CARBONYLATION OF ALCOHOLS AND OLEFINS USING SOLUBLE TRANSITION METAL CATALYSTS

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CARBONYLATION OF ALCOHOLS AND OLEFINS USING SOLUBLE TRANSITION METAL CATALYSTS

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FORM 'A'

Certified that the work incorporated in the thesis entitled: "**Carbonylation of Alcohols and Olefins using Soluble Transition Metal Catalysts**" submitted by **Mr. Tonde Sunil Sopana** was carried out under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

April, 2004 **Dr. R. V. Chaudhari**

Pune (Supervisor/Research Guide)

Dedicated

To

My Parents

ACKNOWLEDGEMENT

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Abstract of the Thesis

A catalyst is known to save process cost through active control of reactions reducing activation energy and making the reaction route attractive not only for economic but also from environmental considerations. Catalysis using soluble metal complexes has been practiced in industry for several years for a number of processes involving carbonylation, hydroformylation, hydrogenation, oligomerization, isomerization, polymerization and oxidation[1]. Industrial significance of catalysis using these homogeneous catalysts was realized after the development of processes like oxo process (hydroformylation technology), Wacker process, carbonylation of methanol to acetic acid, ethylene polymerization by Zeiglar-Natta catalyst, *p*-xylene oxidation to terephthalic acid etc[2]. Though homogeneous catalysis offers high reaction rates and high selectivity towards the desired products, it is only utilized in limited applications because of the catalyst-product separation problems associated with the processes. On the other hand, recent developments in synthesis of new metal complex catalysts and ligands indicate a strong potential of homogeneous catalysis for the synthesis of a wide variety of bulk, specialty and pharmaceutical products[3].

Transition metal catalyzed carbonylation of alcohols and olefins is one of the economically feasible and environmentally benign routes for the synthesis of a variety of carboxylic acids and their derivatives. Acetic Acid is one of the most important commodity chemicals being produced in large quantities for more than 100 years. Worldwide production of acetic acid is 7.8 million tons per annum (TPA). Methanol carbonylation has been the process of choice after the successful development of cobalt catalyst by BASF in early 1960's and rhodium catalyst by Monsanto in 1970's.[3] British Petroleum developed a new iridium catalyzed carbonylation process for the production of acetic acid (1997) (Cativa process). Recently palladium has gained some attention as a catalyst for carbonylation of methanol and methyl iodide[4], though it has yet to be developed as a commercial process. Similarly, palladium catalyzed carbonylation of allylic compounds is also useful for synthesis of unsaturated carboxylic acids, esters and their derivatives[5]. Another interesting example of palladium-catalyzed carbonylation is carbonylation of vinyl acetate (VAM) to methyl-2-acetoxypropionate, which can be easily converted to *dl*-lactic acid. Lactic acid is commercially important in

baking industry, cheese industry, pharmaceutical industry, cosmetic industry, in dying wool, to make plasticisers for resin, etc. The current worldwide production of lactic acid is estimated to be 40,000 TPA. Currently lactic acid is produced industrially by fermentation of molasses, but the process produces large amount of byproducts, making product separation and purification expensive. Any alternative technology yielding lactic acid in lower cost of production using environmentally compatible methods would result in a dramatic increase in the existing market and evolution of a range of new applications. The carbonylation of VAM provides an alternative catalytic route for the synthesis of lactic acid[6]. Very limited efforts in understanding the catalytic chemistry of this route have been made and hence further studies to evolve improved catalyst system would be worthwhile.

The present work is aimed at investigations on the activity and selectivity of palladium catalysts and their kinetics and mechanism. Following specific reactions were chosen for the present work.

- Carbonylation of methanol to acetic acid.
- Carbonylation of allyl alcohol to 3-butenoic acid.
- Methoxycarbonylation of vinyl acetate to methyl-2-acetoxypropionate and subsequent hydrolysis of the carbonylation product to lactic acid.

The thesis is presented in four chapters, a brief summary of which is outlined bellow.

Chapter 1 presents a detailed literature survey of carbonylation reactions with a main focus on carbonylation of aliphatic alcohols and olefins. Carbonylation of methanol has been reviewed critically as it is the process of choice for the synthesis of acetic acid having a bulk worldwide requirement. Though cobalt, rhodium, iridium, nickel, palladium and platinum catalysts were found to be active catalysts for methanol carbonylation, only rhodium, iridium and nickel are well studied[7] for their activity and mechanistic aspects. Rhodium needs higher water concentration (>8%) to achieve higher rates, which on the other hand increases water gas shift reaction decreasing CO selectivity. Literature cites a very scanty information using palladium as a catalyst, where

major concerns are lower catalyst activity and severe reaction conditions[4] (turnover frequency (TOF) 415 h^{-1} at 11 MPa CO pressure and 455 K). Recently Maitlis and coworkers[4] have demonstrated carbonylation of methyl iodide at milder reaction conditions (0.5 MPa CO and 413 K) using palladium (II) salts as catalysts, but the catalyst activity reported is very low (turnover number (TON) 110 in 16 h). Thus, there is scope in improving Pd-based catalysts.

Carbonylation of allylic alcohols is useful in the synthesis of unsaturated carboxylic acid derivatives and lactones. Carbonylation of allyl alcohol to 3-butenoic acid was reported using palladium catalysts and quaternary phosphonium salts as promoters in 100% yield at 373 K and 12 MPa CO pressure[5]. Cyclocarbonylation of allylic alcohols to synthesize butyrolactones has been studied with palladium, cobalt and rhodium catalysts using either syn gas or carbon monoxide and oxygen. Cyclocarbonylation of allyl alcohol to γ-butyrolactone (35% yield) has been reported using $PdCl_2$-$CuCl_2$ as a catalyst in the presence of CO and O_2 at milder reaction conditions[8] (room temperature, atm. pressure). This being a unique approach to synthesize unsaturated carboxylic acids and lactone derivatives, detailed investigations on catalysis, reaction kinetics and mechanism may be very valuable to eventually improve the synthesis process.

Alkoxycarbonylation of VAM has been proposed as an alternative route for the synthesis of lactic acid (currently lactic acid is produced by fermentation of molasses). Palladium and rhodium were found to be active for alkoxycarbonylation of VAM to methyl-2-acetoxypropionate, which is further hydrolyzed to lactic acid having an industrial importance. Carbonylation of VAM is an important step in this route. 62% yield of methyl-2-acetoxypropionate has been achieved using $PdCl_2(PPh_3)_2$ as a catalyst, though the catalyst activity was low even at severe operating conditions (TON = 13 at 373 K and 15.2 MPa)[6]. Review of the subject and the scope of the thesis have been presented in this chapter.

Chapter 2 presents an experimental study on palladium-catalyzed carbonylation of methanol. The effect of different alkali metal iodides, sulfonic acid promoters, N-, and P-containing ligands and solvents was investigated. LiI, NaI and KI were found to promote

carbonylation rates in presence of *p*-toluene sulfonic acid (TsOH) generating HI during reaction conditions, whereas use of HI as a promoter worked without TsOH. Using Pd(OAc)$_2$ as a catalyst precursor and HI as a promoter, a TOF of 45 h^{-1} was achieved at 388 K. At higher temperatures (>403 K) palladium precipitation was predominant, which was avoided using N-, and P-containing ligands (e.g. NEt$_3$, NPh$_3$, 2,2'-bipyridine, PPh$_3$). High TOF of 1052 h^{-1} can also be achieved using Pd(OAc)$_2$ as a catalyst in the presence of HI and PPh$_3$ at 448 K and 5.4 MPa, which is a substantial improvement over the activity reported in earlier literature[4] (TOF 415 h^{-1} at 455K and 11 MPa). Water gas shift reaction does not occur during palladium-catalyzed carbonylation as no CO$_2$ was traced in gas phase as analyzed after the carbonylation reactions. Considering the high catalytic activity of Pd complexes at milder reaction conditions, they have potential as alternative catalysts for the synthesis of acetic acid. An iodide bridged palladium dimeric complex, (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ was isolated from the carbonylation reaction mixture for the first time and characterized by X-ray crystallography and ^{31}P NMR spectroscopy. The isolated dimeric complex was carbonylated to a monomeric species, [PdI$_3$CO]$^-$ at room temperature and atmospheric pressure, which was characterized by IR spectroscopy. Reaction mechanism was proposed based on IR and UV-vis spectroscopic characterizations of the catalytic species involved in the catalytic cycle. The effect of various reaction parameters such as catalyst loading, methanol, water, iodide, triphenyl phosphine concentration, and CO partial pressure was studied in a temperature range of 388 K-433 K.

Chapter 3 presents a detailed study on carbonylation of allyl alcohol using palladium catalyst (e.g. PdCl$_2$, Pd(acac)$_2$, Pd(OAc)$_2$) with a quaternary salt (e.g. tetrabutyl ammonium chloride, tetrabutyl ammonium bromide or benzyl triethyl ammonium chloride) and TsOH as promoters. The role of different quaternary salts was investigated wherein quaternary ammonium chlorides were found to be superior among the other halides. Higher TOF (256 h^{-1}) was achieved using PdCl$_2$ as a catalyst and benzyl triethyl ammonium chloride as a promoter in the presence of TsOH. Activity of the palladium catalyst was strongly influenced by the solvent used. Five fold decrease in TOF was observed when 4 equiv. PPh$_3$ was used as a ligand. Kinetics of this reaction was

studied in the temperature range of 363 K-383 K. The rate of reaction was found to be 0.8^{th} order with respect to catalyst, first order with respect to allyl alcohol at lower concentration (<1 kmol/m^3) and nearly zero order at higher allyl alcohol concentrations. Similarly, first order dependence of the rate was observed with respect to CO partial pressure. The activation energy of the reaction was found to be 38.72 kJ/mol. Mechanism of carbonylation of allyl alcohol was proposed.

Chapter 4 presents results on methoxycarbonylation of VAM to methyl-2-acetoxypropionate and methyl lactate, which were further hydrolyzed in the presence of acid catalysts to *dl*-lactic acid. Methoxycarbonylation of VAM gives carbonylation products (methyl-2-acetoxypropionate and methyl lactate) along with the side products (methyl acetate and dimethyl acetal). Different palladium catalysts such as $PdCl_2(PPh_3)_2$, $PdCl_2(AsPh_3)_2$, $PdCl_2Py_2$ were synthesized, characterized and tested for the methoxycarbonylation reaction. $PdCl_2(PPh_3)_2$ was found as the best catalyst for VAM methoxycarbonylation, which gave TOF of 102 h^{-1} at 373 K and 5.4 MPa CO pressure. This was a significant improvement over the previous reports[6] (TON = 13 at 373 K and 15.2 MPa). Different quaternary ammonium salts were screened as promoters for this reaction where the activity trend was observed in the order: Cl > Br >> I (using tetrabutyl ammonium halides the TOF were 52, 10, 0 h^{-1} for TBACl, TBABr and TBAI respectively). Various acidic and basic ligands (-N and O- donor ligands) were screened for VAM methoxycarbonylation reaction along with $PdCl_2(PPh_3)_2$ as a catalyst in the presence and absence of TsOH. The ligands having basic nature were effective to achieve higher carbonylation selectivity for $PdCl_2(PPh_3)_2$-TsOH catalyst system, whereas the ligands with acidic nature increased the conversion of VAM with decrease in selectivity. Significant effect of PPh$_3$ concentration was observed. Increasing the PPh$_3$ concentration from 0.1 mmol to 1 mmol decreased the yield of carbonylation product from 52 to 4%. The effect of different solvents was also studied. The strongly coordinating solvents such as acetonitrile, DMF reduced the rate of carbonylation reaction. Kinetics of methoxycarbonylation of VAM was studied in the temperature range of 363- 383 K using $PdCl_2(PPh_3)_2$ as a catalyst. Methoxycarbonylation of VAM was found to be first order with respect to catalyst and CO, whereas it was first order tending to zero order with respect

to VAM and methanol. Activation energy of the catalytic reaction was found to be 81.62 kJ/mol. The palladium catalyzed methoxycarbonylation route proposed here provides an efficient method for the synthesis of methyl-2-acetoxypropionate, which can be hydrolyzed to lactic acid. The carbonylation product, methyl-2-acetoxypropionate was separated from the reaction mixture, characterized by ^{1}H NMR spectroscopy and was further hydrolyzed to lactic acid using acid or base catalysts. Similarly, methyl lactate was also isolated form the reaction mixtures and hydrolyzed to lactic acid using acidic catalysts. 100% conversion of methyl-2-acetoxypropionate to lactic acid was achieved using TsOH as a catalyst.

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CHAPTER 1

Introduction and Literature Survey

1.1. Introduction

Catalysis is widely used in nature for affecting various kinds of chemical transformations since the evolution of life, though human being knows it since 400 years. Today catalysis is used to satisfy human needs right from food and clothing to drugs, plastics, detergents, fuels, agrochemicals and pesticides accounting for more than one sixth of the value of all goods manufactured worldwide. Furthermore, catalysis is playing an important role in environmental protection by providing cleaner alternative routes for stoichiometric organic synthesis and converting hazardous emissions to harmless streams. Stoichiometric organic reactions produce large amount of byproducts and mineral salts creating environmental threat to dispose them off. Thus, the importance of catalysis to society is not only in economic aspects but also from the environmental considerations.

Catalysis in broader terms has been classified in two different types as homogeneous and heterogeneous catalysis depending on the physical nature of the catalyst employed. In homogeneous catalysis, the catalyst is soluble in the reaction medium making a single phase whereas in heterogeneous catalysis the catalyst is present as a separate phase (a solid or an immiscible liquid phase). Though, both the type of catalysts have contributed significantly to the industry, homogeneous catalysts have distinct advantages like high activity at milder operating conditions, selectivity control, feasibility to understand detailed mechanistic aspects at microscopic level to tailor it further and negligible diffusion limitations. These advantages of homogeneous catalysts have been used in industry for several years for a number processes involving carbonylation, hydroformylation, hydrogenation, oligomerization, isomerization, polymerization and oxidation reactions[1]. Industrial significance of homogeneous catalysis was realized several decades ago after the development of oxo process[2] (hydroformylation technology), Wacker process (olefin oxidation)[3], Acetic Acid manufacture by BASF[4], Monsanto[5] and BP[6] processes (methanol carbonylation technology), ethylene polymerization by Zeigler-Natta catalysts[7] and *p*-xylene oxidation to terephthalic acid. Initially, the application of homogeneous catalysts was limited to Lewis and Bronsted acids, bases, simple metal salts and simple organic molecules. As the need for more specialized products increased, transition metals with tailored coordination

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environment were preferred as catalysts to achieve selectivity control at milder reaction conditions. Selectivity control is the main advantage of homogeneous catalysts, which is achieved by ligand design utilizing the knowledge of organometallic, coordination and theoretical chemistry. Chemistry of chiral synthesis via asymmetric catalysis is mainly based on homogeneous catalysis. Despite these advantages, about 80% of the industrial catalytic processes employ heterogeneous catalysts for easier catalyst-product separation, which is often a tedious job in homogeneous catalysis. On the other hand, recent development in synthesis of new metal complex catalysts, novel ligands, new designs for tandem reactions and asymmetric catalysis indicates a strong potential of homogeneous catalysis for the synthesis of a wide variety of bulk, specialty and pharmaceutical products.

The main objective of this thesis was to investigate the catalysis aspects of carbonylation of aliphatic alcohols and olefins to the carboxylic acids and esters, which also have several industrial applications. Carbonylation of methanol, allyl alcohol and vinyl acetate were chosen as reaction systems with the goal of understanding the performance of various catalytic systems followed by a study on kinetics and mechanism. This chapter presents a brief literature survey on carbonylation of aliphatic alcohols and olefins with respect to catalysis, reaction kinetics and mechanism.

1.2. Carbonylation Reactions and their Applications

Catalytic carbonylation reactions involve insertion of CO around the central metal atom that leads to chemical transformation of a particular substrate to a carbonyl compound such as aldehyde, ketone, carboxylic acid, ester, amide etc. Reactivity of carbon monoxide has been established for a variety of substrates such as olefins, alkynes, alcohols, amines, nitro compounds and organic halides yielding various useful compounds (Scheme 1.1).

Carbonylation chemistry was pioneered by Otto Roelen[8] with the discovery of a landmark oxo synthesis, which was first commercialized at Ruhrchemie and further explored by Walter Reppe[9] at BASF. Further, the work of Wilkinson[10], Heck[11] and
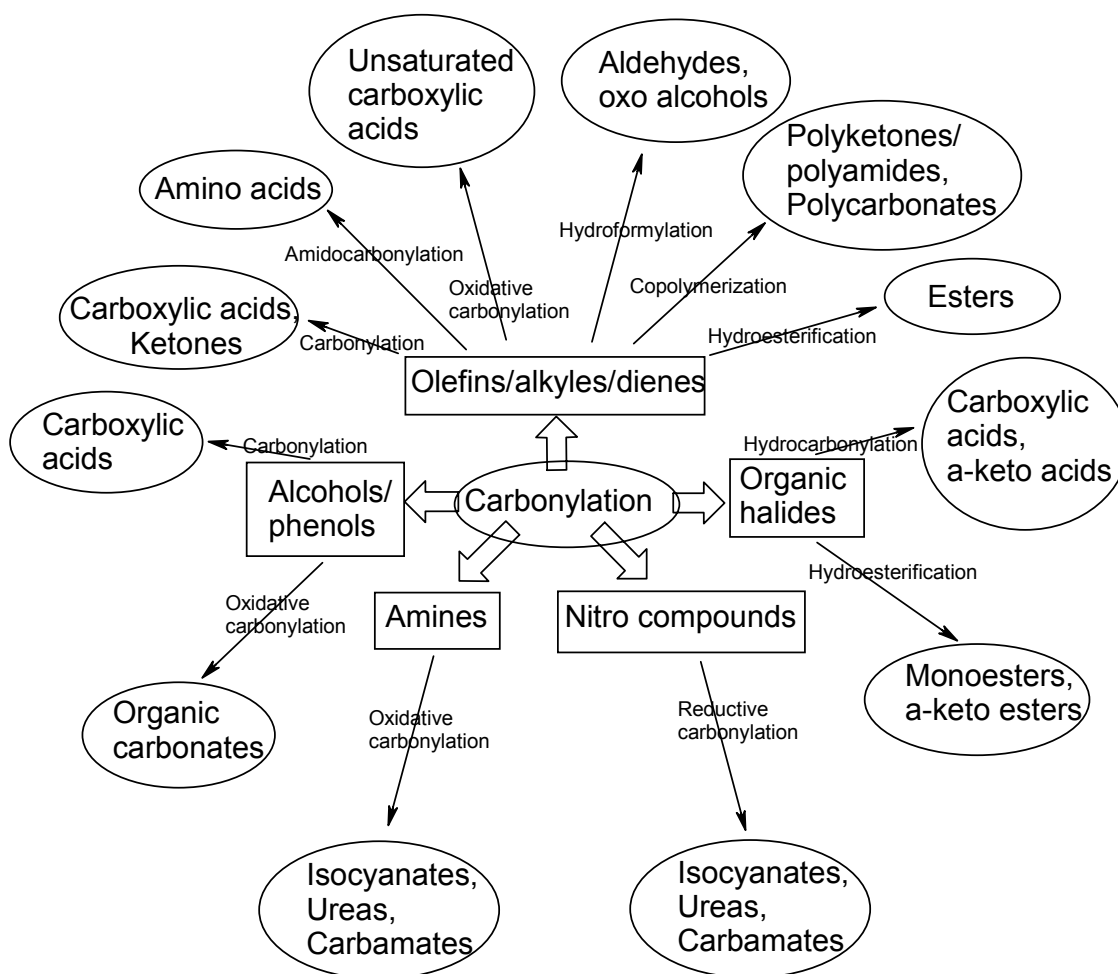
Scheme 1.1. Useful products through carbonylation reactions

Tsuji[12] on organophosphine complexes achieved significant improvements in the field of carbonylation chemistry. As a result, a number of processes utilizing carbonylation reactions have been commercialized worldwide till date for the production of aldehydes, ketones, carboxylic acids, esters, organic carbonates and amides etc, some of which are given in Table 1.1. C_1 chemistry using homogeneous catalysis was established in a true sense after 1950, after which the organometallic chemistry has also grown at an exponential rate with significant advances in their synthesis, characterization techniques and catalytic applications.

Table 1.1. Industrial processes involving carbonylation reactions

No.	Process	Catalyst	Company	Reference
1	Methanol to acetic acid	$Co_2(CO)_8$	BASF	Falbe (1975)[4]
		$[Rh(CO)_2I_2]^-$	Monsanto	Roth (1975)[5]
		$IrCl_3$-$RuCl_3$	BP	Watson (1998)[6]
2	Acetylene to acrylic acid	$NiBr_2$-$CuBr_2$	BASF	Weissermel and Arpe (1993)[13]
3	Ethylene to propionic acid	$Ni(OCOC_3H_5)_2$	BASF	Weissermel and Arpe (1993)[13]
4	Methanol to dimethyl carbonate	$PdCl_2$-$CuCl_2$	Assoreni	Ugo et al. (1980)[14]
5	Propene to butyraldehyde	$HCo(CO)_3(PBu)_3$	Shell	Johnson (1985)[15]
6	Methyl acetate to acetic anhydride	$RhCl_3$	Estman	Mayfield (1986)[16]
7	Benzyl chloride to phenyl acetic acid	$Na[Co(CO)_4]$	Montedison	Cassar et al. (1969)[17]
8	Butadiene to adipic acid	$HCo(CO)_4$	BASF	Chem.Week (1984)[18]
9	Isobutylphenyl ethanol to Ibuprofen	$PdCl_2(PPh_3)_2$	Hoechst Celanese	Armor (1991)[19]
10	Propylene to methyl methacrylate	Pd-pyridyl Phosphine	Shell	Schwaar (1994)[20]
11	Ethylene copolymerization to polyketones	$Pd(OAc)_2$/dppp/ TsOH	Shell	Ash (1994)[21]

The first thirty years of carbonylation chemistry were based on only metal carbonyls as catalysts employing high pressure and high temperature conditions. At such severe conditions, the metal carbonyl catalysts could give the carbonylation products with lower selectivities and large amount of byproducts, which needed tedious procedures and higher cost for product separation. Further developments in catalyst design using ligands changed the scenario of industrial carbonylation processes and showed that a given carbonylation reaction can be operated even at lower operating conditions with improved

product selectivity. The advanced knowledge of coordination chemistry and theoretical calculations (using molecular modeling) indeed could help in achieving a deeper insight into the steric and electronic properties of the ligands and the coordination environment to tailor the catalysts as per need. Homogeneously catalyzed carbonylation reactions are important in chemical industry producing more than eight million tons of carbonylation products per annum (TPA). Some examples of the carbonylation reactions are reviewed in following sections.

1.3. Carbonylation of Alcohols

Carbonylation of alcohols is an economical and environmentally benign route for the synthesis of carboxylic acids and esters as demonstrated by BASF for acetic acid by methanol carbonylation[4]. Methanol carbonylation processes initially used cobalt[4] catalysts but were further shifted to rhodium[5] and iridium[6] catalysts for better selectivities and economics.

