxide picks up with decrease in the concentration of aniline.

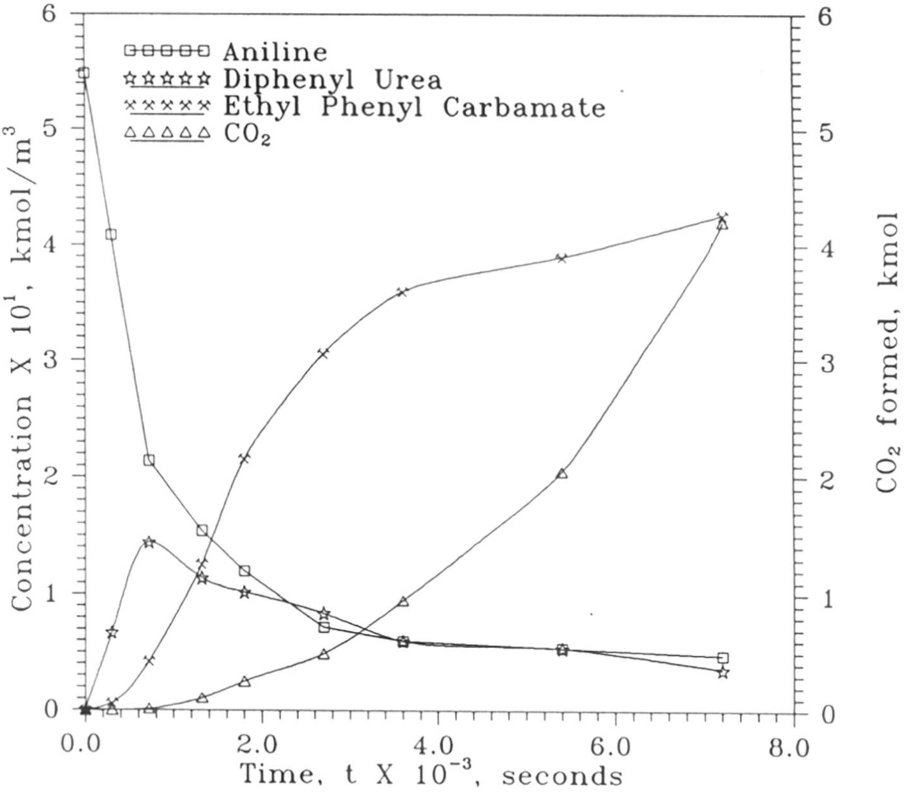


FIGURE 2.2 CONCENTRATION TIME PROFILE FOR THE OXIDATIVE CARBONYLATION OF ANILINE

Reaction conditions:

Aniline : 0.55, kmol/m^3;
Ethanol : 1.73, kmol/m^3;
Catalyst, 5 % Rh/C : 0.4, kg/m^3;
LiI : 8.7×10^{-3}, kmol/m^3;
Carbon monoxide : 4.48, MPa;
Oxygen : 0.32, MPa;
Temperature : 443, K;
Solvent : Ethyl acetate;
Agitation speed : 600, rpm.

TABLE 2.3

SCREENING OF CATALYSTS

Sr. No.	Catalyst	Average activity	Selectivity Aniline based	
			DPU	EPC
		kmol/kg/hr	%	%
1	$Rh(CO)_2(acac)$	0.2685	36.2	62.3
2	$HRh(CO)\ (PPh_3)_3$	0.0578	30.1	68.4
3	$Rh(CO)Cl(PPh_3)_2$	0.0685	24.8	74.2
4	$Rh(Py)_3Cl_3$	0.122	33.2	64.7
5	5 % Rh/C	0.503	3.7	94.7

Reaction Conditions
Aniline : 0.55, $kmol/m^3$; NaI : 8.7×10^{-3}, $kmol/m^3$;
Ethanol : 1.73, $kmol/m^3$; P_{CO} : 4.48, MPa;
Catalyst : Equivalent to 0.02 gm of rhodium metal,
P_{O_2} : 0.32, MPa; Agitation speed : 600, rpm;
Solvent : Ethyl acetate; Temperature : 443, K;
DPU : Diphenyl urea, EPC : Ethyl phenyl carbamate.

The above observations indicate that the following reactions take place.

$$2\ C_6H_5NH_2 + CO + \tfrac{1}{2}\ O_2 \longrightarrow C_6H_5NHCONHC_6H_5 + H_2O \qquad (2.9)$$

$$C_6H_5NHCONHC_6H_5 + C_2H_5OH \longrightarrow C_6H_5NHCOOC_2H_5 + C_6H_5NH_2 \qquad (2.10)$$

$$CO + \tfrac{1}{2}\ O_2 \longrightarrow CO_2 \qquad (2.11)$$

The material balance of the reactants, aniline, CO, O_2 and ethanol, consumed and the products, diphenyl urea, ethyl phenyl carbamate and CO_2, formed matched to the extent of 95% and above. However, the selectivity based on carbon monoxide and oxygen consumed was found to be strongly affected by the formation of carbon dioxide via oxidation of carbon monoxide. In reactions with high conversion of aniline, the selectivity for diphenyl urea and ethyl phenyl carbamate together based on carbon monoxide consumed was about 40%. No leaching of rhodium metal was observed.

To determine the role of supported Rh catalysts the following reactions were carried out with and without Rh/C and sodium iodide catalyst system.

- The oxidative carbonylation of aniline was carried out at 373, K with dimethyl formamide as a solvent. The conversion of aniline and selectivity to diphenyl urea was $\approx$ 100 %, in the presence of 5% Rh/C-NaI catalyst system, while no reaction occurred in absence of a catalyst.

- At 443, K with ethanol as a solvent, the conversion of aniline and selectivity to ethyl phenyl carbamate was ≈ 100 % in presence of 5% Rh/C-NaI, while no reaction occurred in the absence of 5 % Rh/C-NaI catalyst system.

- The reaction of diphenyl urea with ethanol at 443, K to ethyl phenyl carbamate was found to be independent of 5 % Rh/C-NaI catalyst.

The conclusions which can be drawn from these preliminary reactions are:

- The oxidative carbonylation of aniline is catalyzed by rhodium and an alkali metal iodide as a catalyst system.

- Heterogeneous catalysts were found to be more active than the homogeneous catalysts.

- The reaction proceeds thorough formation of diphenyl urea.

- Ethanolysis of diphenyl urea to ethyl phenyl carbamate is not catalyzed by rhodium or alkali metal iodides.

2.3.3 Activity and Selectivity of supported Rh catalysts

2.3.3.1 Effect of reducing agents

The supported rhodium catalysts were prepared by reducing the impregnated catalyst using different reducing agents like sodium borohydride, hydrazine hydrate, formaldehyde and potassium hydroxide, methanol and hydrogen. The details of the various methods used are given in Section 2.2.3. The results are presented in Table 2.4. The activity and selectivity to ethyl phenyl carbamate (0.621 kmol/kg/hr and 96.7 % respectively) was found to be highest for the catalyst reduced by sodium borohydride and the lowest (0.530 kmol/kg/hr and 90.5 % respectively) for catalyst reduced with hydrogen. The activity and selectivity varied in a decreasing order of the reducing agents as:

Sodium Borohydride >methanol > hydrazine hydrate > alkaline formaldehyde > hydrogen

The selectivity for carbon monoxide oxidation to carbon dioxide was not affected by the use of different reducing agents. For all subsequent catalyst preparations, sodium borohydride was used as a reducing agent.

2.3.3.2 Effect of Catalyst Precursors

In the present work supported rhodium catalysts containing 5% Rh (w/w) were prepared using different types of Rh salts/complexes as precursors. The different

TABLE 2.4

EFFECT OF REDUCING AGENTS

Run No.	Reducing agent	Average activity	Selectivity				
			CO based			Aniline based	
		kmol/kg catalyst/hr	DPU %	EPC %	CO_2 %	DPU %	EPC %
1	$RhCl_3\ 3H_2O$/A	0.621	4.0	37.0	55.5	1.9	96.7
2	$RhCl_3\ 3H_2O$/B	0.547	4.7	36.5	55.4	2.3	94.9
3	$RhCl_3\ 3H_2O$/C	0.587	4.8	37.3	55.9	3.6	94.8
4	$RhCl_3\ 3H_2O$/D	0.576	5.6	33.6	56.3	5.7	93.2
5	$RhCl_3\ 3H_2O$/E	0.530	6.5	30.4	56.8	6.9	90.5

A : Sodium borohydride; B : Methanol; C : Hydrazine hydrate;
D : Formaldehyde and Potassium hydroxide; E : Hydrogen.

Reaction Conditions
Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3; Catalyst, 5% Rh/C : 0.4, kg/m^3;
LiI : 8.7, $\times 10^{-3}$, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Agitation **speed** : 600, rpm; Solvent : Ethyl acetate;
Temperature : 443, K;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

rhodium salts and complexes used were rhodium chloride trihydrate $RhCl_3 \cdot 3H_2O$, rhodium dicarbonyl acetylacetonate $Rh(CO)_2(acac)$, rhodium chloro bis(triphenyl phosphine) ($RhClCO(PPh_3)_2$) and hydrido carbonyl tris(triphenyl phosphine) ($HRhCO(PPh_3)_3$) The catalyst precursors $Rh(CO)_2(acac)$, ($RhCOCl(PPh_3)_2$) and ($HRhCO(PPh_3)_3$) were prepared and the procedure as described in Section 2.2.2. The results are presented in Table 2.5.

The activity of supported Rh catalysts and selectivity to ethyl phenyl carbamate and carbon dioxide, were found to be independent of the type of catalyst precursors used. Hence, rhodium trichloride was used as a precursor for further catalyst preparations.

2.3.3.3 Effect of Support

The role of supports was studied using activated C, alumina, Silica gel, titanium dioxide, calcium carbonate, ZSM-5 and molecular sieves (5A) in the preparation of 5% Rh/support catalysts. The results on the performance of these catalysts are presented in Table 2.6. It was observed that Rh on activated carbon gave highest activity (0.621 kmol/kg/hr) for oxidative carbonylation of aniline, while molecular sieves (5A) based catalyst showed the lowest activity (0.12 kmol/kg/hr). The selectivity based on aniline consumed was not affected by the type of support used, but the formation of CO_2 varied. Rh/molecular sieves catalyst gave the lowest ethyl phenyl carbamate selectivity based on CO consumed. The selectivity to ethyl

TABLE 2.5

EFFECT OF CATALYST PRECURSORS

Run No.	Catalyst Precursor	Average activity	Selectivity				
			CO based			Aniline based	
		kmol/kg catalyst/hr	DPU %	EPC %	CO_2 %	DPU %	EPC %
1	$RhCl_3$ $3H_2O$	0.621	4.0	37.0	55.5	1.9	96.7
2	$Rh(CO)_2(acac)$	0.613	5.2	37.6	54.6	2.0	95.8
3	$Rh(CO)Cl(PPh_3)_2$	0.603	4.9	38.3	54.8	2.3	94.8
4	$HRh(CO)(PPh_3)_3$	0.623	5.0	38.0	55.7	2.2	95.6

Reaction Conditions
Aniline : 0.55, kmol/m^3;   Ethanol : 1.73, kmol/m^3;
LiI : 8.7×10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Agitation speed : 600, rpm;   Solvent : Ethyl acetate;   Temperature : 443, K;
DPU : Diphenyl urea;   EPC : Ethyl phenyl carbamate.

TABLE 2.6

EFFECT OF CATALYST SUPPORTS

Run No.	Support	Average activity	Selectivity				
			CO based			Aniline based	
		kmol/kg catalyst/hr	EPC %	DPU %	CO_2 %	DPU %	EPC %
1	Carbon	0.621	37.0	4.0	55.5	1.9	96.7
2	Silica	0.157	25.1	2.9	72.6	5.4	92.1
3	Alumina	0.220	26.0	3.8	70.4	5.1	95.4
4	ZSM-5	0.610	52.4	4.6	40.2	5.2	90.4
5	Calcium Carbonate	0.557	30.5	2.6	60.5	3.6	97.3
6	Moleculear Sieves	0.120	8.3	1.1	85.5	4.5	94.2
7	Titania	0.450	23.0	4.8	58.3	3.2	94.7

Reaction Conditions

Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3;
LiI : 8.7×10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Solvent : Ethyl acetate; Agitation speed : 600, rpm; Temperature : 443, K;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

phenyl carbamate, based on CO consumed, decreased in the order C > ZSM-5 > $CaCO_3$ > TiO_2 > Al_2O_3 > SiO_2 > Molecular sieves. Thus, activated C supported Rh catalyst was found to be the most optimal one.

2.3.3.4 Rhodium Content

The effect of Rh content was studied by preparing catalysts with 0.2, 1 and 5% Rh. The results are shown in Table 2.7. The activity of these catalysts decreased with decreasing Rh content, but the specific activity as defined below

Specific activity =

$$\left[\frac{\text{aniline reacted}}{(\text{wt of Rh metal in catalyst charged})\ (\text{time of reaction})}\right],\quad \frac{\text{kmol}}{\text{kg(Rh) hr}} \tag{2.12}$$

was found to be highest for 0.2% Rh/C catalyst (9.11 kmol/kg rhodium/hr) and decreased with increasing Rh content (from 9.11 to 1.65 kmol/kg rhodium/hr). Selectivity of ethyl phenyl carbamate based on aniline was unaffected by a change in Rh content but the formation of CO_2 was found to increase with decrease in Rh content (from 55.5 to 83.5 %).

2.3.3.5 Effect of promoters

The role of promoters on the 5 % Rh/C catalyzed oxidative carbonylation of aniline was investigated by screening a series of metal halide promoters.

TABLE 2.7

EFFECT OF RHODIUM CONTENT

Run No.	Metal Content	Average activity	Specific activity	Selectivity				
				CO based			Aniline based	
	(%)	kmol/kg catalyst/hr	kmol/kg Rh/hr	DPU %	EPC %	CO_2 %	DPU %	EPC %
1	5	0.620	1.65	4.0	37.0	55.5	1.9	96.7
2	1	0.463	4.63	0.5	19.8	68.1	4.2	87.2
3	0.2	0.182	9.11	0.8	15.8	83.5	7.9	80.8

Reaction Conditions
Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3; Catalyst, Rh/C : 0.4, kg/m^3;
LiI : 8.7×10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Solvent : Ethyl acetate; Agitation speed : 600, rpm; Temperature : 443, K;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

- **Alkali metal salts:**

The iodides, bromides and chlorides of lithium, sodium and potassium were screened as promoters. The results are presented in Table 2.8. It was observed that alkali metal iodide promoters are more effective compared to bromides or chlorides. The bromides were more active than chlorides. The activity as well as the selectivity to ethyl phenyl carbamate decreased in following order for the alkali metal iodides.

Lithium > Sodium > Potassium.

for equivalent iodide content.

For the anions, of promoters the trend in a decreasing order was as follows:

Iodide > Bromide > Chloride

From the above study, lithium iodide was found to be the best promoter with 5 % Rh/C catalyst.

- **Other iodide salts:**

Molecular iodine, iodides of tin, copper and nickel were also screened as promoters. The results are presented in Table 2.9 and the effect on the activity and selectivity to ethyl phenyl carbamate is summarized below. Though high activity (0.474 kmol/kg/hr) was obtained with molecular iodine as a promoter, the selectivity for ethyl phenyl carbamate was lower (59.6 %). The activity of copper and nickel iodides was lower (≈ 0.245 kmol/kg/hr) than iodine, but

TABLE 2.8

EFFECT OF ALKALI METAL PROMOTERS

Run No.	Promoter	Average activity	Selectivity				
			CO based			Aniline based	
			DPU	EPC	CO_2	DPU	EPC
		kmol/kg catalyst/hr	%	%	%	%	%
1	-	0.058	0.9	3.2	93.2	20.0	67.3
2	Lithium Iodide	0.620	4.0	37.0	55.5	1.9	96.7
3	Sodium Iodide	0.503	5.3	36.2	56.4	3.7	94.6
4	Potassium Iodide	0.496	5.7	33.3	56.6	57.4	42.1
5	Lithium Bromide	0.394	5.4	22.9	60.2	45.4	53.9
6	Lithium Chloride	0.313	6.7	18.5	69.6	48.7	50.6
7	Sodium Chloride	0.138	7.3	6.9	80.0	64.3	32.4

Reaction Conditions
Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3; Catalyst, 5 % Rh/C : 0.4, kg/m^3;
Promoter concentration : 8.7×10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Solvent : Ethyl acetate; Agitation speed : 600, rpm; Temperature : 443, K;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

TABLE 2.9

EFFECT OF OTHER PROMOTERS

Run No.	Promoter	Average activity	Selectivity				
			CO based			Aniline based	
			DPU	EPC	CO_2	DPU	EPC
		kmol/kg catalyst/hr	%	%	%	%	%
1	Iodine	0.474	22.0	23.4	48.5	5.6	59.6
2	Copper Iodide	0.226	2.73	12.4	75.6	30.3	65.3
3	Tin Iodide	0.480	4.4	33.5	53.0	2.5	90.2
4	Nickel Iodide	0.289	3.8	16.7	62.4	29.8	68.8

Reaction Conditions
Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3; 5 % Rh/C Catalyst : 0.4, kg/m^3;
Promoter concentration : 8.7 × 10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Agitation speed : 600, rpm; Temperature : 443, K; Solvent : Ethyl acetate;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

the selectivity to ethyl phenyl carbamate was higher (≈ 68 %). With SnI_2, the conversion of aniline was lower (≈ 70 %), while the selectivity to ethyl phenyl carbamate was high (90.2 %). This study indicates that for the oxidative carbonylation of aniline, 5 % Rh/C with LiI or SnI_2 gave the highest activity and selectivity for ethyl carbamate.

2.3.3.6 Effect of Co-catalyst

In the present study, a combined influence of metal iodide promoters was investigated. For this purpose, the performance of 5% Rh/C+LiI+$CoCl_2$ and 5% Rh/C+SnI_2+$CoCl_2$ combinations as catalysts was studied and the results are compared with those without $CoCl_2$ (Table 2.10). The addition of cobalt chloride to 5 % Rh/C - LiI catalyst system was found to decrease the activity of catalyst marginally (from 0.62 to 0.517 kmol/kg/hr), however, the addition to 5 % Rh/C- SnI_2 catalyst system was found to enhance the activity of the catalyst from 0.48 to 0.61 kmol/kg/hr. The selectivity to ethyl phenyl carbamate was around 90 %, and was not affected by the addition of cobalt chloride. Further reactions were carried out to investigate the effect of concentration of cobalt chloride on 5 % Rh/C- SnI_2 catalyst system. The activity and selectivity to ethyl phenyl carbamate of the catalyst system was found to pass through a maximum at a concentration of 0.058 kg/m^3 of cobalt chloride (Table 2.11). Manganese, tin and nickel chlorides were also observed to enhance the activity of 5% Rh/C-SnI_2 catalyst system (Table 2.12). The

TABLE NO. 2.10

EFFECT OF CO-CATALYST

Run No.	Catalyst system	Average activity	Selectivity				
			CO based			Aniline based	
		kmol/kg catalyst/hr	DPU %	EPC %	CO_2 %	DPU %	EPC %
1	Rh/C LiI	0.620	4.0	37	55.5	1.9	96.7
2	Rh/C SnI_2	0.480	4.4	33.5	53.03	8.4	90.2
3	Rh/C LiI $CoCl_2$	0.517	4.7	35.74	45.57	5.6	86.5
4	Rh/C SnI_2 $CoCl_2$	0.611	5.4	43.36	50.97	11.21	88.72

Reaction Conditions
Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3; Catalyst, 5% Rh/C : 0.4, kg/m^3;
LiI or SnI_2 : 8.7×10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Solvent : Ethyl acetate; Agitation speed : 600, rpm; Temperature : 443, K;
DPU : Diphenyl urea; EPC: Ethyl phenyl carbamate.

TABLE NO. 2.11

EFFECT OF COBALT CHLORIDE CONCENTRATION

Run No.	Cobalt chloride concentration kmol/m^3	Average activity kmol/kg catalyst/hr	Selectivity				
			CO based			Aniline based	
			DPU %	EPC %	CO_2 %	DPU %	EPC %
1	0	0.480	4.4	33.5	53.0	8.4	90.2
2	0.015	0.563	4.8	37.2	48.8	15.2	86.5
3	0.029	0.573	5.2	37.7	47.2	13.2	87.6
4	0.058	0.611	5.5	43.4	50.97	11.2	88.7
5	0.116	0.577	5.3	42.7	45.5	13.6	86.3
6	0.232	0.536	5.3	41.7	45.6	12.6	83.7

Reaction Conditions
Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3; Catalyst, 5 % Rh/C : 0.4, kg/m^3;
SnI_2 : 8.7 × 10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Solvent : Ethyl acetate; Agitation speed : 600, rpm; Temperature : 443, K;
DPU : Diphenyl urea, EPC: Ethyl phenyl carbamate.

TABLE NO. 2.12

EFFECT OF OTHER METAL CHLORIDES

Run No.	Catalyst system	Average activity	Selectivity				
			CO based			Aniline based	
		kmol/kg catalyst/hr	DPU %	EPC %	CO_2 %	DPU %	EPC %
1	Rh/C SnI_2 $MnCl_2$	0.652	30.5	28.7	36.2	41.7	58.3
2	Rh/C SnI_2 $SnCl_2$	0.515	18.8	45.3	37.7	22.5	75.6
3	Rh/C SnI_2 $NiCl_2$	0.533	38.2	10.5	40.2	80.2	18.6

Reaction Conditions
Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3; Catalyst, 5 % Rh/C : 0.4, kg/m^3;
SnI_2 : 8.7×10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Solvent : Ethyl acetate; Agitation speed : 600, rpm; Temperature : 408, K;
DPU : Diphenyl urea, EPC: Ethyl phenyl carbamate.

enhancement of activity in decreasing order for different co-catalysts is:

$MnCl_2 > SnCl_2 > NiCl_2 > CoCl_2$

The selectivity to ethyl phenyl carbamate changed in the following order

$SnCl_2 > CoCl_2 > MnCl_2 > NiCl_2$

The selectivity to carbon dioxide was found to be independent of the co-catalysts. As the effect of co-catalysts screened was not significant, for further reactions co-catalysts were not used.

2.3.3.7 Effect of Solvents

The effect of various solvents on the oxidative carbonylation of aniline was studied. The solvents used were benzene, toluene, p- xylene, chlorobenzene, dimethyl formamide, ethanol, ethyl acetate, methyl acetate, acetonitrile and water. In reactions with solvents other than ethanol, the concentration of ethanol was thrice the molar quantity of aniline taken. The results are presented in Table 2.13.

The activity of the 5 % Rh/C catalyst was found to be comparable for all the solvents except the highly polar solvents like dimethyl formamide, acetonitrile and water. In water the oxidative carbonylation reaction did not proceed and charring of aniline was observed. In dimethyl formamide and acetonitrile the selectivity to ethyl phenyl carbamate was lower (23% and 19 % respectively), but the selectivity

TABLE 2.13

EFFECT OF SOLVENTS

Run No.	Solvents	Time	Average activity	Selectivity Aniline based	
				DPU	EPC
		min	kmol/kg /hr	%	%
1	Benzene	60		35.8	63.2
		120	0.609	19.2	72.8
2	p-Xylene	60		40.2	57.4
		120	0.616	17.5	74.8
3	Toluene	60		45.6	50.3
		120	0.622	26.2	72.8
4	Chlorobenzene	60		32.4	64.7
		120	0.632	17.5	73.0
5	Ethanol	60		23.4	75.3
		120	0.630	-	97.8
6	Methyl acetate	60		50.4	37.5
		120	0.596	34.5	49.8
7	Ethyl acetate	60		10.2	81.0
		120	0.620	1.9	96.7
8	Acetonitrile	60		87.3	7.3
		120	0.514	76.1	19.9
9	Dimethyl formamide	60		85.3	10.2
		120	0.548	70.8	23.3
10	Water	60	-	-	-
		120	-	-	-

Reaction Conditions
Aniline : 0.55, kmol/m^3; Catalyst, 5 % Rh/C : 0.4, kg/m^3;
LiI : 8.7×10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Agitation speed : 600, rpm; Temperature : 443, K;
Ethanol concentration in other solvents : 1.73, kmol/m^3;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

to diphenyl urea was higher (71% and 76 % respectively). In all other solvents the selectivity to ethyl phenyl carbamate was higher (60 to 96 %). With ethanol as a solvent, the selectivity for ethyl phenyl carbamate was highest (97.8 %), though side products such as, N-ethyl aniline was also observed to be formed in small quantities. The selectivity to ethyl phenyl carbamate was found to decrease in the following order for the various solvents screened:

Ethanol $\approx$ ethyl acetate $>$ p-xylene $>$ chlorobenzene $>$ benzene $\approx$ toluene $>$ methyl acetate $>$ dimethyl formamide $>$ acetonitrile

A surprising observation was that the oxidation of carbon monoxide to carbon dioxide was found to be independent of the solvent used. Ethyl acetate was used as a solvent for further reactions as the selectivity to ethyl phenyl carbamate was high (96.7 %) and no side reactions were observed.

2.3.3.8 Effect of Pretreatment

The pretreatment of catalyst with reactant often has influence on the rate and selectivity in many reactions and such effects have already been reported in hydrogenation (Chaudhari et. al. (1984)) and carbonylation reactions (Gupte and Chaudhari (1988)). To study the effect of pretreatment on the activity and selectivity behavior of 5% Rh/C catalyst, pretreatment with aniline, carbon monoxide, oxygen, hydrogen and carbon dioxide was carried out. The catalyst was pretreated in the reactor for one hour in the presense of solvent, ethyl acetate, at 373, K. The results are presented in Table 2.14. When the catalyst was pretreated with hydrogen, a significant increase in the initial activity (2.1, kmol/kg/hr) compared to that without any pretreatment (1.75, kmol/kg/hr) was observed, while pretreatment with other substances affected the initial activity marginally ($\approx$ 1.8, kmol/kg/hr). The selectivity to both ethyl phenyl carbamate and carbon dioxide was unaffected by the pretreatment. As the effect of pretreatment of 5 % Rh/C catalyst was marginal, further reactions were carried out without any pretreatment.

2.3.3.9 Reusability of Catalysts

In order to investigate the constancy of the catalytic activity and reusability, a few experiments were carried out in which the catalyst from the first batch was recycled. The details of the experimental procedure are given in Section 2.2.5. and the results presented in Table 2.15 It was observed that 5 % Rh/C catalyst could be reused at least seven times without significant loss of activity and selectivity for ethyl phenyl carbamate (0.62 kmol/kg/hr and 96.7 % respectively). The activity of the used catalyst after the first recycle was found to increase to about 20 % of the original activity, indicating a change in the surface crystal structure of the catalyst.