1.3.1. Carbonylation of Methanol

Methanol is a versatile, readily available C_1 compound obtained from synthesis gas. Large-scale methanol synthesis is accessible using highly active copper catalyst. Current production capacity of methanol is surveyed to be around 37.5 million TPA, out of which only 80 % is being utilized for various purposes[22]. This overcapacity is mainly due to new plants where the surplus natural gas is available at lower price[23]. This will introduce new methanol-based processes for motor fuels and organic chemicals in the near future. Availability of methanol in cheaper rates finds versatile applications of methanol in carbonylation reactions as shown in scheme 1.2. Some of these processes have already been commercialized. Though, the production of ethanol, acetaldehyde and ethylene glycol by methanol carbonylation route is uneconomical today, these processes have potential to replace existing ethylene based processes due to the availability of methanol at competitive rates.
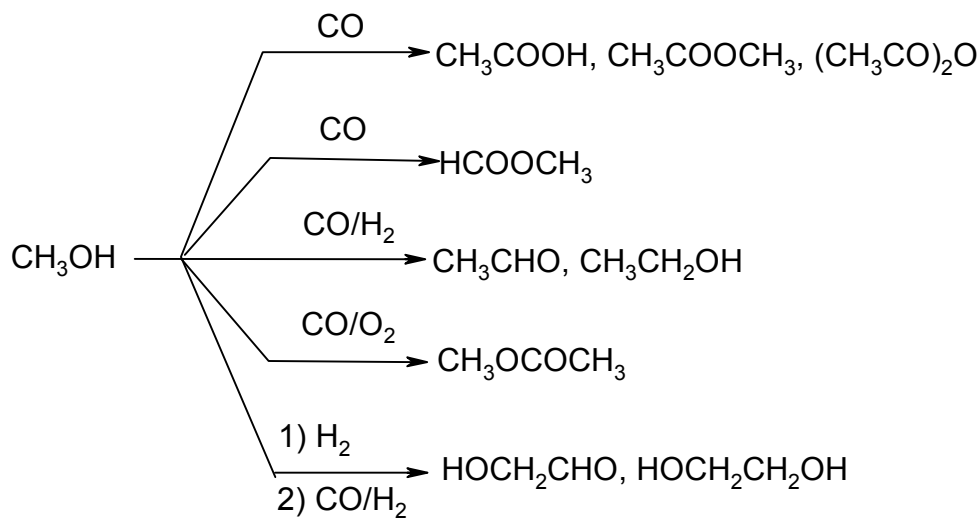
Scheme 1.2. Reactions involved in methanol carbonylation

Acetic acid manufacture is one of the major applications of methanol carbonylation and is one of the most important commodity chemicals being produced in large quantities for more than 100 years. The total world capacity of acetic acid was estimated to be 7.8 million TPA in 1998[24]. It is used in the manufacture of synthetic fibers and resins, acetic anhydride,
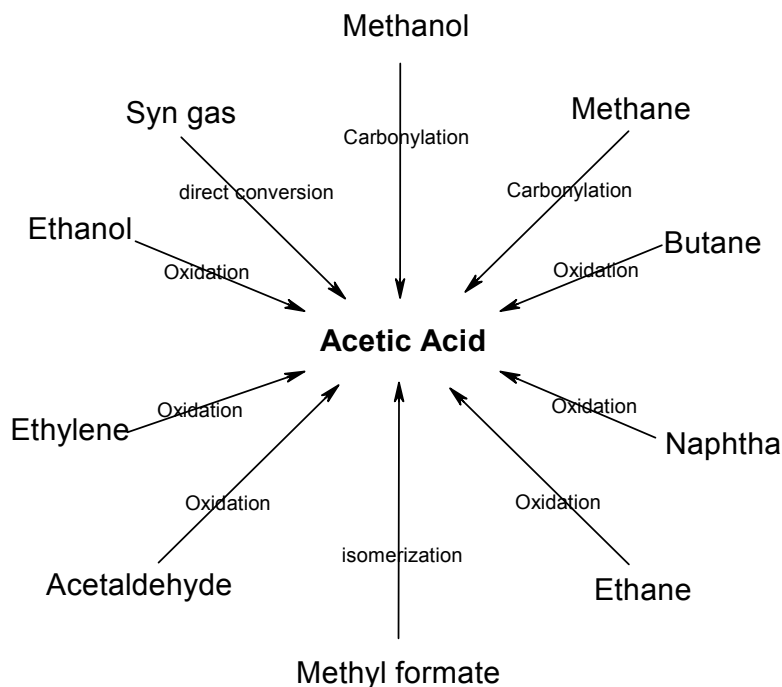
Scheme 1.3. Various routes for acetic acid synthesis

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vinyl acetate and as a solvent in polyester fiber production. The demand for acetic acid is growing rapidly as there is increasing demand of major chemical intermediates like PTA, VAM, alkyl acetate solvents and other finished products[25]. Demand for the acetic acid based products is increasing which in turn will increase the demand for acetic acid.

Though various routes for synthesis of acetic acid are known as described in scheme 1.3, major commercial processes being used for the large-scale manufacture of acetic acid are oxidation of acetaldehyde, oxidation of hydrocarbons and carbonylation of methanol (Table 1.2).

Table 1.2. Acetic acid Commercial processes

Process Route	Catalyst	Reaction Conditions (K, MPa.)	Yield, %
Methanol carbonylation	Rh or Ir complexes	453-493, 3-4	MeOH: 99, CO: 85
	$Co_2(CO)_8$	523, 70	MeOH: 90, CO: 70
Acetaldehyde Oxidation	$Mn(OAc)_2$, $Co(OAc)_2$	323-333, 0.1	Acetaldehyde: 95
Ethylene direct oxidation	Pd/Cu/ heteropolyacid	423-433, 8.1	Ethylene: 87
Hydrocarbon oxidation (n-butane, naphtha)	$Co(OAc)_2$, $Mn(OAc)_2$	423-503, 5-6	n-Butane: 50, Naphtha: 40

Reppe's work at BASF demonstrated the efficiency of group VIII transition metal carbonyls as catalysts for carbonylation reactions[4]. The availability of CO in abundant quantities from resources such as natural gas, coal and biomass led to the development of new routes for a wide range of chemicals. Methanol was available in large quantities at cheaper rates from CO and H_2 as a feedstock. Thus, methanol carbonylation has been the process of choice for acetic acid production after the successful development of cobalt carbonyl catalyst by BASF in 1960[4] and rhodium catalyst by Monsanto in 1970[5]. The carbonylation route produces 60% of the total acetic acid production[26]. A variety of transition metals including Co, Rh, Ir, Ni, Ru, Pt and Pd have been found to be active for carbonylation of methanol (eq. 1.1 shows overall methanol carbonylation reaction), out of which only Co, Rh, Ir and Ni have been explored well for their activity, kinetics

$$CH_3OH + CO \longrightarrow CH_3COOH; \triangle H = -33 \text{ kcal/mol} \qquad (1.1)$$
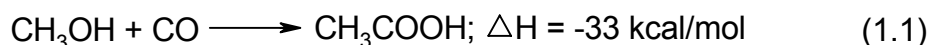
and mechanism. Further, new processes have come up using carbonylation technology to fulfill the current acetic acid need. In 1996, iridium/iodide catalyzed carbonylation process was announced by BP Chemicals[6]. Recently, Chiyoda Corporation has introduced Rh/PVP based heterogeneous catalytic carbonylation process minimizing water and iodide concentration giving less byproducts and less corrosion[27].

1.3.1.1. Cobalt Catalysts

Reppe's work for carbonylation reactions led to the development of a first methanol carbonylation process for acetic acid, at high pressure (70 MPa), temperature (523 K) and using cobalt iodide catalyst, which was commercialized in 1960 by BASF at Ludwigshafen, Federal Republic of Germany[4]. Initially the plant was operated for 36000 TPA. In 1966 Borden Chemical Co. started an acetic acid unit in Geismar, Louisiana, United State, based on BASF technology, which was expanded in 1981 from the capacity of 45,000 to 64,000 TPA[28]. Cobalt (II) iodide was used as a catalyst precursor with HI as a promoter to generate $Co_2(CO)_8$. Severe operating conditions (as mentioned above) were required to maintain the catalyst in an active form and to achieve commercially acceptable rates. The rate of reaction in BASF process was found to be dependent both on the partial pressure of CO and the concentration of methanol. The process gives 90 % yield of acetic acid based on methanol and 70% based on carbon monoxide.

Hohenschutz *et. al.*[4] have proposed a mechanism for cobalt-catalyzed carbonylation of methanol, which is summarized in the following reaction scheme (eq. 1.2-1.9). Formation of $HCo(CO)_4$ from $Co_2(CO)_8$ as the first step took place using hydrogen generated via water gas shift reaction. $HCo(CO)_4$, thus formed subsequently generated $[Co(CO)_4]^-$ anion, which is an active catalyst in the BASF process. Nucleophilic attack of methyl iodide and subsequent methyl migration gave tricarbonyl cobalt acyl intermediate, which gave tetracarbonyl cobalt acyl species after CO addition. This tetracarbonyl cobalt acyl intermediate regenerated the active catalytic species $[Co(CO)_4]^-$ after reaction with HI producing acyl iodide which was further hydrolyzed in presence of water yielding the product acetic acid and simultaneously regenerating the iodide promoter.

$$Co_2(CO)_8 + H_2O + CO \longrightarrow 2HCo(CO)_4 + CO_2 \qquad (1.2)$$

$$CH_3OH + HI \rightleftharpoons CH_3I + H_2O \qquad (1.3)$$

$$HCo(CO)_4 \rightleftharpoons H^+ + [Co(CO)_4]^- \qquad (1.4)$$

$$[Co(CO)_4]^- + CH_3I \longrightarrow CH_3Co(CO)_4 + I^- \qquad (1.5)$$

$$CH_3Co(CO)_4 \longrightarrow CH_3\overset{\displaystyle O}{\overset{\|}{C}}-Co(CO)_3 \qquad (1.6)$$

$$CH_3Co(CO)_4 + CO \rightleftharpoons CH_3\overset{\displaystyle O}{\overset{\|}{C}}-Co(CO)_4 \qquad (1.7)$$

$$CH_3\overset{\displaystyle O}{\overset{\|}{C}}-Co(CO)_4 + HI \longrightarrow CH_3COI + H^+ + [Co(CO)_4]^- \qquad (1.8)$$

$$CH_3COI + H_2O \longrightarrow CH_3COOH + HI \qquad (1.9)$$
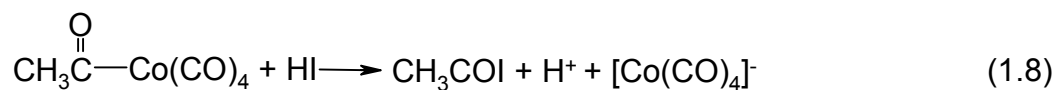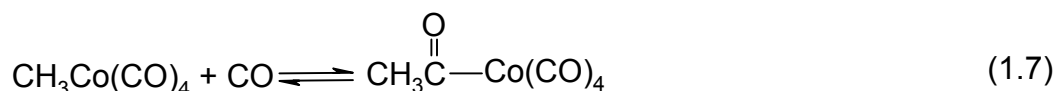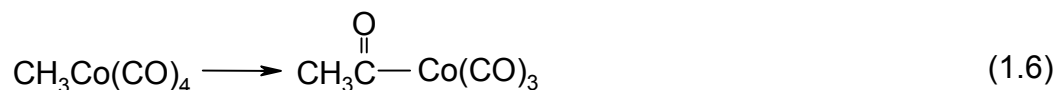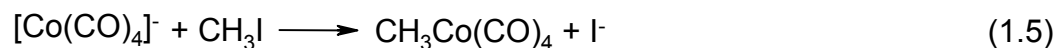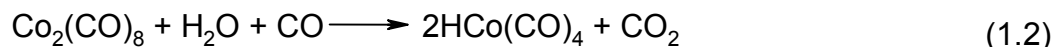
BASF process produced CH_4, CH_3CHO, C_2H_5OH, CO_2, C_2H_5COOH, alkyl acetates and 2-ethyl-1-butanol as byproducts. Water gas shift reaction was very much prominent (~10% of converted CO goes to CO_2) in cobalt-catalyzed process decreasing CO based selectivity of acetic acid.

A highly active cobalt catalyst system, $[CpCo(CO)_2]$-PEt_3-H_2O, was reported by Cole-Hamilton and coworkers[29] at milder reaction conditions (10 MPa CO, 393 K) yielding an initial rate as high as 44 mol/l/h at higher concentration of the cobalt catalyst (0.15 mol/l). Considering the concentration of cobalt charged, the rates were found to be 1.5 times higher than those with rhodium catalyst at similar conditions. The authors have isolated a species, $[CoI(CO)_2(PEt_3)_2]$ from the reaction mixture and characterized by X-ray crystallography. They proposed that, species $[CpCo(CO)I]^-$ generated insitu was an active catalyst for the methanol carbonylation reaction.

1.3.1.2. Rhodium Catalysts

Monsanto initiated development of rhodium iodide catalyzed carbonylation of methanol as a process for acetic acid production in 1966[5]. It is one of the most successful examples of homogeneously catalyzed reactions in industry. After the successful commercialization of the Monsanto process, methanol carbonylation route was found to be the cheapest way for acetic acid manufacture. Monsanto process achieved significant improvement over the BASF process by reducing the operating conditions (423-473 K, 3-6 MPa CO), which reduced construction cost and thus saving the capital cost. Furthermore, the process gave high selectivity (99% based on methanol and 85% based on CO) towards the product acetic acid leading to easier product purification[30]. Though the process used very expensive rhodium catalyst, cost of rhodium was counterbalanced by a lower cost of production and capital investment. In 1986, BP Chemicals acquired ownership of the Monsanto technology and further extended it for the co-production of acetic anhydride using methyl acetate carbonylation technology[26]. Similar technology was used by Eastman[16] for the manufacture of acetic anhydride. The improved methanol carbonylation process operated at lower water concentration (2%) using alkali metal iodide promoters in combination with methyl iodide to the Monsanto process was first commercialized by Celanese and Daicel in 1980s[31]. This improved process, as operated at lower water level reduced the byproduct formation via water gas shift reaction thus improving the CO selectivity and decreasing downstream separation costs.

Though, Monsanto process offered higher rates, it needed higher water concentration (14-15%) to achieve high catalyst activity and also to maintain the catalyst stability[32], which in turn increased water gas shift reaction and generated CO_2 (eq. 1.10-1.11) decreasing CO based selectivity of acetic acid (85%). At the reaction conditions,

$$[Rh(CO)_2I_2]^- + 2\ HI \longrightarrow [Rh(CO)_2I_4]^- + H_2 \qquad (1.10)$$

$$[Rh(CO)_2I_4]^- + H_2O + CO \longrightarrow [Rh(CO)_2I_2]^- + CO_2 + 2\ HI \qquad (1.11)$$
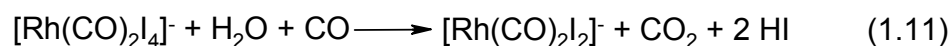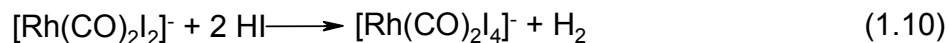
the rate-determining step was of oxidative addition methyl iodide, which can be shifted to reductive elimination process at lower concentration of water (<8%)[33]. At higher water

concentrations, the rate of reaction was necessarily first order with respect to catalyst as well as methyl iodide (eq. 1.12), while it was observed to be independent of methanol concentration and carbon monoxide pressure at higher water concentration (>8%).

$$\text{Rate} \propto [\text{catalyst}] \times [CH_3I] \qquad\qquad (1.12)$$

Propionic acid was found as a major byproduct (1200-2000 ppm) in the Monsanto process. Rhodium can catalytically generate acetaldehyde by methanol carbonylation. Acetaldehyde is further hydrogenated to ethanol, which on successive carbonylation can form propionic acid as a byproduct. Acetaldehyde formed can again undergo self-condensation or aldol condensation yielding butenal and higher aldehydes. This homologation process produces unsaturated compounds and alkyl iodides having even number of carbon atoms along with long chain carboxylic acids having odd number of carbon atoms as byproducts (Scheme 1.4)[6]. The byproducts obtained in such a way create difficulties in the product separation consuming high energy.
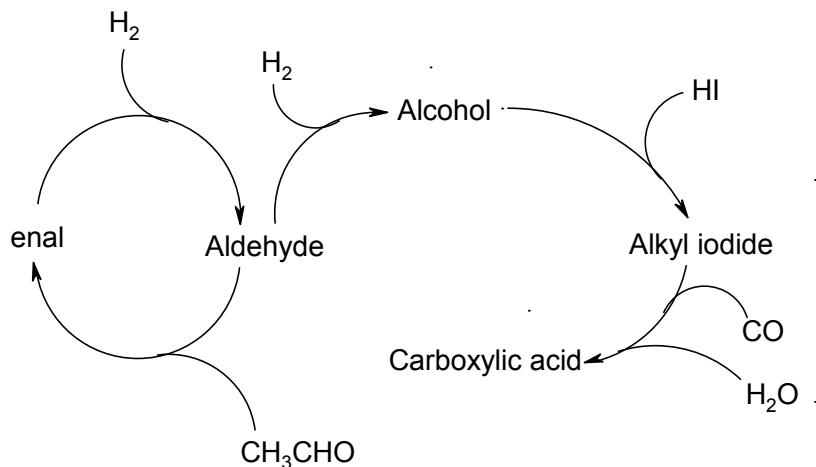
Scheme 1.4. Higher aldehydes, higher alkyl iodides, and higher carboxylic acid formation in rhodium process.

Though this process gives high selectivity to the product acetic acid, there is room for improvements[6]. A major drawback of the rhodium catalyzed process is the formation of inactive rhodium species such as $[Rh(CO)I_4]^-$ in CO deficient areas, which eventually forms insoluble RhI_3 loosing rhodium catalyst (eq. 1.13, 1.14). Minimum CO pressure

has to be maintained to avoid catalyst decomposition. Certain concentrations of methyl iodide, methyl acetate and water are again necessary to achieve higher rates[33]. On the other hand higher concentration of water decreases CO selectivity with increasing product separation cost as discussed above.

$$[RhI_3(CO)(COCH_3)]^- + HI \longrightarrow [RhI_4(CO)]^- + CH_3CHO \qquad (1.13)$$

$$[RhI_4(CO)]^- \longrightarrow RhI_3 + I^- + CO \qquad (1.14)$$

In order to overcome the limitations of the homogeneous catalyst system, heterogeneous catalyst systems were suggested using Rh/C and inorganic oxides or zeolites supported rhodium as catalysts for vapor phase operation. However, the processes lack in lower reaction rates and selectivities[34]. Chiyoda and UOP[24] have jointly developed a heterogeneous catalytic process for methanol carbonylation called Acetica Process. Catalyst stability was tested in a continuous-recycle pilot plant and showed no catalyst deactivation after continuous operation for more than 7000h[24]. The acetic acid production capacity of the plant is 36000TPA[27] (Guizhou Crystal Organic Chemical Group Co., Ltd. of Guizhou Province, People's Republic of China (PRC) took license from Chiyoda to produce acetic acid by Acetica Process). The process used Rh catalyst immobilized on poly vinyl pyridine resin operated in a bubble column loop reactor to improve gas-liquid contact. The process designed in such a way, achieved 99% and 92% yields of acetic acid with respect to methanol and carbon monoxide respectively and enables use of low purity CO and lower iodide concentration. The process was operated at lower concentration of water to minimize byproduct formation.

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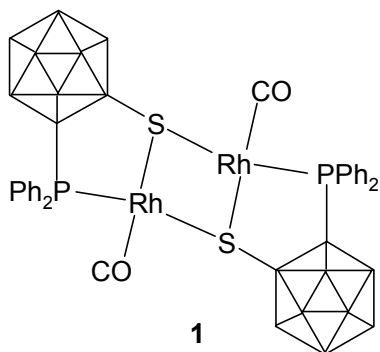
Rhodium complexes containing P- and S-containing carborane ligands have been reported for methanol carbonylation reaction showing much higher activity than Monsanto catalyst, $[Rh(CO)_2I_2]^-$. At the optimum conditions (453 K, 4.8 MPa CO) the activity of $[Rh(\mu\text{-S-Cab-P,S})(CO)]_2$ (**1**) was reported to be 1290 h^{-1} against 590 h^{-1} for

Rh(CO)$_2$I$_2^-$. Das *et. al.*[35] have reported a catalytic system consisting of [Rh(COD)Cl]$_2$ and phosphine oxide, sulfide or selenide ligands achieving TOF of 800 h^{-1} at 403 K and 1.5 MPa for the complex (**4**) formed insitu whereas under similar conditions, the Monsanto catalyst could yield only TOF of 200 h^{-1}. Rhodium complex supported on PVP was used for carbonylation reaction at 423 K, 4 MPa CO in supercritical CO$_2$ as a solvent with minimum leaching (>0.3 ppm against 52.2 ppm) of the Rh catalyst yielding 50% rates to that of liquid phase[36]. Rankin *et. al.*[37] have reported a catalyst [RhI(CO(PEt$_3$)$_2$] with higher activity at milder reaction conditions (393-423 K, 2.7 MPa). Oxidative addition of methyl iodide to the [RhI(CO(PEt$_3$)$_2$] catalyst to form [RhI$_2$Me(CO)(PEt$_3$)$_2$] was found to be 57 times faster than to [Rh(CO)$_2$I$_2$]$^-$ complex. The complex after oxidative addition of methyl iodide was characterized by single crystal X-ray crystallography. Migratory insertion of CO formed acyl rhodium species [RhI$_2$(COMe)(CO)(PEt$_3$)$_2$]. The authors have also speculated a mechanism for methanol carbonylation reaction using [RhI(CO(PEt$_3$)$_2$] as a catalyst precursor.
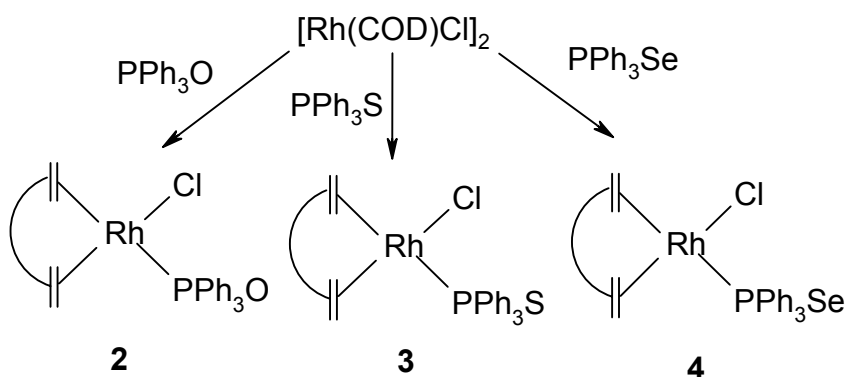
Forster and coworkers[5] investigated the mechanism of methanol carbonylation reaction showing [Rh(CO)$_2$I$_2$]$^-$, species **A**, as an active catalytic species as evidenced by *in situ* IR spectroscopy (Scheme 1.5). Oxidative addition of methyl iodide (formed from methanol and HI) to the species **A** to form methyl rhodium species, **B** is proposed to be the rate-determining step in this reaction. Further, methyl migration generating an acyl rhodium species, **C** was the first isolated intermediate for this reaction. It was also observed that the species **C** generates initial complex **A** and methyl iodide indicating reversibility of the oxidative addition and methyl migration steps. The monocarbonyl rhodium species, **C** was then carbonylated to a six coordinate dicarbonyl species **D**,

which reductively eliminates acyl iodide to regenerate [Rh(CO)$_2$I$_2$]$^-$, **A**. Thus, the cycle continues to produce acyl iodide, which is hydrolyzed in the presence of water to give the product acetic acid, and generates HI to form methyl iodide from methanol. Rhodium catalyzed methanol carbonylation reaction can be carried out using various rhodium (I) or rhodium (III) complexes as precursors, which are converted to the active catalyst [Rh(CO)$_2$I$_2$]$^-$ at reaction conditions[38].
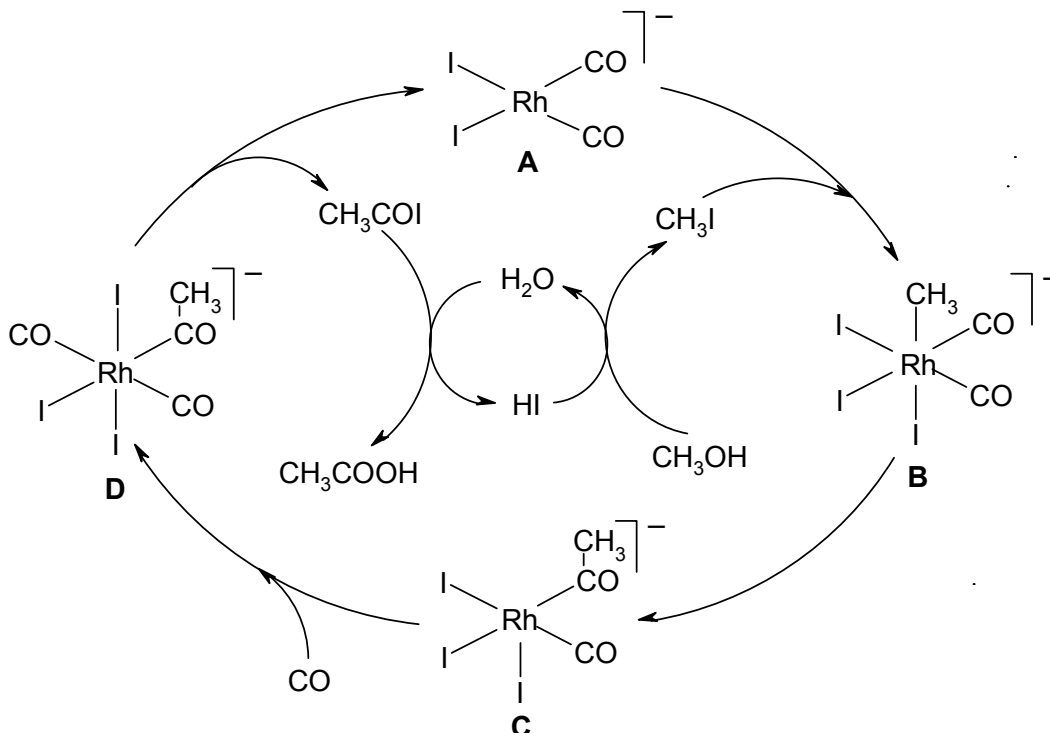
Scheme 1.5. mechanism of rhodium catalyzed carbonylation of methanol