2.3.3.10 Characterization of Catalysts

In order to understand the nature of changes undergoing during the oxidative carbonylation, some catalyst samples (Rh/C) were characterized by ESCA, XRD and TEM techniques. The details of characterization of 5% Rh/C catalyst are given

TABLE 2.14

EFFECT OF CATALYST PRETREATMENT

Run No.	Pretreatment with	Contact time	Initial activity	Selectivity				
				CO based			Aniline based	
				DPU	EPC	CO_2	DPU	EPC
		min	kmol/kg/hr	%	%	%	%	%
1	-	30	1.75	-	-	-	32.1	66.5
	-	120	0.62	4.0	37.0	55.5	1.9	96.7
2	Carbon monoxide	30	1.93	-	-	-	28.2	69.7
		120	0.63	4.2	36.9	54.3	1.8	96.1
3	Oxygen	30	1.87	-	-	-	29.7	69.7
		120	0.62	4.5	37.2	55.3	1.9	96.4
4	Carbon Dioxide	30	1.90	-	-	-	28.7	70.2
		120	0.61	3.5	36.4	56.3	1.6	97.4
5	Hydrogen	30	2.10	-	-	-	25.5	73.6
		120	0.62	2.4	37.7	57.3	1.3	96.8
6	Aniline	30	1.79	-	-	-	30.9	67.9
		120	0.62	5.6	34.6	54.5	3.3	94.5

Reaction Conditions

Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3; Catalyst, 5 % Rh/C : 0.4, kg/m^3;
LiI : 8.7×10^{-3}, kmol/m^3; Solvent : Ethyl acetate; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Agitation speed : 600, rpm; Temperature : 443, K;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

TABLE 2.15

CATALYST REUSABILITY

Run No.	Number of recycles	Average activity kmol/kg catalyst/hr	Selectivity Aniline based	
			DPU %	EPC %
1	0	0.62	1.9	96.7
2	1	0.79	1.0	97.9
3	2	0.76	1.3	96.6
4	3	0.73	1.7	96.4
5	4	0.71	1.9	96.3
6	5	0.70	2.2	95.8
7	6	0.66	2.3	94.9
8	7	0.63	2.5	92.4

Reaction Conditions
Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3;
Catalyst, 5 % Rh/C : 0.4, kg/m^3; LiI : 8.7×10^{-3}, kmol/m^3;
P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Solvent : Ethyl acetate; Agitation speed : 600, rpm;
Temperature : 443, K;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

below.

A. ESCA

The ESCA spectrum of the catalysts were determined by using a VG Scientific ESCA 3 Mk spectrophotometer, using a monochromated Al Kα radiation. The ESCA of fresh and used catalyst are shown in Fig 2.3 (A) and (B). The spectrum shows that the peak heights at 307 and 312.5 eV values in both 2.3 (A) and 2.3(B) are similar, thus indicating the presense of rhodium in zero valent state. Obviously, Rh° undergoes change in oxidation state during the reaction, but the transient species may not be stable enough and hence reduce to zero valent state once the CO/O_2 atmosphere is removed.

B. TEM

The catalysts were examined by model 1200 JEOL Japan, transmission electron microscope (TEM), with a 120 KeV electron source. The micrographs of fresh and used catalyst are shown in Figs 2.4 and 2.5 respectively. The micrographs indicate that the size of rhodium metal crystallite on the support is reduced during the reaction. This can be interpreted as a result of redispersion of Rh metal, which is also observed earlier under CO environment [Basu et. al. (1988), Bergeret et. al. (1987), Buchanan et. al. (1990), Takahashi et. al. (1992, 1993)].

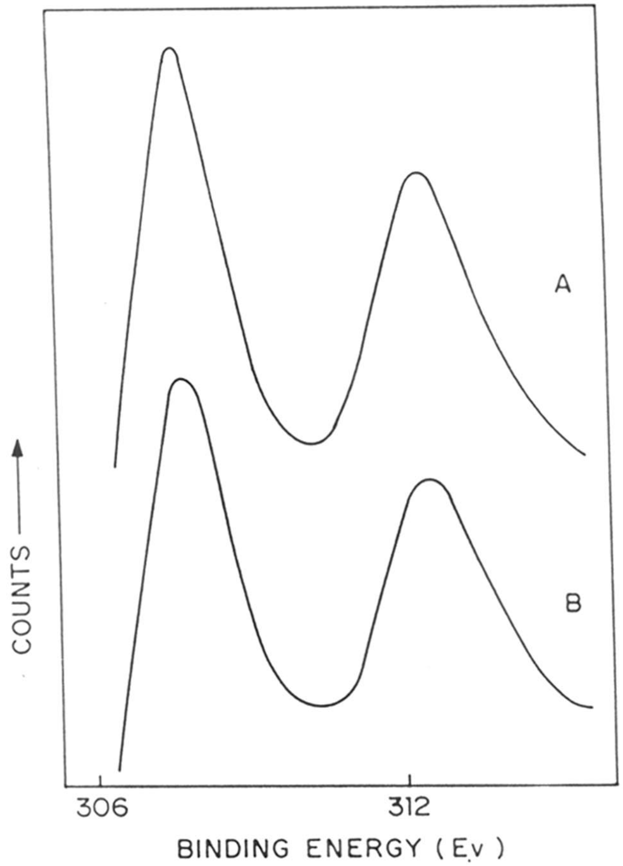


FIGURE 2.3 ESCA SPECTRUM OF 5 % Rh/C CATALYST, SHOWING RHODIUM 3d ELECTRONS, (A) BEFORE REACTION (B) AFTER REACTION

FIGURE 2.4 TEM OF FRESH 5 % Rh/C CATALYST

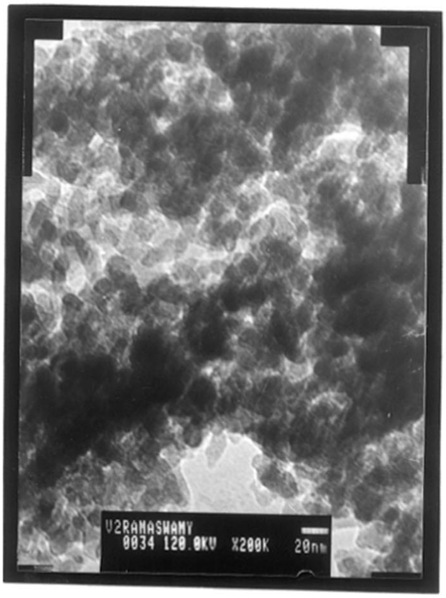


FIGURE 2.5 TEM OF USED 5 % Rh/C CATALYST

C. XRD

The X-ray diffraction patterns of the 5 % Rh/C catalyst were made by using a Phillips PW-1730 X-Ray diffractometer employing copper Kα radiation. The XRD patterns are shown in Fig 2.6(A) and (B). The fresh catalyst, Fig 2.6(A), shows the presence of large particle size rhodium on the support surface. In Fig 2.6(B) the XRD pattern does not show any peak corresponding to that of rhodium metal at the 2θ value. This also shows a decreased Rh metal crystallite size in the used catalyst.

2.3.3.11 Effect of catalyst loading

The catalyst loading was varied between 0.2 to 0.5 kg/m^3 and the results are presented in Table 2.16. The activity of the catalyst was found to increase (from 0.3 to 0.621 kmol/kg/hr) with the increase in catalyst loading upto 0.4 kg/m^3, but increased marginally thereafter (from 0.621 to 0.635 kmol/kg/hr). The non linear behavior for the catalyst loading effect may be due to the catalyst Rh metal to promoter ratio. The optimum ratio of catalyst metal to promoter was observed to be 1:1. In case of higher catalyst loading due to the decrease in the optimum ratio, the activity of the catalyst increases non linearly.

2.3.3.12 Effect of aniline concentration

The effect of aniline concentration on the activity and selectivity to ethyl phenyl

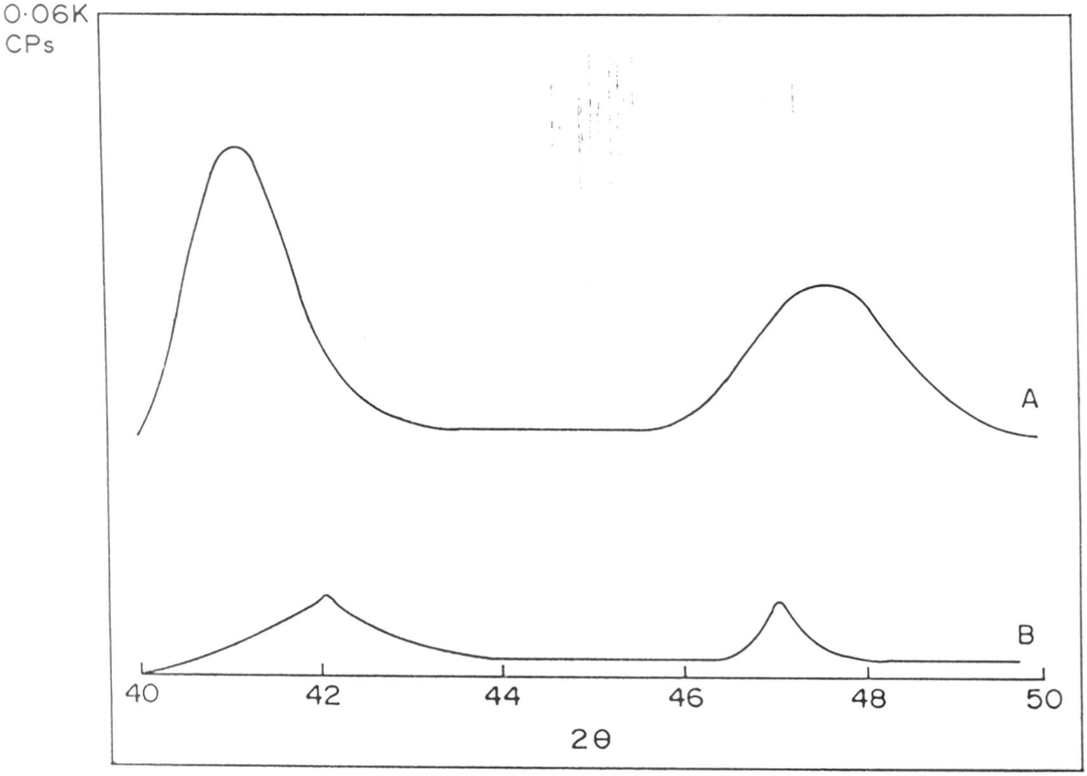


FIGURE 2.6 XRD SPECTRUM OF 5 % Rh/C CATALYST, BETWEEN 2Θ VALUES 40-50 FOR RHODIUM, (A) BEFORE REACTION (B) AFTER REACTION

TABLE 2.16

EFFECT OF CATALYST LOADING

Run No.	Catalyst loading kg/m^3	Average activity kmol/kg/hr	Selectivity Aniline based DPU %	EPC %
1	0.2	0.310	45.5	53.7
2	0.3	0.441	32.5	66.8
3	0.4	0.621	1.9	96.7
4	0.5	0.635	0.8	97.6

Reaction Conditions
Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3;
LiI : 8.7×10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa;
Solvent : Ethyl acetate; P_{O_2} : 0.32, MPa;
Agitation speed : 600, rpm; Temperature : 443, K;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

carbamate of 5% Rh/C catalyst was studied by varying the concentration of aniline between 0.548 kmol/m^3 and 1.645 kmol/m^3. The results are presented in Table 2.17. The activity of the catalyst was found to decrease (from 0.62 to 0.321 kmol/kg/hr), while the selectivity to diphenyl urea increased (from 1.9 to 50.3 %) with increase in the concentration of aniline. An interesting observation was that the selectivity for carbon dioxide decreased (from 55.5 % to 38.8 %) with increase in concentration of aniline. The observed trend may be due to the blocking of active catalytic sites by aniline, thus preventing the oxidation of carbon monoxide.

2.3.3.13 Effect of Partial pressure of carbon monoxide

The partial pressure of carbon monoxide was varied from 1.92 MPa to 5.76 MPa. The partial pressure of oxygen was kept at 0.32 MPa. The results are presented in Table 2.18. The average activity of the catalyst was found to increase linearly (from 0.17 to 0.62 kmol/kg/hr)with increase in partial pressure of carbon monoxide upto 4.48 MPa, above which the increase was very marginal. The selectivity to ethyl phenyl carbamate also increased (from 76.4 to 97.8 %) with increase in partial pressure of carbon monoxide. The formation of carbon dioxide showed marginal increase (from 53.5 to 64.5 %) with increase in partial pressure of carbon monoxide.

2.3.3.14 Effect of partial pressure of oxygen

The partial pressure of oxygen was varied between 0.23 and 1.61 MPa. The partial pressure of carbon monoxide was kept constant at 4.48, MPa. The results

TABLE 2.17

EFFECT OF ANILINE CONCENTRATION

Run No.	Aniline concentration	Average activity	Selectivity		
			Aniline based		CO based
			DPU	EPC	CO_2
	kmol/m^3	kmol/kg catalyst/hr	%	%	%
1	0.548	0.621	1.9	96.7	55.5
2	0.878	0.432	25.5	71.2	45.2
3	1.645	0.321	50.3	45.8	38.7

Reaction Conditions
Ethanol : 1.73, kmol/m^3;   Catalyst, 5% Rh/C : 0.4, kg/m^3;   LiI : 8.7×10^{-3}, kmol/m^3;
P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;   Solvent : Ethyl acetate;
Agitation speed : 600, rpm;   Temperature : 443, K;
DPU : Diphenyl urea;   EPC : Ethyl phenyl carbamate.

TABLE 2.18

EFFECT OF P_{CO}

Run No.	P_{CO} MPa	Average activity kmol/kg /hr	Selectivity				
			CO based			Aniline based	
			DPU %	EPC %	CO_2 %	DPU %	EPC %
1	1.92	0.174	9.7	34.5	53.5	20.6	76.4
2	2.56	0.211	7.4	35.4	56.5	15.8	82.3
3	3.22	0.300	6.3	35.7	57.4	10.5	84.6
4	3.84	0.387	5.3	36.9	55.9	7.9	87.2
5	4.48	0.621	4.0	37.0	55.5	1.9	96.7
6	5.12	0.632	3.6	34.5	58.4	1.2	97.6
7	5.76	0.680	2.7	32.1	64.5	1.2	97.8

Reaction Conditions
Aniline : 0.55, kmol/m^3; Catalyst, 5 % Rh/C : 0.4, kg/m^3;
Ethanol : 1.73, kmol/m^3; LiI : 8.7×10^{-3}, kmol/m^3;
Solvent : Ethyl acetate; P_{O_2} : 0.32, MPa;
Agitation speed : 600, rpm; Temperature : 443, K;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

are presented in Table 2.19. The activity of the catalyst was found to increase (from 0.587 to 7.23 kmol/kg/hr) with increase in partial pressure of oxygen. The selectivity to ethyl phenyl carbamate and carbon dioxide also increased (from 86.5 % to 97.5 % and from 53.5 % to 63.8 % respectively) with increase in the partial pressure of oxygen.

2.3.3.15 Effect of ethanol concentration

The effect of ethanol concentration on activity and selectivity of 5 % Rh/C catalyst was investigated. The concentration of ethanol was varied between 0.869 and 8.768 kmol/m^3. The results are presented in Table 2.20. The average activity of the catalyst was found to increase marginally (from 0.62 to 0.625 kmol/kg/hr) while, the increase in selectivity to ethyl phenyl carbamate was higher (from 82.4 % to 96.7 %), with increase in ethanol concentration.

2.3.3.16 Effect of water concentration

Water is one of the co-products formed during the oxidative carbonylation reaction (Eqn. 2.9). The results on solvent effect, (Section 2.3.9), indicated that water inhibits the reaction totally, when used as a solvent. To understand the effect of water in small quantities some reactions were carried out by adding water to the reaction mixture. The results are presented in Table 2.21. The activity of the 5% Rh/C catalyst and selectivity to ethyl phenyl carbamate was found to decrease with increase in water concentration. There was a significant increase in the formation

TABLE 2.19

EFFECT OF P_{O_2}

Run No.	P_{O_2}	Average activity	Selectivity				
			CO based			Aniline based	
			DPU	EPC	CO_2	DPU	EPC
	MPa	kmol/kg /hr	%	%	%	%	%
1	0.23	0.587	5.3	38.7	53.5	6.1	86.5
2	0.32	0.621	4.9	37.3	54.9	6.5	87.2
3	0.69	0.685	4.0	37.0	55.5	1.9	96.7
4	1.61	0.723	3.8	39.3	63.8	1.2	97.5

Reaction Conditions
Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3;
Catalyst, 5 % Rh/C : 0.4, kg/m^3; LiI : 8.7×10^{-3}, kmol/m^3;
P_{CO} : 4.48, MPa; Agitation speed : 600, rpm;
Solvent : Ethyl acetate; Temperature : 443, K;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

TABLE 2.20

EFFECT OF ETHANOL CONCENTRATION

Run No.	Ethanol concentration kmol/m^3	Average activity kmol/kg/hr	Selectivity Aniline based DPU %	Selectivity Aniline based EPC %
1	0.869	0.610	16.1	82.4
2	1.734	0.621	1.9	96.7
3	8.768	0.625	1.0	97.7

Reaction Conditions
Aniline : 0.55, kmol/m^3; Catalyst, 5% Rh/C : 0.4, kg/m^3;
LiI : 8.7×10^{-3}, kmol/m^3; Solvent : Ethyl acetate;
P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;
Agitation speed : 600, rpm; Temperature : 443, K;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

TABLE 2.21

EFFECT OF WATER CONCENTRATION

Run No.	Water concentration	Average activity	Selectivity		Carbon dioxide formed
			Aniline based		
			DPU	EPC	
	%	kmol/kg catalyst/hr	%	%	kmol/m^3
1	0	0.621	1.9	96.7	0.09264
2	0.1	0.432	10.98	88.7	0.108
2	1.0	0.322	15.67	79.2	0.121
3	10	0.198	59.76	37.2	0.1347

Reaction Conditions

Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3; Catalyst, 5% Rh/C : 0.4, kg/m^3;

LiI : 8.7×10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa;

Solvent : Ethyl acetate; Agitation speed : 600, rpm; Temperature : 443, K;

DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

of carbon dioxide (from 0.09 kmol/m^3 to 0.17 kmol/m^3) in the presense of water. This is consistent with earlier work in which the oxidation of carbon monoxide has been shown to be catalyzed in the presense of water (Hadman et. al. (1932)).

2.3.3.17 Effect of Temperature

The effect of temperature on the activity and selectivity of 5 % Rh/C catalyst was studied in a temperature range of 373 to 473 K. The results are presented in Table 2.22. The activity of the catalyst was found to increase (from 0.173 to 0.621 kmol/kg/hr), with temperature, but the selectivity to ethyl phenyl carbamate showed a maximum at 443, K (96.7 %) and decreased to 67.3 % at 473, K. This decrease in selectivity may be due to thermal degradation of ethyl phenyl carbamate above 453, K (Arnold et. al. (1957)). The selectivity to carbon dioxide increased (from 47.9 % to 68.8 %) with the increase in temperature.

2.3.4 Kinetic Study

In the previous section, the effect of catalyst precursors, solvents, supports, rhodium content, pretreatment and reaction conditions on the oxidative carbonylation of aniline using 5 % Rh/C catalyst has been discussed. The intrinsic kinetics of the reaction was also studied at 443, K. The details are given below:

The kinetics of oxidative carbonylation of aniline using 5% Rh/C catalyst and

TABLE 2.22

EFFECT OF TEMPERATURE

Run No.	Temperature	Average activity	Selectivity				
			CO based			Aniline based	
			DPU	EPC	CO_2	DPU	EPC
	K	kmol/kg catalyst/hr	%	%	%	%	%
1	373	0.153	21.9	6.1	47.9	80.1	11.2
2	408	0.437	18.9	31.1	38.2	54.4	44.8
3	443	0.620	4.0	37.0	55.5	1.9	96.7
4	473	0.397	-	17.4	68.8	-	67.3

Reaction Conditions
Aniline : 0.55, kmol/m^3; Ethanol : 1.73, kmol/m^3; Catalyst, 5 % Rh/C : 0.4, kg/m^3;
LiI : 8.7×10^{-3}, kmol/m^3; P_{CO} : 4.48, MPa; P_{O_2} : 0.32, MPa; Solvent : Ethyl acetate;
Agitation speed : 600, rpm;
DPU : Diphenyl urea; EPC : Ethyl phenyl carbamate.

lithium iodide as a promoter was studied at 443, K. As discussed in Section 2.3.2, the oxidative carbonylation of aniline to ethyl phenyl carbamate proceeds through the formation of diphenyl urea (Eqns. 2.9, 2.10). The side reaction of oxidation of carbon monoxide to carbon dioxide also occurred under the reaction conditions (Eqn. 2.11). To study the kinetics, the initial rate of the reaction was calculated from the region of high concentration of diphenyl urea wherein carbon dioxide and ethyl phenyl carbamate formation is negligible. The results presented here are thus, representative of the kinetics of oxidative carbonylation of aniline to diphenyl urea (Eqn. 2.9). The effect of concentration of aniline, catalyst loading, partial pressures of carbon monoxide and oxygen on the initial rate of the reaction was investigated.

2.3.4.1 Initial rate calculations

The procedure used for kinetic runs is described in Section 2.2.5. In each experiment, the amount of carbon monoxide and oxygen consumed as a function of time was observed and the typical plots for different sets of conditions are shown in Figs 2.7- 2.10. From these plots, only the initial region (< 10% conversion of aniline) was chosen for rate analysis. The initial rate of aniline consumed, (R_A, kmol/m^3/s), was calculated as:

$$R_A \quad = \quad \frac{\text{Slope of } CO+O_2 \text{ consumed vs time}}{\text{Volume of liquid}} \times 1.33, \quad \frac{\text{kmol/s}}{\text{m}^3} \qquad (2.12)$$

For the kinetic studies, the liquid phase concentrations of carbon monoxide and

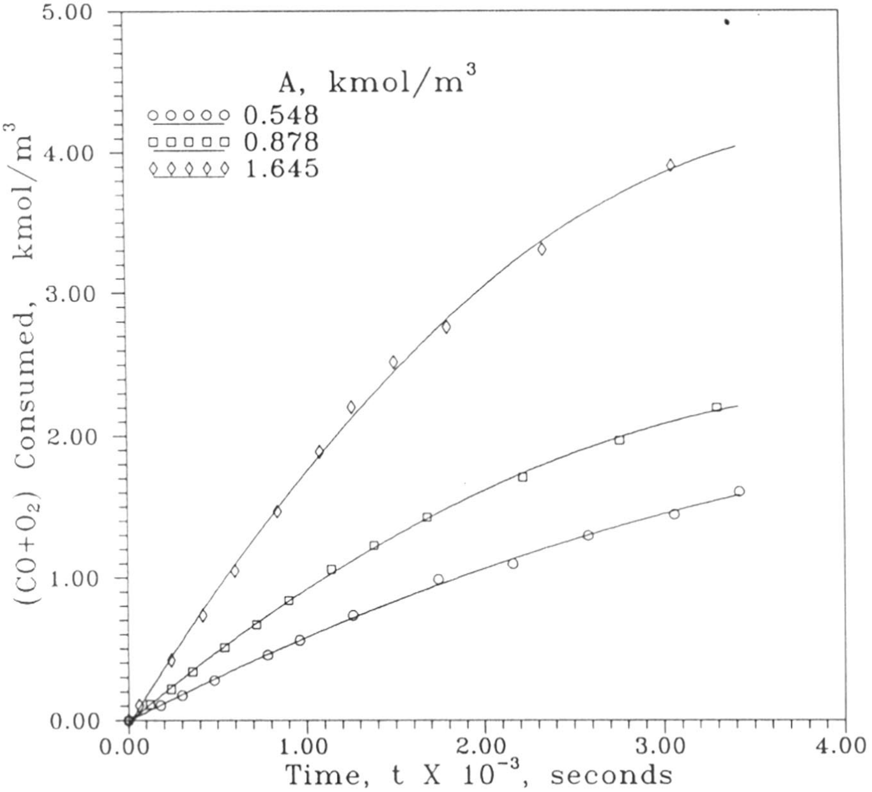


FIGURE 2.7 PLOT OF CO + O_2 CONSUMED VS TIME, EFFECT OF CONCENTRATION OF ANILINE

Reaction conditions:

Ethanol : 1.73, kmol/m^3;
Catalyst, 5 % Rh/C : 0.4, kg/m^3;
LiI : 8.7×10^{-3}, kmol/m^3;
Carbon monoxide : 4.48, MPa;
Oxygen : 0.61, MPa;
Temperature : 443, K;
Solvent : Ethyl acetate;
Agitation speed : 600, rpm.

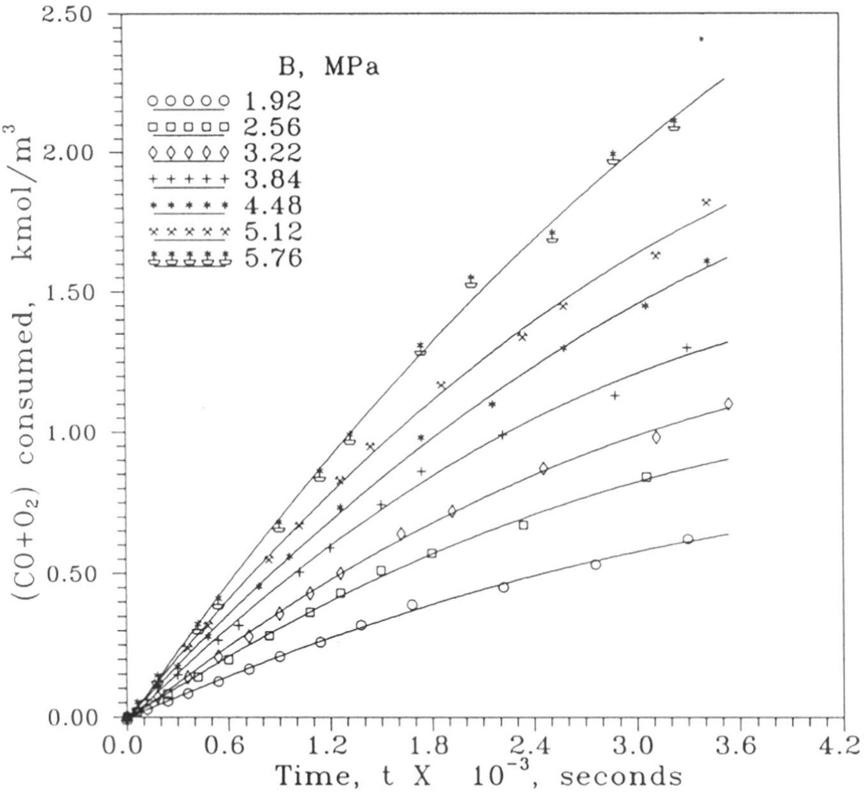


FIGURE 2.8 PLOT OF CO + O_2 CONSUMED VS TIME, EFFECT OF PARTIAL PRESSURE OF CARBON MONOXIDE

Reaction conditions:

Aniline : 0.55, kmol/m^3;

Ethanol : 1.73, kmol/m^3;

Catalyst, 5 % Rh/C : 0.4, kg/m^3;

LiI : 8.7 × 10^{-3}, kmol/m^3;

Oxygen : 0.61, MPa;

Temperature : 443, K;

Solvent : Ethyl acetate;

Agitation speed : 600, rpm.