BP did considerable work in collaboration with Sheffield University, UK on rhodium-catalyzed carbonylation of methanol with respect to kinetics and mechanism[30]. The initial work at Sheffield focused on the rate-determining step in the catalytic cycle[30]. The product after oxidative addition of methyl iodide, **B** was successfully shown by the reaction of complex **A** in neat methyl iodide by IR (v_{CO} = 2104 cm^{-1}) and ^{13}C NMR spectroscopy in ^{13}CH$_3$I (d −0.65; ^1J(Rh-C) 14.6 and ^1J(C-H) 143 Hz)[39]. The monocarbonyl acyl complex **C** decomposed loosing methyl iodide rather than acyl

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iodide. However, addition of CO formed the dicarbonyl rhodium species **D**, which reductively eliminated acyl iodide to regenerate complex **A.**

The reaction was found to obey first order kinetics with respect to catalyst **A** as well as methyl iodide. Protic polar solvents were found to enhance the oxidative addition step compared to aprotic solvents. Chaudhari and coworkers[40] have studied the kinetics of rhodium-catalyzed carbonylation of methanol in acetic acid and water media and found that the carbonylation reaction behaves differently in water medium. Rate of reaction was found to be zero order with respect to methanol concentration in acetic acid medium similar to that reported by Paulik and Roth[5]. When water is used as a solvent, the rate of reaction was found to increase with increasing methanol concentration. Increase in temperature beyond 443 K decreased the rate of reaction. A linear dependence on CO partial pressure was observed at lower CO pressure (< 1 MPa) above which it was independent of CO pressure. Rate equations were proposed for the reactions in water and acetic acid solvents, which are shown in equations 1.15 and 1.16 respectively.

$$R = \frac{k_1[CO][catalyst][HI][MeOH]^p}{1+ K_1[CO]} \quad (1.15)$$

$$R = \frac{k_2[CO][catalyst][HI]}{1+ K_2[CO]} \quad (1.16)$$

Where, R is rate of reaction, $kmol/m^3/s$; k_1 and k_2 are rate constants $(m^3/kmol)^{(p+2)}.s^{-1}$ and $(m^3/kmol)^2.s^{-1}$ respectively; K_1 and K_2 constants, $m^3/kmol$ and p is the order of reaction with respect to methanol

1.3.1.3. *Iridium Catalysts*

Keeping in mind the drawbacks of the Monsanto process, BP developed iridium based catalytic process named 'Cativa Process' for carbonylation of methanol and successfully commercialized at two plants: the Sterling Chemicals Texas City acetic acid plant in November 1996 and the Samsung-BP acetic acid plant in Ulsan, Republic of Korea in August 1997. The new process is considered to be a significant breakthrough in this industry in 25 years[6]. The process operated at lower water concentration (<8%) at

463 K and 2.8 MPa CO pressure using an iridium catalyst along with a promoter such as ruthenium, gave higher catalytic activity with lower byproducts consuming lower energy for product purification[24]. Though, early studies showed that the rhodium is superior to iridium for methanol carbonylation[5], iridium was found to be extremely robust catalyst than rhodium at higher temperatures[41]. Iodide complexes of zinc, cadmium, mercury, gallium and indium and carbonyl iodide complexes of tungsten, rhenium, ruthenium and osmium were found to enhance the catalytic activity of iridium catalyst[6]. Unlike rhodium system, carbonylation rate increased with decrease in water concentration up to 5% (w/w) in iridium system promoted by ruthenium. In this process, when the water concentration was above 5% (w/w), the catalyst was observed to be in two forms viz $[Ir(CO)_2I_4]^-$ (inactive species generated though water gas shift reaction) and $[Ir(CO)_2I_3Me]^-$ (active species)[33]; whereas at lower water concentration (bellow 5% (w/w)), the forms of the catalyst were active neutral species such as $[Ir(CO)_3I]$ and inactive species as $[Ir(CO)_3I_3]$. Byproduct formation was significantly suppressed in the Cativa Process as it operates at lower water concentration. Acetaldehyde formation was very low with further reduction of acetaldehyde to ethanol and subsequent carbonylation to propionic acid being very fast, higher unsaturates, higher alkyl iodides and higher carboxylic acids were negligibly small[6].

BP has investigated the reaction mechanism for iridium catalyst (Scheme 1.6) with a close partnership with Sheffield University[30] and observed key differences with rhodium catalysts. Model studies have shown that the oxidative addition of methyl iodide to the iridium center is 150 times faster than that to the rhodium center (A + CH$_3$I → B). This higher rates of oxidative addition process shift the rate determining step to migratory CO insertion to form an acyl intermediate D, which involves the elimination of ionic iodide and the coordination of an additional CO. Further reductive elimination of acyl iodide to generate an active catalytic species A, completes the catalytic cycle. The

$$\text{Rate} \propto \frac{[\text{catalyst}][\text{CO}]}{[\text{I}^-]} \qquad (1.17)$$

migratory insertion being the rate-determining step involved elimination of iodide and addition of CO, suggesting a totally different form of rate law as in equation 1.17. This

rate expression suggested that very high rates should be achieved by operating the process at lower iodide concentration. This also suggested that the addition of promoters
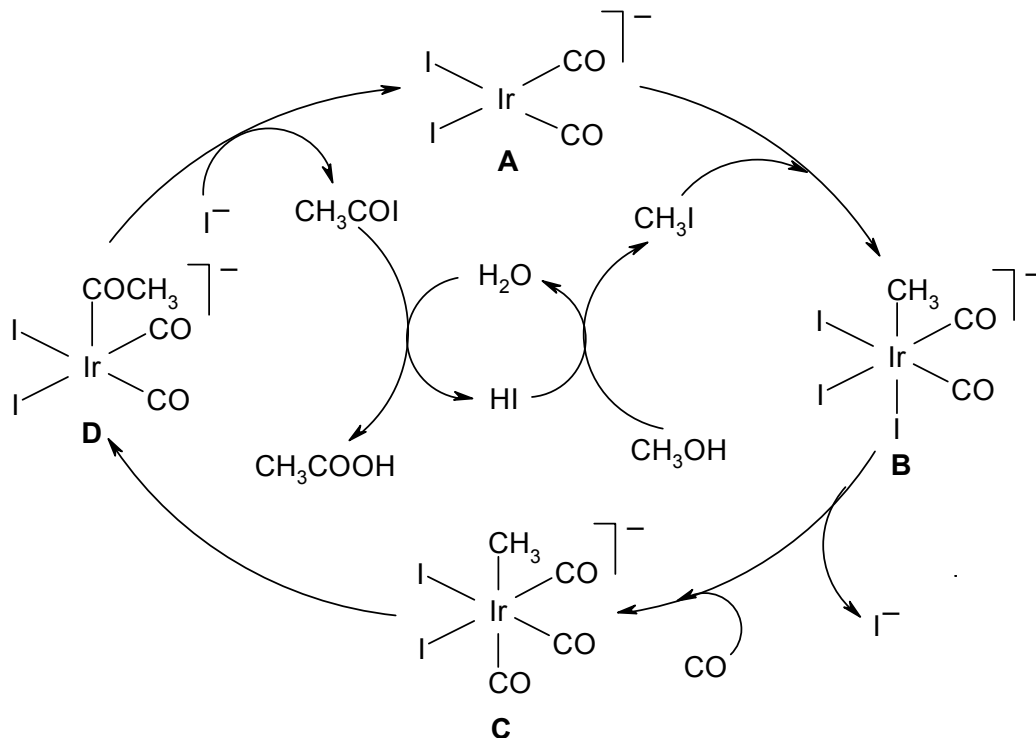
Scheme 1.6. Mechanism for iridium catalyzed carbonylation of methanol.

capable of removing ionic iodide should promote the rate-determining step to enhance the catalytic activity. Though, the above rate expression doesn't include any term specifying the concentration of water, it was found to have a very significant effect on the rate.

Until the early 1990s, the lower price of iridium (US$ 60/oz) over rhodium (US$ 500/oz) was the driving force for replacing the rhodium-catalyzed process. However, the price increase for iridium in 2001 (US$ 450/oz) negated the advantage in catalyst[24], which has still come down to US$ 90/ troy oz as per recent prices[42].

1.3.1.4. Nickel Catalysts

Earlier literature on nickel-catalyzed carbonylation indicated that severe operating conditions were required (523-573 K and 20 MPa bar) to achieve significant rates of acetic acid production[43]. Further, this process was modified using different promoters consisting of iodide (specifically methyl iodide) to reduce the operating temperature and

pressure. Recent studies have shown that nickel catalysts can be operated at milder reaction conditions for the carbonylation of methanol (463-498 K and 7 MPa.)[44]. This development is particularly important due to the extreme cost difference between nickel and rhodium. The activity of nickel catalysts was found to enhance by addition of organo-phosphorous, -nitrogen, -tin or -antimony compounds, alkali metals, and molybdenum as promoters[43]. As a result, nickel system was found to be much more robust in which Ni species can be charged in any form and was found to be tolerant to lower grade CO with impurities such as H_2O, N_2, CO_2[45]. Addition of H_2 significantly increases the rate without any side product formation[44]. For NiI_2-PPh_3[46] and $Ni(PPh_3)_2(CO)_2$-PPh_3[47] catalysts with methyl iodide as a promoter, 98% conversion of methanol with a selectivity of 75-90% has been reported. A highly active catalyst, $Ni(isoq)_4Cl_2$ has been reported by Kelkar et al.[48], which gave 99% conversion of methanol with 90-98% selectivity. Vapour phase carbonylation of methanol using supported Ni catalysts were also reported[44]. Thus, nickel catalysts can achieve activity and selectivities comparable to rhodium; nickel being a cheaper catalyst precursor, it may be rewarding to develop an economic process for the production of acetic acid by methanol carbonylation route. Recently, Ni/C catalyst has been described by Merenov *et. al.*[49] for vapour phase carbonylation of methanol in which a strong influence of support was observed on carbonylation reaction rate.

In order to achieve higher rates and selectivities, higher concentration of iodide promoters is needed, which on the other hand creates a severe problem of corrosion of the reactor under the reaction conditions. Although nickel catalysts have the advantage of being cheaper, possible formation of $Ni(CO)_4$ poses safety limitations to operate this process on a large scale and hence to commercialize the process.

A kinetic study has been reported by Kelkar et al[44] in a temperature range of 478-508 K for Ni-isoquinoline catalyst system. Linear dependence of the reaction rates were observed for catalyst, methyl iodide and H_2 whereas the rate was observed to increase with increase in methanol concentration and CO partial pressure bellow a certain limit of concentrations beyond which they were independent of methanol concentration and CO partial pressure at all temperatures. Further, it was shown that the presence of water in the

system inhibits the rate of carbonylation. The rate equation proposed[44] for methanol carbonylation reaction for Ni-isoquinoline catalyst system is given in equation 1.18. The activation energy for the reaction was reported to be 5.88×10^4 kJ/kmol.

$$R = \frac{k_0 A^* B C^{0.89} E (1 + 0.0014 D^{0.9})}{(1 + K_A A^*)(1 + K_B B)(1 + K_p P)^2} \qquad (1.18)$$

1.3.1.5. Palladium Catalysts

While Rh and Ir complexes have been found to be most attractive in commercial processes for methanol carbonylation, investigations on Pd catalysts may be worthwhile as an alternative catalyst at milder operating conditions.

Van Leeuwen[50] suggested palladium catalyst system consisting of $Pd(OAc)_2$, N-containing ligand, CH_3I and NaI for carbonylation of methanol to achieve high activity (5.8 mol/l/h and 100 % conversion) at 11-20 MPa and 451-573 K. Rates of the order of 10 mol/l/h have been considered reasonable for commercial operation that was the benchmark set by the Monsanto process[6]. Though, Van Leeuwen's[50] patent provided good activity palladium catalysts for methanol carbonylation, the process was operated at severe reaction conditions with higher concentration of iodide promoters (iodide/Pd ratio = 470), N-containing ligands and sulfolane solvent to achieve such higher rates. Further, the process needed 5-30 % water concentration that could be troublesome for product separation consuming high energy as discussed in previous sections. Later, the process was improved[51] to achieve the highest activity (TOF = 480) at milder operating conditions (448 K, 4.13 MPa) using a nickel additive (NiI_2 and/ $Ni(OAc)_2.4H_2O$), higher iodide concentration (methyl iodide/Pd ratio = 212 for the highest activity) and sulfolane or sulfoxide solvents, without which the catalyst was found to be inactive for methanol carbonylation reaction. Drent et al.[52] have reported palladium catalyst ($Pd(OAc)_2$) with $NiCl_2$ as an additive and N- and P-containing ligands in presence of sulfolane or sulfoxide as a solvent to achieve TOF of $90h^{-1}$ at 398-473 K and 7 MPa pressure.

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Recently Maitlis and coworkers[53] have shown that the palladium catalysts can carbonylate methyl iodide at still milder operating conditions (0.5 MPa CO, 413 K) to obtain a TON of 110 in 16 hours. The authors have proposed a mechanism for Pd-catalyzed carbonylation of methanol using $PdCl_2(PPh_3)_2$ as a catalyst along with Bu_4NI as a promoter (scheme 1.7). ^{31}P NMR spectroscopy showed that PPh_3 was detached from Pd center and formed $[PPh_3Me]I$ showing a signal at $\delta = 22.2$. Though the authors have speculated a mechanism for carbonylation of methanol showing PdI_3CO^- as an active catalytic species, direct evidence for this species was not given. In an analogous study using Pt-catalyst system (K_2PtCl_4-CH_3I-Bu_4NI), FTIR characterizations of carbonylation reaction mixture showed the formation of PtI_3CO^-. Similar Pd-carbonyl species, **A** (PdI_3CO^-) was speculated to be an active catalytic species in $PdCl_2(PPh_3)_2$-CH_3I-Bu_4NI
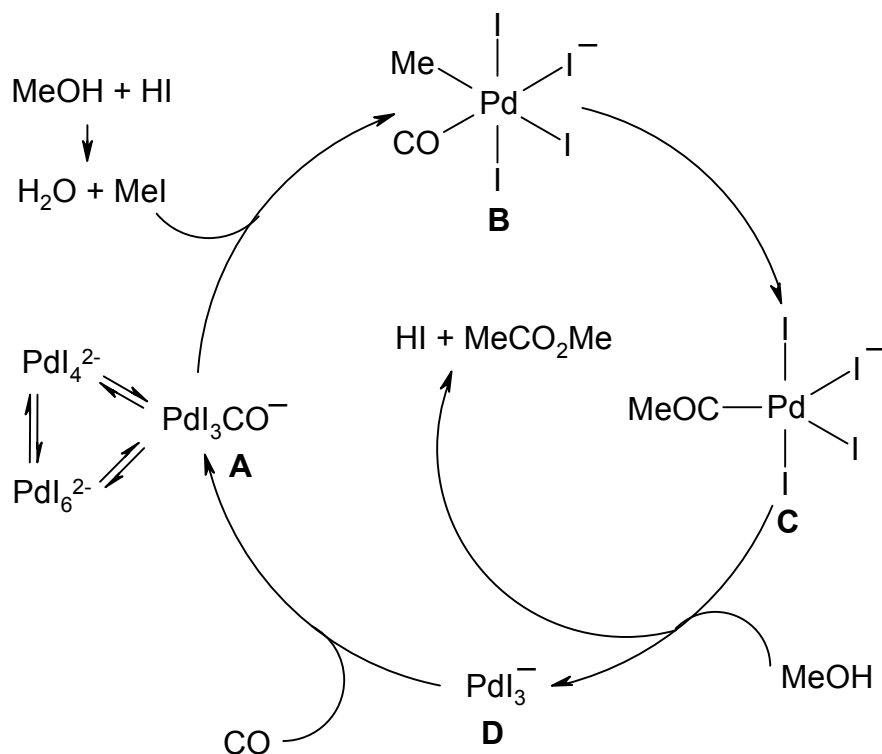
Scheme 1.7. Mechanism of palladium catalyzed carbonylation of methanol. catalyzed carbonylation of methyl iodide, which undergoes oxidative addition of methyl iodide to give methyl-palladium species **B**, which forms the species **C** after CO insertion. Reductive elimination of acyl iodide from **C** forms the species **D**, which after successive carbonylation regenerates the active Pd-carbonyl species **A**.

1.3.1.6. Other Processes for Acetic Acid

Though, methanol carbonylation route dominates the production of acetic acid today, early developments were mostly based on oxidation routes. These processes involve oxidation of acetaldehyde, ethanol, naphtha or n-butane. Other than oxidation, direct conversion of syn gas and methane carbonylation are continuously being explored for their application in acetic acid synthesis. Catalytic oxidation of acetaldehyde was initially started in the United States in 1920 using manganous acetate as a catalyst[54]. Single stage vapour phase ethylene oxidation to acetic acid has been studied extensively using $PdCl_2$ and V_2O_5 supported on Al_2O_3, 2%Pd-25%H_3PO_4 on SiO_2, Pd-V_2O_5-Sb_2O_3 on Al_2O_3 and 1% Pd on V_2O_5 as catalysts with the selectivities in the range of 60-90% based on ethylene[24]. The liquid phase oxidation of aliphatic hydrocarbons can be used to synthesize carboxylic acids. n-Butane is suitable for the production of acetic acid by oxidation route. This process has been used by number of companies such as Celanese, Union Carbide, and Russian Refinery since 1952 for the large-scale production of acetic[54]. Various other routs have been proposed for the synthesis of acetic acid based on oxidation and carbonylation technologies such as oxidation of ethane, carbonylation of methane, direct conversion of syn gas and methyl formate isomerization. Ethane oxidation has been attempted using various metal catalysts and their combinations such as $Mo_xV_yZ_z$ and $Re_xV_yZ_z$[55] (Z is Nb, Sb or Ca). Nishiguch et al[56] first disclosed methane carbonylation to acetic acid using $Pd(OAc)_2$/$Cu(OAc)_2$/$K_2S_2O_8$/CF_3COOH. Further, in 1994 it was reported that $RhCl_3$ can carbonylate methane in presence of CO and O_2 in an aqueous medium[57]. Formation of acetic acid has been demonstration by methyl isomerization route in presence of rhodium catalysts[58]. It has been reported that methyl formate can be produced by methanol dehydration route (eq. 1.19-1.21), using Ru-Sn[59] and Fe-Sn[60] catalyst systems.

$$2CH_3OH \longrightarrow 2HCHO + H_2 \qquad (1.19)$$

$$3HCHO \longrightarrow HCOOCH_3 \qquad (1.20)$$

$$HCOOCH_3 \longrightarrow CH_3COOH \qquad (1.21)$$
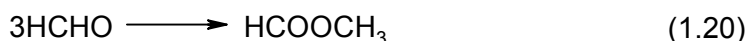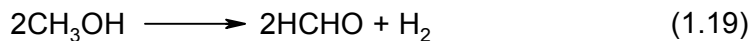
Table 1.3. Literature on methanol carbonylation

No.	Catalyst system	Reaction Conditions			Activity		Reference
		Temperature, K	Pressure, MPa	Other Details	Conv, %	Sel, %	
1	MeI-Rh(CO)$_2$I$_2$/polymer support	383	2.9	Divinylbenzene vinyl pyridine derivatives-support	--	99.8[a]	Tempesti $et.$ $al.$[61]
2	RhI(CO)(PEt$_3$)$_2$-MeI	393-423	2.7	3.2-17.1% water	9.2 mol/l/hr (initial rate)		Rankin $et.$ $al.$[62]
3	Rh(OAc)$_3$-GrV oxide-HI-MeI	448	2.75	4-12% water	2.25 mol/l/hr (initial rate)		Hinnenkamp $et.$ $al.$[63]
4	Rh/Ys zeolite	458	1.2		86	99	Jiang $et.$ $al.$[64]
5	Rh-CeO$_2$-MeI	463	21	Gas phase CO-H$_2$ Pressure	73.4	54.3	Chateau $et.$ $al.$[65]
6	Rh-Iodide	Review					Lodal P. N.[66]
7	Rh, Ir, Ni-iodide	Review					Zoeller J. R.[67]
8	Rh, Ir-iodide	Mechanistic investigations					Maitlis $et.$ $al.$[68]
9	Rh-zeolite	Mechanistic investigations					Maneck $et.$ $al.$[69]
10	Li[RhI$_2$(CO)$_2$]-MeI	463	2.75	Kinetic and mechanistic studies	28.5 mol/l/hr		Murphy et. al[70]
11	Rh-Iodide	Review					Forster $et.$ $al.$[71]
12	Rh, Ir, Ni, Co	Review					Eby $et.$ al[72]
13	Rh-Iodide	Mechanism					Forster D.[73]
14	RhCl$_3$-N-chelating ligand-Cl, Br	508	7-8.3		17.7	9.07%a, 85.3%b	Nakamura K.[74]
15	[MeIr(CO)$_2$I$_3$]$^-$, SnI$_2$			Mechanistic studies			Maitlis $et.$ $al.$[75]
16	Ir-MeI-Pt	463	3	--	TOF = 1190 h^{-1}		Kalck $et.$ $al.$[76]

Table 1.3. Literature on methanol carbonylation (continued)

17	Ir-Ru-Li	463	2.8		30.8 mol/l/hr (initial rate)		Sunley et al[77]
18	Ir-Ru-MeI	463	3	2% H_2 in CO; 5% H_2O	20.3 mol/l/hr		Willams *et. al.*[78]
19	Ni(OAc)$_2$-SnPh$_4$-MeI	423	3.44	12 h	91	67.03[ab]	Rizkalla et al.[79]
20	Ni(PPh$_3$)$_2$(CO)$_2$- PPh$_3$-MeI	423	2	CO or CO-H_2 mixture, 5 h	--	100[ab]	Rizkalla. et al.[79]
21	NiI$_2$-Cr, Mo, W(CO)$_6$-MeI-alkali MI	473	3.6-4.1	4.8:36.6-CO:H_2	--	74-100[ab]	Rizkalla[79]
22	Ni(CO)$_4$-KI-MeI	393-513	6-15	CO-(33%)H_2, NMP solv.	--	100[ab]	Gauthier *et. al.*[84b]
23	Ni(OAc)$_2$-VO(acac)$_2$-MeI	473	7-15	Acetic acid solvent	--	69[a]	Gauthier *et. al.*[84c]
24	Ni(OAc)$_2$-La(OAc)$_3$-MeI	473	7-15	Acetic acid solvent	--	87[ab]	Gauthier *et. al.*[84d]
25	NiI$_2$-MeI-PBu$_3$-MeI	463	10	--	99	98[b]	Erpenbach *et. al.*[80]
26	5%Ni-5%Sn/C	523	0.1	Vapour phase, CO:MeOH:MeI:Ar = 10:9:1:5	39.1	90.3[b]	Liu *et. al.*[81]
27	Ni/C-MeI	498	--	Vapour phase, MeOH:CO:MeI = 17:82:1 mol	15	21[b]	Merenov *et. al.*[82]
28	Ni/C-MeI	523-553	0.6-1	Vapour phase, CO:MeOH:MeI:H_2 = 43:9:1:11	--	10[a], 84[b]	Fujimoto *et. al.*[83]

Table 1.3. Literature on methanol carbonylation (continued)

29	$Co_2(CO)_8$-alkali MI or quaternary iodide-alkyl iodide	433	25	CO-(5-20%)H_2 mixture	--	97[ab]	Gauthier et. al.[84a]
30	Sulfided Co-Mo/C	523-573	7.5	CO or CO-(50%)H_2, GHSV=2000 l/h/kg	36.5	62.8[b]	Calafat et. al.[85]
31	RuO_2-$Co_2(CO)_8$-NBu_4Br	442	23.3	18 h	56	90[b]	Lin[86]
32	RuO_2-$Co_2(CO)_8$-$MePh_3PBr$-$MeSO_3H$	473-493	26.8-45.2	Other bromides and sulfonic acid promoters	--	(33-35)[a]	Vanderpool et. al.[87]

[a]Selectivity to acetic acid; [b]Selectivity to methyl acetate

1.3.2. Carbonylation of Higher Aliphatic Alcohols

Carbonylation of higher aliphatic alcohols is of interest to synthesize useful higher saturated carboxylic acids. For example, carbonylation of ethanol produces propanoic acid, which is an important raw material in the manufacture of polyester resins, food preservatives, insecticides and cosmetic products. Carbonylation of primary alcohols was reported using Ru, Rh or Co catalysts along with iodine promoter at 473 K and 45 MPa[88]. For higher alcohol carbonylation, Ru was found to give better activity than Rh and Co catalysts unlike methanol carbonylation. Iodide promoted Ir catalyzed carbonylation of ethanol has been reported by Patil *et. al.*[89] with ethanol and CO selectivities in the range of 85-99% and 77-99% respectively, where effect of solvents was found to be predominant. The rate of reaction varied with the change in solvents in the order nonanoic acid> Propionic acid> acetic acid> toluene> water. Kinetics of Ir-isoquinoline-HI catalyst system has been reported for ethanol carbonylation in the temperature range 443-473 K[90]. The reaction orders with respect to CO (beyond 3.85 MPa) pressure, ethanol and catalyst concentrations were reported to be zero, 0.71 and 0.62 respectively. Activation energy was found to be 106.81 KJ/mol. Kinetics of $RhCl_3.3H_2O$-HI catalyzed carbonylation of ethanol has also been reported at the temperature in the range of 443 – 488 K and showed that the rate of reaction was zero, 0.81, 0.855 and 0.66 orders with respect to CO partial pressure, catalyst, HI and ethanol respectively[91]. Base catalyzed carbonylation of higher alcohols has been reported by Tonner *et. al.*[92] at 323-363 K and 4 MPa CO pressure using alkali metal alkoxides as catalysts. Dake and Chaudhari[93] have reported the carbonylation of n-alcohols (C_1-C_4) using $RhCl_3.3H_2O$ as a catalyst, HI as a promoter and acetic acid as a solvent. n-Propanol was found to be carbonylated via n-propyl iodide and n-propyl acetate intermediates leading to n- and iso-butyric acid respectively with the ratio of 3.5:1. Further the authors have reported that the rate of n-alcohol carbonylation reaction varied in the order: methanol> ethanol> Propanol> butanol; and the rate determining step being oxidative addition of alkyl iodide to Rh(I) complex. The activation energies were found to be 97.48 and 102.46 kJ/mol for n-propanol and n-butanol carbonylation reactions respectively. Mineral acid catalyzed carbonylation of t-butanol yielding pivalic acid proceeds via isobutelene intermediate were known in literature[94]. An attempt to synthesize pivalic acid

(60% selectivity) from t-butanol using a novel palladium catalyst has been reported at 388 K and 5.54 MPa CO pressure[96].

1.3.3. Carbonylation of Aryl Alcohols

Carbonylation of aryl alcohols especially 1-arylethanols have gained attention in recent years due to the applications of 2-arylpropionic acid derivatives in pharmaceutical industry. Hoechst Celanese[19] successfully applied this technology at Texas for the synthesis of Ibuprofen on the large scale (3,500 TPA) by the carbonylation of 1-(4-isobutylphenyl)ethanol (IBPE) in 1992. The process used $PdCl_2(PPh_3)_2$ as a catalyst with 10% aq. HCl as a promoter in a biphasic medium consisting of methyl ethyl ketone (MEK) and water at 403 K and 5-35 MPa pressure. Seayad et. al.[95] have reported $PdCl_2(PPh_3)_2$ catalyst with inorganic halide and organic sulfonic acid promoters (LiCl and TsOH) for higher selectivity (>95%) to Ibuprofen at milder reaction conditions (388 K, 5.4 MPa). Further enhancement in catalytic activity (TOF= 800-2600 h^{-1}) and regioselectivity (99%) was achieved using novel palladium complex **(5)** with different N- and P- containing ligands[96]. Mukhopadhyay et. al.[97] have reported a novel heterogeneous recyclable palladium catalyst anchored in MCM-41 and MCM-48 at similar reaction conditions with 97.5 % selectivity to Ibuprofen and 450 h^{-1} TOF. Rhodium and Nickel catalysts were also found to be active for IBPE carbonylation yielding 80-87% selectivity to Ibuprofen at 3-10 MPa and 360-450 K^{98}. Palladium catalysts with TsOH as promoter was reported for 1-(6-methoxy-2-napthyl)ethanol carbonylation reaction with 100% (TsOH/Pd=13.1) selectivity to methyl ester of Naproxen at 6 MPa and 373 K[99].
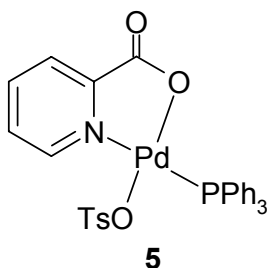
1.4. Carbonylation of Olefins and Acetylenes

Unsaturated substrates such as alkynes, alkenes and dienes, through different carbonylation reactions produce wide range of useful products like carboxylic acids, esters, aldehydes and alcohols as shown in Scheme 1.1. Carbonylation of unsaturated compounds often needs the source of hydrogen along with carbon monoxide, which is

generally obtained from variety of sources such as gaseous hydrogen, carboxylic acids, water, alcohols, amines, thiols etc. Carbonylation reactions utilizing water or alcohols as hydrogen source are of practical interest as they produce valuable carboxylic acids and esters with complete atom utilization. Transition metal complexes of Co, Rh, Ir, Ni, Pd and Pt are found to be active catalysts for these reactions.

Acetylene carbonylation yielding acrylic acid was one of the first large scale processes that used carbonylation technology, which used $NiBr_2$-$CuBr_2$ catalysts at 4-10 MPa and 453-478 K to obtain 90% selectivity to acrylic acid[13]. Today this process
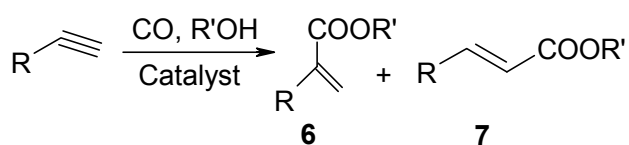
R = H, alkyl or aryl; R' = H, alkyl or aryl

produces around 150,000 TPA acrylic acid. Carbonylation of alkynes produces two isomeric products (**6** and **7**) and thus the reactions often face the problem of regioselectivity control[100]. Catalyst environment modified with different ligands plays an important role in deciding the regioselectivity. Recent developments are focused on the modified t-phosphine complexes of Ni, Pd and Pt to achieve maximum selectivity towards the desired product[101]. A highly active Pd(II) catalysts modified with 2-pyridylphosphine and weakly acidic promoters was reported to give very high TOF (40,000 h-1) for propyne carbonylation to achieve methyl methacrylate in 98.9-99.9% selectivity at 333 K and 6 MPa[102]. Recently Chaudhari and coworkers[103] have reported the carbonylation of terminal as well as internal acetylenes at 0.1-0.3 MPa CO pressure using $Pd(OAc)_2$/pyridine-2-carboxylic acid/PPh_3 catalyst system to achieve the TOF of 3500 h^{-1} and selectivity of 98%.

Before the use of transition metal catalysts by Reppe, olefin carbonylation was limited to carboxylic acids and esters synthesis using phosphoric acids, heteropolyacids, and boron triflourides etc. as catalysts. Such carbonylation is known as Koch carbonylation[104], which needed severe reaction conditions (573 K and 70-90 MPa). Further developments in transition metal catalysts showed that the olefin carbonylation could yield various saturated carboxylic acids, esters, anhydrides, amides, amino acids and copolymers.

Hydroxy-carbonylation generally produces branched (**8**) and linear (**9**) carboxylic acids. Selectivity control was often a problem in higher olefin carbonylation reactions, where catalyst design became a challenging task. Early processes for olefin carbonylation mostly required severe operating conditions (473-573 K, 20-30 MPa), which on the other hand increased side reactions such as water-gas shift reaction, hydrogenation of reactant olefins, polymerization, isomerization etc. Thus the processes needed to be modified in order to achieve maximum selectivity to the required product at milder operating conditions. Co, Rh, Ir, Pd and Pt complexes were found to be active at relatively milder conditions[105]. Hydroesterification of 1-octene was reported using cobalt catalysts along with pyridine ligands with a ratio of 15-35:1 giving maximum conversion at 433 K, 16-18 MPa, whereas in absence of pyridine 1-octene was isomerized to internal olefins yielding only 12% of the hydroesterification product[106]. Rhodium[107] and iridium[108] catalysts were reported for hydrocarbonylation of olefins to achieve predominantly branched carboxylic acids. Thus, $Ir(PPh_3)_2(CO)Cl$ was reported as a catalyst for propylene carbonylation in presence of aqueous HI in acetic acid medium to yield 83.3% branched butyric acid at 4.8 MPa (1.3 MPa CO in propylene) and 448 K, whereas rhodium could give 1.6:1 (branched:linear) butyric acid at similar reaction conditions. $Rh(CO)_2(acac)$-pyridine catalyst system was patented by Schafer *et. al.* at 373 K and 10 MPa to achieve 200-1280 h^{-1} TOF and > 95% selectivity to propionic acid[109]. Nickel salts forming $Ni(CO)_4$ insitu, have been known since 1943 to catalyze ethylene carbonylation reaction[110]. Nickel catalyzed carbonylation of ethylene is an important commercial process for the manufacture of propionic acid, which is run by BASF since 1952 which used halogen free Nickel-propionate catalyst to give 95% selectivity to propionic acid with byproducts such as CO_2, ethane, and higher carboxylic acids[13]. Carbonylation of internal olefins has also been reported using Ni-catalysts, where branched carboxylic acid or ester products were predominant[111]. Carbonylation of lower olefins (C_2-C_6) to the corresponding esters was reported at 30-300 MPa and 323-598 K using platinum compounds along with Sn or Ge salts (H_2PtCl_6-$SnCl_2$) in alcoholic medium[112].

$$R\text{—}CH{=}CH_2 \xrightarrow[\text{Catalyst}]{\text{CO, R'OH}} \underset{\textbf{8}}{R\text{—}CH(COOR')\text{—}CH_3} + \underset{\textbf{9}}{R\text{—}CH_2CH_2\text{—}COOR'}$$

R = H, alkyl or aryl; R' = H, alkyl or aryl

Palladium compounds were found to be the most effective catalysts for olefin carbonylation and hence, they have been explored well in literature for their activity, selectivity and mechanism. Majority of palladium catalyzed olefin carbonylation reactions focused on the catalyst developments, selective synthesis of linear fatty acids, branched aryl propionic acids and high activity in polyketone synthesis.

Co-polymerization of CO with olefins, producing polyketones has received considerable attention in recent years due to its high performance and photodegradable nature. Shell International has successfully commercialized the co-polymerization process using ethylene, propylene and CO as raw materials to produce the polymer CARILON that was considered to be the major breakthrough in the field of carbonylation technology. The process producing high molecular weight (20,000) polyketones (**10**) from ethylene and CO was catalyzed by Pd cationic complex formed from Pd(OAc)$_2$, bidentate phosphine ligand and TsOH at 358 K and 4.5 MPa to achieve the catalytic TOF of 6000 g/g/hr[21]. Tsuji[113] reviewed the palladium-catalyzed carbonylation of olefins with respect to phosphine and arsine ligands stabilized Pd catalysts, their complexes with IVB group metal halides such as SnCl$_2$, GeCl$_2$ and PbCl$_2$ etc. and the catalyst activity. Such palladium catalysts when coupled with group IVB metal chlorides were found to be effective for carbonylation of α-olefins to linear carboxylic acids (98% selectivity) at milder reaction conditions (353 K and 30 MPa)[114]. Fenton[115] reported the hydrocarbonylation of higher terminal olefins such as 1-octene using PdCl$_2$-PPh$_3$ catalysts to produce nonanoic acid at 399 K and 0.7–5.4 MPa CO where the n/iso ratio was observed to be dependent on the concentration PPh$_3$, water and CO partial pressure. In 1983, Alper and coworkers[116] reported the carbonylation of higher α-olefins at room temperature and CO-O$_2$ atmosphere using PdCl$_2$ as a catalyst along with CuCl$_2$ and HCl promoters to produce branched carboxylic acids in high selectivities where the concentrations water (<5%) and HCl were found to be important. Hydrocarbonylation and hydroesterification of 4-methyl styrene was reported to produce branched aryl propionic acid or ester in 93% selectivity with a TOF of around 25 h^{-1}, at 373 K and 4.1

MPa using PdCl$_2$-CuCl$_2$-HCl catalyst system in presence of PPh$_3$ as a ligand[117]. Further, the negative effect of presence of O$_2$ in the reaction mixture was shown explaining the formation of PPh$_3$O, which was found to be ineffective as a ligand to Pd catalyzed carbonylation of 4-methyl styrene.

Palladium catalysts have received a considerable attention in recent years in the synthesis of pharmaceutical intermediates such as Ibuprofen and Naproxen through the carbonylation of 4-isobutyl styrene and 2-vinyl-6-methoxynaphthalene respectively. Many companies such as Nippon Petrochemical Company Ltd.,[118] Ethyl Corporation,[119] Montedison,[120] etc., have patented their own processes in this field. Nippon petrochemicals used PdCl$_2$(PPh$_3$)$_2$ as a catalyst at 393 K and 30 MPa in biphasic conditions (10% aq HCl and toluene) to achieve 89% selectivity to Ibuprofen and 100% conversion with low activity (TOF < 2 h^{-1})[121]. Higher activity (TOF 100-500 h-1) was reported for methyl ester of Ibuprofen at 7 MPa of CO and 363 K using CuCl$_2$ as a promoter instead of 10 % HCl$_{(aq)}$. Seayad *et. al.*.[122] have published a detailed study on the hydroesterification of styrene using Pd(OAc)$_2$-PPh$_3$-TsOH catalyst system, where high activities (TOF = 411 h^{-1}) were reported at higher concentration of styrene (6.73 kmol/m^3) at 348 K and 3.4 MPa. PdCl$_2$(PPh$_3$)$_2$-TsOH-LiCl catalyst system was reported carbonylate various olefins to their branched carboxylic acids with high activity (TOF in the range of 77-2250 h^{-1}) at 388 K, 5.4 MPa CO pressure[123]. Carbonylation of various aliphatic and aromatic olefins have been studied using a novel catalyst, (**5**) along with TsOH and LiCl to give a TOF in the range of 400-2600 h^{-1} at similar reaction conditions[124]. The same catalyst was reported in heterogeneous form by anchoring in MCM-41 and MCM 48 for hydrocarbonylation of olefins to achieve effective catalyst-product separation that was demonstrated by catalyst recycle studies[97].

1.4.1. Alkoxycarbonylation of Vinyl Acetate
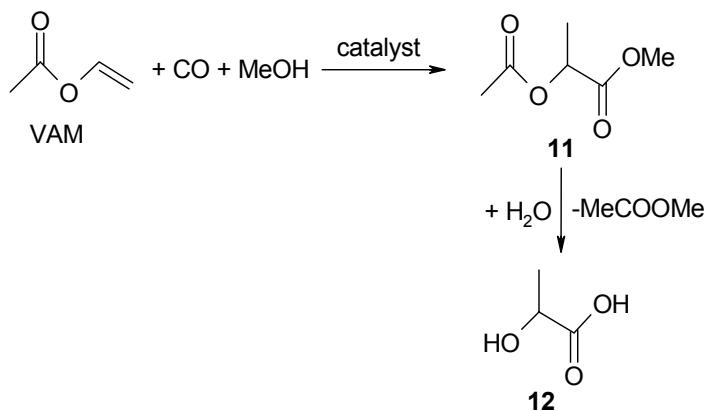
Hydrocarbonylation or alkoxycarbonylation of vinyl acetate is another promising area that produces lactic acid (**12**) after successive hydrolysis of the carbonylated product, methyl-2-acetoxypropionate (**11**). In spite of its importance, literature lacks in the study of this catalytic route for the production of lactic acid.

Today commercial lactic acid is produced by two methods, a) fermentation of molasses, and b) Hydrocyanation of acetaldehyde followed by hydrolysis of cyanohydrin produced.

a) Fermentation of molasses: Today major lactic acid is produced from molasses from sugar production. The fermentation is achieved in industrial scale stirred tank bioreactors with low productivities. Lactic acid is separated from the lactate salts by addition of sulfuric acid and subsequent separation of emerging gypsum. The gypsum has no further use and is an environmental threat to dispose off.

b) Hydrocyanation of acetaldehyde followed by hydrolysis of the cyanohydrin produced: This route produces cyanohydrin upon hydrocyanation of acetaldehyde using toxic HCN. The cyanohydrin produced is hydrolyzed with corrosive and toxic sulfuric acid. In addition to lactic acid this process generates stoichiometric amount of ammonium sulfate, which is problematic for disposal.

The first patented report suggesting three-step process for synthesis of lactic acid from VAM appeared in 1978[125] in which 2-acetoxypropanaldehyde (**13**) formed by hydroformylation of vinyl acetate using Rh(COD)(PPh$_3$)$_2$ catalyst was oxidized to 2-acetoxypropionic acid (**14**) with manganese or cobalt catalysts, which is further hydrolyzed to lactic acid in presence of water using acid catalysts such as TsOH, H$_2$SO$_4$. Maximum yield of lactic acid reported was 75% using Rh catalyst at 373 K and 3.33 MPa syn gas, cobaltous acetate with 0.2 MPa air and TsOH at 423 K for hydroformylation, oxidation and hydrolysis reactions respectively.
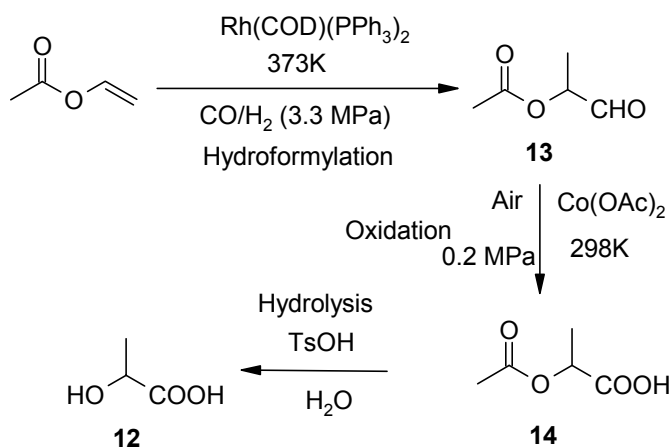
Morris[126] has attempted hydrocarbonylation of VAM to yield 2-acetoxypropionic using Pd-complex catalysts at milder reaction conditions (373-473 K 0.6-6.9 MPa CO). [(allyl)PdCl$_2$]$_2$ was found to give maximum conversion (96%) and selectivity (67%) along with VAM hydrolysis products such as acetaldehyde and acetic acid. Hydrocarbonylation reaction was dominated by hydrolysis in higher ligand (PPh$_3$/Pd ratio > 20) and water concentrations (> 0.9 wt%) in the reaction mixture. Mark-Clark[127], from The Standard Oil Company has demonstrated alkoxycarbonylation of VAM using Pd, Rh and Ni catalysts at 373 K and 6.9 MPa CO pressure where PdCl$_2$(PPh$_3$)$_2$ gave maximum yield (81.6%) of methyl-2-acetoxypropionate and Rh and Ni were very less active catalysts for alkoxycarbonylation. Kiyoshi Kudo et al[128]. have studied the methoxycarbonylation of VAM to methyl-2-acetoxypropionate at high-pressure carbon monoxide (15.2-25.33 MPa.) to obtain 62% yield using palladium catalysts in presence of a base such as pyridine or pyridine derivatives. Though the attractive yield of 2-acetoxypropionate was reported, the TOF achieved was very low (2.5 h^{-1}).

1.4.1.1. Mechanism

Kudo *et. al.*[128] have speculated the reaction mechanism (Scheme 1.8) using in situ IR spectroscopy to show $HPdCl(PPh_3)_2$ (ν_{CO}=2050 cm^{-1}) as an active species (eqns 1.22-1.26). The active catalytic species, $HPdCl(PPh_3)_2$ was detected when $PdCl_2(PPh_3)_2$ was used as a catalyst along with methanol and VAM in the carbonylation reaction mixture at various temperatures (298-373 K), notably, the species was not formed in absence of either methanol or CO (eq. 1.22 and 1.23). Further the formation of CO_2 in the reaction mixture was also evidenced by FTIR spectroscopy (ν_{CO_2} = 2330 cm^{-1}), which was generated as per equation 1.26.

$$PdX_2L_2 + ROH \rightleftharpoons [ROPdXL_2] + HX \qquad (1.22)$$

$$[ROPdXL_2] + CO \rightleftharpoons [Pd(COOR)XL_2] \qquad (1.23)$$

$$[Pd(COOR)XL_2] + ROH \longrightarrow [HPdXL_2] + (RO)_2CO \qquad (1.24)$$

$$[HPdXL_2] + CO \rightleftharpoons [Pd(CO)L_2] + HX \qquad (1.25)$$

$$(RO)_2CO + HX \longrightarrow CO_2 + RX + ROH \qquad (1.26)$$

$$L= PPh_3, X= Cl, R=CH_3$$
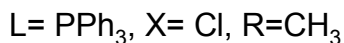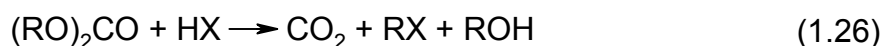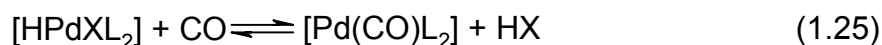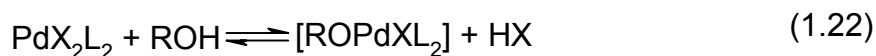
Further, halogen atom in $PdX_2(PPh_3)_2$ catalyst has a strong effect on its activity and was found to vary in the order: Cl>Br>I. As an explanation for this trend, the activity was correlated with the Pd-X bond strength, which varies in the reverse order of the activity trend.