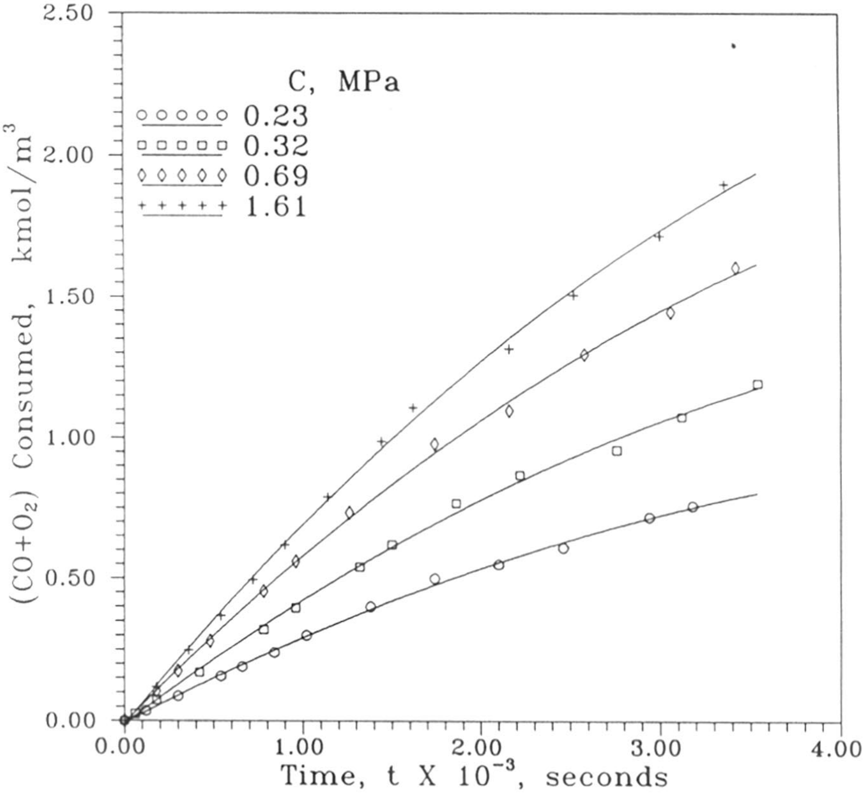


FIGURE 2.9 PLOT OF CO + O_2 CONSUMED VS TIME, EFFECT OF PARTIAL PRESSURE OF OXYGEN

Reaction conditions:

Aniline : 0.55, kmol/m^3;
Ethanol : 1.73, kmol/m^3;
Catalyst, 5 % Rh/C : 0.4, kg/m^3;
LiI : 8.7 × 10^{-3}, kmol/m^3;
Carbon monoxide : 4.48, MPa;
Temperature : 443, K;
Solvent : Ethyl acetate;
Agitation speed : 600, rpm.

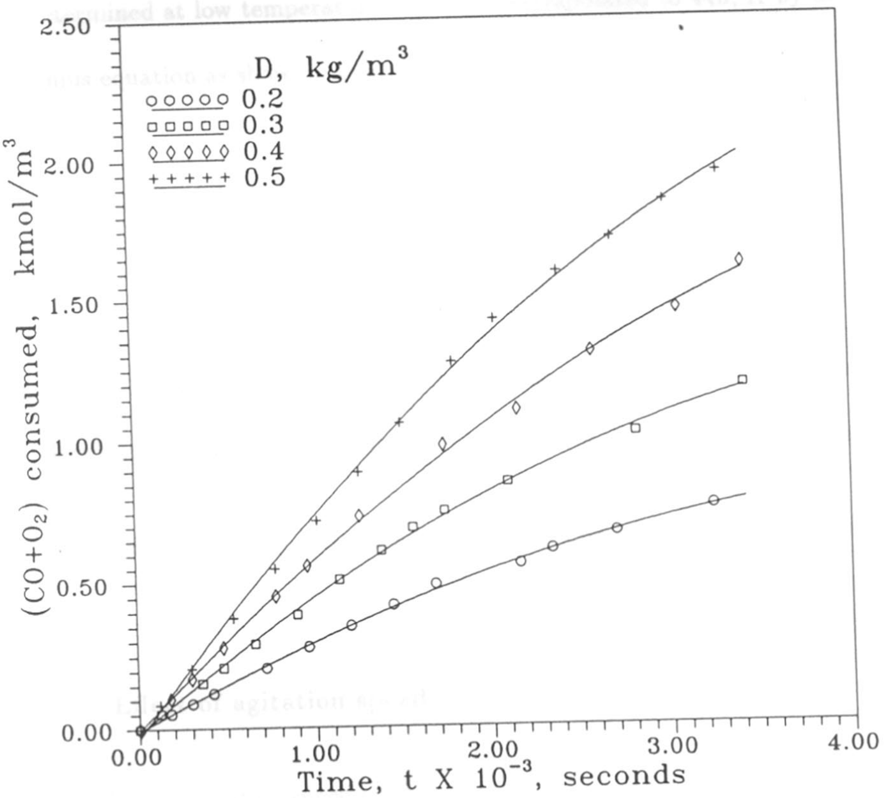


FIGURE 2.10 PLOT OF CO + O_2 CONSUMED VS TIME, EFFECT OF CATALYST LOADING

Reaction conditions:

Aniline : 0.55, kmol/m^3;
Ethanol : 1.73, kmol/m^3;
LiI : Catalyst : 1:1;
Carbon monoxide : 4.48, MPa;
Oxygen : 0.61, MPa;
Temperature : 443, K;
Solvent : Ethyl acetate;
Agitation speed : 600, rpm.

oxygen at 443, K are necessary. The liquid phase concentration of carbon monoxide in ethyl acetate at 443, K. However, for safety reasons, the solubility of oxygen was determined at low temperatures and then extrapolated to 443, K by using the Arrhenius equation as shown below:

$$H_{e_{443}} = H_{e_{353}} \ e^{-\frac{E}{R}} \left[\frac{1}{443} - \frac{1}{353}\right] \qquad (2.13)$$

Where,

$H_{e_{443}}$, $H_{e_{353}}$ are the solubility factors of oxygen at 443 and 353 K respectively (kmol/m^3/atm), R is the gas constant, E is the energy of dissolution in kcal/mol.

The values of solubility factor for carbon monoxide and oxygen are presented in Table 2.23.

2.3.4.2 Effect of agitation speed

The effect of agitation speed on the activity and selectivity of 5 % Rh/C catalyst was studied and the results are shown in Fig 2.11. It was observed that the initial rate of the reaction was dependent on agitation speed below 400, rpm and hence was in the mass controlled regime. Above 400, rpm, the initial rate was independent of the agitation speed, which indicates that the data are mainly in the kinetic regime. Therefore all reactions were carried out at 600, rpm.

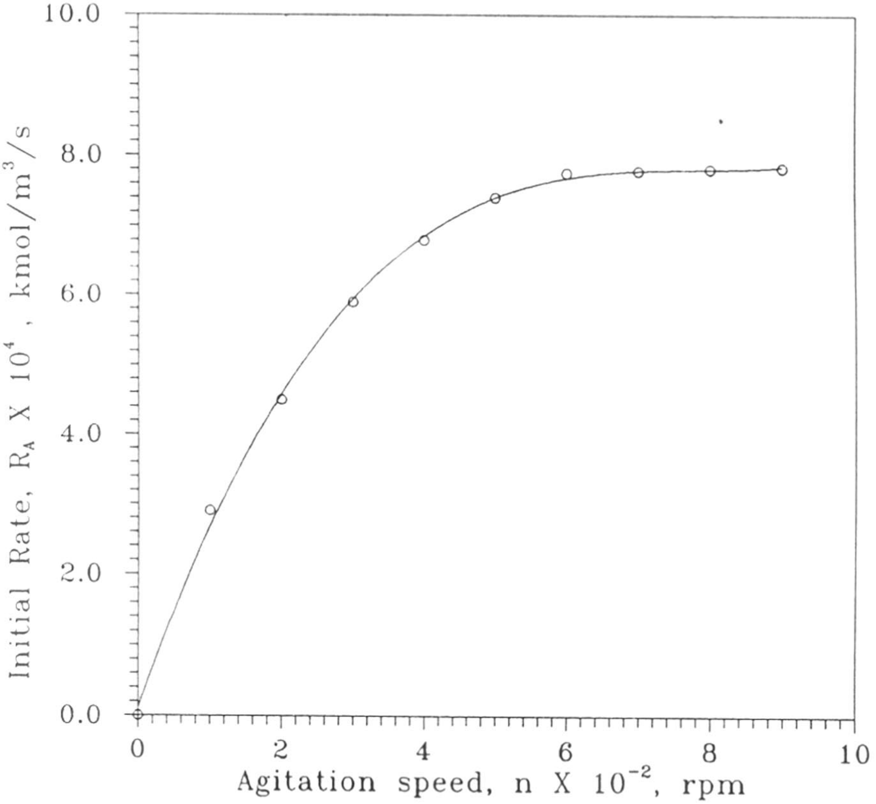


FIGURE 2.11 EFFECT OF AGITATION SPEED ON THE RATE OF OXIDATIVE CARBONYLATION OF ANILINE

Reaction conditions:

Aniline	:	**0.55, kmol/m^3;**
Ethanol	:	**1.73, kmol/m^3;**
Catalyst, 5 % Rh/C	:	**0.4, kg/m^3;**
LiI	:	**8.7×10^{-3}, kmol/m^3;**
Carbon monoxide	:	**4.48, MPa;**
Oxygen	:	**0.61, MPa;**
Temperature	:	**443, K;**
Solvent	:	**Ethyl acetate.**

TABLE 2.23

HENRY'S CONSTANT FOR CO AND O_2 IN ETHYL ACETATE

Sr. No.	Temperature K	Henry's constant $H_e \times 10^4$, kmol/m^3/atm
	For CO	
1	299	0.91
2	318	1.02
3	353	1.23
4	443	1.75
	For O_2	
1	299	0.92
2	318	0.66
3	353	0.35
4	443	0.11**

** Extrapolated

2.3.4.3 Effect of aniline concentration

The concentration of aniline was varied from 0.548 to 1.645 kmol^3 and a plot of initial rate of the reaction vs concentration of aniline is shown in Fig 2.12. The plot is a straight line indicates a linear dependence of the initial rate on the concentration of aniline.

2.3.4.4 Effect of partial pressure of carbon monoxide

The partial pressure of carbon monoxide was varied between 1.92 and 5.76 MPa, at a constant partial pressure of oxygen at 0.61, MPa. The plot of initial rate vs partial pressure of carbon monoxide (Fig 2.13), is a straight line indicating first order dependence on the partial pressure of carbon monoxide.

2.3.4.5 Effect of partial pressure of oxygen

The partial pressure of oxygen was varied between 0.23 to 1.61 MPa while the partial pressure of carbon monoxide was kept constant at 4.48, MPa. The plot of the initial rate vs partial pressure of oxygen (Fig 2.14) shows a linear dependence in the initial stages and above 0.69, MPa, is independent of partial pressure of oxygen.

2.3.4.6 Effect of catalyst loading

The effect of catalyst loading on the initial rate of the the reaction was carried out by keeping Rh-LiI catalyst system in the molar ratio of 1:1. The catalyst loading

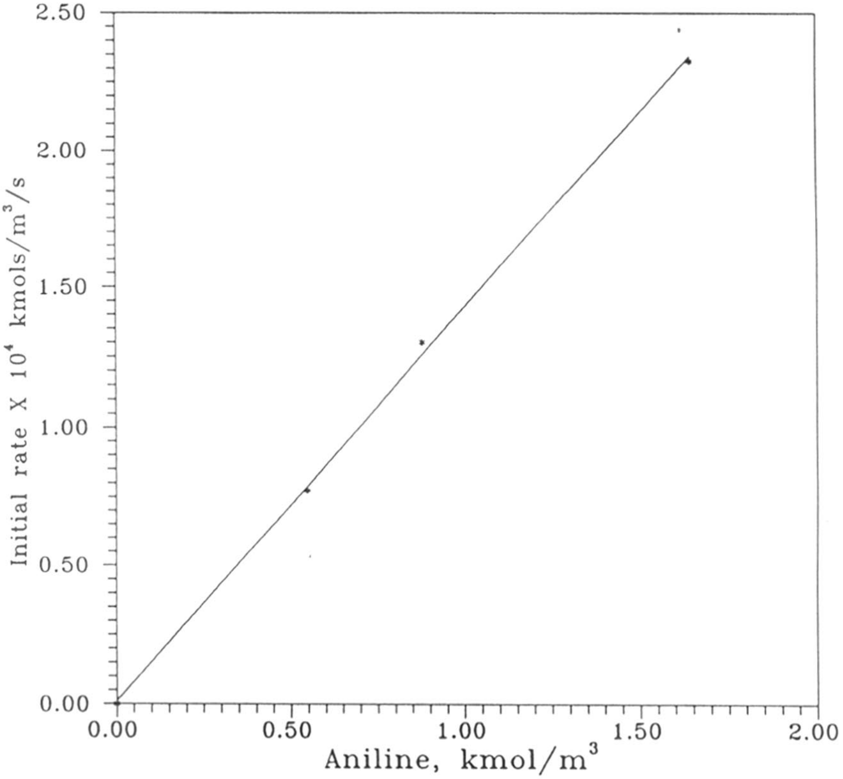


FIGURE 2.12 EFFECT OF ANILINE CONCENTRATION, ON THE RATE OF OXIDATIVE CARBONYLATION OF ANILINE

Reaction conditions:

Ethanol	:	1.73, kmol/m^3;
Catalyst, 5 % Rh/C	:	0.4, kg/m^3;
LiI	:	8.7×10^{-3}, kmol/m^3;
Carbon monoxide	:	4.48, MPa;
Oxygen	:	0.61, MPa;
Temperature	:	443, K;
Solvent	:	Ethyl acetate;
Agitation speed	:	600, rpm.

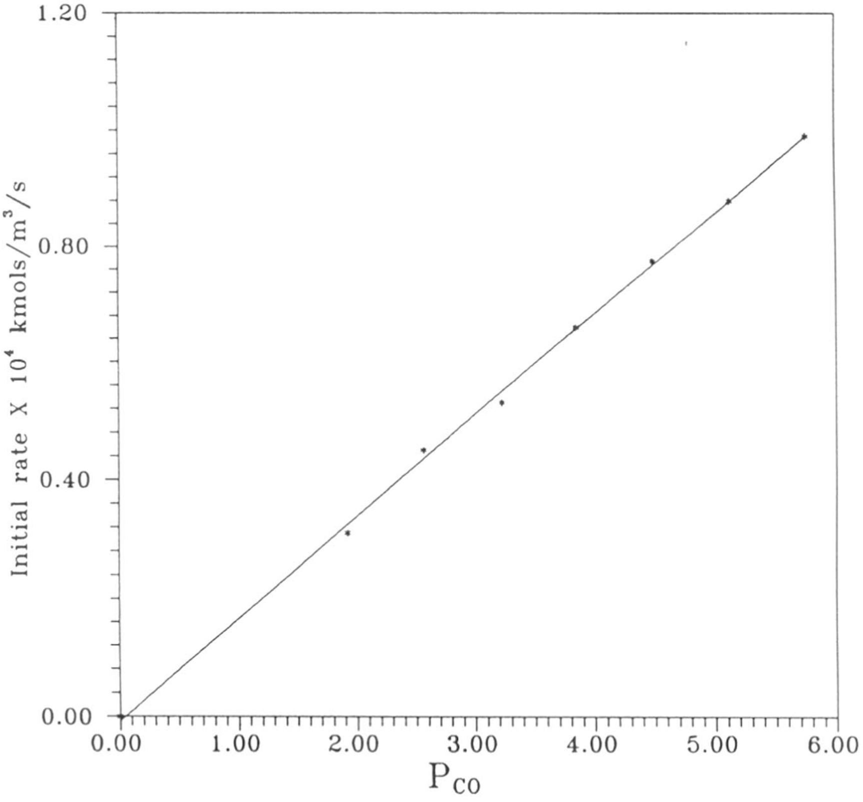


FIGURE 2.13 EFFECT OF PARTIAL PRESSURE OF CO ON THE RATE OF OXIDATIVE CARBONYLATION OF ANILINE

Reaction conditions:

Aniline	:	**0.55, kmol/m^3;**
Ethanol	:	**1.73, kmol/m^3;**
Catalyst, 5 % Rh/C	:	**0.4, kg/m^3;**
LiI	:	**8.7×10^{-3}, kmol/m^3;**
Oxygen	:	**0.61, MPa;**
Temperature	:	**443, K;**
Solvent	:	**Ethyl acetate;**
Agitation speed	:	**600, rpm.**

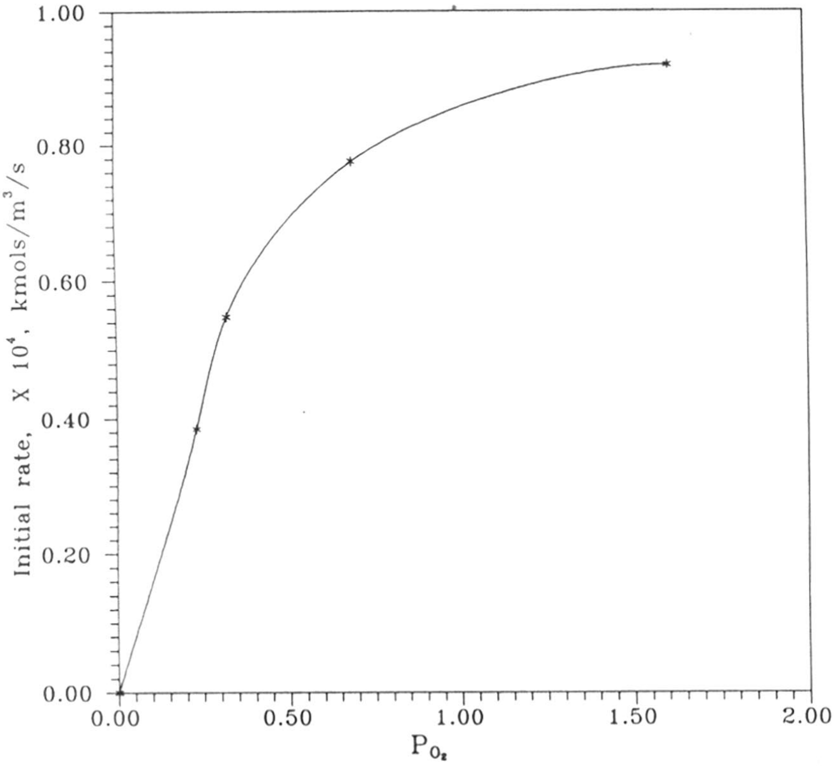


FIGURE 2.14 EFFECT OF PARTIAL PRESSURE OF OXYGEN ON THE RATE OF OXIDATIVE CARBONYLATION OF ANILINE

Reaction conditions:

Aniline	:	**0.55**, kmol/m^3;
Ethanol	:	**1.73**, kmol/m^3;
Catalyst, **5** % Rh/C	:	**0.4**, kg/m^3;
LiI	:	**8.7** $\times$ 10^{-3}, kmol/m^3;
Carbon monoxide	:	**4.48**, MPa;
Temperature	:	**443**, K;
Solvent	:	Ethyl acetate;
Agitation speed	:	**600**, rpm.

was varied between 0.2 to 0.5 kg/m^3. The plot of initial rate as a function of catalyst loading (Fig 2.15) shows that the rate is linearly dependent on the catalyst loading.

2.3.4.7 Kinetic Model

In order to develop a suitable rate equation representing the intrinsic kinetics of oxidative carbonylation of aniline using 5 % Rh/C - LiI catalyst system, the initial rate data from the above study was used. The mass transfer limitations were minimized by taking the reaction in the kinetic regime at 600 rpm.

The observed trends indicate that the rate of oxidative carbonylation reaction is dependent linearly on the concentration of aniline, catalyst and the partial pressure of carbon monoxide. The rate is initially linearly dependent on the partial pressure of oxygen and independent at partial pressure higher than 0.69, MPa.

In the present case, of oxidative carbonylation of aniline using a heterogeneous rhodium - lithium iodide catalyst system, the mechanism is not well established. Therefore to derive a kinetic model for the oxidative carbonylation of aniline using Rh/C-LiI catalyst systems an empirical model was proposed. Based on the above rate data, the following form of empirical rate equation was considered.

$$R_A = \frac{k\ A\ B\ C\ D}{1 + K_C\ C} \qquad (2.14)$$

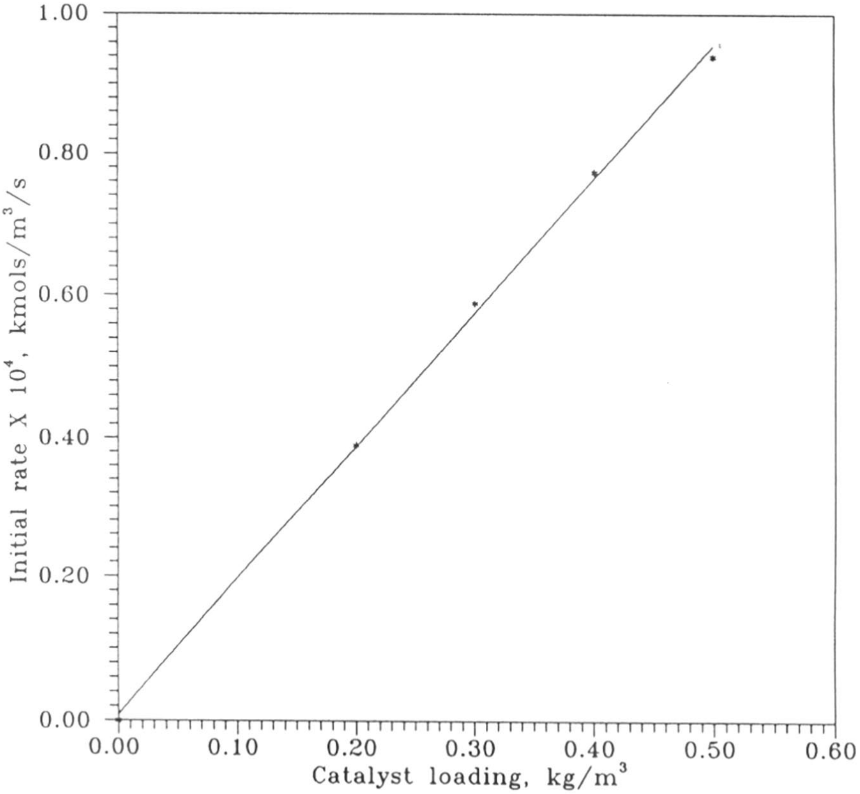


FIGURE 2.15 EFFECT OF CATALYST LOADING ON THE RATE OF OXIDATIVE CARBONYLATION OF ANILINE

Reaction conditions:

Aniline : 0.55, kmol/m^3;
Ethanol : 1.73, kmol/m^3;
LiI : Catalyst : 1:1;
Carbon monoxide : 4.48, MPa;
Oxygen : 0.61, MPa;
Temperature : 443, K;
Solvent : Ethyl acetate;
Agitation speed : 600, rpm.

Where,

R_A is the rate of aniline, kmol/m^3/s; A, B and C, the liquid phase concentrations of aniline, carbon monoxide and oxygen respectively, kmol/m^3; k the rate constant, (m^9/kg/kmol^2/s); K_C, the absorption equilibrium constant, m^3/kmol; D, the concentration of the catalyst, kg/m^3.

The constant K_C was evaluated by keeping constant the partial pressure of carbon monoxide, concentration of aniline and loading of catalyst. Under these conditions the rate equation (Eqn. 2.14) simplifies to:

$$R_A = \frac{K' \; C}{1 + K_C \; C} \qquad (2.15)$$

Where $K' = k \; A \; B \; D$

$$\frac{1}{R_A} = \frac{1 + K_C \; C}{K' \; C} \qquad (2.16)$$

$$\frac{1}{R_A} = \frac{1}{K'C} + \frac{K_C \; C}{K' \; C} \qquad (2.17)$$

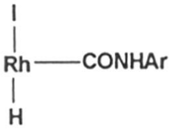
$$\frac{1}{R_A} = \frac{1}{K'C} + K'' \qquad (2.18)$$

Where $K'' = \frac{K_C}{K'}$

The plot of $\frac{1}{R_A}$ vs $\frac{1}{C}$ gives a straight line giving a slope of $\frac{1}{K'}$ and intercept of K''. From the slope and intercept the guess values of K_C and K' were calculated. These guess values were optimized by Marquardt method (Marquardt, (1962)). The values of rate parameters and Φ_{min}, the minimum of squares of the difference between the observed and predicted rates, is presented in Table 2.24. The rates as predicted using these optimized rate parameters were found to agree with experimental data within 5-7% error (Fig 2.16).

2.3.4.8 Mechanism

The mechanism of oxidative carbonylation of amines using supported Rh catalyst is not well understood. From the literature on activation of CO using supported Rh catalysts, formation of metal carbonyl species like $RhI_2(CO)_2^-$ are likely to exist (Mulla et. al. (1991)). In the presence of aromatic amines and metal iodide promoter, carbamoyl species of the type



$$\begin{array}{l} \mathrm{I} \\ | \\ \mathrm{Rh}\text{——}\mathrm{CONHAr} \\ | \\ \mathrm{H} \end{array} \qquad (2.19)$$

is likely to be found similar to that established earlier for Pd catalyzed reactions (Vasapollo et. al. (1985)). However, further work would be necessary to characterize the nature of active catalytic species.