OCOCH$_3$

R'

HPdXL$_2$

OCOCH$_3$

L$_2$XPd

R'

R' OCOCH$_3$

H$_3$C PdXL$_2$

CO

OCOCH$_3$

R'

CO

OCOCH$_3$

R' OCOCH$_3$

H$_3$C CO-PdXL$_2$

OCOCH$_3$

L$_2$XPdOC

R'

MeOH

HPdXL$_2$

MeOH

OCOCH$_3$

MeOOC

R'

R' OCOCH$_3$

H$_3$C COOMe

or

R'

H$_3$C O OMe

O O CH$_3$

L= PPh$_3$, X= Cl, R'= H
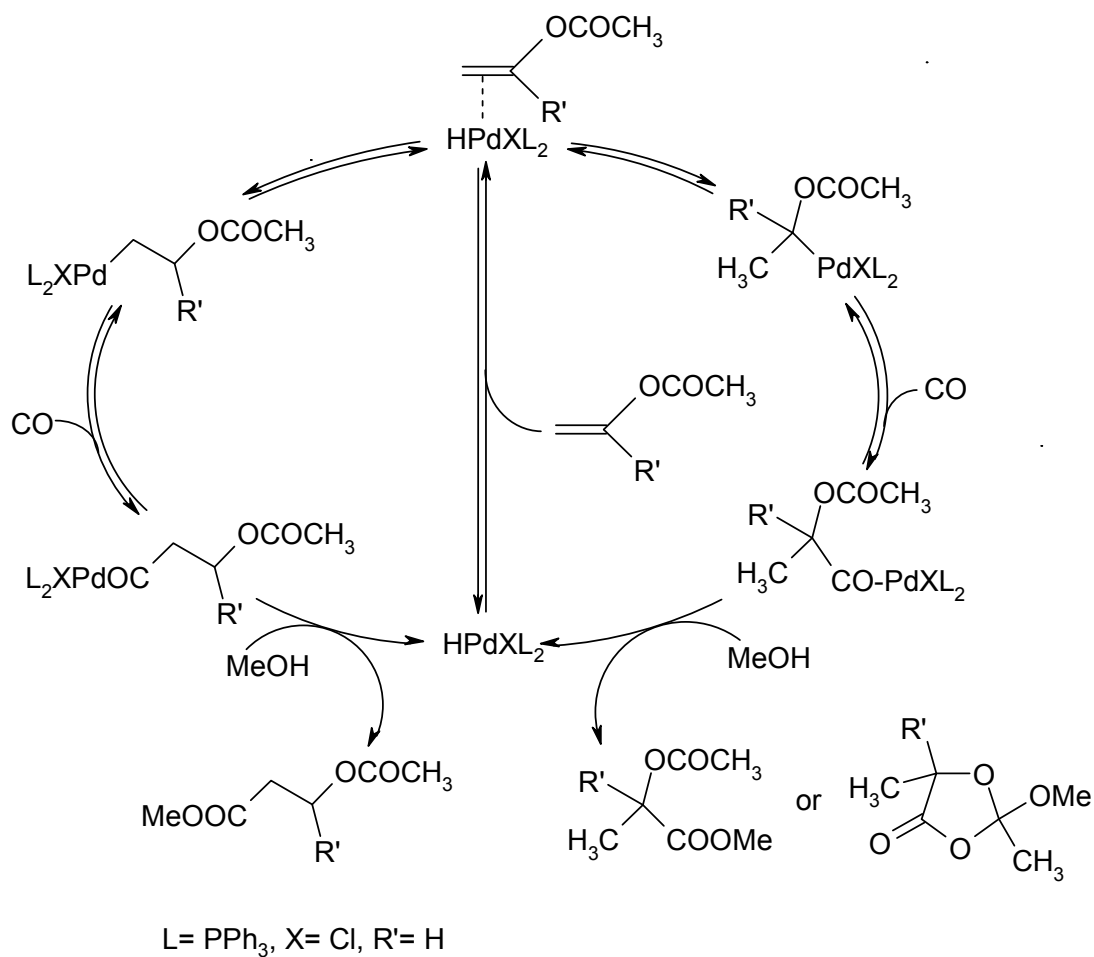
Scheme 1.8. Mechanism of methoxycarbonylation of VAM

Table 1.4. Literature on aliphatic olefin carbonylation

No.	Catalyst system	Substrate	Reaction conditions			Conv, %	Selectivity, %		Reference
			T, K	P_{CO}, MPa	Others		Linear, %	Branched, %	
1	Pd(II)-bisphosphines	Ehtene, α-C_{14} olefin	333-388	2.5	10h	--	>99 80	-- 20	Pugh[129]
2	$PdCl_2(PPh_3)_2$-PPh_3	1-hexene	368	12.2	--	65	Mechanistic investigations		Cavinato[130]
3	PtO_2-H_2SO_4	C_5-C_{10} olefins	Rt	0.1	96% H_2SO_4	--	39-70% t-acids		Xu[131a]
4	$Rh_4(CO)_{12}$-H_2SO_4	C5-C10 olefins	Rt	0.1	96% H_2SO_4	--	30-68% t-acids		Xu[131b]
5	$PdSO_4$-H_2SO_4	C5-C10 olefins	Rt	0.1	96% H_2SO_4	--	29-48% t-acids		Xu[131c]
6	Au_2O_3-H_2SO_4	C5-C10 olefins	Rt	0.1	96% H_2SO_4	--	33-53% t-acids		Xu[131d]
7	$Cu(CO)n$-BF_3, $Ag(CO)n$-BF_3	C_5-C_{10} olefins	293	0.1	Conc. H_2SO_4	--	47-60 t-acids		Souma[132]
8	$PdCl_2(PPh_3)_2$-Resin	1-pentene	100	2.75	--	5.4	94	6	Pittman[133]
9	Rh-Pyridine derivatives	Ethene	303-473	3-20	--	--	40-94	--	Schaefer et. al.[134]
10	$Ru(acac)_3$-UO_2SO_4	Ethene	453	5	5h	--	92	--	Drent[135a]
11	$Pd(OAc)_2$-PPh_3-TsOH-Bu_3PO	Ethene	383	3	5h	--	100	--	Drent[135b]
12	$Pd(OAc)_2$-dppb-TsOH	Et-crotonate	428	4	--	100	31	69	Drent[135c]
13	$PdCl_2$-CuCl	Ethene	373	3.44	--	--	97%, double carbonylation product		Hsu[136]

14	NiI_2-EtI-$Mo(CO)_6$	Ethene	448	2.75	2h	--	~100	--	Rizkalla [137]
15	Pd-Cu	Propene	Rt	0.1	Alcohol solvent	--	--	95	Bertoux *et. al.*[138]
16	$PdCl_2(PPh_3)_2$-Py	VAM	373	15.2	Methanol solvent, 5 h	82	--	76	Kudo *et. al.*.[128]
17	[(allyl)$PdCl_2$]$_2$-PPh_3	VAM	373-473	4.12	H_2O (<0.9%)	96	--	67	Moris[126]
18	$PdCl_2(PPh_3)_2$	VAM	373	6.9	Methanol:VAM = 5.5, THF solvent	84.5	--	96.5	Mark-Clerk[127]

1.5. Carbonylation of Unsaturated Alcohols

Allylic alcohols are functional olefins, which on carbonylation yield unsaturated carboxylic acid derivatives or lactones. Structure of an allyl alcohol plays an important role in the synthesis of the selective product.

1.5.1. Carbonylation of Allylic Alcohols to Lactones

Alper and Ali[139] have reviewed the cyclocarbonylation reactions of allylic substrates yielding different lactones. Intromolecular cyclocarbonylation of bromovinyl or iodoaryl compounds has been reported to give corresponding bicyclic lactones (15) in 71-93% yields using $Ni(CO)_4$-NEt_3 catalyst at 203-308 K[140]. Such intramolecular cyclocarbonylation of hydroxyvinyl vinyl triflets have also been reported to give bicyclic α,β-butenolides in 60-95% yields using $Pd(PPh_3)_4$-NBu_3 catalyst system at 388 K[141]. Oxidative cyclocarbonylation of allyl alcohols yielded 2(5H)-furanones (16) in 31-77% yields using $RuCl_2(PPh_3)_2$ as a catalyst in presence of allyl acetate[142].
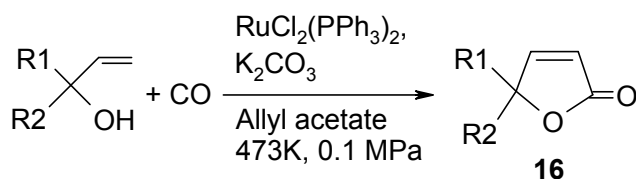
One-step synthesis of γ-butyrolactone (GBL) (18) is possible through allyl alcohol cyclocarbonylation, which is generally obtained by multistep synthesis involving allyl alcohol and butanediol (17) as intermediates as used by Lyondell Company. $Co_2(CO)_8$ catalyzed synthesis of GBL was reported using N,N,N',N'-tetramethylethylenediamine promoter under syngas pressure of 6.99 MPa at 357 K[143]. Alper and coworkers[144] reported $PdCl_2$-$CuCl_2$ catalyzed cyclocarbonylation of various substituted and unsubstituted allylic alcohols in
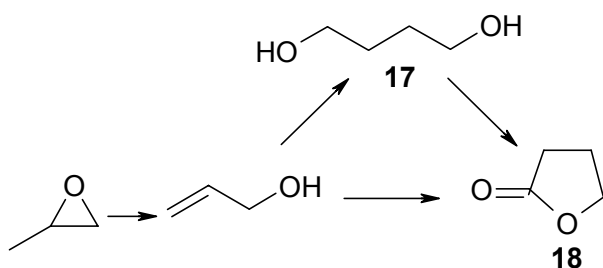
presence of CO/O$_2$ atmosphere to obtain corresponding GBLs and valerolactones (35-70% yields) at milder reaction conditions (room temp, atm. press.). Asymmetric synthesis of butyrolactones was reported using palladium catalysts along with chiral ligands[144].

PdCl$_2$, CuCl$_2$, L*

CO, O$_2$, 0.1MPa

THF, HCl, r.t.

19
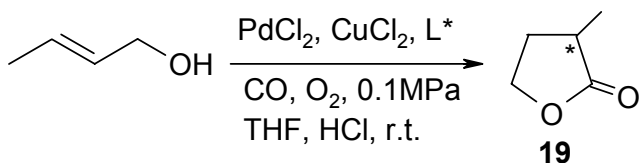
PdCl$_2$-CuCl$_2$ catalysts in presence of poly-L-lucine and CO-O$_2$ atmosphere gave 61% enentiomeric excess of lactones **(19)**. Similar synthesis was reported using Pd$_2$(dba)$_3$.CHCl$_3$ catalyst and (2S, 4S)-N-(t-butoxycarbonyl)-4-(diphenylphosphino)-2-((diphenylphosphino)methyl)pyrolidine in syngas pressure of 5.52 MPa at 373 K to achieve 44-84% *ee*. Secondary and tertiary allyl alcohols were successfully carbonylated to achieve 42-100% yields using Pd(dba)$_2$-dppb catalyst system at 40.53 MPa CO and 373 K[145].

1.5.2. Carbonylation of Allylic Alcohols to Unsaturated Carboxylic Acids

Carbonylation of allyl alcohol is very useful method for the synthesis of β,γ-unsaturated carboxylic acid derivatives. Though, the literature sites efficient methods for such synthesis from allyl carbonates, esters and halides, allyl alcohol carbonylation route have received a least attention for the synthesis of unsaturated carboxylic acid esters, despite of its ready availability. Allyl alcohol carbonylation route known to literature is discussed in this section.

PdCl$_2$ catalyzed carbonylation of allylic alcohols was reported at high pressures and temperatures (353-403 K and 1.5-20MPa) to achieve lower yields (42-64%) of carboxylic acid esters[146]. Gabriele *et. al.*[147] have reported the synthesis of β,γ-unsaturated carboxylic acid derivatives from various substituted allylic alcohols at milder reaction conditions with good yields (40-88%) using PdI$_2$ as a catalysts along with thiourea as a ligand and methanol or methanol-dimethylacetamide mixture as a solvent. Carbonylation of allyl alcohol at 2.53 MPa CO and 373 K have been reported to produce 3-butenoic acid esters in 85%yields using stoichiometric amounts of Ti(IV) alkoxide and LiCl[148]. Catalytic carbonylation of 3-phenyl-2-buten-ol **(20)** in presence of phenol at 0.5 MPa CO

and 373 K was reported to produce phenyl-3-butenoate **(21)** in 80% yield. Denis *et. al.*[149] have obtained 3-butenoic acid (60%) and allyl 3-butanoate (30%) using PdCl$_2$ catalyst along with quaternary ammonium or phosphonium halides at 353 K and 20.0 MPa. Addition of water to the reaction mixture was noted to be beneficial to achieve 100% yield of 3-butenoic acid. Allyl alcohol carbonylation to 3-butenoic acid and allyl-3-butenoate (73% acid, 22% ester) was reported using 5% Pd/C heterogeneous catalyst and hydrohalic acid promoters at 423-573 K and 13.78-34.47 MPa[150].
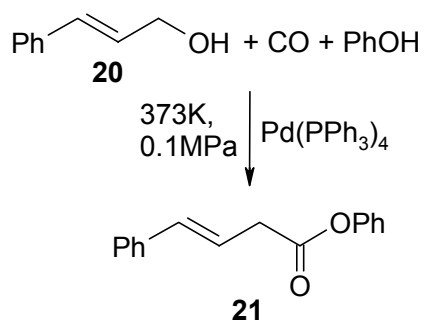
Ph⌒⌒OH + CO + PhOH

20

373K, 0.1MPa | Pd(PPh$_3$)$_4$

Ph⌒⌒OPh

O

21

Table 1.5. Literature on allylic alcohol carbonylation

No.	Catalyst system	Substrate	Reaction conditions			Selectivity, %		Reference
			T, K	P_{CO}, MPa	Others	Lactone	Un-saturated acid/ester	
1	Pd, Rh, Co, Ni complexes	Allylic alcohols	Review on synthesis of ring lactones and lactums					Alper[151a]
2	Pd(OAc)$_2$, dppb	(E)-PhCH:CMeCH$_2$OH	383	5.5 syngas	--	63%-trans-β-methyl-α-phenyl-γ-butyrolactone		Alper[151b]
3	Pd(OAc)$_2$-Montmorrinilite-PPh$_3$-HCl	Sec. Allylic alc.	398-453	4.13-5.52	48-27 hrs	--	39-56	Alper[151c]
4	Pd(OAc)$_2$-PPh$_3$-TsOH	Allyl alc., thiols	373-393	2.75	48-27 hrs	--	93	Xiao[152]
5	Pd(OAc)$_2$-PPh$_3$	Allyl alc. phenols	353-373	0.5	--	--	80	Satoh[153]
6	Pd(PPh$_3$)$_4$, LiCl, Ti-isopropoxide	Allyl alc., Cinamyl alc.	373	2.53	18 hrs	--	85	Itoh[154]
7	Rh$_2$(Oac)$_4$, PEt$_3$	Allyl alc.	393	1-5	Ethanol solvent, syngas	<50	--	Simpson[155]
8	5% Pd/C- HCl	Allyl alc.	373	20.7	6h	--	93	Baugh[156]
9	PdCl$_2$-PPh$_3$	Substituted allyl alc.	373	60	17h	--	92	Himmele[157]
10	Rh$_6$(CO)$_{16}$- N ligands.	Allyl alc.	353	0.5	Water gas shift conditions	68 (GBL)	21 (BDO)	Kaneda[158]
11	PdCl$_2$-HOAc	Allyl alc.	353	9	21h	--	82	Kurkov[159]
12	PdCl$_2$-PPh$_3$	Substituted allyl alc.	323-423	20-70	Methanol solvent	--	92	Himmele et. al.[160]

1.6. Aim and Scope of the Thesis

Carbonylation of alcohols and olefins is very useful method for the synthesis of carboxylic acids and esters. Detailed literature survey of olefins and alcohol carbonylation reactions showed that Gr. VIII transition metal complexes in homogeneous and heterogeneous forms are excellent catalysts for these reactions, out of which Pd, Rh, Ir and Co are being used industrially for the synthesis of various carboxylic acids and esters. The literature report reveals that Pd-catalyzed carbonylation has a potential to operate at relatively milder operating conditions and there are very few studies on Pd-catalyzed carbonylation of alcohols. The present work is aimed at investigations on the activity and selectivity of palladium catalysts and their kinetics and mechanism. The following specific reactions have been studied.

- Carbonylation of methanol to acetic acid

Carbonylation of methanol is industrially carried out using rhodium and iridium catalysts leaving the issues such as the use of high water concentration, dominant water gas shift reaction, high cost and limited resources of catalyst components etc. Considering the industrial significance of methanol carbonylation for acetic acid manufacture, it is always rewarding to search new catalysts as alternatives to existing ones. Pd-catalysts, though well known for a variety of carbonylation reactions, have not been explored for methanol carbonylation. Available literature on Pd-catalyzed carbonylation of methanol shows lower catalytic activity (110 TON in 16 hours), severe operating conditions (11-20 MPa and 451-573 K) and lack of understanding of kinetics and mechanism. In the present work $Pd(OAc)_2$-TsOH-Alkali metal iodide, $Pd(OAc)_2$-HI and $Pd(OAc)_2$-HI-PPh$_3$ catalyst systems were evaluated for their catalytic activity, selectivity, stability and mechanism for carbonylation of methanol.

- Carbonylation of allyl alcohol to 3-butenoic acid.

Carbonylation of allyl alcohol is an important reaction, which gives β,γ-unsaturated carboxylic acid derivatives. The published information is very limited, where the issues are severe reaction conditions and lack of understanding of the kinetics and mechanism and hence there is a need for further development of catalysts and processes in this area.

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This thesis presents a detailed study on carbonylation of allyl alcohol using Pd-BTEACl (benzyl triethyl ammonium chloride)-TsOH catalyst system with respect to catalytic activity, selectivity and kinetics.

- Alkoxycarbonylation of vinyl acetate to methyl-2-acetoxypropionate and subsequent hydrolysis of the carbonylation product to lactic acid.

Lactic acid is an industrially important product and is commercially produced by two methods: a) fermentation of molasses and b) Hydrocyanation of acetaldehyde followed by hydrolysis of cyanohydrin produced. Both the processes use toxic and corrosive chemicals and produce stoichiometric amount of byproducts, which is undesirable from environmental point of view. The methoxycarbonylation of VAM provides an economic and environmentally benign catalytic method for synthesis of a precursor (methyl-2-acetoxypropionate) to lactic acid, which can be easily converted to lactic acid by hydrolysis. Literature sites very limited published information for this route, where the issues are low catalyst activity and lack of understanding of kinetics of this reaction. In the present work, methoxycarbonylation of VAM was undertaken to study the catalyst activity, selectivity and kinetics using $PdCl_2(PPh_3)_2$ as a catalyst. Hydrolysis of the carbonylation products was also carried to give *dl*-lactic acid using acidic catalysts such as HCl, TsOH and Amberlite-IR20 resin.

This thesis presents detailed understanding of Pd-catalyzed carbonylation of methanol, allyl alcohol and VAM with their activity, selectivity, kinetics and mechanism. The work presented in this thesis shows a great potential for developing industrially competitive Pd-catalysts for the carbonylation processes for industrially important products.

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CHAPTER 2

Carbonylation of Methanol

2.1. Introduction

Acetic Acid is one of the most important commodity chemicals used in the manufacture of synthetic fibers, resins, acetic anhydride, vinyl acetate and as a solvent in polyester fiber production[1]. Carbonylation of methanol is the preferred route for the production of acetic acid after the successful development of cobalt catalyzed process by BASF in 1960's[2] and the low pressure Rh and Ir catalyzed processes by Monsanto[3] and BP[4] respectively.

$$CH_3OH + CO \longrightarrow CH_3COOH; \quad \triangle H = -33 \text{ kcal/mol}$$

Scheme 2.1. Methanol carbonylation reaction

The overall methanol carbonylation reaction is shown in Scheme 2.1. BASF process used $Co_2(CO)_8$ as a catalyst and iodide promoters at severe operating conditions (523 K, 68 MPa CO pressure) to achieve 90 % selectivity towards acetic acid based on methanol. High temperatures and pressure were necessary for maintaining the cobalt catalyst in its active form. Rhodium catalyzed iodide promoted carbonylation of methanol, discovered by Monsanto[3] in 1970's, gave high selectivity (>99% based on methanol) at milder operating conditions (423-473K and 3-6 MPa). In 1996, a process using Ir/Iodide catalyst with Ru promoter, named as Cativa Process was announced by BP Chemicals[4]. The Cativa Process operated under lower water concentration and higher reaction rates, improved carbon monoxide selectivity and minimized liquid by-products. Methanol carbonylation reaction yielding acetic acid using Co, Rh and Ir based catalysts has been reviewed[5] in the literature by several authors though other transition metal catalysts such as Ru[6], Ni[7], Pd and Pt[8] are also known to catalyze this reaction. For NiI_2-PPh_3[9] and $Ni(PPh_3)_2(CO)_2$-PPh_3[10] catalysts with methyl iodide as a promoter, 98% conversion of methanol with a selectivity of 75-90% has been reported. A highly active catalyst, $Ni(isoq)_4Cl_2$ has been reported by Kelkar et al.[11], which gave 99% conversion of methanol with 90-98% selectivity. Vapour phase carbonylation of methanol using supported Ni catalysts has also been reported[12].

Palladium compounds have gained some attention recently as catalysts for methanol carbonylation reaction mainly due to the possibility of lower effective cost, simple recovery and being known for other carbonylation reactions. Van Leeuwen[13]

reported palladium catalysts along with iodide promoters in 1983 for carbonylation of methanol with high activity (5.8 mol/l/h) at severe operating conditions (11-20 MPa and 451-573 K). The process used higher iodide concentration (iodide/Pd ratio = 470), higher water concentration (5-30%), N- containing ligands and sulfolane like solvents to achieve such higher rates. Further improvements in this process achieved the TOF of 480 h^{-1} at milder reaction conditions (448 K, 4.13 MPa) using Pd(OAc)$_2$ as a catalyst along with a nickel additive and higher iodide concentration (methyl iodide/Pd ratio = 212) in presence of sulfolane or sulfoxide solvents[14]. Drent *et al.*[15] have reported palladium catalyst with Ni additive and N- and P-containing ligands to achieve TOF of 90 h^{-1} at 398-473 K and 7 MPa pressure. Recently, Maitlis and coworkers[8] have reported palladium and platinum catalyzed carbonylation of methyl iodide at milder reaction conditions (413 K, 0.5 MPa) where the activity was very low (110 TON in 16 hours). These authors have proposed a mechanism for Pd-catalyzed carbonylation of methanol using PdCl$_2$(PPh$_3$)$_2$ as a catalyst along with Bu$_4$NI as a promoter showing PdI$_3$CO$^-$ as an active catalytic species. ^{31}P NMR spectroscopy showed that PPh$_3$ was detached from Pd center and formed [PPh$_3$Me]I showing a signal at δ 22.2. FTIR studies of the Pt analogue showed the formation of PtI$_3$CO$^-$, but the direct evidence for PdI$_3$CO$^-$ species was not shown.

Thus, severe reaction conditions (11-20 MPa and 451-573 K), higher iodide concentration (iodide/Pd ratio = 212 to 600), use of specific solvent (reaction doesn't occur without sulfolane or sulfoxide solvents), lower activity (110 TON in 16 hours) and detailed kinetic and mechanistic understanding were the key issues in palladium catalyzed carbonylation of methanol.

This chapter presents experimental results on palladium-catalyzed carbonylation of methanol. A detailed study of methanol carbonylation reaction using Pd(OAc)$_2$-Alkali metal iodide-TsOH, Pd(OAc)$_2$-HI and Pd(OAc)$_2$-HI-PPh$_3$ catalyst systems has been presented with respect to activity, catalyst stability and mechanistic aspects. Screening of different N- and P- containing ligands and solvents was done using Pd(OAc)$_2$-HI catalyst system. Effect of different parameters such as concentration of catalyst, methanol, HI, water, PPh$_3$ and CO partial pressure was studied in the temperature range of 388-433K.

An iodide bridged dimeric palladium species was isolated and characterized by X-ray crystallography, which is an insitu generated catalyst precursor for methanol carbonylation reaction. A mechanism has been proposed based on the UV-vis, IR and NMR spectroscopic characterizations of the catalytic species involved in the catalytic cycle.

2.2. Materials

Palladium acetate (Pd(OAc)$_2$), palladium acetyl acetonate (Pd(acac)$_2$), palladium chloride (PdCl$_2$) were purchased from Aldrich Chemicals (Milwaukee, WI). 56% Hydroiodic acid (HI) was purchased from Fluka Chemicals. Methanol AR, lithium iodide (LiI), sodium iodide (NaI), potassium iodide (KI), *p*-toluene sulfonic acid (TsOH), triphenylphosphine (PPh$_3$), methyl iodide AR, Methyl ethyl ketone (MEK) AR and other solvents were purchased from SD Fine Chemicals (Mumbai, India). [Pd(Pyca)(PPh$_3$)(OTs)] was prepared as reported elsewhere[16]. Water was used after distillation in the laboratory. Carbon monoxide (99.9% purity) was supplied by Matheson (Montgomeryville, PA).

2.2.1. Synthesis of (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$

1 mmol of Pd(OAc)$_2$ was dissolved in 10 ml of acetone to which 4 mmol of 57% HI was added and stirred at room temperature for 5 min. 2 mmol of PPh$_3$ was dissolved in 10 ml of methyl iodide separately and was added to the palladium solution while stirring. The resultant black solution was stirred for 1 hour and was evaporated to dryness at 313 K. The black complex obtained was washed 3 times with 10 ml of water and 4 times with diethyl ether. The complex, thus obtained, was re-crystallized from acetone to obtain 97% yield based on Pd(OAc)$_2$. The complex was characterized by elemental analysis [%C: 29.05 (29.8); %H: 2.35 (2.3), %I=49.5 (49.8)] and ^{31}P NMR (δ = 27.62) spectroscopic analysis.

2.2.2. Synthesis of PdI$_2$

PdI$_2$ was prepared as reported in literature[17]. To 50 ml of an aqueous HCl solution

of $PdCl_2$ (0.53 g), a saturated solution of KI (3 ml) was added with stirring at room temperature. Instantaneous precipitation of PdI_2 was observed. The dark brown PdI_2 obtained was filtered, washed with distilled water until all the acidic impurities were removed (washings were tested for pH) and was dried under vacuum to yield 97% PdI_2. Elemental analysis for Iodine was 70.3% (consistent with 70.55% theoretical).

2.3. General Procedure for Carbonylation Reactions
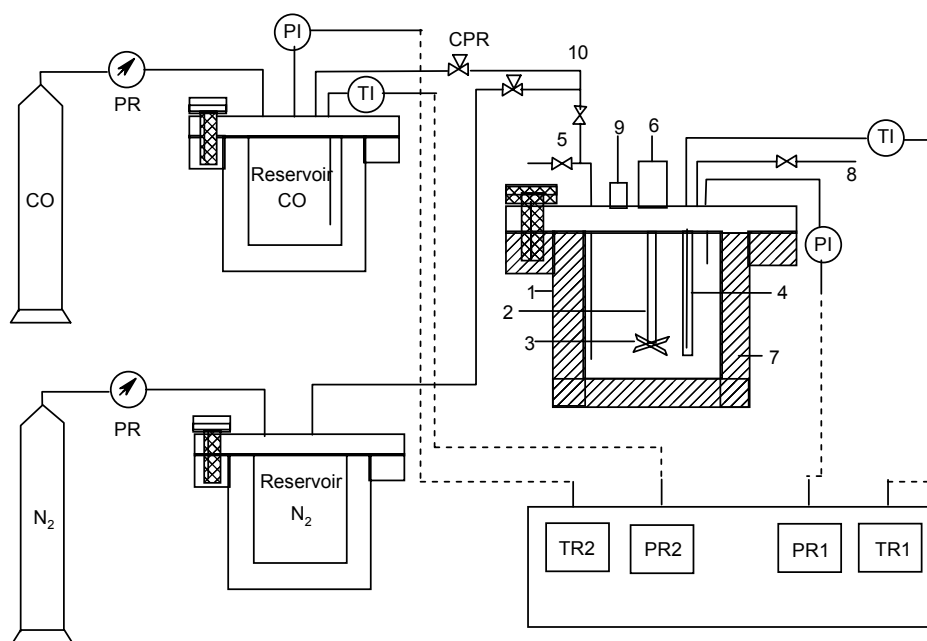
Fig. 2.1. A schematic of the reactor setup for carbonylation reactions

(1) Reactor, (2) Stirrer Shaft, (3) Impeller, (4) Thermo-well, (5) Sampling valve, (6) Magnetic Drive Stirrer, (7) Furnace, (8) Outlet, (9) Rupture Disc, (10) CO-gas Inlet, TI: Thermocouple, PI: Pressure Transducer, CPR: Constant Pressure Regulator, PR: Pressure Regulator, TR1: Reactor Temperature Indicator, PR1: Reactor Pressure Indicator, PR2: Reservoir Pressure Indicator, TR2: Reservoir Temperature Indicator

All carbonylation reactions were carried out in a 50 ml Parr Autoclave made of Hastelloy-C-276. The autoclave was provided with gas inlet, gas outlet, intermediate sampling arrangements, a safety rupture disc (gold faced-14 MPa), digital temperature, pressure and agitation speed indicators with temperature control (±1K) and magnetically driven stirrer having variable agitation speed adjustment (Fig. 2.1). In a typical experiment, weighed quantities of $Pd(OAc)_2$, PPh_3, HI (or TsOH and iodide promoters), H_2O and

53

methanol were added to MEK (solvent) so as to make the total volume to 25 ml and charged in the autoclave. The autoclave was then purged once with nitrogen and thrice with carbon monoxide from respective reservoirs at room temperature and the contents were heated to the desired temperature after which the autoclave was pressurized with carbon monoxide to the desired pressure and the reaction was started at 16.66 Hz. The reaction was carried out at a constant pressure by feeding CO from a reservoir vessel with the help of a constant pressure regulator. The progress of the reaction was monitored by observing a change in pressure drop in CO reservoir vessel to evaluate CO consumed as a function of time. Intermediate samples were also taken in a few cases to determine liquid components concentration with time. The reaction was continued for specific time duration, the contents were cooled to room temperature and the gas was vented off after analyzing by gas chromatography (GC). The reactor was opened and a small amount of the liquid phase was withdrawn and quantitatively analyzed by GC for the reactant and product concentrations. Details of gas and liquid analysis are given in the section below.

2.4. Analytical Methods

Liquid samples were analyzed on HP 6890 GC, controlled by HP Chemstation software using HP1 methyl siloxane capillary column (length 30 m, diameter 30 μm, film thickness 0.25 μm). Gas samples were analyzed on Hayesep (10 feet, 8/100 mesh) and Molecular AR Sieves (13 feet, 45/60 mesh) packed columns, which were operated through a programmed valve switching. Conditions for GC analysis are given in Table 2.1. The

Table 2.1. Conditions used for GC analysis

	Liquid phase analysis	Gas phase analysis
Inlet	Split ratio 100:1, 523K	Split-less, 523K
Column	HP1, 303-523K (programmed), 0.034-0.206 MPa (prog.)	Hayesep & Molecular sieves (operated through prog. valve switching), 323K, 0.206 MPa
Detector	FID, 523K	TCD, 473K
Carrier gas	He, 1 ml/min	He, 1 ml/min

quantitative analysis was determined using a calibration curve prepared based on synthetic standards. Conversion of methyl groups, selectivity to acetic acid and methyl acetate,

Turnover number (TON) and Turnover frequency (TOF) were calculated according to the formulae given in equations 2.1-2.5.

$$\%Conversion = \frac{100 \times [(Initial\ Mol_{MeOH+MeI})-(Final\ Mol_{MeOH+MeI})]}{(Initial\ Mol_{MeOH+MeI})} \qquad (2.1)$$

$$\%Selectivity_{HOAc} = \frac{100 \times (Final\ Mol_{HOAc})}{[(Initial\ Mol_{MeOH+MeI})-(Final\ Mol_{MeOH+MeI})]} \qquad (2.2)$$

$$\%Selectivity_{MeOAc} = \frac{100 \times 2(Final\ Mol_{MeOAc})}{[(Initial\ Mol_{MeOH+MeI})-(Final\ Mol_{MeOH+MeI})]} \qquad (2.3)$$

$$TON = \frac{Moles\ of\ carbonylation\ products\ formed}{Moles\ of\ catalyst\ charged} \qquad (2.4)$$

$$TOF = \frac{Moles\ of\ carbonylation\ products\ formed}{Moles\ of\ catalyst\ charged \times time} \qquad (2.5)$$

IR analysis was obtained on Bio Rad FTS 175C spectrophotometer. UV-vis spectroscopic analysis was done on Schimadzu UV-160A spectrophotometer. NMR were obtained from a Brucker-MSL300 and Brucker-AC200 machines. Elemental analysis of the complexes was carried out on a CHNS-O EA1108, Elemental analyzer of Carlo Erba Instruments and the ion chromatography on a Waters Ion Chromatograph, having Waters 432 Conductivity detector, Waters 600S Controller and Waters 626 Pump.

2.5. Results and Discussion

Palladium catalyzed carbonylation of methanol for the synthesis of acetic acid has been documented in literature leaving a wide scope for improvements. Severe operating conditions, requirement of higher iodide concentration, lower activity and poor understanding of mechanism were the key issues. Different palladium catalyst systems (Pd(OAc)$_2$-Alkali metal iodide-TsOH, Pd(OAc)$_2$-HI and Pd(OAc)$_2$-HI-PPh$_3$) were evaluated for carbonylation of methanol with the aim of improvement in the catalytic activity, catalyst stability and understanding of kinetics and mechanism.

Preliminary reactions were carried out using $Pd(OAc)_2$ as a catalyst along with an alkali metal iodide and TsOH as promoters. Effect of different alkali metal iodides in the presence of TsOH was studied at different concentrations of water. During this

$$MI + TsOH \longrightarrow MOTs + HI \qquad\qquad (2.6)$$

$$HI + CH_3OH \rightleftharpoons CH_3I + H_2O \qquad\qquad (2.7)$$
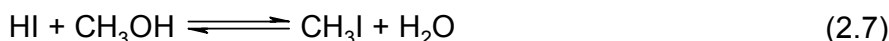
$$M = Li, Na, K$$

investigation it was observed that the use of alkali metal iodide and TsOH as promoters liberated HI in the reaction medium (eq. 2.6), which was further utilized for the formation of methyl iodide, a reactive intermediate for carbonylation of methanol, as per the equilibrium reaction (eq. 2.7). Hence, only HI was used as a promoter in further studies. Detailed study on the effect of solvents, palladium precursors, N- and P-containing ligands was done using HI as a promoter along with $Pd(OAc)_2$ as a catalyst ($Pd(OAc)_2$-HI catalyst system). As catalyst deactivation was prominent at higher temperatures, PPh_3 was used as a ligand to achieve catalyst stability. Effect of catalyst, methanol, HI, water and ligand (PPh_3) concentrations and partial pressure of CO was investigated using $Pd(OAc)_2$-HI-PPh_3 catalyst system at four different temperatures (388-433K) and the results are discussed in this section.

2.5.1. Pd(OAc)₂-Alkali Metal Iodide-TsOH Catalyst System

The effect of different alkali metal iodide promoters in the presence of TsOH and $Pd(OAc)_2$ as a catalyst system on carbonylation of methanol was studied in MEK as a solvent at 388K and 5.4 MPa CO pressure[18]. Alkali metal iodides LiI, NaI and KI as promoters showed almost similar activity giving a TOF in the range of 21-25 h^{-1} at 4% water concentration (Table 2.2, run # 3-5). Significant effect of water concentration was observed. On increasing the water concentration from 4% to 20%, the rate was found to be doubled when KI and TsOH were used as promoters with $Pd(OAc)_2$ as a catalyst (Table 2.2, run # 5, 6). At lower water concentration (4%), the precipitation of a white salt, KOTs was observed when the reactor was discharged, unlike at higher water concentration due to its solubility in water. Formation of such a salt generated HI in the

reaction medium according to the equation 2.6, which was the actual promoter for this reaction. Thus, an alkali metal iodide was effective as a promoter only in the presence of TsOH, as shown in run no. 1 and 2 (Table 2.2). However, HI as a promoter was found to be as effective as alkali metal iodides even in the absence of TsOH (Table 2.2, run # 7). Organic iodide such as methyl iodide gave very low activity, as an ionic iodide is necessary to generate a key intermediate active catalytic species, PdI_3CO^- (see mechanism, Section 2.6). Other palladium precursors such as $PdCl_2$, $Pd(acac)_2$, $Pd(Pyca)(PPh_3)(OTs)$ were used for this reaction to show that the activity of these is almost similar to $Pd(OAc)_2$ as a precursor under the same conditions (Table 2.2, run # 10 - 12).

Table 2.2. Effect of Iodide promoters in presence of sulfonic acid for the carbonylation of methanol[a]

Run No.	Promoter	H_2O, % (V/V)	Conversion, %	Selectivity to CH_3COOH,%	Selectivity to CH_3COOCH_3,%	TOF, h^{-1}
1	—	4	0	0	0	0
[b]2	LiI	4	0	0	0	0
3	LiI	4	94.25	65.12	4.23	24
4	NaI	4	97.06	78.83	5.06	25
5	KI	4	97.07	73.96	3.20	21
[c]6	KI	20	92.86	89.86	2.95	50
[d]7	HI	20	87.51	92.54	2.02	45
8	CH_3I	4	23.27	trace	43.67	8
[e]9	LiI	4	59.29	trace	8.29	2
[f]10	LiI	4	96.67	67.74	4.20	23
[g]11	LiI	4	97.36	67.55	4.08	24
[h]12	LiI	4	93.84	72.54	5.98	23

[a]*Reaction Conditions: $Pd(OAc)_2$, 4×10^{-3} kmol/m^3; CH_3OH, 1.25 kmol/m^3; Promoter, 4×10^{-1} kmol/m^3; TsOH, 4×10^{-1} kmol/m^3; Solvent, MEK; Total Volume, 2.5×10^{-5} m^3; Temperature, 388K; P_{CO}, 5.4 MPa; Time, 10 hr; A, Acetic acid; B, Methyl acetate;* [b,d]*Without TsOH;* [c,d]*4.5 hr;* [e]*Benzene sulfonic acid instead of TsOH;* [f]*$PdCl_2$ instead of $Pd(OAc)_2$;* [g]*$Pd(acac)_2$ instead of $Pd(OAc)_2$;* [h]*$Pd(pyca)(PPh_3)(OTs)$ instead of $Pd(OAc)_2$.*

Palladium metal catalyst was also used in heterogeneous form along with LiI and TsOH as promoters for carbonylation of methanol. Use of 5%Pd supported on activated carbon was found to be as effective as the homogeneous Pd(OAc)$_2$ catalyst, but the successive recycles of the heterogeneous catalyst showed decrease in the catalyst activity probably due to leaching of palladium from the support (Table 2.3). Decrease in conversion in successive recycles has been shown in Fig. 2.2.
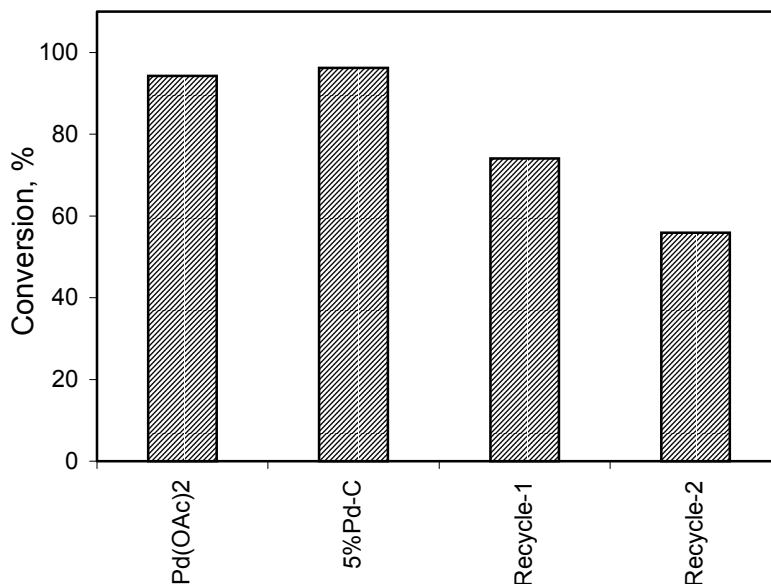
Fig. 2.2. Recycle studies of 5%Pd/C with LiI and TsOH promoters in carbonylation of methanol
Reaction conditions: Pd, 4 × 10^{-3} kmol/m^3(for recycle-n, the catalyst was used from n-1 recycle); CH$_3$OH, 1.25 kmol/m^3; LiI, 4 × 10^{-1} kmol/m^3; TsOH, 4 × 10^{-1} kmol/m^3; Water, 4% (V/V); Solvent, MEK; Total Volume, 2.5 × 10^{-5} m^3; Temperature, 388K; P$_{CO}$, 5.4 MPa; Time, 10 hr; A, Acetic acid; B, Methyl acetate

Table 2.3. Heterogeneous catalyst for LiI and TsOH promoted carbonylation of methanol[a].

Run No.	Catalyst	Conversion, %	Selectivity, %		TOF, h^{-1}
			A	B	
1[b]	Pd(OAc)$_2$	94.25	65.12	4.23	24
2	5%Pd/C	96.22	66.06	4.52	22
3	Recycled from 2	74.09	59.55	9.55	13
4	Recycled from 3	55.87	55.5	12.5	9

[a]*Reaction Conditions:* As in Fig. 2.2; [b]Pd(OAc)$_2$, 4×10^{-3} kmol/m^3 (homogeneous catalyst)

2.5.2. Pd(OAc)$_2$-HI Catalyst System

Effect of water concentration in Pd(OAc)$_2$-HI catalyzed reaction showed a trend similar to that with Pd(OAc)$_2$-KI-TsOH catalyst system. Increase in the catalytic activity was noted when water concentration was increased from 4% to 20%, which remained unchanged beyond that. Significant improvement in selectivity to acetic acid was observed at higher water concentrations as shown in Table 2.4. This improvement was consistent with the equilibrium reaction (eq. 2.8) of acetic acid with unreacted methanol

$$CH_3COOH + CH_3OH \rightleftharpoons CH_3COOCH_3 + H_2O \qquad (2.8)$$
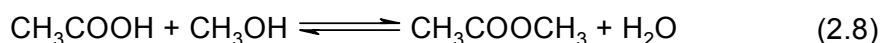
at higher water concentration. PdI$_2$ as a catalyst was found to be inactive for methanol carbonylation reaction probably because PdI$_2$ is insoluble in the reaction solvent (Solubility of PdI$_2$ in MEK was separately checked. Also, after the carbonylation reaction black precipitate of PdI$_2$ was found in the reactor).

Table 2.4. Effect of concentration of water in Pd(OAc)$_2$-HI catalyzed carbonylation of methanol[a]

Run No.	H$_2$O, % (V/V)	Conversion, %	Selectivity, %		TOF, h^{-1}
			A	B	
1	4	84.24	71.92	13.78	30
2	20	87.51	92.54	2.02	45
3	30	72.59	93.23	1.05	44
[b]4	20	0	0	0	0

[a]*Reaction Conditions*: Pd(OAc)$_2$, 4×10^{-3} kmol/m^3; CH$_3$OH, 1.25 kmol/m^3; HI, 4×10^{-1} kmol/m3; Solvent, MEK, Total Volume, 2.5×10^{-5} m^3; Temperature, 388K; P$_{CO}$, 5.4 MPa; Time, 4.5 hr; A, Acetic acid; B, Methyl acetate; [b]PdI$_2$ as a catalyst instead of Pd(OAc)$_2$

2.5.2.1. Effect of Temperature

Significant effect of temperature was observed in Pd(OAc)$_2$-HI catalyzed carbonylation of methanol. At 388 K, a TOF of 82 h^{-1} was observed without catalyst deactivation. When the temperature was increased from 388 K to 403 K, in Pd(OAc)$_2$-HI

catalyst system, substantial amount of catalyst was found to be decomposed, giving black particles in the reaction mixture, thus decreasing the catalyst activity (TOF = 56 h^{-1}) (Table 2.5, run # 1, 2). However, using a ligand (PPh$_3$) along with Pd(OAc)$_2$ as a catalyst

Table 2.5. Effect of temperature on Pd(OAc)$_2$-HI and Pd(OAc)$_2$-HI-PPh$_3$ catalyzed carbonylation of methanol[a]

Run	Temp,	Time,	Conversion,	Selectivity, %		TOF,
No.	K	h	%	A	B	h^{-1}
[b]1	388	2	16.47	22.29	64.46	82
[b]2	403	2	13.05	5.72	74.36	56
4	388	2	20.54	27.10	56.66	110
5	403	1	26.77	21.23	57.27	260
6	418	1	46.46	28.45	57.46	533
7	433	1	62.34	54.39	42.45	863
8	448	1	64.77	61.33	33.74	1052

[a]*Reaction conditions: Pd(OAc)$_2$, 2 × 10^{-3} kmol/m^3; HI, 2 × 10^{-1} kmol/m^3; PPh$_3$, 8 × 10^{-2} kmol/m^3; CH$_3$OH, 4 kmol/m^3, H$_2$O, 10% (v/v); Solvent, MEK; Total Volume, 2.5 × 10^{-5} m^3; P$_{CO}$, 5.4 MPa; A, Acetic acid; B, Methyl acetate; [b]Without PPh$_3$*

and HI as a promoter at higher temperatures (> 388 K) eliminated this problem showing an increase in the catalytic activity with increasing temperature without any catalyst precipitation (Table 2.5). Use of PPh$_3$ as a ligand in Pd(OAc)$_2$-HI catalyst system at 388K gave marginal improvement in catalytic activity, but was much significant at higher temperatures (>388 K). Increase in temperature from 388-403 K increased the conversion as well as catalytic activity (Table 2.5, run # 4, 5). With further increase in temperature this catalyst system (Pd(OAc)$_2$-HI-PPh$_3$) could achieve the highest methyl conversion (64.77 %) and catalytic TOF (1052 h^{-1}) at 448 K in one hour (Table 2.5, run # 8). Simultaneously, increase in conversion levels increased the selectivity to acetic acid, decreasing the selectivity to methyl acetate (eq. 2.8). Thus, use of PPh$_3$ as a ligand in Pd(OAc)$_2$-HI catalyst system avoided catalyst precipitation and increased the catalyst stability at higher temperatures, which helped in achieving higher catalytic activity.