TABLE 2.24

RATE PARAMETERS BY MARQUARDT OPTIMIZATION PROGRAM

Sr. No.	Rate Parameter	
1	k	1.53×10^4
2	K_C	2.27×10^4
3	ϕ_{min}	8.15×10^{-9}

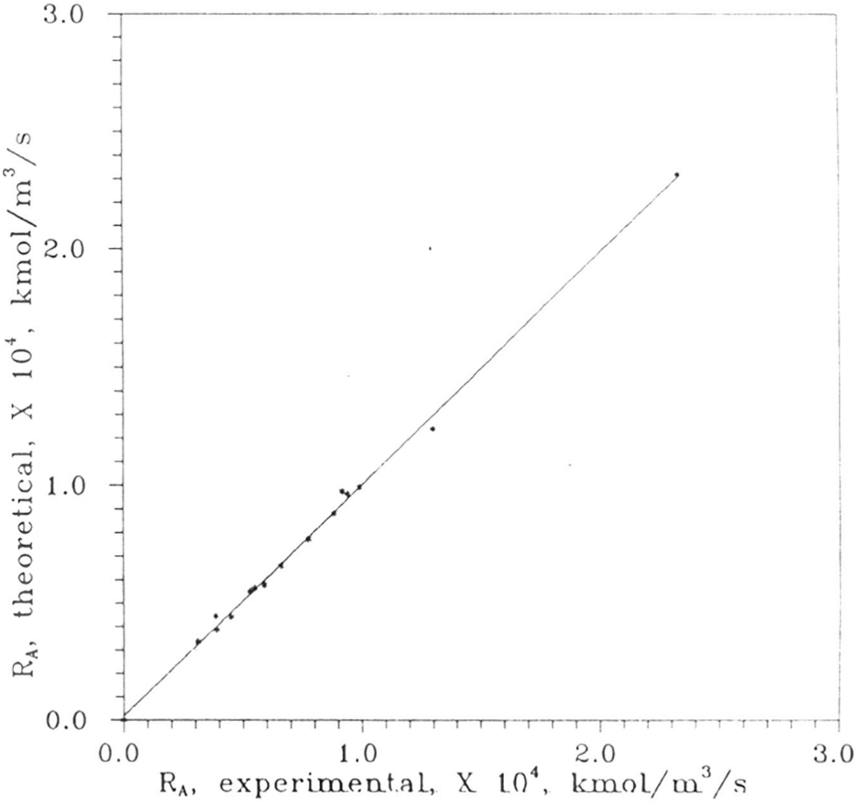


FIGURE 2.16 PLOT OF R_A PREDICTED vs R_A EXPERIMENTAL

2.4 CONCLUSIONS

The oxidative carbonylation of aniline using rhodium catalysts has been investigated. The major products of the reaction are ethyl phenyl carbamate, diphenyl urea and carbon dioxide.

The screening of catalysts for the reaction indicated that heterogeneous catalysts are more active than the homogeneous catalysts, under the present reaction conditions. Iodide species, as promoters, are essential for the carbonylation of aniline at 443, K using supported rhodium catalysts.

The effect of catalyst preparation methods, catalyst precursors, supports, metal content, reusability, promoters, solvents, and pretreatment on the activity and selectivity of supported Rh catalyst has been investigated.

The activity of the supported Rh catalyst was found to depend on the type of support, rhodium content, promoters, concentration of aniline, catalyst loading, partial pressures of carbon monoxide and oxygen, ethanol and water concentrations and temperature. Active carbon supported catalyst, with 5 % metal loading was found to be the most active catalyst. Of the different promoters screened, LiI and SnI_2 were found to be the most active promoters. The activity of the 5 % Rh/C catalyst decreased with increase in aniline and water concentrations, while it increased with increase in the partial pressures of carbon monoxide and oxygen, catalyst loading, ethanol concentration and temperature.

Carbon dioxide formation was found to be dependent on the nature of support, the metal content and reaction temperature. The selectivity to ethyl phenyl carbamate was found to be independent of catalyst preparation methods, nature of supports, metal content and dependent on the reaction temperature upto 443, K, beyond which the selectivity decreased. Alkali metal iodides, as promoters, gave higher selectivity for ethyl phenyl carbamate and lower selectivity for carbon dioxide. Other metal iodides, like NiI_2, SnI_2, were also found to promote the reaction and gave good selectivity for ethyl phenyl carbamate. The selectivity to ethyl phenyl carbamate was found to be higher in moderately polar and non polar solvents. In highly polar solvents like dimethyl formamide and acetonitrile, the major product was diphenyl urea.

Addition of cobalt, manganese, tin and nickel chlorides on the activity and selectivity behavior of 5 % Rh/C-SnI_2 catalyst system was investigated. The activity of the catalyst was found to be enhanced by the addition of cobalt, manganese or tin chlorides, however, the selectivity to ethyl phenyl carbamate was unaffected. Pretreatment of the catalyst with carbon monoxide, oxygen, carbon dioxide, hydrogen and aniline was found to have a very marginal effect on the initial activity of the catalyst. The catalyst 5 % Rh/C could be used seven times without significant loss of activity.

The characterization of fresh and used catalyst was done by ESCA, XRD and TEM. The analysis indicated that (a) Rh exists in zero valent state and (b) redispersion of Rh occurs during carbonylation leading to lower Rh metal crystallite size.

The intrinsic kinetics has been investigated at 443, K. The rate of reaction was found to be linearly dependent on concentration of aniline, partial pressure of carbon monoxide and catalyst loading. The rate of the reaction was also found to be linearly dependent on oxygen partial pressure upto 0.69, MPa, above which it was found to be independent of oxygen partial pressure. The following empirical rate model has been proposed and the rate parameters evaluated.

$$R_A = \frac{k\ A\ B\ C\ D}{(1 + K_C\ C)} \qquad (2.20)$$

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CHAPTER 3

ETHANOLYSIS OF DIPHENYL UREA

3.1 INTRODUCTION

The oxidative carbonylation of amines to substituted ureas and carbamic acid derivatives is an industrially important reaction as it provides a non phosgene route for the manufacture of commercially important substituted ureas and carbamic acid derivatives. This route is particularly attractive as it eliminates corrosive by-products and is a single step process.

The oxidative carbonylation of aniline to ethyl phenyl carbamate is the first step in the non-phosgene route for synthesis of methylene diphenyl diisocyanate (MDI) (Fukuoka et. al. (1984)). In Chapter 2, the results on rhodium catalyzed oxidative carbonylation of aniline to ethyl phenyl carbamate are presented. It was observed during this study that the catalytic oxidative carbonylation of aniline to ethyl phenyl carbamate proceeds through the following steps :

$$2C_6H_5NH_2 + CO + \frac{1}{2}O_2 \longrightarrow C_6H_5NHCONHC_6H_5 + H_2O \qquad (3.1)$$

$$C_6H_5NHCONHC_6H_5 + C_2H_5OH \longrightarrow C_6H_5NHCOOC_2H_5 + C_6H_5NH_2 \qquad (3.2)$$

The first step is the formation of the diphenyl urea by oxidative carbonylation of aniline and the second step involves ethanolysis of diphenyl urea to ethyl phenyl carbamate. Aniline formed in the second reaction is recycled through the first step. A knowledge of the kinetics of ethanolysis step is essential in order to understand the overall kinetics of the reaction leading to synthesis of ethyl phenyl carbamate. Ayyangar et. al. (1988) and Giannoccarro (1988), have reported the catalytic synthesis of ethyl phenyl carbamate from diphenyl urea using concentrated sulfuric acid and homogeneous palladium copper catalysts respectively, though the kinetics of the reaction has not been reported. The relevant literature on the subject is presented in Section 1.3, of Chapter 1.

In the present work, the effect of different types of catalysts, solvents and reaction conditions on the conversion and selectivity of ethanolysis reaction was investigated. The intrinsic kinetics of the reaction was studied over a temperature range of 413-433 K.

3.2 EXPERIMENTAL

3.2.1 Materials

Aniline and ethanol were procured from SD Fine Chemicals Ltd., India, and were of analytical grade. Urea was purchased from Ranbaxy Laboratories Ltd., Punjab. The metal salts, Cobalt (II) Chloride dihydrate (Wilson Laboratories, Bombay), Manganese (II) Chloride quadrahydrate (Thomas Baker Pvt. Ltd., Bombay), Tin (II) Chloride quadrahydrate (SD Fine Chemicals Ltd., India) were used as received. Phenyl isocyanate was procured from BDH Chemicals. The catalysts, 5 % Pd/C and

5% Rh/C, were obtained from Arrora Mathey, Calcutta. The solvents ethyl acetate, benzene, toluene, dimethyl formamide were of laboratory grade and distilled before use. Nitrogen gas was supplied by Indian Oxygen Ltd., Bombay. Diphenyl urea and ethyl phenyl carbamate were synthesized by organic methods.

3.2.2 Analytical Methods

The analytical method for analysis of products (ethyl phenyl carbamate and aniline) and reactant (diphenyl urea) was by gas chromatography and high performance liquid chromatography respectively. The columns and other conditions for analysis were similar to those described in Section 2.2.2, of Chapter 2.

3.2.3 Synthesis of Diphenyl Urea

Diphenyl urea, for the purpose of this study, was synthesized from aniline and urea. The method of Ayyangar et. al. (1988) was used for the synthesis.

30.3, gms of urea was added to 150, ml freshly distilled aniline and this mixture was refluxed for 24 hours on an oil bath. The solution was cooled and diluted with two liters of dilute hydrochloric acid solution. Addition of dilute hydrochloric acid resulted in precipitation of diphenyl urea. The solution was filtered and the crystals were washed first with dilute hydrochloric acid and then repeatedly with distilled water till the acid was washed off. The crystals were finally washed with benzene and dried under vacuum. The yield obtained was more than 97%.

Diphenyl urea was confirmed by mass spectrum, IR, HPLC and melting point (512, K).

3.2.4 Synthesis of Ethyl Phenyl Carbamate

Ethyl phenyl carbamate, required as a standard, was synthesized by mixing phenyl isocyanate and ethanol. About 100, ml of ethanol was cooled to 278, K, and to this cold solution, phenyl isocyanate was added. A total of 25, ml was added drop wise from a burette over a period of 30 minutes with constant stirring. The temperature of the solution was kept at 278, K throughout the addition. After complete addition the solution was stirred and the temperature brought to room temperature over a period of 30 minutes. The solution was distilled to remove excess ethanol. Ethyl phenyl carbamate was obtained as fine crystals and was purified by recrystallization from hot ethanol. The yield was more than 99%.

Ethyl phenyl carbamate was confirmed from melting point (326, K) and mass spectral analysis. The purity was confirmed by gas chromatography.

3.2.5 Experimental Set-up

The ethanolysis experiments were carried out in a stirred pressure reactor as described in Chapter 2. A schematic diagram of the set-up is shown in Fig 2.1 (see section 2.2.4, Chapter 2).

In a typical experiment, the reactants diphenyl urea, ethanol and solvent ethyl acetate were charged to the autoclave reactor. The contents were flushed with nitrogen before the heating was started. After the required temperature was reached, the stirrer was started. The progress of the reaction was monitored by withdrawing liquid samples from the autoclave and analyzing for ethyl phenyl carbamate and aniline by gas chromatography.

The mass balance of the reactants consumed and products formed matched to more than 97 % as per the stoichiometery of the reaction (Eqn. 3.2).

3.3 RESULTS AND DISCUSSIONS

The ethanolysis of diphenyl urea to ethyl phenyl carbamate was studied at 423 K. The aim of the present work was to investigate the role of catalysts, solvents and effect of reaction conditions on the conversion of diphenyl urea to ethyl phenyl carbamate.

Several experiments were carried out to check the material balance and reproducibility of the experimental data, at 423 K. The material balance of products (ethyl phenyl carbamate and aniline), formed and the reactant (diphenyl urea) consumed was found to be more than 98 % by gas chromatographic analysis. The reproducibility of the data was found to be within ± 5 % error. The results are presented as conversion of diphenyl urea and selectivity of ethyl phenyl carbamate as defined below.

The conversion of diphenyl urea (DPU) is defined as:

$$\text{Conversion } (\%) = \left[\frac{(\text{ DPU charged}) - (\text{ DPU reacted})}{\text{DPU charged}} \times 100\right], \quad (3.3)$$

The selectivity to ethyl phenyl carbamate (EPC) is defined as

$$\text{Selectivity}_{\text{EPC}} \ (\%) = \left[\frac{\text{EPC formed}}{\text{DPU consumed}} \times 100\right], \quad (3.4)$$

3.3.1 Effect of Catalysts

To study the effect of catalyst types on the ethanolysis reaction, several reactions were carried out in the presence of 5% Pd/C, 5%Rh/C, 5% Pd/C-LiI, 5%Rh/C-LiI, $CoCl_2$, $MnCl_2$ and $SnCl_2$ as catalysts. This was important to assess whether ethanolysis is a catalytic reaction or not. The results are presented in Table 3.1. It was observed that the conversion of diphenyl urea to ethyl phenyl carbamate (≈ 63 %) was not affected by the presense of any of the catalysts screened. A variation

TABLE 3.1

EFFECT OF DIFFERENT CATALYSTS ON ETHANOLYSIS REACTION

Sr.No	Catalyst	Concentration kmol/m^3	Conversion %
1	-	-	61.4
2	Pd/C	0.4*	62.2
3	Pd/C-LiI**	0.4 *	62.5
4	Rh/C	0.4 *	61.9
5	Rh/C-LiI**	0.4 *	62.2
6	$MnCl_2$ $2H_2O$	5.14×10^{-3}	63.1
7	$SnCl_2$ $6H_2O$	8.93×10^{-4}	65.3
8	$CoCl_2$ $4H_2O$	7.23×10^{-4}	66.7
9	$CoCl_2$ $4H_2O$	2.51×10^{-3}	68.2
10	$CoCl_2$ $4H_2O$	9.87×10^{-3}	69.5

* : kg/m^3; ** : 8.7×10^{-3}, kmol/m^3

<u>Reaction Conditions</u>

Diphenyl urea	:	0.27, kmol/m^3;
Ethanol	:	1.73, kmol/m^3;
Temperature	:	423, K;
Agitation speed	:	600, rpm;
Reaction time	:	2, hours.

in the concentration of $CoCl_2$, from 0 to 9.87×10^{-3}, kmol/m^3, also showed a very marginal increase in conversion of diphenyl urea (from 61 to 69 %). As the effect of catalyst on the ethanolysis of diphenyl urea was marginal, further reactions were carried out in the absence of catalysts.

3.3.2 Effect of Solvents

The ethanolysis of diphenyl urea was carried out in different solvents such as dimethyl formamide, benzene, toluene, ethyl acetate and ethanol at 423, K. The reactions were carried out for 3 hours and the results are presented in Table 3.2. For all solvents, except dimethyl formamide, the conversion of diphenyl urea was greater than 90%. The observed trend may be due to the formation of a 1:1 complex between diphenyl urea and dimethyl formamide (Kozlova and Zharkov (1974)), which may inhibit further reaction. Of the solvents screened, the conversion was higher in ethanol and ethyl acetate (100 and 97.5 % respectively). However, to study the effect of ethanol concentration on ethanolysis reaction, ethyl acetate was used as a solvent in further reactions.

3.3.3 Effect of water concentration

Water is produced in stoichiometric amounts in the oxidative carbonylation reaction (Eqn. 3.1) and was found to inversely affect the rate of the reaction (Section 2.3.3.16,

TABLE 3.2

EFFECT OF SOLVENT

Sr.No	Solvent	Conversion %
1	Benzene	92.1
2	Toluene	94.3
3	Dimethyl formamide	20.3
4	Ethyl acetate	97.5
5	Ethanol	100

Reaction Conditions

Diphenyl urea	:	0.27, kmol/m^3;
Ethanol	:	1.73, kmol/m^3;
Temperature	:	423, K;
Agitation speed	:	600, rpm;
Reaction time	:	3, hours.

Chapter 2). It was also observed to enhance the side reaction, leading to oxidation of carbon monoxide to carbon dioxide. Hence, it was thought necessary to investigate effect of water on ethanolysis reaction. To study the effect of water concentration, several experiments were carried out by varying concentration of water between a concentration range of 0 to 5.56 kmol/m^3. The results are presented in Table 3.3. The selectivity to ethyl phenyl carbamate was found to decrease from 98.25 to 20.75 % with increase in concentration of water from 0 to 5.56, kmol/m^3 respectively and the major side product formed was aniline.

3.3.4 Effect of Ethyl Phenyl Carbamate concentration

The effect of ethyl phenyl carbamate concentration on conversion of diphenyl urea, was investigated by adding ethyl phenyl carbamate externally to the reaction mixture. The experiments were carried out at 423, K and the concentration of ethyl phenyl carbamate was varied between 0 and 0.548 kmol/m^3. The results are presented in Table 3.4. The results indicate that ethyl phenyl carbamate has negligible effect on ethanolysis reaction.

3.3.5 Effect of diphenyl urea concentration

The effect of concentration of diphenyl urea on the ethanolysis of diphenyl urea to ethyl phenyl carbamate was investigated at 423 K. The concentration of diphenyl

TABLE 3.3

EFFECT OF WATER CONCENTRATION

Sr.No	Concentration kmol/m^3	Selectivity to EPC %
1	0	98.3
2	0.28	90.4
3	0.56	78.6
4	2.77	50.2
5	5.56	20.7

Reaction Conditions

Diphenyl urea : 0.27, kmol/m^3;
Ethanol : 1.73, kmol/m^3;
Temperature : 423, K;
Agitation speed : 600, rpm;
Reaction time : 2, hours.

TABLE 3.4

EFFECT OF CARBAMATE CONCENTRATION

Sr.No	Concentration kmol/m^3	Conversion %
1	0	61.4
2	0.27	59.7
3	0.55	58.3

<u>Reaction Conditions</u>

Diphenyl urea	:	0.27, kmol/m^3;
Ethanol	:	1.73, kmol/m^3;
Temperature	:	423, K;
Agitation speed	:	600, rpm;
Reaction time	:	2, hours.

urea was varied from 0.034 to 0.548 kmol/m^3 and the results are presented in Table 3.5. The conversion of diphenyl urea was found to decrease (from 96.5 to 50.3 %) with increase in diphenyl urea concentration (from 0.034 to 0.548 kmol/m^3). The selectivity to ethyl phenyl carbamate ($\approx$ 98 %) was not affected by increase in the concentration of diphenyl urea.

3.3.6 Effect of ethanol concentration

The effect of ethanol concentration, on the conversion of diphenyl urea to ethyl phenyl carbamate, was studied in a concentration range of 0.57 to 7.32 kmol/m^3 at 423, K. The results are presented in Table 3.6. The conversion of diphenyl urea was found to increase from 52.2 % to 98.9 % with the increase in concentration of ethanol from 0.57 to 7.32 kmol/m^3. The selectivity to ethyl phenyl carbamate was more than 98 % at all concentrations.

3.3.7 Effect of aniline concentration

To study the effect of aniline concentration on ethanolysis of diphenyl urea to ethyl phenyl carbamate, several experiments were carried out at 423, K by adding aniline externally to the reaction mixture. The concentration of aniline was varied between 0 and 0.55, kmol/m^3 and the results are presented in Table 3.7. It was observed that increase in aniline concentration in the reaction mixture decreases the conversion

TABLE 3.5

EFFECT OF DIPHENYL UREA CONCENTRATION

Sr.No	Concentration $\times 10^1$, $kmol/m^3$	Conversion %
1	0.34	96.5
2	0.69	89.2
3	1.30	72.6
4	2.74	61.4
5	5.48	50.3

<u>Reaction Conditions</u>

Ethanol	:	1.73, $kmol/m^3$;
Temperature	:	423, K;
Agitation speed	:	600, rpm;
Reaction time	:	2, hours.

TABLE 3.6

EFFECT OF ETHANOL CONCENTRATION

Sr.No	Concentration kmol/m^3	Conversion %
1	0.57	52.2
2	0.87	58.8
3	1.73	61.4
4	7.32	98.9

Reaction Conditions

Diphenyl urea : 0.27, kmol/m^3;
Temperature : 423, K;
Agitation speed : 600, rpm;
Reaction time : 2, hours.

TABLE 3.7

EFFECT OF ANILINE CONCENTRATION

Sr.No	Concentration kmol/m^3	Conversion %
1	0	61.4
2	0.11	48.8
3	0.33	38.2
4	0.55	18.1

Reaction Conditions

Diphenyl urea	:	0.27, kmol/m^3;
Ethanol	:	1.73, kmol/m^3;
Temperature	:	423, K;
Agitation speed	:	600, rpm;
Reaction time	:	2, hours.

of diphenyl urea from 61.4 % to 18.1 %. However, the selectivity to ethyl phenyl carbamate was more than 98 %.

3.3.8 Effect of Temperature

The effect of reaction temperature on ethanolysis of diphenyl urea to ethyl phenyl carbamate was investigated by varying reaction temperature between 303 and 473, K. The results are presented in Table 3.8. The conversion of diphenyl urea (< 6 %) was found to be negligible below 373, K. With increase in temperature from 393 to 473, K the conversion of diphenyl urea increased from 30.3 to 100 %. The selectivity to ethyl phenyl carbamate was more than 98 % for all reactions.

Diphenyl urea is known to decompose on heating to give equimolar amounts of phenyl isocyanate and aniline (Hoshino et. al. (1952), Csuros et. al. (1971)) as shown below.

$$C_6H_5NHCONHC_6H_5 \rightleftharpoons C_6H_5NCO \quad + \quad C_6H_5NH_2 \qquad (3.5)$$

The reactions of phenyl isocyanate with substrates having acidic hydrogen are well known (Arnold et. al.(1957)). In the present reaction system, phenyl isocyanate may react with aniline, ethanol or water to give diphenyl urea, ethyl phenyl carbamate and aniline and carbon dioxide respectively as shown below:

TABLE 3.8

EFFECT OF TEMPERATURE

Sr.No	Temperature K	Conversion %
1	303	-
2	333	01.9
3	373	05.3
4	393	30.3
5	413	48.8
6	423	61.4
7	433	84.7
8	443	100.0

Reaction Conditions

Diphenyl urea : 0.27, kmol/m^3;
Ethanol : 1.73, kmol/m^3;
Agitation speed : 600, rpm;
Reaction time : 2, hours.

$$C_6H_5NCO \quad + \quad C_2H_5OH \longrightarrow \quad C_6H_5NHCOOC_2H_5 \tag{3.6}$$

$$C_6H_5NCO \quad + \quad C_6H_5NH_2 \longrightarrow \quad C_6H_5NHCONHC_6H_5 \tag{3.7}$$

$$C_6H_5NCO \quad + \quad H_2O \longrightarrow \quad C_6H_5NH_2 + CO_2 \tag{3.8}$$

These reactions are spontaneous reactions and the rates of addition of phenyl isocyanate with each of the substrate depends on it's concentration. Thus an increase in the concentration of any one of these substrates will decrease the rate of the other two reactions. This has been observed, in the present work, for the effect of water, ethanol and aniline concentrations on the conversion of diphenyl urea to ethyl phenyl carbamate (Section 3.3.3, 3.3.6 and 3.3.7 respectively). The reaction of aniline with phenyl isocyanate is known to be catalyzed by diphenyl urea and aniline (Borsus et. al. (1982)) and hence an increase in concentration of diphenyl urea and aniline (Section 3.3.5 and 3.3.7 respectively) decreases the conversion of diphenyl urea to ethyl phenyl carbamate.

The following conclusions may be drawn from the above investigations:

1. The ethanolysis of diphenyl urea to ethyl phenyl carbamate is not catalyzed by 5 % Pd/C, 5 % Rh/C, 5 % Pd/C-LiI, 5 % Rh/C-LiI, $MnCl_2$, $SnCl_2$ and $CoCl_2$.

2. The ethanolysis reaction was found to be independent of the nature of solvents, though in highly polar dimethyl formamide the conversion of diphenyl urea to ethyl phenyl carbamate was low.

3. The conversion of diphenyl urea was affected inversely by the presence of water and with increase in water concentration, the major side product being aniline.

4. The conversion of diphenyl urea to ethyl phenyl carbamate decreased with increase in diphenyl urea and aniline concentrations.

5. An increase in ethanol concentration was found to increase the conversion of diphenyl urea.

3.3.9 Kinetic Study

In the previous sections, the results on the ethanolysis of diphenyl urea to ethyl phenyl carbamate are presented and the effect of reaction conditions is discussed. Further to this work, it was also the objective of this work to investigate the kinetics of ethanolysis of diphenyl urea to ethyl phenyl carbamate. A knowledge of the reaction kinetics is essential as it describes the variation of rate of reaction with concentration of different species involved and temperature. It is also useful in understanding the reaction mechanism. Such studies are also important in developing rate equations which are useful for design and scale up of reactors. The kinetics of thermal dissociation of diphenyl urea in aliphatic carboxylic acids like acetic, propionic and butyric acids, and alcohols like cyclohexanol has been reported (Hoshino et. al. (1952), Csuros et. al. (1971)), though there have been no reports on the kinetics of ethanolysis of diphenyl urea.

The kinetics of the ethanolysis of diphenyl urea to ethyl phenyl carbamate was studied in a temperature range of 413 to 433 K. Several experiments were carried out by varying the concentrations of diphenyl urea, ethanol and aniline. The range of variables for the kinetic study are given in Table 3.9. The progress of each kinetic run was monitored by taking samples from the reactor at different time intervals and analyzing for ethyl phenyl carbamate and aniline by gas chromatography. The typical plots of ethyl phenyl carbamate formed with time for aniline, ethanol and diphenyl urea concentrations at 413, 423,and 433 K are shown in Figs 3.1, 3.2 and 3.3 respectively.

The material balance of reactant, diphenyl urea, to products, ethyl phenyl carbamate and aniline, corresponded to more than 98 %, as per the stoichiometery of Eqn. 3.2. Hence, the initial rate of the ethanolysis of diphenyl urea to ethyl phenyl carbamate was calculated from the plot of ethyl phenyl carbamate formed vs time. The initial region, corresponding to about 10 % conversion of diphenyl urea, was chosen for the calculation of the initial rate. The initial rate, R_A (kmol/m^3/s), of the reaction was calculated as

$$R_A = \frac{\text{Slope of plot of a EPC formed vs time}}{\text{Volume of liquid}}, \quad \frac{\text{kmol/s}}{\text{m}^3} \tag{3.9}$$

TABLE 3.9

RANGE OF VARIABLES STUDIED FOR KINETICS

Sr.No	Variables Studied	Range kmol/m^3
1	Diphenyl urea	0.03-0.55
2	Ethanol	0.57 - 7.32
3	Aniline	0 - 0.55
4	Temperature	413 - 433, K

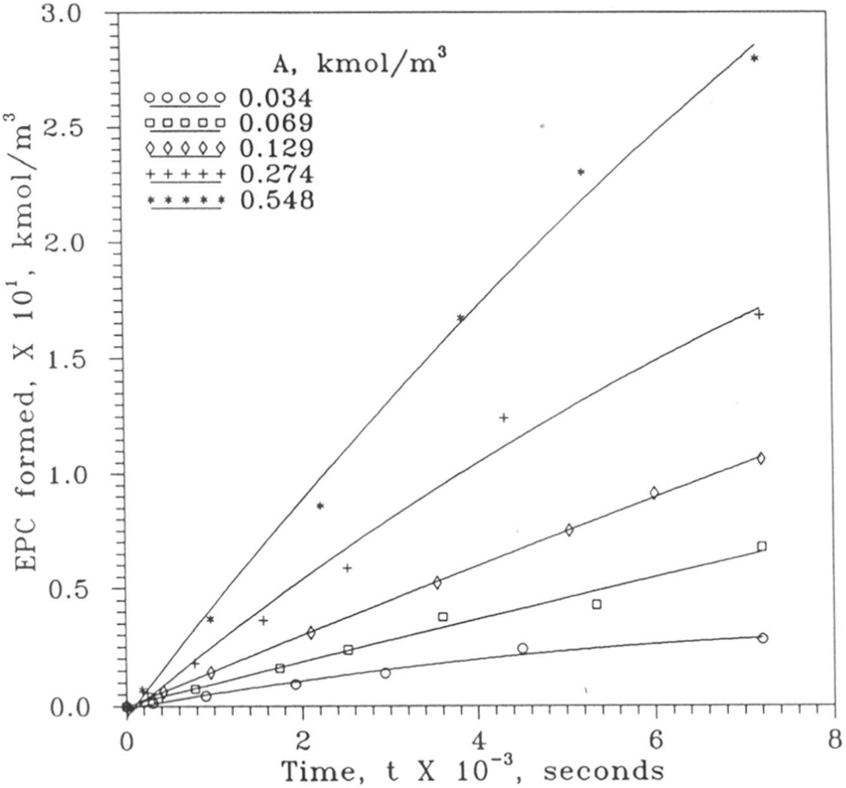

FIGURE 3.1 PLOT OF EPC FORMED WITH TIME, EFFECT OF DIPHENYL UREA CONCENTRATION

Reaction conditions:

Ethanol	:	**1.73, kmol/m^3;**
Temperature	:	**413, K;**
Solvent	:	**Ethyl acetate;**
Agitation speed	:	**600, rpm.**

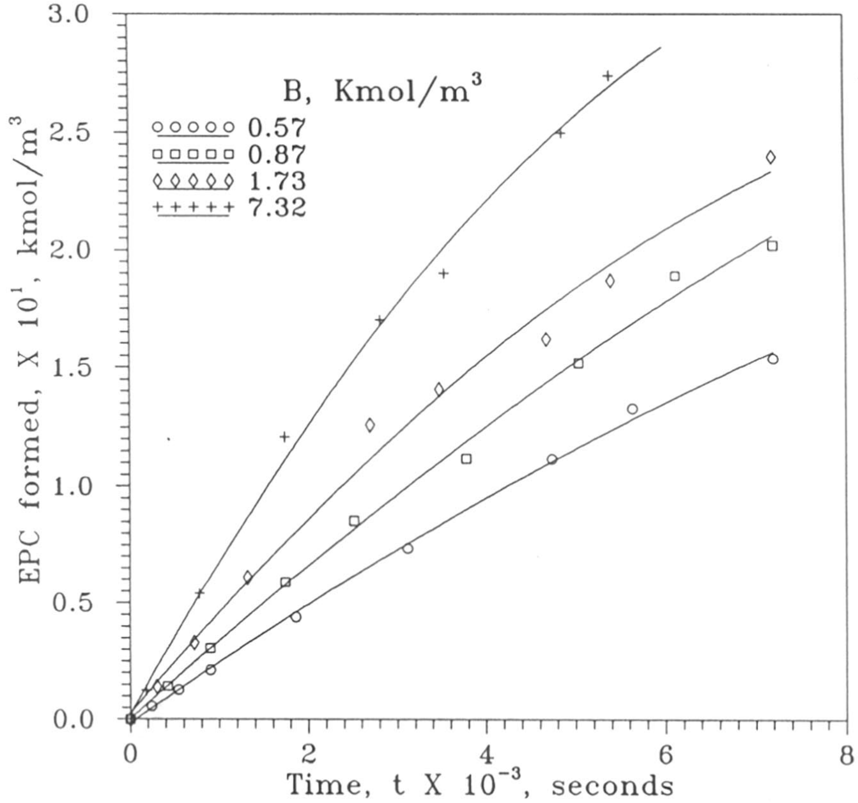

FIGURE 3.2 PLOT OF EPC FORMED WITH TIME, EFFECT OF ETHANOL CONCENTRATION

Reaction conditions:

Diphenyl urea	**:**	**0.27, kmol/m³;**
Temperature	**:**	**423, K;**
Solvent	**:**	**Ethyl acetate;**
Agitation speed	**:**	**600, rpm.**

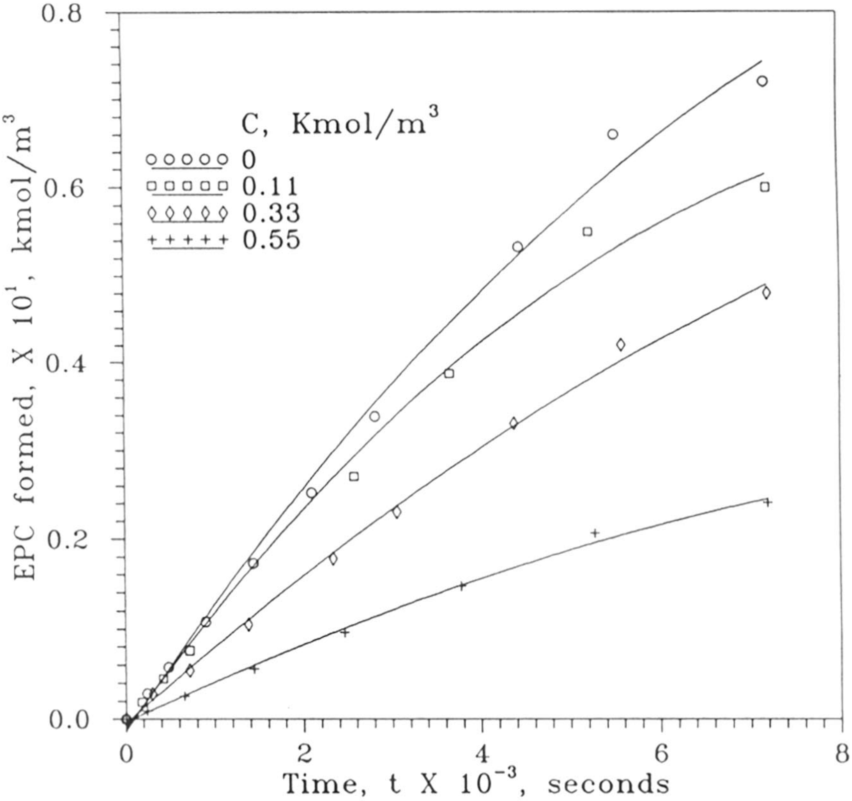

FIGURE 3.3 PLOT OF EPC FORMED WITH TIME, EFFECT OF ANILINE CONCENTRATION

Reaction conditions:

Diphenyl urea	:	**0.27, kmol/m^3;**
Ethanol	:	**1.73, kmol/m^3;**
Temperature	:	**433, K;**
Solvent	:	**Ethyl acetate;**
Agitation speed	:	**600, rpm.**

The effect of concentration of diphenyl urea, ethanol and aniline on the initial rate of the reaction was investigated and the results are shown in Figs 3.4-3.6. The important observations are summarized below:

- The initial rate of the reaction was found to increase linearly at lower concentration of diphenyl urea and marginally at higher concentrations (Fig 3.4).
- The initial rate of the reaction was found to increase linearly at lower concentrations and independent at higher concentrations of ethanol (Fig 3.5).
- The initial rate of the reaction decreases linearly with increase in concentration of aniline (Fig 3.6).

In order to develop a suitable rate equation to represent the kinetics of ethanolysis of diphenyl urea to ethyl phenyl carbamate, the initial rate data presented above over a temperature range of 413-433 K was used. The observed trends indicate that the rate of the reaction is dependent linearly at lower concentrations of diphenyl urea and ethanol and independent at higher concentrations. The rate decreases linearly with increase in aniline concentration.

Several rate equations were examined to fit the above rate data and these are presented in Table 3.10. The various rate parameters were optimized by using an optimization program (Marquardt, 1962). The evaluated rate parameter values and the minimum of squares of the difference between the observed and predicted initial rates, $\phi_{\min}$ are also presented in Table 3.10. The rates

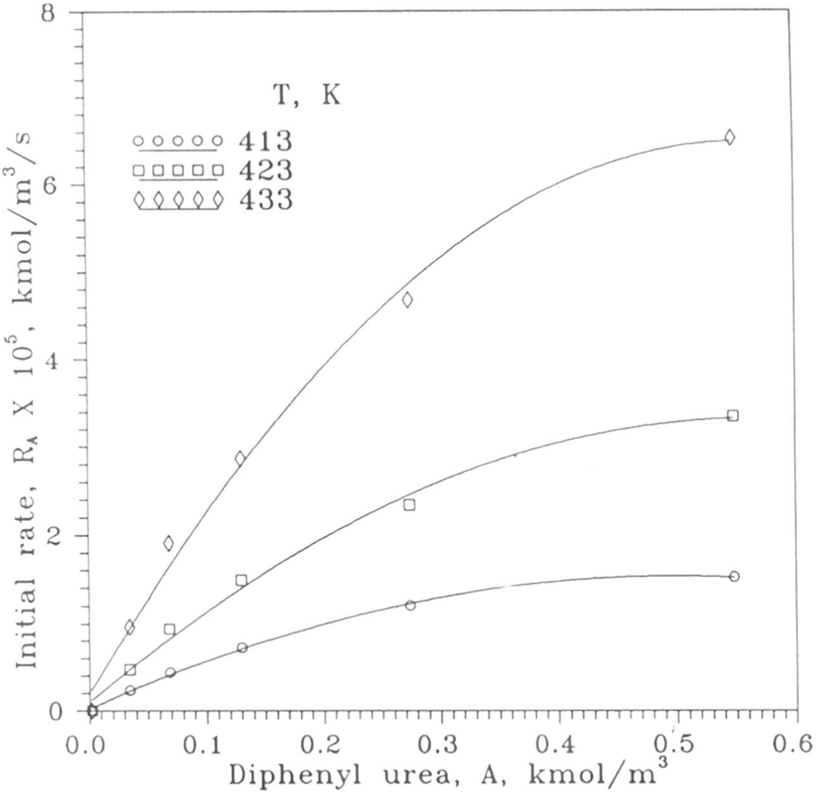

FIGURE 3.4 EFFECT OF DIPHENYL UREA CONCENTRATION ON THE RATE OF ETHANOLYSIS OF DIPHENYL UREA

Reaction conditions:

Ethanol	:	**1.73, kmol/m^3;**
Solvent	:	**Ethyl acetate;**
Agitation speed	:	**600, rpm.**

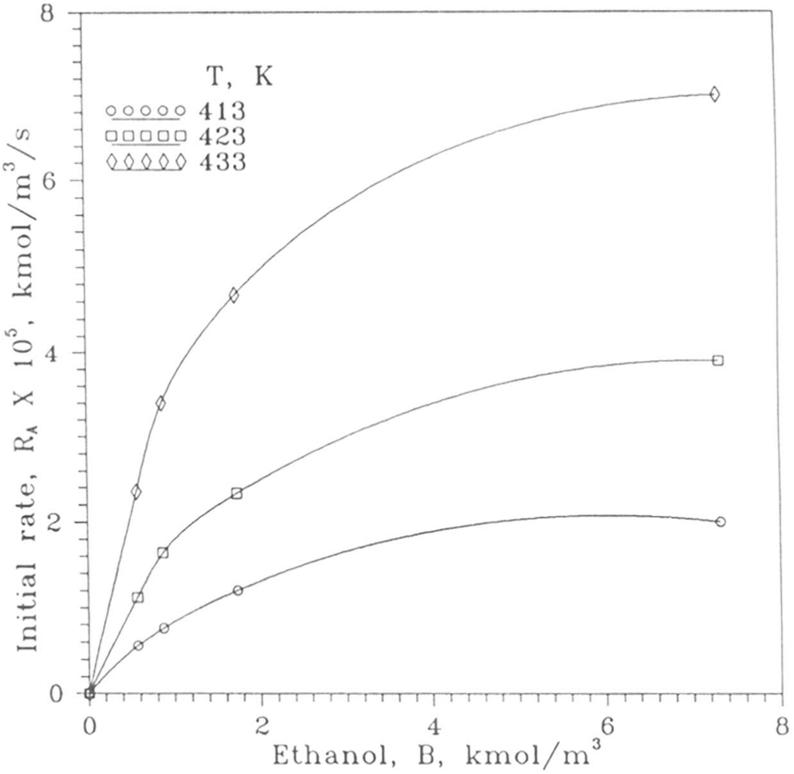

FIGURE 3.5 EFFECT OF ETHANOL CONCENTRATION ON THE RATE OF ETHANOLYSIS OF DIPHENYL UREA

Reaction conditions:

Diphenyl urea	:	0.27, kmol/m^3;
Solvent	:	Ethyl acetate;
Agitation speed	:	600, rpm.

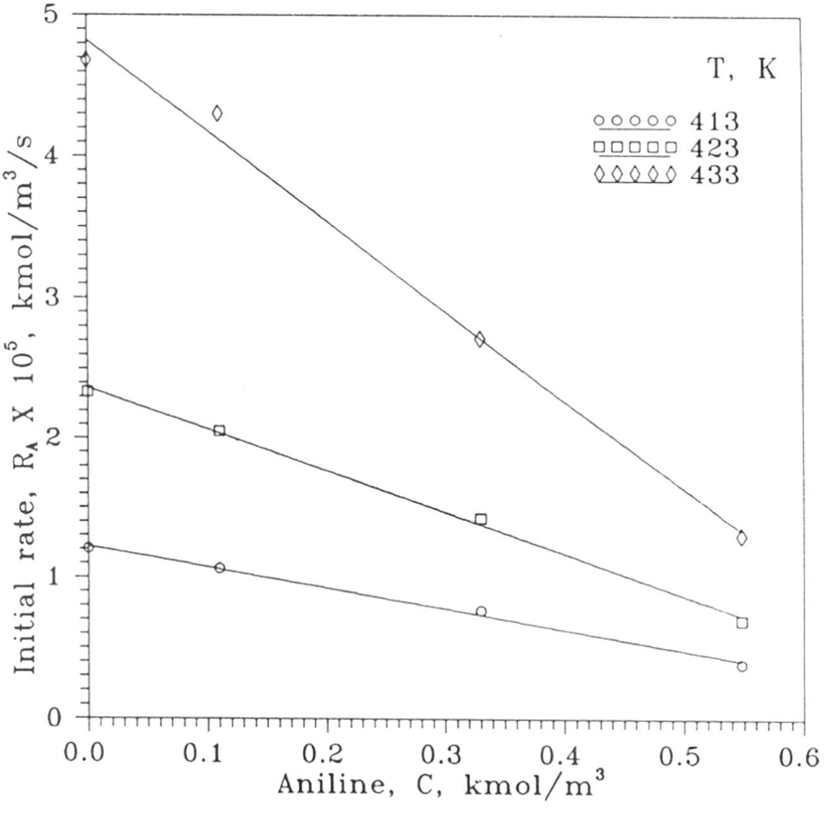

FIGURE 3.6 EFFECT OF ANILINE CONCENTRATION ON THE RATE OF ETHANOLYSIS OF DIPHENYL UREA

Reaction conditions:

Diphenyl urea	:	0.27, kmol/m^3;
Ethanol	:	1.73, kmol/m^3;
Solvent	:	Ethyl acetate;
Agitation speed	:	600, rpm.

TABLE 3.10

RATE MODELS EXAMINED TO FIT THE DATA FOR ETHANOLYSIS OF DIPHENYL UREA

Sr. No.	Rate model	Temp K	k $m^3/kmol/s$	K_A $m^3/kmol$	K_B $m^3/kmol$	K_C $m^3/kmol$	ϕ_{min}
1	$\frac{kAB}{(1+K_A A)(1+K_B B)(1+K_C C^{2.4})}$	413 423 433	9.3×10^{-5} 1.8×10^{-4} 3.6×10^{-4}	3.85 3.20 3.06	0.48 0.54 0.55	8.2 10.0 11.2	1.8×10^{-12} 6.6×10^{-12} 2.9×10^{-11}
2	$\frac{kAB}{(1+K_A A)(1+K_B B)(1+K_C C)}$	413 423 433	9.7×10^{-5} 1.9×10^{-4} 4.6×10^{-4}	3.96 3.40 3.03	0.50 0.57 0.80	2.2 2.6 2.6	5.2×10^{-12} 1.7×10^{-11} 9.1×10^{-11}
3	$\frac{kA^{0.9}B}{(1+K_B B)(1+K_C C^2)}$	413 423 433	3.2×10^{-5} 6.9×10^{-5} 1.7×10^{-4}	- - -	0.36 0.43 0.63	4.5 5.7 6.0	3.7×10^{-11} 9.6×10^{-11} 4.1×10^{-10}
4	$\frac{kAB^{0.6}}{(1+K_A A)(1+K_C C^2)}$	413 423 433	4.6×10^{-5} 7.3×10^{-5} 1.4×10^{-4}	2.63 1.42 1.25	- - -	4.1 4.7 4.7	3.3×10^{-11} 1.5×10^{-10} 9.9×10^{-10}
5	$\frac{kA^{0.7}B^{0.75}}{1+K_C C^{3.5}}$	413 423 433	1.4×10^{-5} 2.9×10^{-5} 5.5×10^{-5}	- - -	- - -	9.5 12.0 12.1	8.5×10^{-11} 3.7×10^{-10} 2.0×10^{-9}

predicted by models 2, 3, 4 and 5 were not consistent with the observed rates. The rates as predicted by model 2 for the effect of aniline concentration was higher (5.3×10^{-6} as against observed 3.9×10^{-6} kmol/m^3/s at 413, K), while model 3 gave higher rates for the concentration of diphenyl urea (3.3×10^{-6} as against observed 2.34×10^{-6} kmol/m^3/s at 423, K), rates predicted by model 4 were inconsistent with the effects of diphenyl urea and aniline and rates predicted by model 5 were inconsistent with the observed rates of ethanol and diphenyl urea concentration effects. Hence these models were rejected.

The rates predicted by model 1, were found to represent the observed trends satisfactorily and the model is given below:

$$R_A = \frac{k\ A\ B}{(1 + K_A\ A)(1 + K_B\ B)\ (1 + K_C\ C^{2.4})} \tag{3.10}$$

Where

R_A = Rate of reaction, kmol/m^3/s; A = Concentration of diphenyl urea, kmol/m^3; B = Concentration of ethanol, kmol/m^3; C = Concentration of aniline, kmol/m^3; k = rate constant of the reaction, (kmol/m^3/s)$^{-1}$; K_A = rate parameter dependent on A, m^3/kmol; K_B = rate parameter dependent on B, m^3/kmol; K_C = rate parameter dependent on C, (m^3/kmol)$^{2.4}$.

The rates predicted using the above rate model were found to agree within ± 6 % with the experimental data, thus indicating that model 1 fits the rate data satisfactorily at all temperatures (Fig 3.7). The Arrhenius plot of ln k

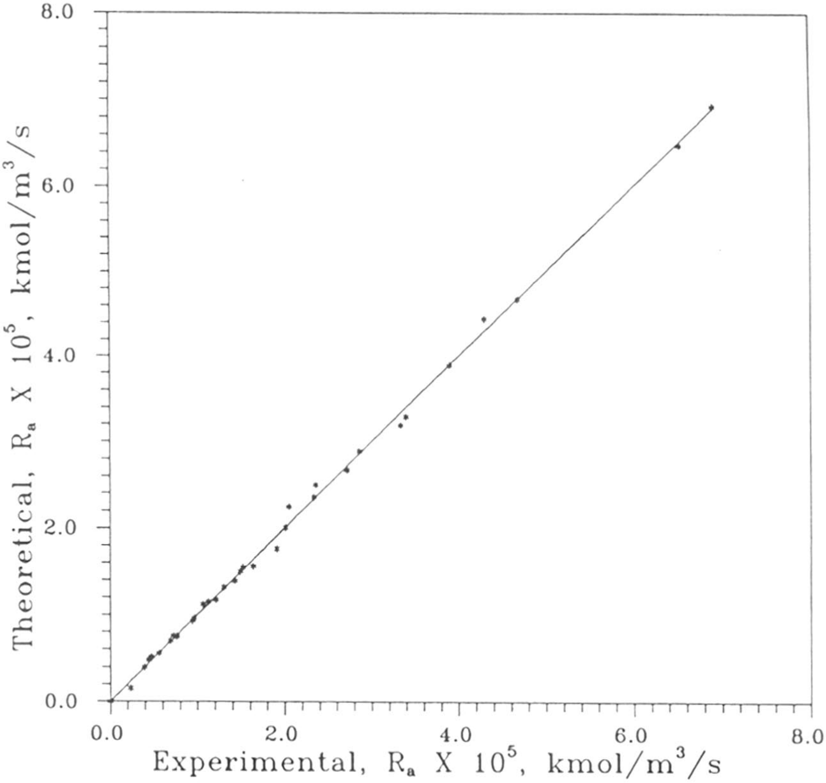

FIGURE 3.7 PLOT OF R_A PREDICTED
vs R_A EXPERIMENTAL

vs $\frac{1}{T}$ is shown in Fig 3.8 and the activation energy was calculated to be 26.9 kcal/mol.

3.4 CONCLUSIONS

The ethanolysis of diphenyl urea to ethyl phenyl carbamate has been investigated. The effect of catalysts, solvents and reaction conditions on the conversion of diphenyl urea and selectivity to ethyl phenyl carbamate have been evaluated. The following observations were drawn from the study :

- The conversion of diphenyl urea to ethyl phenyl carbamate was independent of the catalysts tested.
- The conversion of diphenyl urea was low in dimethyl formamide ($\approx$ 20 %), though in other solvents it was higher than 90 %.
- The selectivity to ethyl phenyl carbamate is adversely affected by the presence of water in the reaction mixture.
- The conversion of diphenyl urea decreases with increase in diphenyl urea and aniline concentrations.
- The ethanolysis of diphenyl urea increases with the increase in the concentration of ethanol.

The kinetics of ethanolysis of diphenyl urea to ethyl phenyl carbamate was investigated over a temperature range of 413 to 433 K. The following observa-

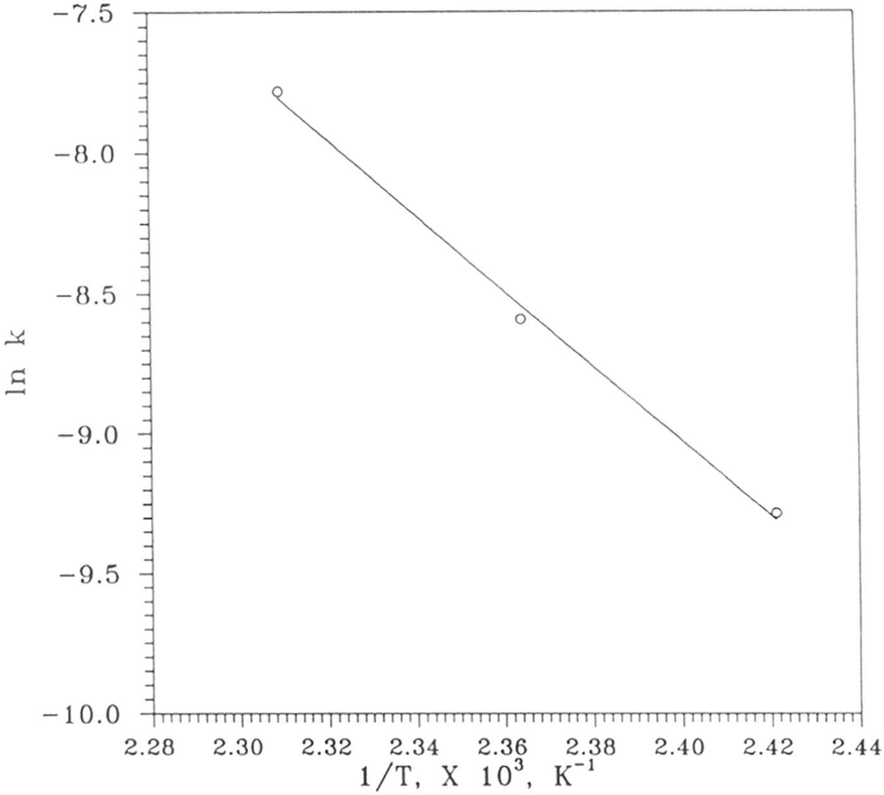

FIGURE 3.8 ARRHENIUS PLOT OF ln k vs $\frac{1}{T}$

tions were made :

- The rate of the reaction was found to increase linearly with increase in concentration of diphenyl urea and ethanol, however, at higher concentrations the rate was found to be a mild function of concentrations.
- The rate of the reaction was found to decrease linearly with increase in concentration of aniline in the reaction mixture.

The following rate equation was found to represent the kinetics of the reaction.

$$R_A = \frac{k\ A\ B}{(1 + K_A\ A)\ (1 + K_B\ B)\ (1 + K_C\ C^{2.4})} \qquad (3.11)$$

The various rate parameters have been evaluated at different temperatures and the activation energy was found to be 26.9 kcal/mol.