2.5.2.2. Effect of Ligands

Use of PPh$_3$ as a ligand in Pd(OAc)$_2$-HI catalyst system helped in avoiding catalyst deactivation at higher temperatures, thus improving catalyst stability and activity, as discussed in the previous section. The effect of different N- and P- containing ligands on the activity and selectivity of Pd(OAc)$_2$-HI catalyst system was investigated at 418 K and 5.4 MPa CO partial pressure (Table 2.6). All the ligands studied, improved the activity of Pd(OAc)$_2$-HI catalyst system (TOF = 43 to 182 *Vs* TOF = 22)., When used with Pd(OAc)$_2$-HI catalyst system, monodentate ligands gave higher conversions (54-75%) with the TOFs in the range of 74-182 h^{-1} (Table 2.6, run # 2-6), whereas, under the same reaction conditions, bidentate ligands gave lower conversions (48-69%) with TOFs in the range of 43-61 (Table 2.6, run # 7-9). At higher conversion of methyl groups, the selectivity to acetic acid was higher, as it is dictated by the equilibrium reaction of the product acetic acid and unreacted methanol (eq. 2.8). Use of triphenyl amine (NPh$_3$) as a ligand in Pd(OAc)$_2$-HI catalyst system showed only 19 h^{-1} TOF, perhaps due to the solubility limitation of NPh$_3$ in the reaction system (white solid NPh$_3$ was found in the reactor when discharged and analyzed by elemental analysis: %C = 88.21 (88.16), %H = 6.25 (6.12) and %N = 5.78 (5.71)). Though, the extent of quaternization (Scheme 2.2) of a ligand with methyl iodide decides the formation of an active catalytic species, PdI$_3$CO$^-$ (see Section 2.6), use of higher concentration of a ligand was found to be beneficial to achieve a higher catalytic activity. Thus, bidentate ligands were comparatively less active
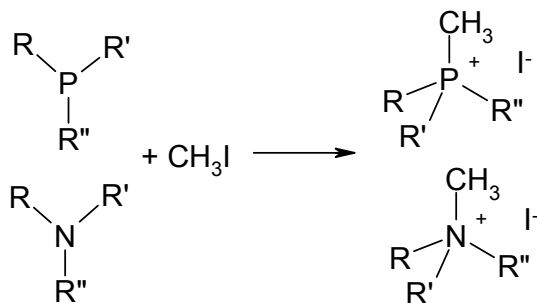
Scheme 2.2. Quaternization of N- and P- containing ligands with methyl iodide

than monodentate ligands for the methanol carbonylation reaction, when used with Pd(OAc)$_2$ as a catalyst and HI as a promoter. During this study PPh$_3$ was found to be the best ligand giving 53% conversion in one hour with a TOF of 182 h^{-1}.

Table 2.6. Effect of ligands on $Pd(OAc)_2$-HI catalyzed carbonylation of methanol[a]

Run No.	Ligand	Time, h	Conversion, %	Selectivity, %		TOF, h^{-1}
				A	B	
1	–	4	19.89	79.79	13.73	22
2	PPh$_3$	1	54.56	49.70	35.90	182
3	NPh$_3$	5	23.16	68.52	22.63	19
4	N(n-Bu)$_3$	4	74.47	83.37	12.06	95
5	NEt$_3$	4	77.12	79.86	8.74	83
6	Pyridine	4	75.65	73.27	11.10	74
7	[b]2,2'-Bipy.	5	67.44	76.20	17.02	59
8	[c]TMPDA	5	48.23	74.95	21.00	43
9	[d]DADPM	5	69.94	84.88	12.72	61

[a]*Reaction conditions: $Pd(OAc)_2$, 2×10^{-3} kmol/m^3; HI, 2×10^{-1} kmol/m^3; Ligand, 8×10^{-2} kmol/m^3; CH_3OH, 1.25 kmol/m^3; H_2O, 10% (v/v); Solvent, MEK; Total Volume, 2.5×10^{-5} m^3; Temperature, 418K; P_{CO}, 5.4 Mpa; A, Acetic acid; B, Methyl acetate;* [b]*2,2'-Bipyridine;* [c]*N,N,N',N'-tetramethyl phenylene diamine;* [d]*N,N'-diaminodiphenyl methane.*

2.5.3. $Pd(OAc)_2$-HI-PPh$_3$ Catalyst System

2.5.3.1. Effect of Solvents

Effect of different solvents was studied using $Pd(OAc)_2$-PPh$_3$-HI catalyst system at 418K and 5.54 MPa CO partial pressure (Table 2.7). Increase in the polarity of solvents (from 2.21 to 18.5 debye for 1,4-dioxan and MEK respectively) increased the conversion level (16-54%) and catalytic activity (from TOF: 7 to 182 h^{-1}) as shown in Figure 2.3, where, dielectric constant of a solvent is considered as a measure of polarity. This effect can be correlated to the stability of the active catalyst species in polar solvents. As polar solvents can stabilize the ionic species PdI_3CO^-, the increase in activity was observed. Acetonitrile being highly polar, the activity was expected to be the highest in it among the solvents studied, but was observed to be lower than that in MEK. This is because acetonitrile can act as a ligand forming the species $Pd(MeCN)_2I_2$ in the reaction mixture thus decreasing the concentration of an active catalytic species, PdI_3CO^-, consequently decreasing the activity. When DMF was used as a solvent, no carbonylation

reaction took place. This effect was due to the quaternization (Scheme 2.2) of N-containing solvent (DMF), which consumed methyl iodide making it unavailable for carbonylation. When the liquid phase of the reaction containing DMF as a solvent was analyzed after the carbonylation reaction, it showed no methyl iodide, though 22.58% of the charged methanol was converted. Methanol in presence of HI forms methyl iodide, according to the equation 2.7 showing the conversion of methanol, which on the other hand is consumed for quaternization of DMF.

Table 2.7. Effect of solvents on $Pd(OAc)_2$-HI-PPh_3 catalyzed carbonylation of methanol[a]

Run No.	Solvent	Time, h	Conversion, %	Selectivity, %		TOF, h^{-1}
				A	B	
1	MEK	1	54.56	49.70	35.90	182
2	Acetonotrile	1	46.28	34.74	45.29	126
3	1,4-Dioxan	4	16.45	1.01	64.83	7
4	DMF	1	22.58	0	0	0
5	THF	4	74.74	73.95	19.55	80

[a]*Reaction conditions: $Pd(OAc)_2$, 2×10^{-3} kmol/m³; PPh_3, 8×10^{-2} kmol/m³; HI, 2×10^{-1} kmol/m³; CH_3OH, 4 kmol/m³; H_2O, 10% (v/v); Total Volume, 2.5×10^{-5} m³; P_{CO}, 5.4 MPa; Temperature, 418K; A, Acetic acid; B, Methyl acetate*
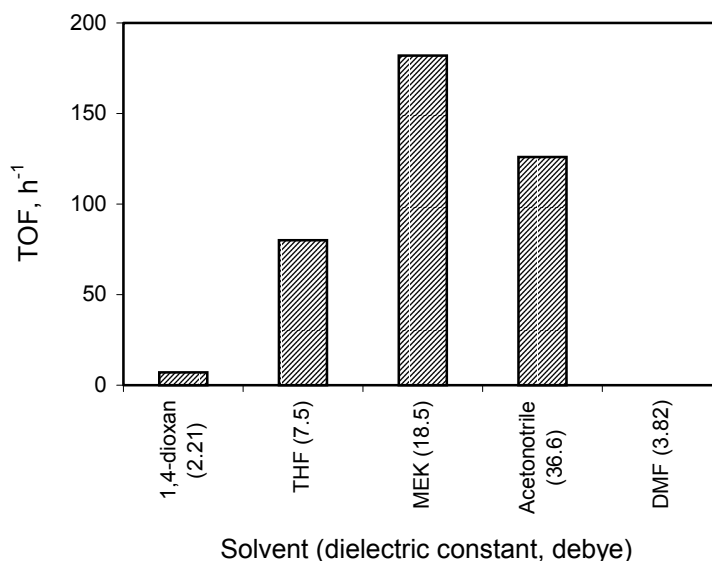
Fig. 2.3. Effect of solvents on $Pd(OAc)_2$-HI-PPh_3 catalyzed carbonylation of methanol
Reaction conditions: As in Table 2.7

2.5.3.2. Parametric Effects

Effect of different reaction parameters such as catalyst, methanol, water, PPh_3 and HI concentrations and CO partial pressure was investigated at four different temperatures in the range of 388-423K. Such parametric effects are very important in reaction engineering studies to first understand kinetics and develop rate equations. The range of conditions used for this study is given in Table 2.8.

Table 2.8. Range of conditions used for parametric study

No.	Parameter	Range of conditions
1	$Pd(OAc)_2$, kmol/m^3	$(1 \times 10^{-3}) - (6 \times 10^{-3})$
2	PPh_3, kmol/m^3	$(2 \times 10^{-2}) - (4 \times 10^{-2})$
3	HI, kmol/m^3	$(2 \times 10^{-1}) - (6 \times 10^{-1})$
4	CH_3OH, kmol/m^3	$0.975 - 6.905$
5	H_2O, kmol/m^3	$3.33 - 11.11$
6	P_{CO}, MPa	$200 - 1200$
7	Temperature, K	$388 - 433$
8	Agitation speed, Hz	$10 - 20$

The rates of reactions were calculated based on CO absorption as a function of time, as the entire CO consumed accounted for the formation of acetic acid or methyl acetate. GC analysis of the gas phase showed no formation of CO_2 or other gaseous products consuming CO. This also indicates that the catalyst system is resistant to water gas shift reaction even at higher water concentrations. The rates obtained were preferentially initial rates for less than 15% conversion of the methyl groups. In order to investigate the balance of all of the components at different intervals of time, in a few cases, reactions were carried out with intermediate sampling. Typical concentration-time profiles at 418 and 433K are shown in Figures 2.4 and 2.5 respectively.
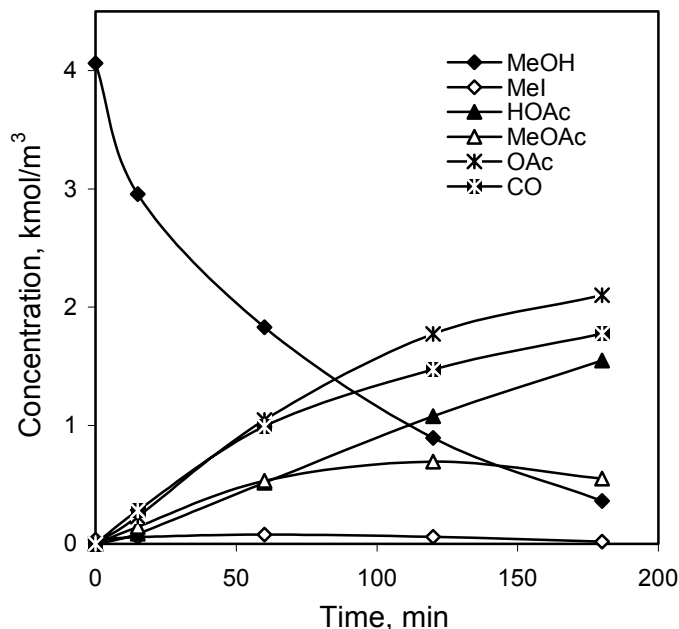
Fig. 2.4. Concentration-time profiles at 418 K

Reaction conditions: *Catalyst Pd(OAc)$_2$, 2 × 10^{-3} kmol/m^3; PPh$_3$, 8 × 10^{-2} kmol/m^3; CH$_3$OH, 4 kmol/m^3; HI, 2 × 10^{-1} kmol/m^3; H$_2$O, 6% (V/V); Solvent, MEK; Total Volume, 2.5 × 10^{-5} m^3; Temperature, 418K; P$_{CO}$, 5.4 MPa; Agitation Speed, 16.66 Hz*

In these concentration-time (CT) profiles, it was observed that decrease in methanol concentration in the initial period (this period depends upon the reaction conditions used) of the carbonylation reaction generates methyl iodide prior to carbonylation step (eq. 2.2), thus increasing the concentration of methyl iodide, which further decreases as a function of time. Increase in the concentration of carbonylation products with time was observed and shown in the respective figures. Concentration-time profile at 433 K showed very sharp decrease in methanol concentration and increase in the concentration of products. Also, it can be noted that the increase in methyl iodide concentration is predominant in initial period, which is a key intermediate in the carbonylation reaction. Effect of various parameters on methanol carbonylation reaction using Pd(OAc)$_2$-HI-PPh$_3$ catalyst system is presented in the following sections.
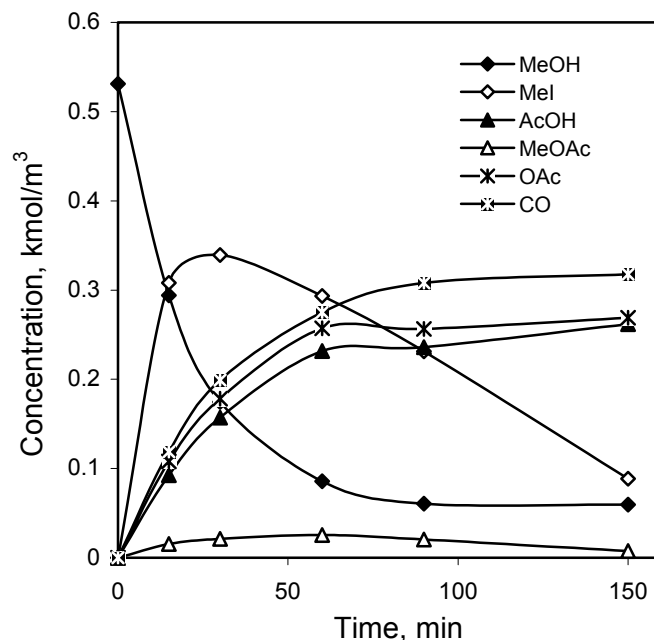
Fig. 2.5. Concentration-time profile at 433 K
Reaction conditions: $Pd(OAc)_2$, 2×10^{-3} $kmol/m^3$; PPh_3, 8×10^{-2} $kmol/m^3$; CH_3OH, 4 $kmol/m^3$; HI, 2×10^{-1} $kmol/m^3$; H_2O, 6% (V/V); Solvent, MEK; Total Volume, 2.5×10^{-5} m^3; Temperature, 433K; P_{CO}, 5.4 MPa; Agitation Speed, 16.66 Hz

2.5.3.2.1. Effect of Agitation Speed
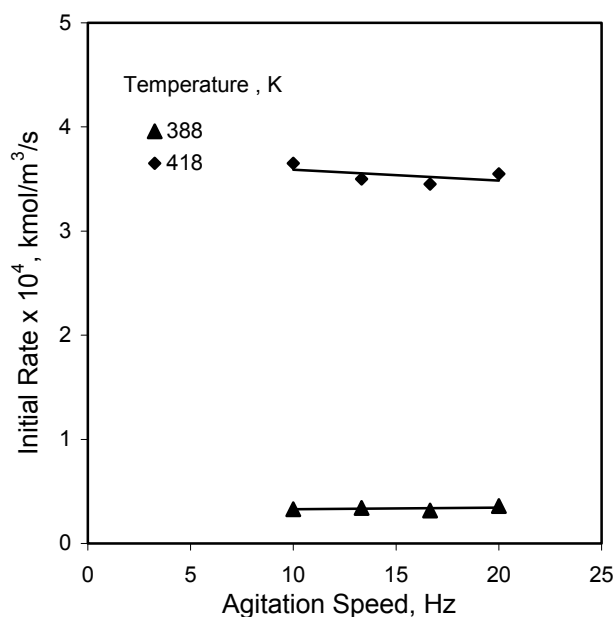
Fig. 2.6. Effect of agitation speed
Reaction conditions: $Pd(OAc)_2$, 2×10^{-3} $kmol/m^3$; PPh_3, 8×10^{-2} $kmol/m^3$; CH_3OH, 4 $kmol/m^3$; HI, 2×10^{-1} $kmol/m^3$; H_2O, 6% (V/V); Solvent, MEK; Total Volume, 2.5×10^{-5} m^3; P_{CO}, 5.4 MPa

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Initially, a few experiments were carried out using $Pd(OAc)_2$-HI-PPh_3 catalyst system at various agitation speeds at 388 and 418K. Increase in the agitation speed from 10 to 20 Hz showed no change in the rate of reaction at both the temperatures indicating that there was no gas-liquid mass transfer barrier at the reaction conditions studied (Fig. 2.6). In order to investigate the parametric effects in the kinetic regime, the reactions were carried out at the agitation speed of 16.66 Hz.

2.5.3.2.2. Effect of Pd(OAc)₂ Concentration

As the amount of catalyst ($Pd(OAc)_2$ only) was increased, increase in the reaction rate was observed that confirmed the reaction to be in kinetic regime. Reaction rates increased with increase in temperature. Effect of $Pd(OAc)_2$ concentration is shown in Figure 2.7. Increase in the reaction rate with catalyst concentration was almost linear at 388 K, whereas it did not vary linearly at higher temperatures indicating the formation of different catalytic species. The formation of different palladium species in the reaction mixture is presented in Scheme 2.3. As the reaction mixture contains $Pd(OAc)_2$ and HI, it can generate H_2PdI_4 species (**1**). This species may be an active species, as the reactions using $Pd(OAc)_2$-HI catalyst system without PPh_3 or any other ligand (Table 2.2, run # 7) showed the catalytic activity comparable to $Pd(OAc)_2$-HI-PPh_3 catalyst system. Further, in presence of PPh_3 as a ligand, the catalytic species H_2PdI_4 (**1**) can form $PdI_2(PPh_3)_2$ (**2**), which forms $PdI_3(PPh_3)^-$ (**3**) species in equilibrium as reported elsewhere[19]. $Pd(OAc)_2$ in presence of PPh_3 can form a Pd(0) species, $Pd(PPh_3)_4$ (**5**) that can be speculated as an active species, as it can undergo oxidative addition of methyl iodide[20] to form a methyl-palladium species, which is considered to be the rate determining step in carbonylation of methanol. Also, quaternization of PPh_3 in presence of methyl iodide can lead to the formation of a dimeric palladium species $(PPh_3CH_3)_2Pd_2I_6$ (**4**) in the presence of $Pd(OAc)_2$ and HI, which can subsequently form PdI_3CO^-, an active catalytic species (see mechanism section, Section 2.6). Thus, the formation of different catalytic species in the reaction mixture deviates the linearity of reaction rates with catalyst loading.
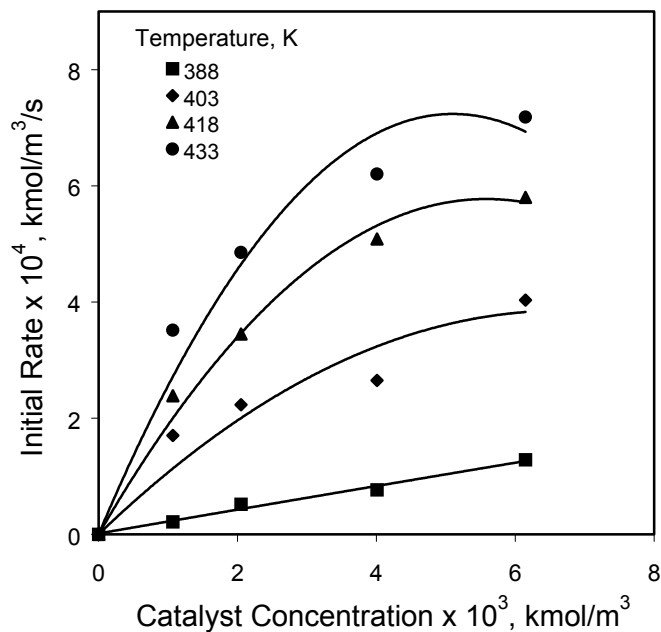
Fig. 2.7. Effect of catalyst loading on the initial rate

Reaction conditions: PPh$_3$, 8 × 10^{-2} kmol/m^3; CH$_3$OH, 4 kmol/m^3; HI, 2 × 10^{-1} kmol/m^3; H$_2$O, 6% (V/V); Solvent, MEK; Total Volume, 2.5 × 10^{-5} m^3; P$_{CO}$, 5.4 MPa; Agitation Speed, 16.66 Hz
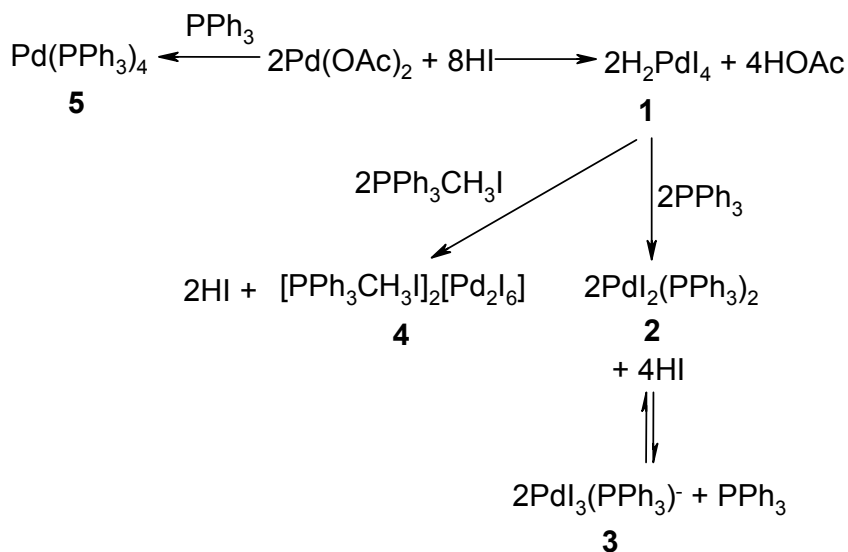
Scheme 2.3. Formation of different catalytic species in palladium catalyzed carbonylation of methanol

2.5.3.2.3. Effect of CO Partial Pressure
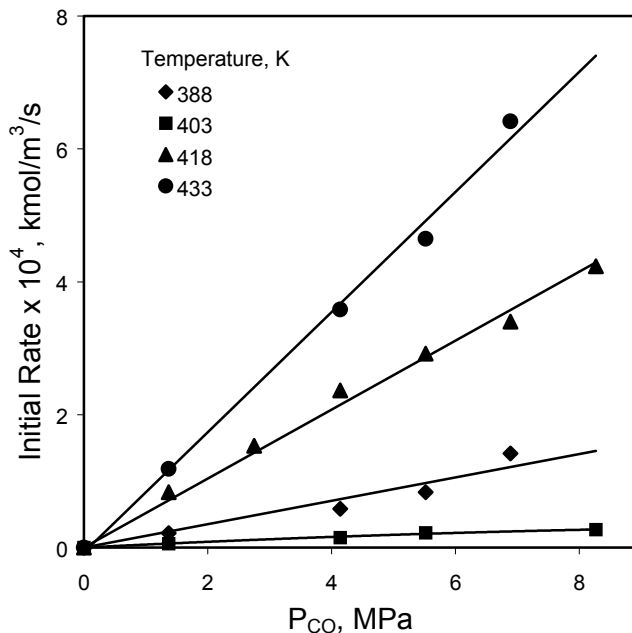
Fig. 2.8. Effect of partial pressure of CO

Reaction conditions: $Pd(OAc)_2$, 2×10^{-3} kmol/m^3; PPh_3, 8×10^{-2} kmol/m^3; CH_3OH, 4 kmol/m^3; HI, 2×10^{-1} kmol/m^3; H_2O, 6% (V/V); Solvent, MEK; Total Volume, 2.5×10^{-5} m^3; Agitation Speed, 16.66 Hz

The effect of CO partial pressure on the carbonylation reaction rate was studied at four different temperatures in the range of 388-433 K. The rate of reaction showed linear dependence on CO partial pressure in the range studied (1.37-8.27 MPa). The graphical representation of the dependence of the reaction rate on CO partial pressure is shown in Figure 2.8.