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CHAPTER 4

CARBONYLATION OF ALLYL CHLORIDE OVER PALLADIUM CATALYSTS

4.1 GENERAL INTRODUCTION

The carbonylation of organic substrates is a synthetically important reaction and a variety of products such as unsaturated acids, esters, ketones or aldehydes and lactones, lactams, amides, carbonates and urethanes can be synthesized by this route (Coloquohn et. al.(1991)). Most of these reactions use soluble metal complex catalysts, which very often give high selectivity to the desired products. In recent years, new reactions involving carbonylation of allylic substrates have been reported leading to novel routes for the synthesis of unsaturated acid chlorides and carboxylic acids (Hegedus (1991)). These reactions are known to be catalyzed by transition metal catalysts consisting of mainly palladium and nickel complexes [Trost and Verhoeven (1982), Tsuji (1982,1985) and Jolly (1982), Chiusoli and Salerno (1985) respectively]. Palladium catalysts may be used in the form of salts, complex or metal (Dent et. al. (1964), Kiji et. al. (1988)).

A summary of palladium based catalysts for the carbonylation of allyl chloride is presented in Table 1.4 of Chapter 1. The main products formed are the isomers of butenoic acids or their esters and unsaturated acid chlorides as shown below:

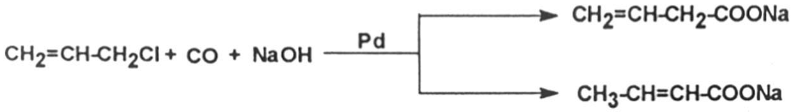
$$\mathrm{CH_2{=}CH\text{-}CH_2\text{-}Cl} \;+\; \mathrm{CO} \;\xrightarrow{\mathrm{Pd}}$$

$$\mathrm{CH_2{=}CH\text{-}CH_2COOH} \;+\; \mathrm{CH_3\text{-}CH{=}CH\text{-}COOH} \qquad (4.1)$$

$$\mathrm{CH_2{=}CH\text{-}CH_2\text{-}Cl} + \mathrm{CO} \xrightarrow{\mathrm{Pd}} \mathrm{CH_2{=}CH\text{-}CH_2COCl} + \mathrm{CH_3\text{-}CH{=}CH\text{-}COCl} \qquad (4.2)$$

Kiji et. al. (1988) have recently reported that using Na_2PdCl_4 catalyst in a biphasic medium (the aqueous phase containing sodium hydroxide) carbonylation of allyl chloride is feasible at 298, K and 1 atmosphere of carbon monoxide. The selectivity of the reaction to vinyl acetic acid is also high (> 88 %). The previous work on this reaction has mainly addressed the synthesis of unsaturated acid/chloride derivatives and very limited published information on the reaction kinetics and role of reaction conditions on activity and selectivity of Pd catalyst is available. Hence, the present work was undertaken to study the effect of reaction conditions and kinetics of carbonylation of allyl chloride in a biphasic medium. The carbonylation of allyl chloride in a biphasic medium is also an unique example of a multiphase catalytic reaction involving gas-liquid- liquid-solid phases. Hence the importance of interface mass transfer in the rate of carbonylation also needs to be considered in the kinetic analysis.

The stoichiometric reaction is :



(4.3)

and the main products are the sodium salt of vinyl acetic and crotonic acids.

In the present work, screening of various catalyst precursors, ligands, solvents, liquid phase hold-up and the effect of temperature, partial pressure of carbon monoxide and concentrations of sodium hydroxide and allyl chloride on the activity and selectivity, of palladium catalysts has been investigated.

4.2 EXPERIMENTAL

4.2.1 Materials

Allyl chloride, pyridine, triphenyl phosphine, potassium iodide and sodium hydroxide of AR grade were procured from SD Fine Chemicals Ltd., India. The solvents benzene, toluene, cyclohexane, hexane and ethanol were of AR grade and distilled before use. Palladium chloride was procured from Arrora Mathey, Calcutta. Carbon monoxide of more than 99 % purity was used directly from a cylinder.

4.2.2 Catalyst Preparation

Palladium sponge was prepared by reducing palladium chloride with hydrazine hydrate. Some complexes of palladium were prepared by well known synthetic methods as described below:

- **Bis($\eta^3\pi$-allyl)di-μ-chlorodipalladium (II), $(Pd(\pi\text{-allyl})Cl)_2$**

The complex was synthesized by a method used by Tatsuno et. al. (1973). Allyl chloride (5 gm) was added to a solution of palladium chloride (4.45 gm) and sodium chloride (2.95 gm) in 60 ml aqueous methanol over a period of 20 minutes. After complete addition, carbon monoxide gas was bubbled through the solution for one hour. The reddish brown solution changed to a bright yellow colloidal solution with the passing of carbon monoxide. The suspension was diluted with distilled water and extracted with chloroform. The extract was washed twice with water and then dried. Evaporation of organic solvent gave yellow crystals (4.3 gm, 93 % yield). The recrystallization was done from a 1:1 dichloromethane and hexane mixture. The complex was confirmed from the elemental analysis as shown below:

	Theoretical (%)	Experimental (%)
C	19.72	19.71
H	2.74	2.77
Cl	19.45	19.40
Pd	58.09	57.9

- **Palladium iodide, PdI_2**

Palladium iodide was prepared from palladium chloride and potassium iodide by the method described by Roolsten (1961). To an aqueous hydrochloric acid solution of palladium chloride (2 gm), a saturated aqueous solution of potassium iodide (5ml) was added. The precipitation of palladium iodide was instantaneous. It was filtered out and washed with water till all traces of acid was removed. The yield was about 98 %.

- **Palladium bis (pyridine) dichloride, $Pd(py)_2Cl_2$**

The complex was prepared by a method described by Gupte (1989). To a solution of palladium chloride (5.64 mmol) in 25 ml water, pyridine (22.5 mmol) was added. The solution was refluxed for 4.5 hours. The colour of the solution changed from wine red to yellow after 30 minutes of refluxing. 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 ethanol giving a yield of 92 %. The elemental analysis of the complex given below:

	Theoretical (%)	Experimental (%)
C	35.82	35.80
H	2.98	3.00
N	8.36	8.30
Cl	21.19	21.20
Pd	31.64	31.23

- **Palladium bis(triphenyl phosphine) dichloride, $Pd(PPh_3)_2Cl_2$**

The complex was prepared by the method reported by Itatani and Bailor (1967). Palladium chloride (5.64 mmol), triphenylphosphine (17 mmol) were added to a solution of 150 ml of ethanol and 50 ml of water with two drops of conc. sulfuric acid. The solution was refluxed for four hours. On cooling the solution, yellow complex of $Pd(PPh_3)_2Cl_2$ precipitated out. It was filtered and washed with 500 ml of ethanol and dried in vacuum. The yield of the reaction was 95 %. The complex was confirmed from its elemental analysis as shown below.

	Theoretical (%)	Experimental (%)
C	61.6	61.5
H	4.28	4.25
P	8.84	8.80
Cl	10.12	10.08
Pd	15.12	14.94

4.2.3 Experimental Set Up

The carbonylation experiments were carried out in a 300 ml stirred autoclave reactor made of SS-316 (supplied by Parr Instrument Co, USA). The experimental setup was similar to that described in Fig. 2.1, Chapter 2.

4.2.4 Experimental Procedure

In a typical experiment allyl chloride, 0.61, kmol/m^3, sodium hydroxide, 1.88, kmol/m^3, catalyst Pd metal, 0.59, kg/m^3 and triphenyl phosphine, 5.7×10^{-3}, kmol/m^3 were charged into the autoclave. The reaction was carried out in a biphasic medium consisting of toluene and water in the ratio of 6:4. The total volume of the liquid was 100, ml (1×10^{-4} m^3). The autoclave was first flushed with nitrogen and then with carbon monoxide. The reactor was heated to the required temperature and pressurized with carbon monoxide to 2.0, MPa. The pressure in the reactor was kept constant by supplying carbon monoxide from a reservoir vessel via a constant pressure regulator. The reaction was monitored by observing a drop in pressure in the reservoir vessel with time. At the end of the reaction, the autoclave was discharged of its gaseous components and the liquid components were separated out for analysis. The kinetic runs were carried out at a constant agitation speed of 600 rpm. In each of the kinetic runs, initial and final samples were analyzed and only those runs were taken into consideration in which the material balance of reactants to products matched to more than 95 %.

4.2.5 Analytical Methods

The analysis of allyl chloride and products, vinyl acetic acid and crotonic acid, was done by gas chromatography after the usual workup. They were analyzed on a Dani-3800 gas chromatograph using 8 ' 5 % OV-17 on chromosorb column. The various conditions used for the analysis are presented in Table 4.1. Allyl chloride was analyzed in both initial and final samples of the organic phase. The aqueous phase was separated and analysed for the acid products the following procedure :

TABLE 4.1

GAS CHROMATOGRAPHY CONDITIONS FOR LIQUID ANALYSIS

Sr.No.		Conditions
1.	Column	8', 5% OV-17 on Chromosrb
2.	Carrier gas	Nitrogen, 20 ml/min.
3.	Injector temperature	473 K
4.	Oven Temperature	
	Initial	333 K for 2 mins
	Final	373 K for 8 mins
	Rate of heating	10 K/min
5.	FID Temperature	533 K

- The alkaline aqueous layer was neutralized with hydrochloric acid.
- The neutralized aqueous phase was solvent extracted thrice with dichloromethane.
- The dichloromethane layers were collected and concentrated by the removal of the solvent by distillation.
- The concentrated solution was diluted to 60 ml with dichloromethane and then analyzed by gas chromatography.

The above procedure was standardized for synthetic samples containing vinyl acetic and crotonic acids and the analysis matched to more than ± 3 % error.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Preliminary Observations

Several experiments were carried out on the carbonylation of allyl chloride using palladium catalysts with the aim of investigating the product distribution and role of promoters, solvents, liquid phase holdup and reaction conditions. The results are discussed as activity and selectivity of Pd catalyst defined as :

$$\text{Average activity} = \frac{\text{Allyl chloride reacted}}{\text{(wt of catalyst) (time)}} \quad , \quad \frac{\text{kmol}}{\text{kg sec}} \qquad (4.4)$$

The selectivity to vinyl acetic acid (VAA) was defined as:

$$\text{Selectivity for VAA (\%)} = \frac{\text{VAA formed}}{\text{allyl chloride reacted}}, \times 100 \qquad (4.5)$$

The selectivity to crotonic acid (CA) was defined as:

$$\text{Selectivity for CA (\%)} = \frac{\text{CA formed}}{\text{allyl chloride reacted}}, \times 100 \qquad (4.6)$$

A few initial experiments were carried out with $PdCl_2 + PPh_3$ as a catalyst precursor system and NaOH as a promoter to check the material balance. The important observations made were:

- The reaction involves contacting of four phases as Pd catalyst is precipitated under reaction conditions. Hence CO is the gas phase reactant, Pd catalyst is in a suspended solid state and the liquid phase consist of two immiscible phases (namely toluene and aqueous sodium hydroxide). It is likely in this case that the catalytic cycle involves dissolution-precipitation of Pd complex catalyst.
- An unique observation is the presense of Pd catalyst at the liquid- liquid interface.

- The amount of carbon monoxide and allyl chloride consumed was found to match with the products (vinyl acetic and crotonic acids) formed as per the stoichiometry. Also nearly complete conversion of allyl chloride is achievable.
- In the absence of NaOH, no reaction occurs and also a certain critical concentration of NaOH is necessary for the carbonylation to initiate.
- No gaseous side products were observed.

Further experiments were carried out to investigate the influence of different catalysts, ligands, solvents, liquid phase holdup and reaction conditions on the palladium catalyzed carbonylation of allyl chloride and the results are discussed below.

4.3.2 Screening of Palladium Catalysts

Various palladium catalysts were examined for the carbonylation of allyl chloride to vinyl acetic acid and the results are presented in Table 4.2. The different catalysts screened were $Pd(PPh_3)_2Cl_2$, PdI_2, $Pd(py)_2Cl_2$, $(Pd(\pi\text{- allyl})Cl)_2$ and Pd metal. An important observation was that for all the catalysts used, palladium metal was found to be precipitated after the reaction and adhering to the interface of the organic and aqueous phases. The activity and selectivity, to vinyl acetic acid, ($\approx 2.7 \times 10^{-4}$ kmol/kg/s and 84-88 % respectively) was found to be independent of the Pd catalyst type used. Since, in all these cases the precursors are converted to Pd metal (the content of which was maintained constant in these experiments), similar activity is

TABLE 4.2

SCREENING OF PALLADIUM CATALYSTS

Sr. No.	Catalyst	Average activity, × 10^4, kmol/kg/s	Selectivity VAA %	Selectivity CA %
1	$PdCl_2$	2.57	88.3	10.1
2	PdI_2	2.59	86.4	11.2
3	$Pd(Py)_2Cl_2$	2.62	87.3	11.1
4	Pd metal	2.66	87.8	10.4
5	$(Pd(\pi\text{-allyl})Cl)_2$	2.67	88.1	10.2
6	$Pd(PPh_3)_2Cl_2$	2.42	86.3	12.0

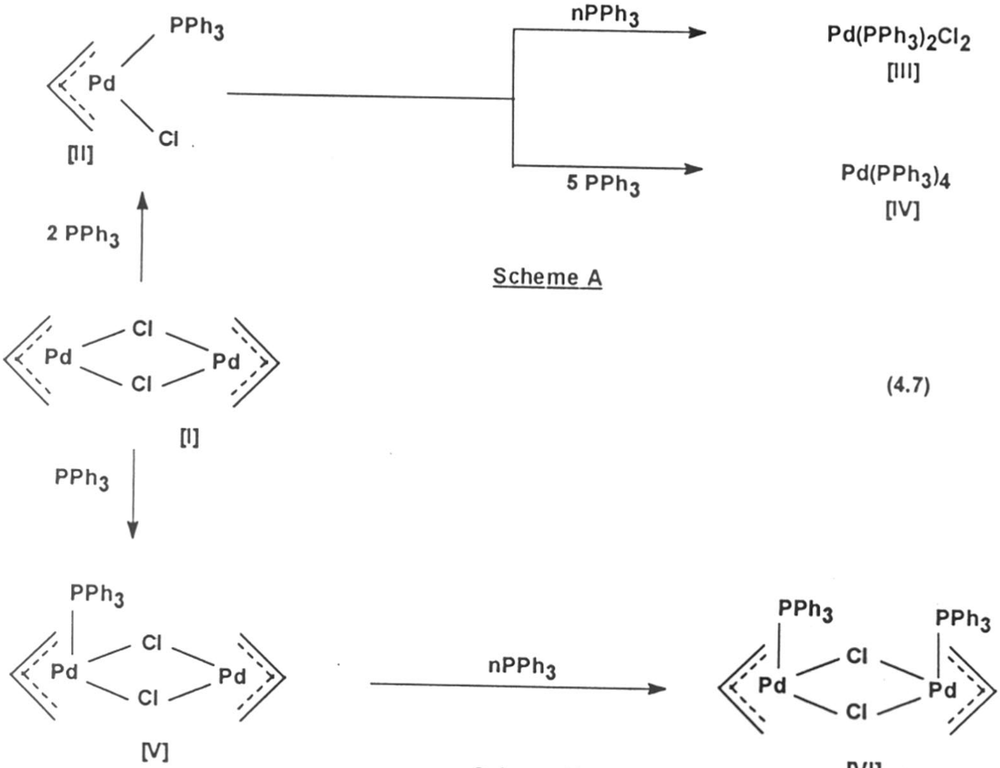
Reaction Conditions

Allyl chloride : 0.61, kmol/m^3;
Catalyst : Equivalent to 0.59, kg/m^3 of Pd;
PPh_3 : 5.7×10^{-3}, kmol/m^3;
Carbon Monoxide : 2.0, MPa;
Temperature : 308, K;
Stirring speed : 600, rpm;
Sodium hydroxide : 1.88, kmol/m^3;
VAA : Vinyl acetic acid;
CA : Crotonic acid.

only expected. These results indicate a significantly higher activity (2.66 × 10 $^{-4}$ kmol/m^3/s) compared to that of a homogeneous (Pd (π-allyl)Cl)$_2$ catalyst [(1.677 × 10^{-5} kmol/kg Pd/s) Medema et. al.(1969)], even though the latter is carried at high temperature and pressure (363, K and 75 atms.). The observation of catalyst particles adhering to the liquid-liquid interface has been made for the first time in the carbonylation of allyl chloride. However, such a behavior is well known in the separation of metals by selective segregation at the liquid-liquid interface (Lloyd et. al. (1989)). The adhesion of palladium could be the result of sodium hydroxide, which might make it surface active, or it may be imperfectly wetted by the either of the solvents (Guastalla and Coste (1975)). The existence of Pd at the liquid-liquid interface can be useful to achieve higher effective rates as the local concentration of Pd is significantly higher at the interface, where a higher concentration of dissolved CO in the organic phase accessible. This could also be a reason for the feasibility of this catalyst system at milder operating conditions compared to the homogeneous catalysts (76.8 atms, 363, K (Medema et. al. (1969))). In order to understand the effect of other parameters, Pd metal as a catalyst was used in all the experiments.

4.3.3 Effect of Triphenyl Phosphine Concentration

The carbonylation of allyl chloride to vinyl acetic acid proceeds smoothly in the absence of triphenyl phosphine, however, the activity of Pd catalyst is found to be enhanced in the presense of triphenyl phosphine. The results on the effect of concentration of triphenyl phosphine are presented in Table 4.3. The activity of the catalyst was found to increase (from 2.17 to 2.66 × 10^{-4} kmol/kg/s) with increase in the concentration of triphenyl phosphine upto a molar ratio of 1:1 of Pd: PPh_3. Further increase in the concentration resulted in a sharp decrease in the activity of the catalyst (2.66 to 0.69 × 10^{-4} kmol/kg/s). The selectivity, to vinyl acetic acid, (≈ 85-88 %) was found to be independent of the triphenyl phosphine concentration. Thus, there exists an optimum in the activity level with respect to triphenyl phosphine concentration. It is well known that allyl chloride reacts with Pd in the presence of water and CO to form a bridged allyl chloride complex [I] (Nicholson et. al. (1966))



Scheme A

(4.7)

Scheme B

TABLE 4.3

EFFECT OF TRIPHENYL PHOSPHINE : Pd METAL RATIO

Sr. No.	PPh_3 : Pd ratio	Average activity × 10^4, kmol/kg/s	Selectivity	
			VAA %	CA %
1	0	2.17	85.3	07.5
2	0.5	2.47	86.4	08.2
3	1	2.66	87.8	10.4
4	2	1.88	87.4	10.2
5	4	1.16	87.6	10.7
6	6	0.83	87.5	10.9
7	8	0.69	87.2	11.3

Reaction Conditions

Allyl chloride : 0.61, kmol/m^3;
Catalyst, Pd metal : 0.59, kg/m^3;
Carbon Monoxide : 2.0, MPa;
Temperature : 308, K;
Stirring speed : 600, rpm;
Sodium hydroxide : 1.88, kmol/m^3;
VAA : Vinyl acetic acid;
CA : Crotonic acid.

and is reported to be the active catalytic species (Medema et. al. (1969)). The chloride bridged complex is split by addition of equimolar amount of triphenyl phosphine to give (Pd(π-allyl)ClPPh$_3$) complex (II) (See Scheme A, above) (Powell et. al. (1965)). With addition of excess phosphine, the complex (II) is known to disproportionate to give Pd(PPh$_3$)$_2$Cl$_2$ complex (III) (Powell and Shaw (1967)) or Pd(PPh$_3$)$_4$ (IV) (Becconsall et. al. (1967)). This is, however, a reversible reaction and in the presense of excess allyl chloride (Pd(π-allyl)ClPPh$_3$) complex (II) is formed (Powell and Shaw (1968)) from Pd(PPh$_3$)$_4$. Medema et. al. (1969) and Volger et. al. (1970) have observed similar trends for the effect of triphenyl phosphine concentration and have explained on the basis of the reactions shown in Scheme B. Complex (I) is formed from allyl chloride, and palladium metal. In presense of triphenyl phosphine, for a molar ratio of 1:0.5 of palladium to triphenyl phosphine, complex (V) is formed from (I) and in excess of triphenyl phosphine it is converted to inactive Pd(PPh$_3$)$_2$(allyl)$_2$ complex (VI).

Thus, in the absence of any triphenyl phosphine, allyl chloride forms an activated complex with Pd shown as (I), which under carbonylation conditions yields products. However, in the presence of small amount of triphenyl phosphine, a more active complex (II) or (V) may be formed. The observed maximum with respect to triphenyl phosphine concentration could be due to that the complexes (II) or (V) could have higher activity than (I). In presense of excess triphenyl phosphine, complex (IV) or (VI) are formed which could be inactive for carbonylation. It is not clear at this stage whether the actual pathway follows Scheme A or B. While Scheme A (Powell et. al. (1965), Powell and Shaw (1967, 1968)) is proposed based on detailed characterization of species (II) and (IV), the Scheme B (Medema et. al. (1969)), is mainly speculative and there is no evidence for the bridged complexes (V) and (VI) under the conditions of this work. In order to resolve this question, further work on characterization of catalytic intermediates in the presense of carbon monoxide is necessary.

4.3.4 Effect of Sodium Hydroxide Concentration

The effect of sodium hydroxide concentration was investigated at 308, K and the results are presented in Table 4.4. The activity of Pd metal catalyst as well as its selectivity to vinyl acetic acid was found to depend strongly on sodium hydroxide concentration. While the average activity determined for 100 % conversion level of allyl chloride was found to increase (0.78 to 3.15 $\times 10^{-4}$ kmol/kg/s) with increase in concentration of sodium hydroxide, the selectivity of vinyl acetic acid decreased (from 88.3 to 35.3 %). An important observation was that the sodium hydroxide concentration was the only parameter which affected the selectivity of products significantly.

Joó and Alper (1985) have also observed that the isomerization of vinyl acetic acid to crotonic acid is accelerated in the presense of sodium hydroxide during

TABLE 4.4

EFFECT OF SODIUM HYDROXIDE CONCENTRATION

Sr. No.	Concentration kmol/m^3	Average activity × 10^4 kmol/kg/s	Selectivity	
			VAA %	CA %
1	0.94	-	-	-
2	1.25	0.78	88.3	06.4
3	1.88	2.66	87.8	10.4
4	2.81	2.96	64.2	25.7
5	3.75	3.15	35.3	45.5

Reaction Conditions

Allyl chloride	:	0.61, kmol/m^3;
Catalyst, Pd metal	:	0.59, kg/m^3;
PPh_3	:	5.7×10^{-3}, kmol/m^3;
Carbon Monoxide	:	2.0, MPa;
Temperature	:	308, K;
Stirring speed	:	600, rpm;
VAA	:	Vinyl acetic acid;
CA	:	Crotonic acid.

carbonylation of allyl chloride using nickel complex catalyst. Kiji et. al. (1988) have made similar observations in Pd catalyzed reactions.

The exact role of sodium hydroxide in increasing the activity of the catalyst is not well understood. However, the reductive elimination of the product (see proposed mechanism, Fig 4.12) from the catalyst surface is likely to be accelerated in the presense of sodium hydroxide producing the sodium salt of the acid and Pd metal. This is also likely because in the absence of sodium hydroxide vinyl acetic and crotonic acids are not formed.

4.3.5 Effect of Solvent

The effect of solvents on the activity and selectivity of palladium metal catalysts was investigated at 308 k and 2.0, MPa of carbon monoxide. The various organic solvents screened were benzene, toluene, hexane and cyclohexane. The results are presented in Table 4.5. It was observed that the reaction was feasible only in a biphasic medium with the aqueous phase essentially containing sodium hydroxide. It was observed that may be noted that pure allyl chloride as an organic phase, inhibits the reaction (entry 1, Table 4.6) completely. The activity and selectivity, to vinyl acetic acid, ($\approx 2.7 \times 10^{-4}$ kmol/kg/s and 84-88 % respectively) was found to be independent of the nature of organic solvent used. Addition of 5ml of ethanol to the toluene water solvent system was found to inhibit the reaction. This deac-

TABLE 4.5

EFFECT OF SOLVENT

Sr. No.	Solvent	Average activity × 10^4 kmol/kg/s	Selectivity	
			VAA	CA
			%	%
1	Toluene	2.66	87.3	10.4
2	Benzene	2.52	84.2	14.1
3	Hexane	2.67	86.3	11.2
4	Cyclohexane	2.63	87.7	11.2
5	Ethanol*	-	-	-

Reaction Conditions

Allyl chloride : 0.61, kmol/m^3;
Catalyst, Pd metal : 0.59, kg/m^3;
PPh_3 : 5.7×10^{-3}, kmol/m^3;
Carbon Monoxide : 2.0, MPa;
Temperature : 308, K;
Stirring speed : 600, rpm;
Sodium hydroxide : 1.88, kmol/m^3;
Solvent holdup : 6 : 4 (Organic : aqueous);
VAA : Vinyl acetic acid;
CA : Crotonic acid.

* 5 ml of ethanol with 50 ml toluene and 40 ml water

tivation may be due to the decomposition of $(Pd(\pi\text{- allyl})Cl)_2$ complex in aqueous alkaline solutions with the addition of ethanol (Belov et. al. (1970)) as shown below.

$$(Pd(\pi\text{-allyl})Cl)_2 + 2\,OH^- \xrightarrow{C_2H_5OH} C_3H_6 + C_3H_4O + Pd + 2\,Cl^- + H_2O \quad (4.8)$$

4.3.6 Liquid Phase Hold-Up

The effect of liquid phase holdup on the activity and selectivity of Pd metal catalyst was studied using a solvent system of toluene and water. The organic phase contained allyl chloride and the solvent, while sodium hydroxide was present in the aqueous phase. The ratio of toluene to water phases was varied from zero to one, maintaining the total volume of liquid phases constant. The results are presented in Table 4.6. It was observed that the reaction didn't occur in the absence of either of the two solvents, however, at solvent holdup ratio of 1:9 of organic:aqueous, the activity was highest (2.84×10^{-4} kmol/kg/s). The activity of palladium metal catalyst was found to decrease (from 2.84 to 2.66×10^{-4} kmol/kg/s) with increase in the organic phase holdup. At a holdup ratio above 8:2 (organic:aqueous phases), the reaction was completely inhibitted. The selectivity to vinyl acetic acid (≈ 85-89%) was not affected by the variation in liquid phase holdup.

The observed decrease in the activity with increase in the organic phase with almost complete inhibition at the organic : aqueous phase ratio of 8:2 needs to be understood. The reaction system involves contacting of gas phase reactant, CO,

TABLE 4.6

EFFECT OF LIQUID PHASE HOLDUP

Sr. No.	Liquid phase holdup AC : Org : Aq	Average activity × 10^4 kmol/kg/s	Selectivity	
			VAA %	CA %
1	5 : 0 : 95	-	-	-
2	5 : 5 : 90	2.84	89.5	09.1
3	5 : 15 : 80	2.81	89.1	09.9
4	5 : 25 : 70	2.78	88.7	10.1
5	5 : 45 : 50	2.72	88.3	10.3
6	5 : 55 : 40	2.66	87.8	10.4
7	5 : 65 : 30	2.11	85.3	12.3
8	5 : 75 : 20	-	-	-
9	5 : 95 : 0	-	-	-

Reaction Conditions

Allyl chloride : 0.61, kmol/m^3;
Catalyst, Pd metal : 0.59, kg/m^3;
PPh_3 : 5.7×10^{-3}, kmol/m^3;
Carbon Monoxide : 2.0, MPa;
Temperature : 308, K;
Stirring speed : 600, rpm;
Sodium hydroxide : 1.88, kmol/m^3;
AC : Allyl chloride;
VAA : Vinyl acetic acid;
CA : Crotonic acid
Org : Toluene
Aq : Water.

liquid phase reactant, allyl chloride, present in organic phase and a catalyst present at the liquid-liquid interface in the presense of aqueous sodium hydroxide. Since the presense of sodium hydroxide is most essential for the reaction to occur, with increase in organic phase holdup, some part of catalyst may become inaccessible to aqueous sodium hydroxide and hence a decrease in the catalytic activity is expected.

4.3.7 Effect of Allyl Chloride Concentration

The effect of allyl chloride concentration on the activity and selectivity of palladium catalysts for the carbonylation of allyl chloride was investigated at 308 K and 2.0, MPa of carbon monoxide. The concentration of allyl chloride was varied from 0.31, to 1.84, kmol/m^3. The results are presented in Table 4.7. The activity of the catalyst was found to decrease (from 3.5 to 1.8 $\times$ 10^{-4} kmol/kg/s) with increase in the concentration of allyl chloride. The selectivity to vinyl acetic acid ($\approx$ 86-88 %) was not affected by the variation in the concentration of allyl chloride. A slow decrease in the activity with increase in ally chloride concentration indicates that, there is a constant build up of an inactive species with increase in the concentration of allyl chloride. While the stoichiometric reaction of palladium salts with allyl chloride has been investigated by Powell et. al. (1965), Powell and Shaw (1967), and have indicated the formation of species (I) and (II), the effect of allyl chloride concentration on the nature of such species is not known particularly in the presense of carbon monoxide. A possible reason of such an observation is the likelihood of the

TABLE 4.7

EFFECT OF ALLYL CHLORIDE CONCENTRATION

Sr. No.	Concentration kmol/m^3	Average activity × 10^4, kmol/kg/s	Selectivity VAA %	 CA %
1	0.31	3.50	86.8	09.8
2	0.37	2.97	87.8	10.4
3	0.61	2.66	86.3	12.3
4	1.23	1.93	86.1	12.6
5	1.84	1.86	86.4	12.7

Reaction Conditions

Catalyst, Pd metal : 0.59, kg/m^3;
PPh_3 : 5.7×10^{-3}, kmol/m^3;
Carbon Monoxide : 2.0, MPa;
Temperature : 308, K;
Stirring speed : 600, rpm;
Sodium hydroxide : 1.88, kmol/m^3;
VAA : Vinyl acetic acid;
CA : Crotonic acid.

formation of a dimeric inactive species of the type $(PdCl(PPh_3)(C_3H_5)_n$. However, further work will be necessary to support the results.

4.3.8 Effect of Partial Pressure of Carbon Monoxide

The effect of partial pressure of carbon monoxide on the activity and selectivity of the palladium catalyst was investigated at 308 K. The results are presented in Table 4.8. The activity of Pd metal catalyst was found to increase (from 1.39 to 3.13×10^{-4} kmol/kg/s) with increase in partial pressure of carbon monoxide. The formation of active catalytic species $(Pd(\pi\text{-allyl})Cl)_2$ (I) is known to be promoted by carbon monoxide (Dent et. al. (1964)) as shown below :

$$2\,CH_2{=}CH\text{-}CH_2Cl + 2\,Pd \xrightarrow{CO} (Pd(\pi\text{-allyl})Cl)_2 \qquad (4.9)$$

Increase in the partial pressure of carbon monoxide thus increases the concentration of carbon monoxide in the reaction mixture, resulting in increased rate of formation of the active catalytic species (I). Scheben and Mador (1976), Volger et. al. (1970) and Medema et. al. (1969) have also observed similar trends for the effect of partial pressure of carbon monoxide. The selectivity to vinyl acetic acid was independent (≈ 80-88 %) of the partial pressure of carbon monoxide.

TABLE 4.8

EFFECT OF PARTIAL PRESSURE OF CARBON MONOXIDE

Sr. No.	Pressure MPa	Average activity × 10^4 kmol/kg/s	Selectivity VAA %	CA %
1	0.68	1.39	80.2	14.2
2	1.36	2.15	84.8	12.4
3	2.04	2.66	87.3	10.4
4	2.72	3.13	88.2	09.3

Reaction Conditions

Allyl chloride : 0.61, kmol/m^3;
Catalyst, Pd metal : 0.59, kg/m^3;
PPh_3 : 5.7×10^{-3}, kmol/m^3;
Temperature : 308, K;
Stirring speed : 600, rpm;
Sodium hydroxide : 1.88, kmol/m^3;
VAA : Vinyl acetic acid;
CA : Crotonic acid.

4.3.9 Effect of Catalyst Concentration

The effect of catalyst concentration on activity and selectivity of Pd metal catalyst was studied at 308, K and 2.0, MPa of carbon monoxide. The concentration of catalyst was varied between 0.29 and 4.4 kg/m^3. The results are presented in Table 4.9. The activity of Pd catalyst was found to increase initially (from 1.96 to 2.66 × 10^{-4} kmol/kg/s) with increase in concentration of catalyst, however, decreased (from 2.66 to 0.56 × 10^{-4} kmol/kg/s) at higher concentrations. The above observation could be due to decrease in Pd: PPh_3 ratio as the experiments were carried out at constant concentration of triphenyl phosphine. As observed in Section 4.3.3, the optimum molar ratio of Pd:PPh_3 is 1:1 and with decrease in this ratio, the activity of Pd catalyst decreases. Another possible explanation is the rate of formation of active catalytic species from palladium metal may depend on the solubility of palladium metal in the solvent, as suggested by Scheben and Mador (1976), for the homogeneous single phase carbonylation of allyl chloride with $PdCl_2$ as the catalyst. It is reported that the active catalyst species, $(Pd(\pi\text{-allyl})Cl)_2$ (I), can decompose by reaction in the presense of Pd metal (Belov et. al. (1971)). With increase in Pd concentration, such a side reaction can reduce the effective concentration of active catalytic species (I) and hence a decrease in the rate. The selectivity to vinyl acetic acid ($\approx$ 86-88 %)of was found to be independent of the catalyst concentration.

TABLE 4.9

EFFECT OF CATALYST CONCENTRATION

Sr. No.	Concentration kg/m^3	Average activity × 10^4 kmol/kg/s	Selectivity VAA %	Selectivity CA %
1	0.29	1.96	86.2	08.3
2	0.59	2.66	87.8	10.4
3	1.11	1.71	87.9	10.2
4	2.22	0.92	87.9	10.4
5	4.44	0.56	88.1	10.5

Reaction Conditions

Allyl chloride : 0.61, kmol/m^3;
PPh_3 : 5.7×10^{-3}, kmol/m^3;
Carbon Monoxide : 2.0, MPa;
Temperature : 308, K;
Stirring speed : 600, rpm;
Sodium hydroxide : 1.88, kmol/m^3;
VAA : Vinyl acetic acid;
CA : Crotonic acid.

4.3.10 Effect of Temperature

The effect of temperature on activity and selectivity, to vinyl acetic acid, of palladium metal catalyst was studied in a temperature range of 298-318 K and the results are presented in Table 4.10. It was observed that the average activity increased (from 0.96 to 3.15 × 10^{-4} kmol/kg/s) with increase in the reaction temperature. The selectivity to vinyl acetic acid was found to be independent (≈ 80-88 %) of the effect of temperature.

4.4 KINETICS OF ALLYL CHLORIDE CARBONYLATION

In the preceding sections, the effect of catalysts, ligands, solvents, solvent holdup and reaction conditions on palladium metal catalyzed carbonylation of allyl chloride in a biphasic medium has been discussed. The aim of the present work was also to investigate the kinetics of this reaction. A knowledge of the reaction kinetics is useful in understanding the reaction mechanism and the variation in rate with concentration of different species and temperature. Kinetic studies are also useful for designing of reactors and scaling up of processes. The kinetics of the carbonylation of allyl chloride using homogenous palladium has been reported by Medema et. al. (1969) at 363, K and 76.8, atm. partial pressure of carbon monoxide. However, the kinetics in a biphasic medium with palladium metal catalyst has not been reported.

TABLE 4.10

EFFECT OF TEMPERATURE

Sr. No.	Temperature K	Average activity × 10^4 kmol/kg/s	Selectivity	
			VAA %	CA %
1	298	0.96	80.2	12.1
2	308	2.66	87.8	10.4
3	318	3.15	84.3	14.4

Reaction Conditions

Allyl chloride : 0.61, kmol/m^3;
Catalyst, Pd metal : 0.59, kg/m^3;
PPh_3 : 5.7×10^{-3}, kmol/m^3;
Carbon Monoxide : 2.0, MPa;
Stirring speed : 600, rpm;
Sodium hydroxide : 1.88, kmol/m^3;
VAA : Vinyl acetic acid;
CA : Crotonic acid.

Therefore the kinetics of palladium metal catalyzed biphasic carbonylation of allyl chloride was investigated. The rate data presented here represent overall kinetics of carbonylation of allyl chloride to unsaturated acid products.

For the purpose of kinetic study reactions were carried out at different concentrations of allyl chloride, sodium hydroxide and palladium metal catalyst and partial pressure of carbon monoxide over a temperature range of 298-318, K. The range of variables used for the kinetic study are presented in Table 4.11. In each case, the amount of carbon monoxide consumed as a function of time was observed and the typical plots for different parameters are shown in Figs 4.1- 4.3. These figures show the effect of partial pressure of carbon monoxide, catalyst and allyl chloride concentrations at 298, 308 and 318 K respectively.

The material balance of carbon monoxide and allyl chloride consumed to products, vinyl acetic and crotonic acids, was found to agree to the extent of 97 % (Section 4.3.1), as per the stoichiometry of Eqn. 4.3. The initial rates of carbonylation of allyl chloride were calculated from the observed data on consumption of carbon monoxide as a function of time, in the region, wherein the conversion of allyl chloride was ≈ 10 % as follows:

$$R_A = \frac{\text{Slope of CO consumed vs time plot}}{\text{Volume of liquid}} \qquad (4.11)$$

The effect of agitation speed, triphenyl phosphine-Pd metal ratio, concentra-

TABLE 4.11

RANGE OF VARIABLES FOR KINETIC STUDIES

Sr. No.	Parameter	Range
1	Allyl chloride concentration	0.31 - 1.84, kmol/m^3
2	Sodium hydroxide concentration	0.94 - 3.75, kmol/m^3
3	Catalyst, Pd metal concentration	0.29 - 4.44, kg/m^3
4	Partial pressure of carbon monoxide	0.67 - 2.71, MPa
5	Temperature	298 - 318, K

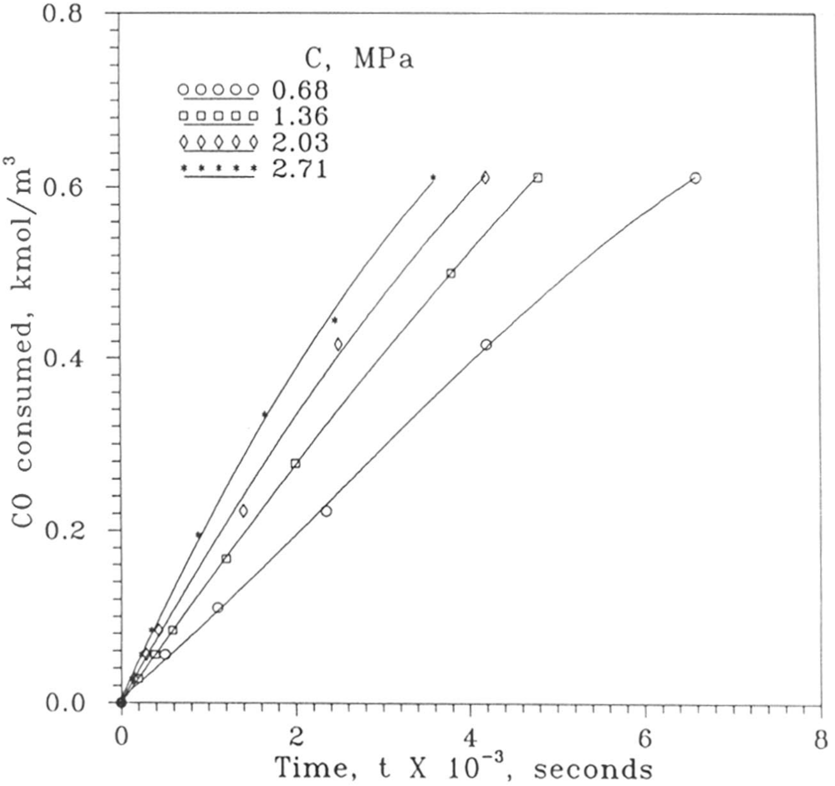


FIGURE 4.1 PLOT OF CO CONSUMED WITH TIME, EFFECT OF PARTIAL PRESSURE OF CARBON MONOXIDE

Reaction conditions:

Allyl chloride	:	0.61, kmol/m^3;
Sodium hydroxide	:	1.88, kmol/m^3;
Pd metal	:	0.59, kg/m^3;
PPh_3	:	5.7×10^{-3}, kmol/m^3;
Agitation speed	:	600, rpm;
Temperature	:	298, K.

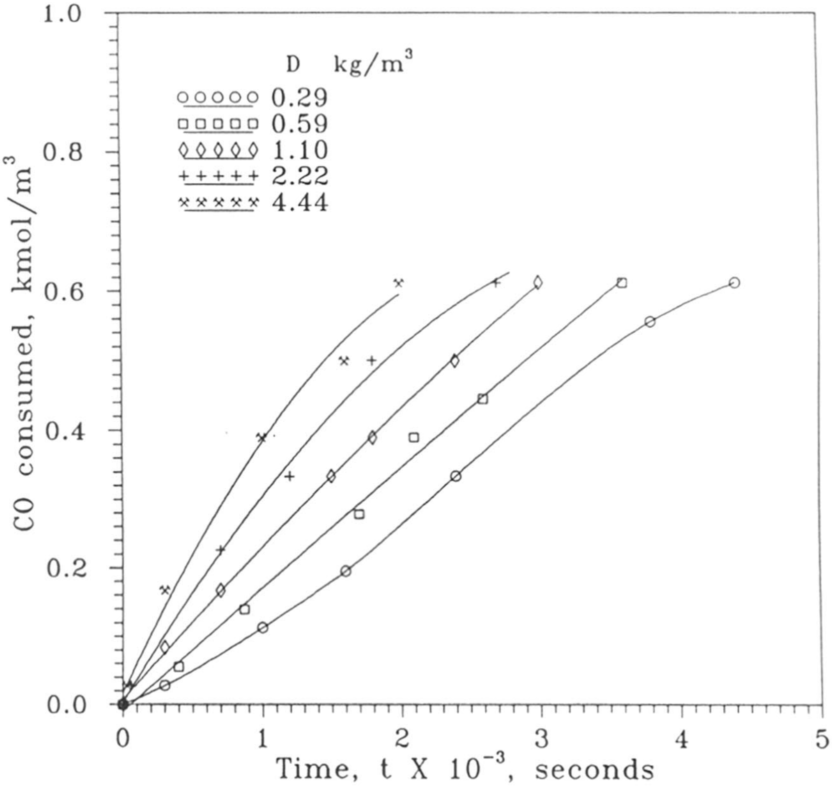


FIGURE 4.2 PLOT OF CO CONSUMED WITH TIME, EFFECT OF CATALYST, Pd METAL, CONCENTRATION

Reaction conditions:

Allyl chloride	:	**0.61, kmol/m^3;**
Sodium hydroxide	:	**1.88, kmol/m^3;**
Carbon monoxide	:	**2, MPa;**
Pd : PPh$_3$ ratio	:	**1:1;**
Agitation speed	:	**600, rpm;**
Temperature	:	**308, K.**

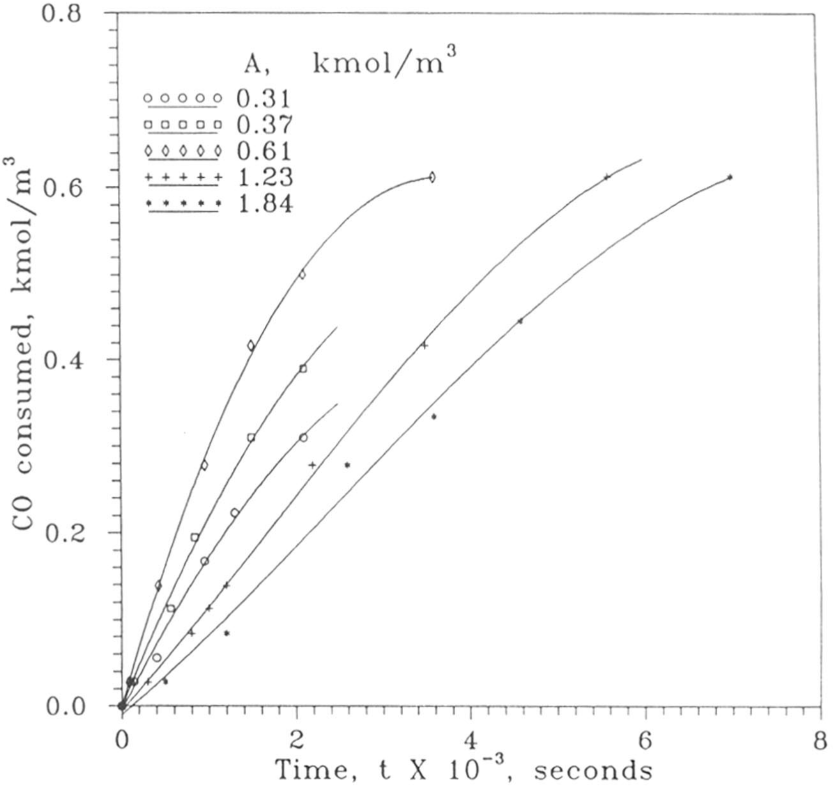


FIGURE 4.3 PLOT OF CO CONSUMED WITH TIME, EFFECT OF ALLYL CHLORIDE CONCENTRATION

Reaction conditions:

Sodium hydroxide : 1.88, kmol/m^3;
Carbon monoxide : 2, MPa;
Pd metal : 0.59, kg/m^3;
PPh$_3$: 5.7 × 10^{-3}, kmol/m^3;
Agitation speed : 600, rpm;
Temperature : 318, K.

tions of allyl chloride, catalyst, sodium hydroxide and partial pressure of carbon monoxide on the initial rate of the reaction was investigated and the results are shown in Figs 4.4-4.9. The important observations are summarized below:

- The agitation speed, beyond 400 rpm, had no influence on the rate of the reaction (Fig 4.4) and hence further reactions were carried out at 600 rpm.
- The initial rate was found to pass through a maximum (Fig 4.5) at a ratio 1:1 of triphenyl phosphine : Pd metal for all temperatures.
- The plot of rate vs allyl chloride concentration passed through a maximum (Fig 4.6), with a sharp decrease beyond 0.61, kmol/m^3.
- The initial rates were found to increase linearly at lower catalyst concentration and marginally at higher concentrations (Fig 4.7).
- The initial rates increased linearly at lower sodium hydroxide concentrations and were independent at higher concentrations (Fig 4.8).
- The initial rates linearly increased with increase in the partial pressure of carbon monoxide (Fig 4.9).

In order to fit the rate data, several rate equations (Table 4.12) were examined. The rate parameters were optimized by using an optimization program (Marquardt (1962)). The values of rate parameters evaluated for each model along with ϕ_{min}, the minimized sum of squares of the difference between observed and predicted rates,

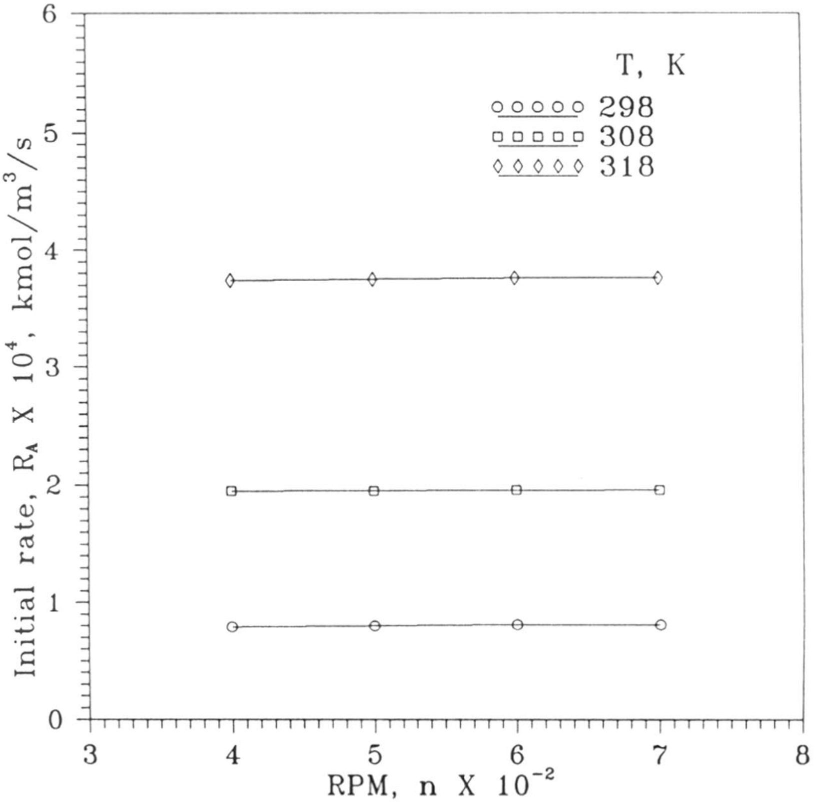


FIGURE 4.4 EFFECT OF AGITATION SPEED ON THE RATE OF CARBONYLATION OF ALLYL CHLORIDE

Reaction conditions:

Allyl chloride	:	**0.61, kmol/m^3;**
Sodium hydroxide	:	**1.88, kmol/m^3;**
Carbon monoxide	:	**2, MPa;**
Pd metal	:	**0.59, kg/m^3;**
PPh$_3$	:	**5.7×10^{-3}, kmol/m^3.**

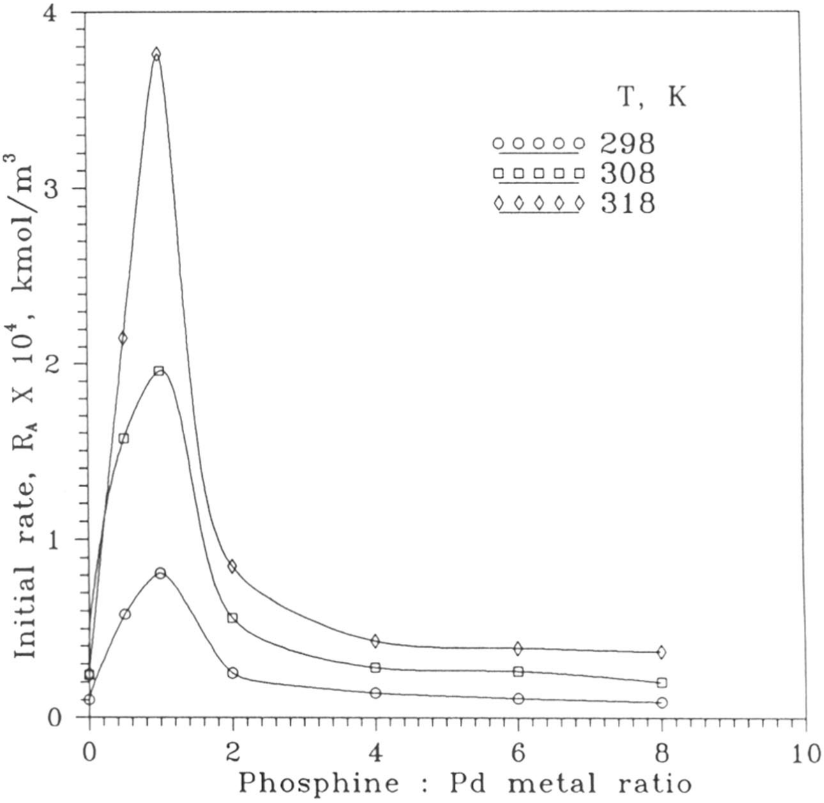


FIGURE 4.5 EFFECT OF PPh_3 : Pd METAL RATIO ON THE RATE OF CARBONYLATION OF ALLYL CHLORIDE

Reaction conditions:

Allyl chloride : 0.61, kmol/m^3;
Sodium hydroxide : 1.88, kmol/m^3;
Carbon monoxide : 2, MPa;
Pd metal : 0.59, kg/m^3;
Agitation speed : 600, rpm.

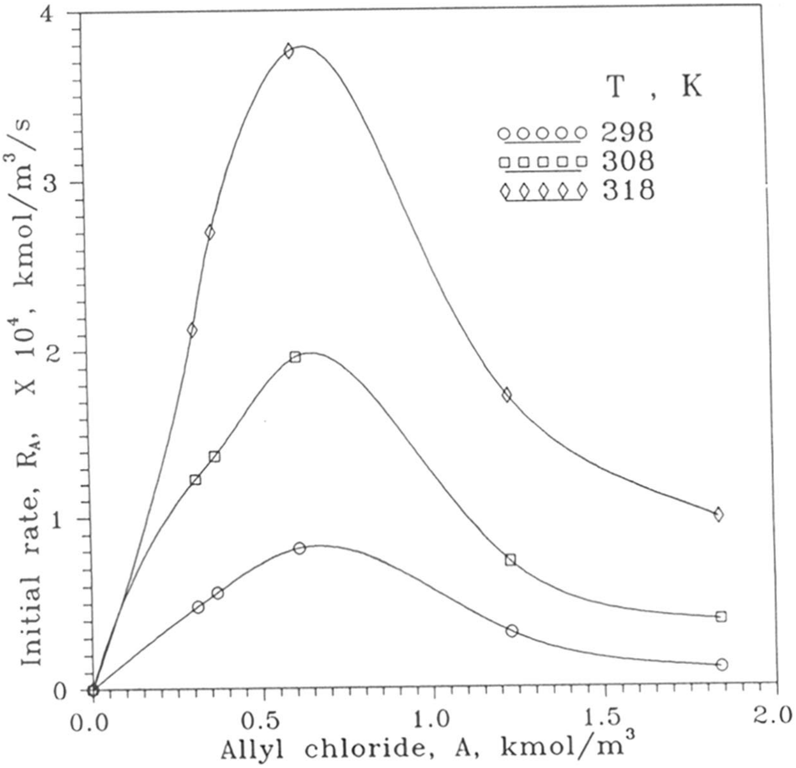


FIGURE 4.6 EFFECT OF ALLYL CHLORIDE CONCENTRATION ON THE RATE OF CARBONYLATION OF ALLYL CHLORIDE

Reaction conditions:

Sodium hydroxide : 1.88, kmol/m^3;
Carbon monoxide : 2, MPa;
Pd metal : 0.59, kg/m^3;
PPh_3 : 5.7×10^{-3}, kmol/m^3;
Agitation speed : 600, rpm.

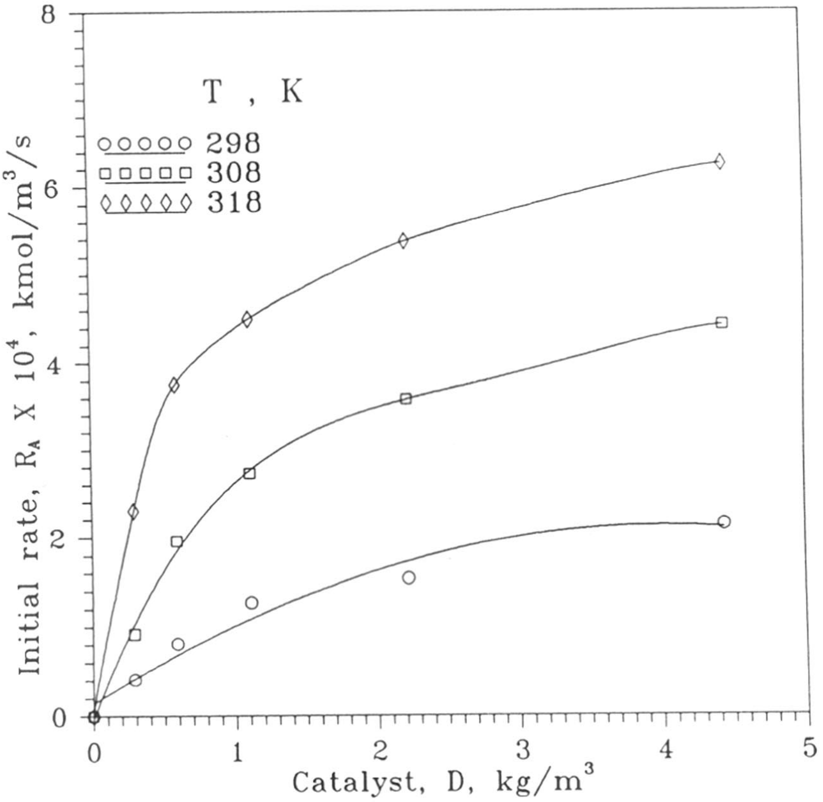


FIGURE 4.7 EFFECT OF CATALYST CONCENTRATION ON THE RATE OF CARBONYLATION OF ALLYL CHLORIDE

Reaction conditions:

Allyl chloride	:	0.61, kmol/m^3;
Sodium hydroxide	:	1.88, kmol/m^3;
Carbon monoxide	:	2, MPa;
Pd : PPh_3 ratio	:	1:1;
Agitation speed	:	600, rpm.

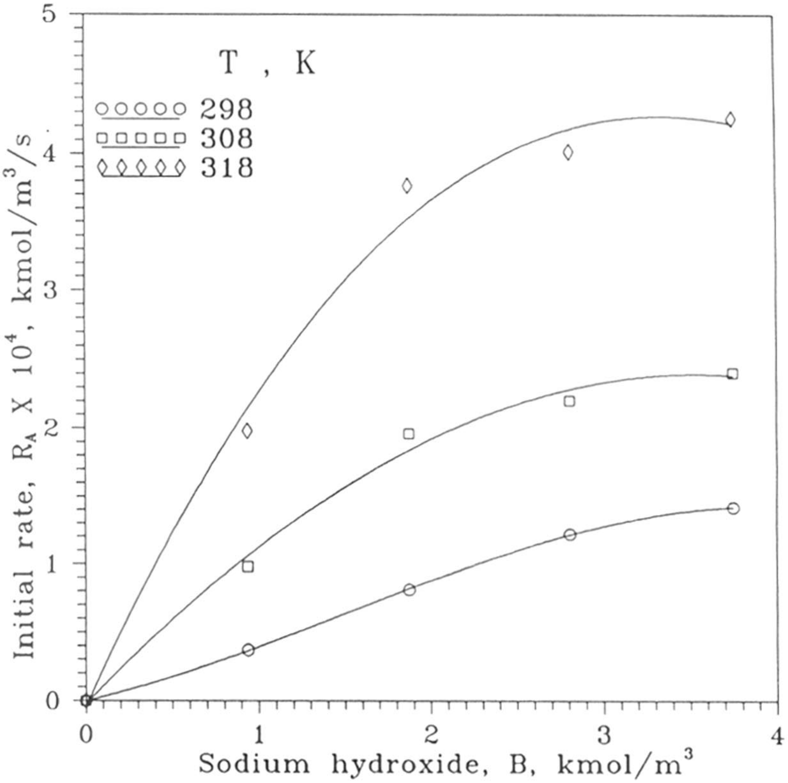


FIGURE 4.8 EFFECT OF SODIUM HYDROXIDE CONCENTRATION ON THE RATE OF CARBONYLATION OF ALLYL CHLORIDE

Reaction conditions:

Allyl chloride : 0.61, kmol/m^3;
Carbon monoxide : 2, MPa;
Pd metal : 0.59, kg/m^3;
PPh$_3$: 5.7 × 10^{-3}, kmol/m^3;
Agitation speed : 600, rpm.

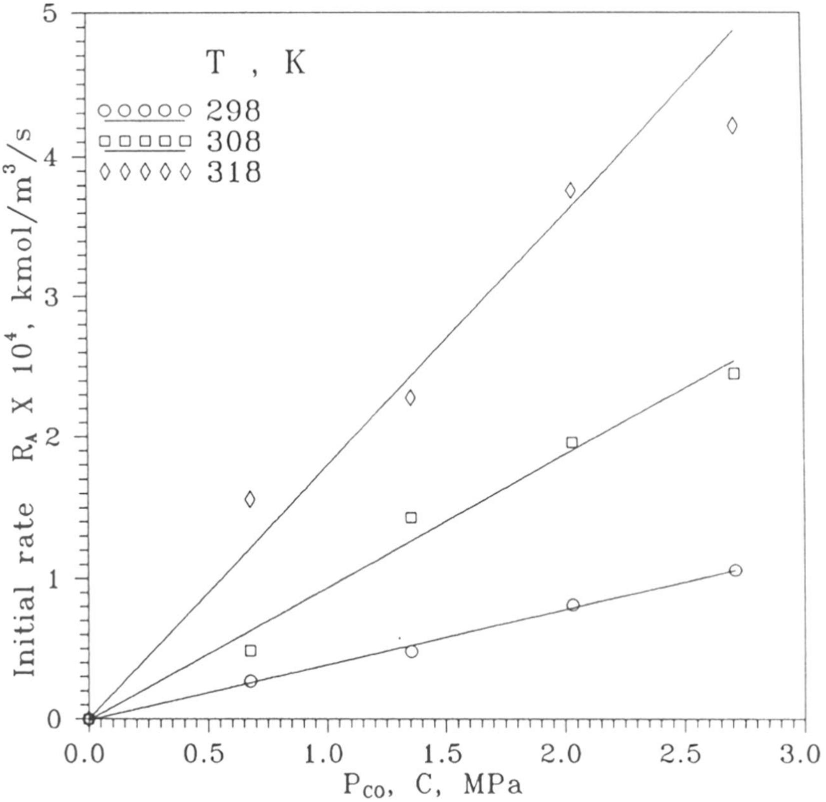


FIGURE 4.9 EFFECT OF PARTIAL PRESSURE OF CO ON THE RATE OF CARBONYLATION OF ALLYL CHLORIDE

Reaction conditions:

Allyl chloride	:	**0.61, kmol/m^3;**
Sodium hydroxide	:	**1.88, kmol/m^3;**
Pd metal	:	**0.59, kg/m^3;**
PPh$_3$	:	**5.7×10^{-3}, kmol/m^3;**
Agitation speed	:	**600, rpm.**

TABLE 4.12

RATE MODELS EXAMINED TO FIT THE DATA FOR ALLYL CHLORIDE CARBONYLATION

Sr. No.	Rate model	Temp K	k m^6/kmol /kg/KPa/s	K_A m^3/kmol	K_B m^3/kmol	K_D m^3/kg	ϕ_{min}
1	$\frac{kABCD}{(1+K_AA)^{3.2}(1+K_BB)(1+K_DD)}$	298	1.23×10^{-4}	2.43	3.10×10^{-2}	0.637	7.95×10^{-10}
		308	5.59×10^{-4}	2.58	0.46	0.80	3.01×10^{-9}
		318	1.53×10^{-3}	2.14	0.63	1.62	1.07×10^{-8}
2	$\frac{kABCD}{(1+K_AA)^2(1+K_BB)(1+K_DD)}$	298	1.47×10^{-4}	3.48	-0.24×10^{-1}	0.53	5.8×10^{-9}
		308	6.21×10^{-4}	3.89	0.27	0.65	2.40×10^{-8}
		318	1.82×10^{-3}	0.34	0.47	1.39	8.02×10^{-8}
3	$\frac{kA^{0.09}BCD}{(1+K_AA)^3(1+K_BB)(1+K_DD)}$	298	1.13×10^{-4}	2.17	$- 0.25 \times 10^{-1}$	0.62	9.86×10^{-10}
		308	5.12×10^{-4}	2.28	0.45	0.79	3.73×10^{-9}
		318	1.41×10^{-3}	1.91	0.61	1.59	1.22×10^{-8}
4	$\frac{kA^{1.4}BCD}{(1+K_AA)^{3.3}(1+K_BB)(1+K_DD)}$	298	3.61×10^{-4}	9.24	0.32×10^{-1}	0.64	8.79×10^{-10}
		308	1.7×10^{-3}	1.01×10^{1}	0.47	0.81	3.39×10^{-9}
		318	4.7×10^{-3}	9.3	0.64	1.63	1.01×10^{-8}
5	$\frac{kA^{0.5}BCD}{(1+K_AA)^2)(1+K_BB)(1+K_DD)}$	298	1.6×10^{-5}	1.49	-0.27×10^{-1}	0.53	5.84×10^{-9}
		308	3.12×10^{-4}	1.59	0.27	0.64	2.34×10^{-8}
		318	9.2×10^{-4}	1.32	0.45	1.34	8.24×10^{-8}

A : Concentration of allyl chloride, kmol/m^3; B : Concentration of catalyst, kg/m^3;
C : Partial pressure of carbon monoxide, MPa; D : Concentration of sodium hydroxide, kmol/m^3;

is shown in Table 4.12. It can be seen that the rate parameters for rate equations 2, 3 and 5 are less than zero and hence were rejected. The model 4 is not consistent with the observed rate dependence, for example, it grossly overestimates the initial rates observed for allyl chloride dependence (4.8×10^{-4} kmol/m^3/s as against 6.3 $\times 10^{-4}$ kmol/m^3/s) and hence was rejected. Model 1, as shown below, was found to predict the rate data satisfactorily.

$$R_A = \frac{k\ A\ B\ C\ D}{(1 + K_A\ A)^{3.2}\ (1 + K_B\ B)\ (1 + K_D\ D)} \tag{4.12}$$

Where

A = Concentration of allyl chloride, kmol/m^3; B = Concentration of sodium hydroxide, kmol/m^3; C = Partial pressure of carbon monoxide, MPa; D = Concentration of catalyst, kg/m^3; k = rate constant of the reaction, m^6/kmol/kg/MPa/s; K_A = rate parameter dependent on A, m^3/kmol; K_B = rate parameter dependent on B, m^3/kmol; K_D = rate parameter dependent on D, m^3/kg.

The rate predicted using the above optimized rate parameters were found to agree within ± 6 % error with experimental data (Fig 4.10). The Arrhenius plot of ln k vs $\frac{1}{T}$ is shown in Fig 4.11 and the energy of activation was calculated as 23.3 kcal/mol.

The mechanism for the carbonylation of allyl chloride using homogeneous pal-

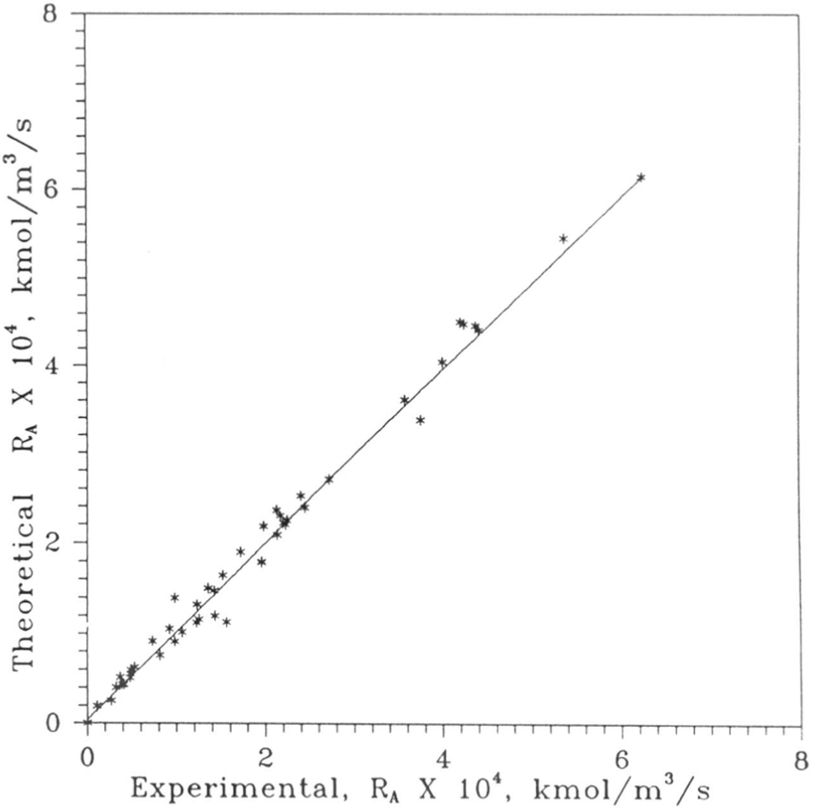


FIGURE 4.10 PLOT OF R_A PREDICTED vs R_A EXPERIMENTAL

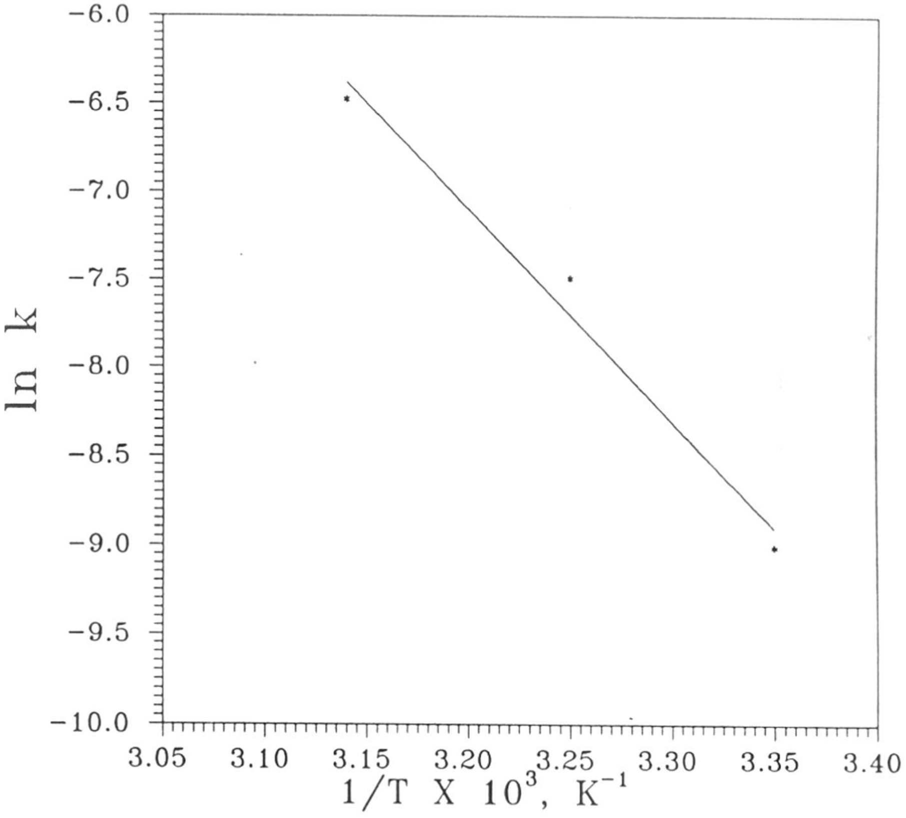
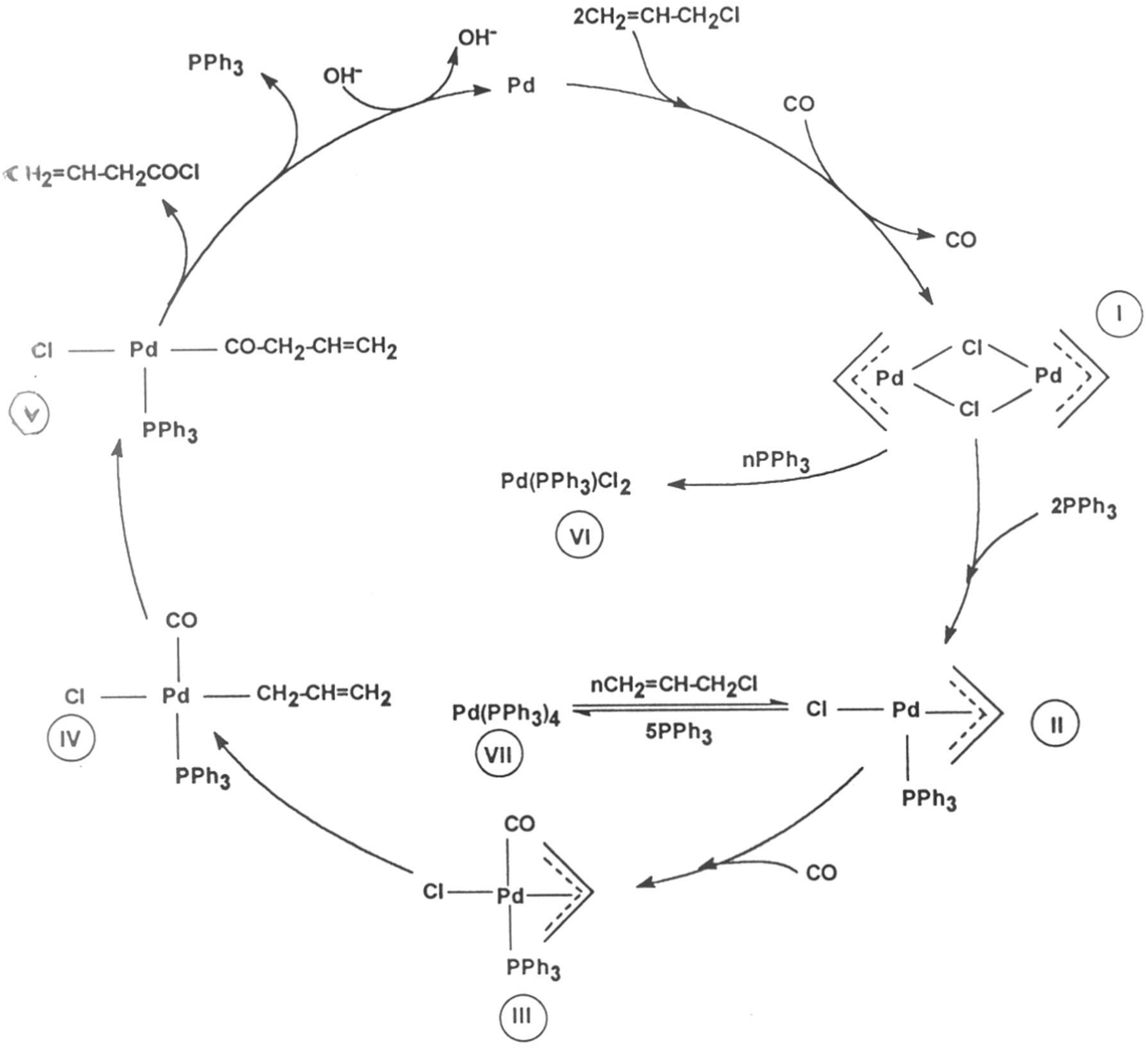


FIGURE 4.11 ARRHENIUS PLOT OF ln k vs $\frac{1}{T}$

ladium catalysts has been proposed by Medema et. al. (1969) and Volger et. al. (1970). Medema et. al. (1969) have proposed a bridged Pd-π-allyl chloride complex, while, Volger et. al. (1970) have proposed a trinuclear Pd-π-allyl chloride complex as the active catalytic intermediate species (See Section 1.4.4 and Figs 1.5, 1.6, 1.7 of Chapter 1).

We propose here a catalytic cycle based on observed trends in our experiments (See Fig 4.12). The catalyst Pd metal in the presense of carbon monoxide reacts with allyl chloride to form a $(Pd(\pi\text{-allyl Cl})_2$ (I) complex (Dent et. al. (1964)). Complex (I) in the presense of equimolar triphenyl phosphine is known to split into $(Pd(\pi\text{-allyl Cl})PPh_3$ (II) complex (Powell et. al. (1965)). Complex (II) reacts with carbon monoxide to form a penta coordinated $(Pd(\pi\text{-allyl Cl})PPh_3(CO)$ (III) complex (Heck (1971)). Due to the presense of electron donating ligands like PPh_3 and CO on palladium metal in complex (III), the π-allyl group acquires a negative charge and changes to a σ-allyl group (complex (IV)) (Vrieze et. al. (1966)). The migration of σ-allyl group to the carbon monoxide takes place giving rise to an acyl palladium complex (V). The reductive elimination of but-3-enoyl chloride from complex (V) in the presense of OH^- ions is the rate determining step. In the elimination step, palladium (I) is reduced to palladium metal and the catalytic cycle is completed. But-3-enoyl chloride reacts with 2 moles of sodium hydroxide to give the sodium salt of vinyl acetic acid and sodium chloride. Thus, the reaction involves dissolution-precipitation cycle for the Pd catalyst and this unique mode of



$$CH_2{=}CH\text{-}CH_2COCl + 2NaOH \longrightarrow CH_2{=}CH\text{-}CH_2COONa + NaCl + H_2O$$

FIGURE 4.12 PROPOSED MECHANISM FOR THE BIPHASIC CARBONYLATION OF ALLYL CHLORIDE WITH Pd METAL CATALYST operation leads to improved activity at ambient conditions.

Complex (I and II) in presense of excess phosphine are converted either to $Pd(PPh_3)Cl_2$ (VI) (Powell and Shaw (1967)) or $Pd(PPh_3)_4$ (VII) (Becconsall et. al. (1967)). In the presense of excess allyl chloride the splitting of complex (I) may not take place, which thus could lead to lower rates. The formation of complex (I) is promoted by carbon monoxide and thus an increase in the partial pressure of carbon monoxide increases the rate of the reaction.

4.5 CONCLUSIONS

The carbonylation of allyl chloride using palladium metal catalysts in a biphasic medium has been investigated over a range of 298-318 K. The biphasic medium used for the reactions comprised of toluene and water in a ratio of 6:4, making total volume of the solution to 1×10^{-4} m^3. A certain minimum concentration of sodium hydroxide necessary, for the reaction to initiate.

The effect of different palladium catalysts, solvents, triphenyl phosphine concentration and reaction conditions on activity and selectivity to, vinyl acetic acid, has been studied. The activity and selectivity was found to be independent of the type of catalyst and nature of organic solvent. An important observation was that all types of catalysts screened, were found to decompose to metal during the reaction and adhered to the interface of the organic and aqueous phases. In pure organic or aqueous phases the reaction was completely inhibitted. With increase in organic phase holdup (from 0 to 1:9), the rate of reaction was high, however, with further increase in organic phase holdup (from 1:9 to 8:2) the activity showed a gradual decrease and beyond (8:2) the reaction was inhibitted totally. Addition of triphenyl phosphine was found to enhance the activity of the catalyst and a maximum at the molar ratio of 1:1 of Pd:PPh_3 was observed. The activity of Pd metal catalyst decreased with increase in allyl chloride concentration, while it increased with increase in partial pressure of carbon monoxide and sodium hydroxide concentrations. A maximum in the activity was observed for the increase in catalyst concentration. The selectivity to vinyl acetic acid was found to depend inversely on the concentration of sodium hydroxide and independent of all other parameters.

The kinetics of Pd metal catalyzed carbonylation of allyl chloride has been investigated over a temperature range of 298- 318 K. The following trends were observed. The rate was found to increase linearly with increase in partial pressure of carbon monoxide, while it increased linearly in the initial stages for the increase in concentration of sodium hydroxide and catalyst and was independent at higher concentrations. A maximum in the rate was observed for increase in allyl chloride concentration showing a substrate inhibited kinetics.

The following rate equation has been proposed based on the rate data and was found to fit the observed rate data within the range of experimental error.

$$R_A = \frac{k\ A\ B\ C\ D}{(1 + K_A\ A)^{3.2}\ (1 + K_B\ B)\ (1 + K_D\ D)} \tag{4.13}$$

The constants k, K_A, K_B and K_D were evaluated and the activation energy was found to be 23.3 kcal/mol.

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