2.5.3.2.4. Effect of Water Concentration

Though, the catalyst system was found to be resistant to water gas shift reaction, prominent effect of water concentration on the reaction rate was observed. At lower concentration of water (<10% V/V), the rate of reaction increased with increasing water concentration, beyond which it showed inverse dependence. At higher concentration of water, methyl iodide formation was probably suppressed according to the equation 2.7. This negative effect of water at higher concentrations confirmed that the reaction

proceeds via methyl iodide intermediate. The results are shown in Figure 2.9.
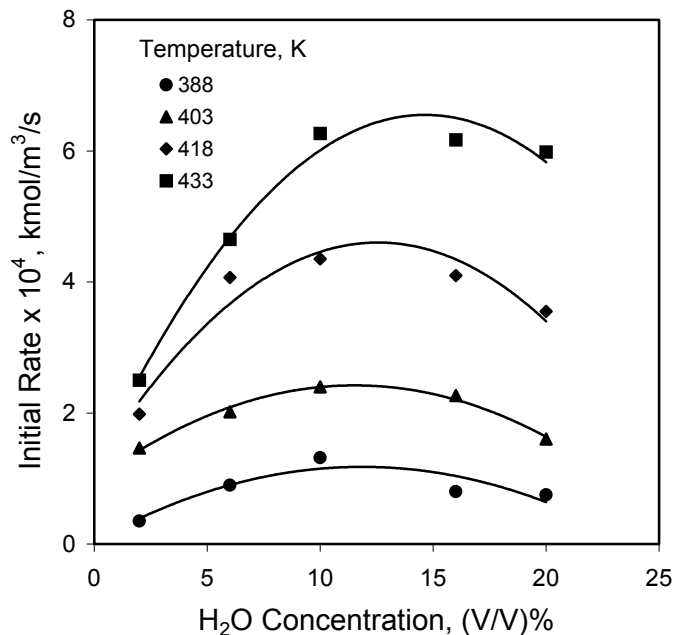
Fig. 2.9. Effect of H_2O concentration

Reaction conditions: $Pd(OAc)_2$, 2×10^{-3} $kmol/m^3$; PPh_3, 8×10^{-2} $kmol/m^3$; CH_3OH, 4 $kmol/m^3$; HI, 2×10^{-1} $kmol/m^3$; Solvent, MEK; Total Volume, 2.5×10^{-5} m^3; P_{CO}, 5.4 MPa; Agitation Speed, 16.66 Hz

2.5.3.2.5. Effect of HI Concentration

Prominent effect of HI concentration was observed on the rate of the reaction. At lower concentration of HI (<0.2 $kmol/m^3$) the rate of the reaction was linearly dependent on HI concentration, whereas at higher concentrations (>0.5 $kmol/m^3$) it was found to be inversely dependent, though the higher concentration of HI favors the formation of methyl iodide intermediate. This inverse dependence may be due to the formation of inactive PdI_2 (Table 2.4, run # 4) at higher HI concentration. Increase in temperature increased the rate of reaction maintaining the similar trend at all temperatures (Figure 2.10).
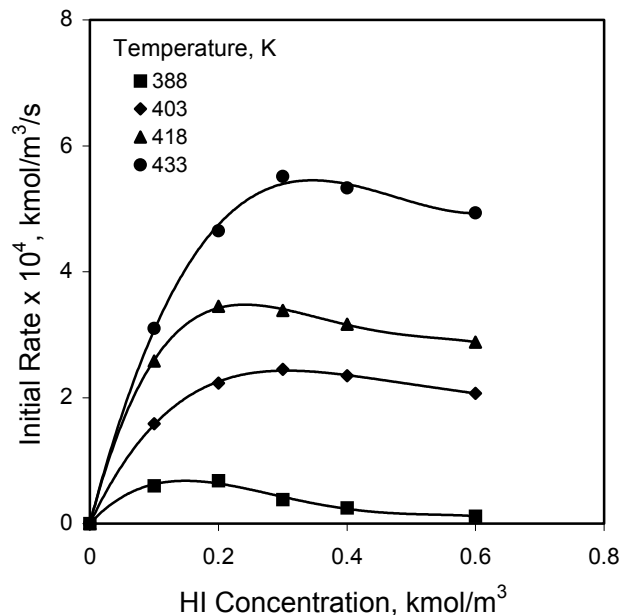
Fig.2.10. Effect of concentration of HI

Reaction conditions: $Pd(OAc)_2$, 2×10^{-3} kmol/m³; PPh_3, 8×10^{-2} kmol/m³; CH_3OH, 4 kmol/m³; H_2O, 6% (V/V); Solvent, MEK; Total Volume, 2.5×10^{-5} m³; P_{CO}, 5.4 MPa; Agitation Speed, 16.66 Hz

2.5.3.2.6. Effect of PPh₃ Concentration

At 388 K, the rate of the reaction was nearly independent of PPh_3 concentration. Effect of PPh_3 concentration was found to be prominent at higher temperatures (>403 K) (Fig. 2.11). At lower concentration range of PPh_3 (<0.07 kmol/m³), the rate of reaction increased with increase in PPh_3 concentration, whereas at higher PPh_3 concentrations, it showed negative effect on the rate. Higher concentration of PPh_3 consumes methyl iodide for its quaternization, making it unavailable for carbonylation reaction. Liquid phase analysis of the reaction mixtures of this set of reactions (reactions with various concentrations of PPh_3) also showed decrease in methyl iodide concentration with increase in PPh_3 concentration. The decrease in concentration of methyl iodide in final liquid samples, with increase in the concentration of added PPh_3 has been shown in Figure 2.12.

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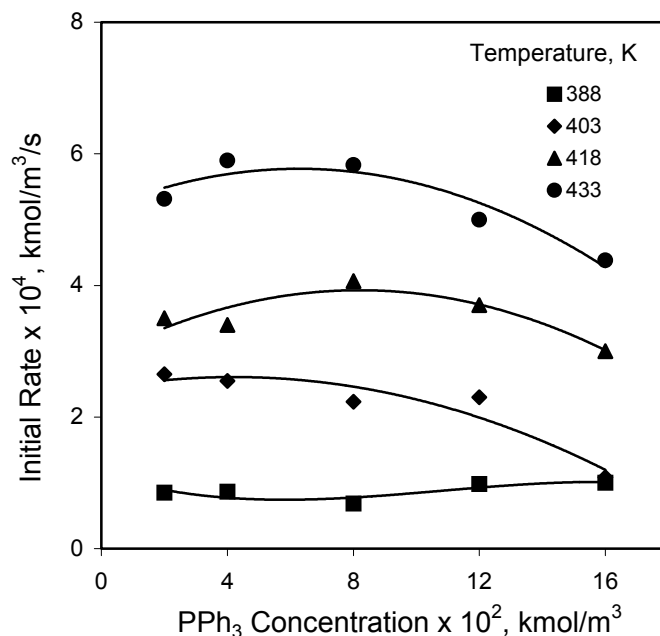
Fig. 2.11. Effect of concentration of PPh$_3$

Reaction conditions: Pd(OAc)$_2$, 2×10^{-3} kmol/m^3; CH$_3$OH, 4 kmol/m^3; HI, 2×10^{-1} kmol/m^3; H$_2$O, 6% (V/V); Solvent, MEK; Total Volume, 2.5×10^{-5} m^3; P$_{CO}$, 5.4 MPa; Agitation Speed, 16.66 Hz
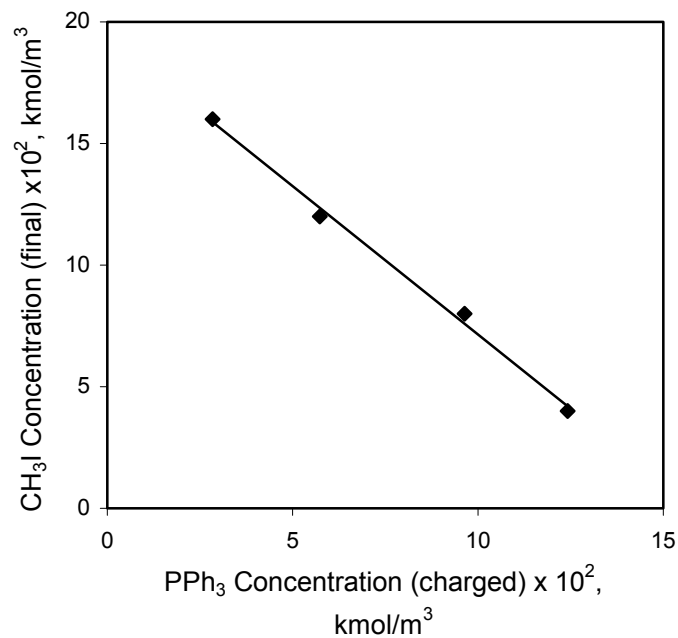
Fig. 2.12. Decrease in Methyl iodide concentration with increase in PPh$_3$ concentration

Reaction conditions: As in Fig 2.11; Temperature, 418 K; Reaction Time, 1 hr

2.5.3.2.7. Effect of Methanol Concentration
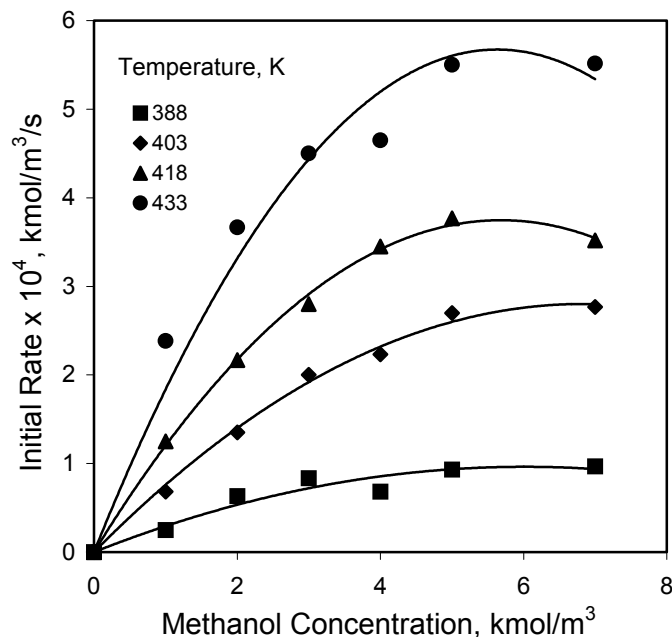
Fig. 2.13. Effect of concentration of methanol

Reaction conditions: _Pd(OAc)$_2$, 2 × 10^{-3} kmol/m^3; PPh$_3$, 8 × 10^{-2} kmol/m^3; HI, 2 × 10^{-1} kmol/m^3; H$_2$O, 6% (V/V); Solvent, MEK; Total Volume, 2.5 × 10^{-5} m^3; P$_{CO}$, 5.4 MPa; Agitation Speed, 16.66 Hz_

The rate of reaction showed linear dependence with methanol in lower concentration range (<5 kmol/m^3), which became independent of methanol concentration at higher concentrations (>5 kmol/m^3). Similar trend of the rate dependence was observed at all temperatures studied. The results are graphically represented in Figure 2.13.

2.6. Mechanistic Study

This section deals with the mechanistic aspects of palladium-catalyzed carbonylation of methanol. Mechanism of palladium-catalyzed carbonylation of methanol in homogeneous solutions was investigated using UV-visible, IR and NMR spectroscopic characterizations of the intermediate catalytic species involved in the catalytic cycle. The observations and results obtained in the previous sections were also used to speculate the mechanism that may be operative for this reaction. During these investigations, a palladium dimeric species, (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ was isolated from the reaction mixture for the first time and characterized by X-ray crystallography, though the use of high

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concentration of PPh$_3$ in the reaction showed the presence of free PPh$_3$ (without quaternization) by GCMS and ^{31}P NMR spectroscopy.

2.6.1. Isolation, Characterization and Catalytic Activity of (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$

Reaction mixtures from a series of catalytic reactions using Pd(OAc)$_2$-HI-PPh$_3$ catalyst system at 418K were collected together and allowed to evaporate at room temperature so as to obtain a black residue, which was washed with water several times and dried in vacuum. The residue was then dissolved in minimum amount of MEK and allowed to evaporate at room temperature from which black to brown crystals were obtained, which were washed with methanol and water several times and analyzed for elemental content (C, H, I), single crystal X-ray crystallography and ^{31}P NMR spectroscopy.

Elemental analysis of the crystalline compound showed the compound to be (PPh$_3$CH$_3$)PdI$_3$. [%C: 29.08 (29.8); %H: 2.5 (2.3) and %I=50.0 (49.8)], ^{31}P NMR spectroscopic analysis is shown in Fig. 2.14. Single crystal X-ray crystallographic data and structure refinement is shown in Table 2.9 with selected bond lengths and bond angles in Table 2.10. ORTEP view of [Pd$_2$I$_6$]$^{2-}$ and packing arrangement of atoms in a crystal lattice are shown in Fig. 2.15a and 2.15b respectively. Such palladium species, (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ has been isolated from the reaction mixture for the first time and characterized by single crystal X-ray crystallography.

Thus the isolated complex showed an anionic, iodide bridged Pd-dimer. The anion [Pd$_2$I$_6$]$^{2-}$ was stabilized by [PPh$_3$CH$_3$]$^+$ cations. The cations were formed due to the quaternization of PPh$_3$ with CH$_3$I (Scheme 2.2). The formation of [PPh$_3$CH$_3$]$^+$ was evidenced by ^{31}P NMR spectroscopy (δ 27.62) with a shift of +5.44 ppm to $^+$PPh$_3$CH$_3$I$^-$, meaning that the I$^-$ ions in $^+$PPh$_3$CH$_3$I$^-$ were replaced by bulky Pd-anion. Single crystal X-ray structure also showed $^+$PPh$_3$CH$_3$ cations around palladium dimer, which are clearly shown in packing arrangement of atoms in the crystal lattice of the isolated complex. (Fig. 2.15b).
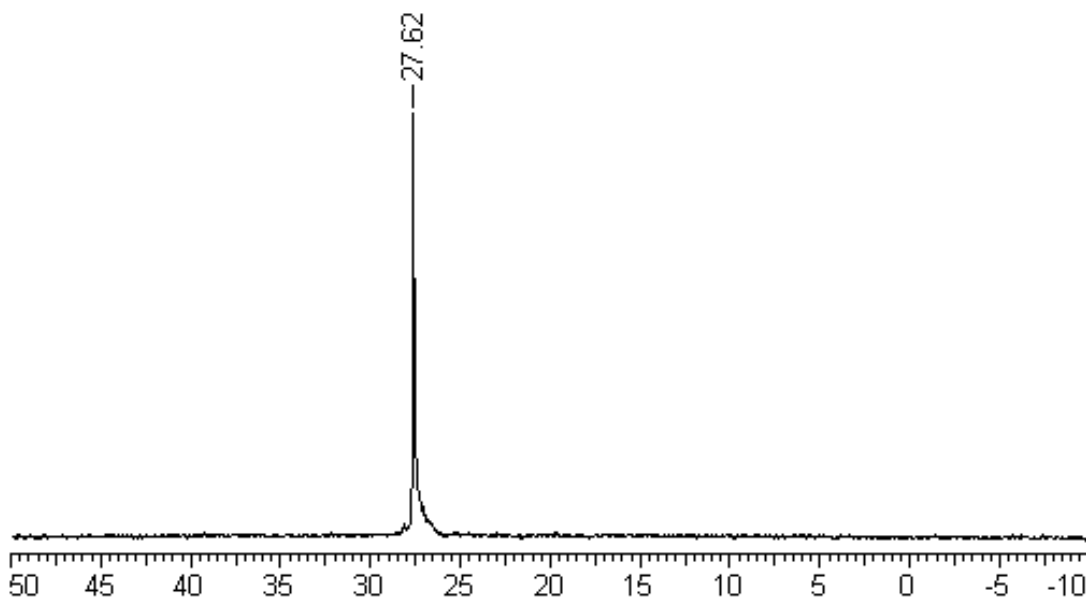
Fig. 2.14. ^{31}P NMR spectra of $(PPh_3CH_3)_2Pd_2I_6$ in Acetone d_6

ORTEP view of the complex $[Pd_2I_6]^{2-}$ along with the bond length distribution is shown in Fig. 2.15a. The bond lengths of iodo bridged Pd-dimer tend to be longer than the terminal Pd-I distances, notably Pd1-I2 of the length 2.6074(5) Å can be suggestive of the initiation of the breakdown of dimeric unit into monomeric anions by CO insertion (see Section 2.6.3).

In order to investigate the reaction mechanism, various stoichometric reactions were carried using the complex $(PPh_3CH_3)_2Pd_2I_6$. As the isolated complex was not in sufficient amount for carrying out these reactions, it was synthesized as in Section 2.2.1 and characterized, which showed good agreement with the complex $(PPh_3CH_3)_2Pd_2I_6$ isolated from the reaction mixture.
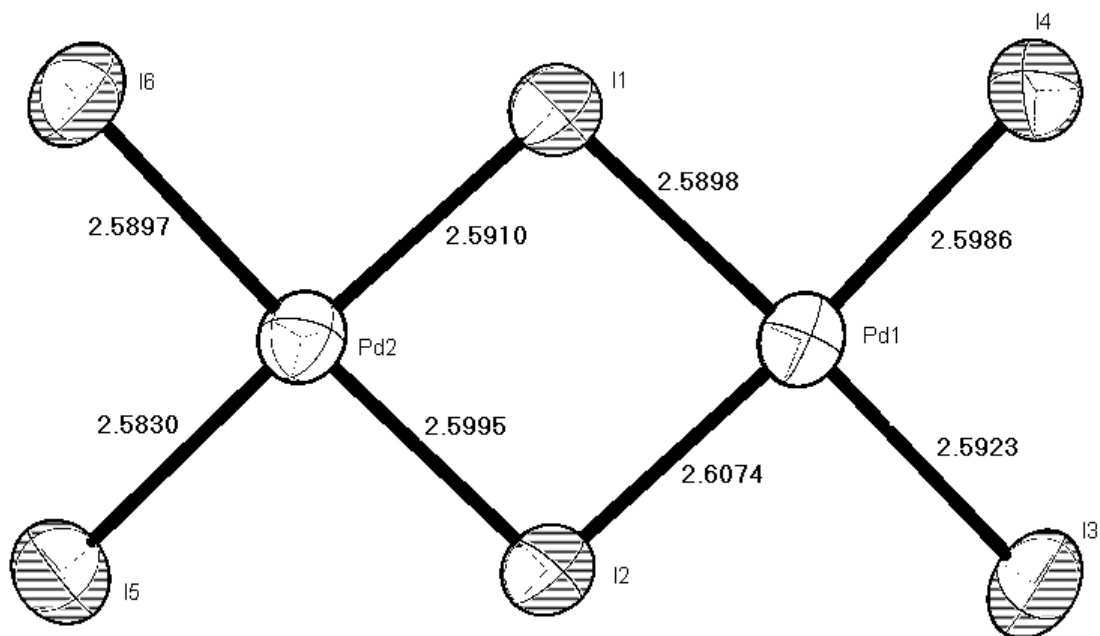
Fig. 2.15a. ORTEP View of the isolated complex, $[Pd_2I_6]^{2-}$.
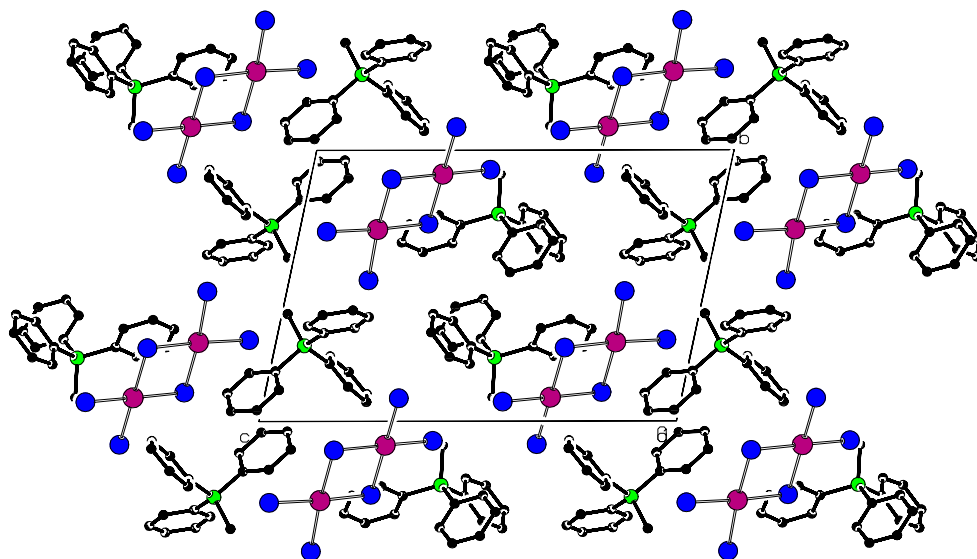
Fig. 2.15b. Packing arrangement of atoms in crystal lattice of $(PPh_3CH_3)_2Pd_2I_6$

Table 2.9. Crystal data and structure refinement for $(PPh_3CH_3)_2Pd_2I_6$

Empirical formula	C12.67 H12 I2 P0.67 Pd0.67
Formula weight	509.60
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic
Unit cell dimensions	a = 10.0013(17) A alpha = 101.540(3) deg.
	b = 12.674(2) A beta = 90.930(3) deg.
	c = 18.552(3) A gamma = 103.252(3) deg.
Volume	2237.9(7) A^3
Z, Calculated density	6, 2.269 Mg/m^3
Absorption coefficient	5.039 mm^-1
F(000)	1408
Theta range for data collection	1.69 to 25.00 deg.
Limiting indices	-11<=h<=11, -15<=k<=15, -22<=l<=21
Reflections collected / unique	21394 / 7835 [R(int) = 0.0364]
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0300, wR2 = 0.0778
R indices (all data)	R1 = 0.0350, wR2 = 0.0813
Extinction coefficient	0.00482(15)
Largest diff. peak and hole	0.733 and -0.999 e.A^-3

Table 2.10. Bond lengths [Å] and angles [deg] for $[Pd_2I_6]^{2-}$

I(1)-Pd(1)	2.5898(5)
I(1)-Pd(2)	2.5910(5)
Pd(2)-I(5)	2.5830(5)
Pd(2)-I(6)	2.5897(5)
Pd(2)-I(2)	2.5995(5)
I(2)-Pd(1)	2.6074(5)
Pd(1)-I(3)	2.5923(5)
Pd(1)-I(4)	2.5986(5)
Pd(1)-I(1)-Pd(2)	94.500(14)
I(5)-Pd(2)-I(6)	93.042(15)
I(5)-Pd(2)-I(1)	174.958(15)
I(6)-Pd(2)-I(1)	90.178(14)
I(5)-Pd(2)-I(2)	91.242(14)
I(6)-Pd(2)-I(2)	173.629(15)
I(1)-Pd(2)-I(2)	85.878(14)
Pd(2)-I(2)-Pd(1)	93.881(14)
I(1)-Pd(1)-I(3)	176.574(15)
I(1)-Pd(1)-I(4)	89.847(14)
I(3)-Pd(1)-I(4)	93.405(14)
I(1)-Pd(1)-I(2)	85.737(14)
I(3)-Pd(1)-I(2)	91.055(14)
I(4)-Pd(1)-I(2)	175.037(14)

When the isolated complex and the prepared complex, $(PPh_2CH_3)_2Pd_2I_6$ were tested for carbonylation reaction along with PPh_3 and HI, they gave the activity similar to $Pd(OAc)_2$-PPh_3-HI catalyst system (Table 2.11). This observation means that the presence of PPh_3 and HI along with $Pd(OAc)_2$ in a methanol carbonylation reaction mixture readily generates the catalyst precursor $(PPh_2CH_3)_2Pd_2I_6$ and carbonylates methanol.

Table 2.11. Comparison of $Pd_2I_6^{2-}$ catalysts for methanol carbonylation reaction[a]

Run No.	Catalyst	Conversion, %	Selectivity, %		TOF, h^{-1}
			A	B	
1	$Pd(OAc)_2$	54.56	49.70	35.90	182
[b]2	$(PPh_2CH_3)_2Pd_2I_6$	56.37	48.74	35.29	181
[c]3	$(PPh_2CH_3)_2Pd_2I_6$	56.85	49.01	34.89	182

[a]*Reaction conditions: Catalyst, 2×10^{-3} kmol/m³; PPh_3, 8×10^{-2} kmol/m³; CH_3OH, 4 kmol/m³; HI, 2×10^{-1} kmol/m³; H_2O, 6% (V/V); Solvent, MEK; Total Volume, 25 ml; P_{CO}, 5.4 MPa; Agitation Speed, 16.66 Hz; Temperature, 418K; Reaction Time, 1 hour; A, Acetic acid; B, Methyl acetate;* [b]*Catalyst isolated from the reaction mixtures as in Section 2.7.1;* [c]*Catalyst prepared as in Section 2.2.1*

2.6.2. UV-vis. Spectroscopic Investigations
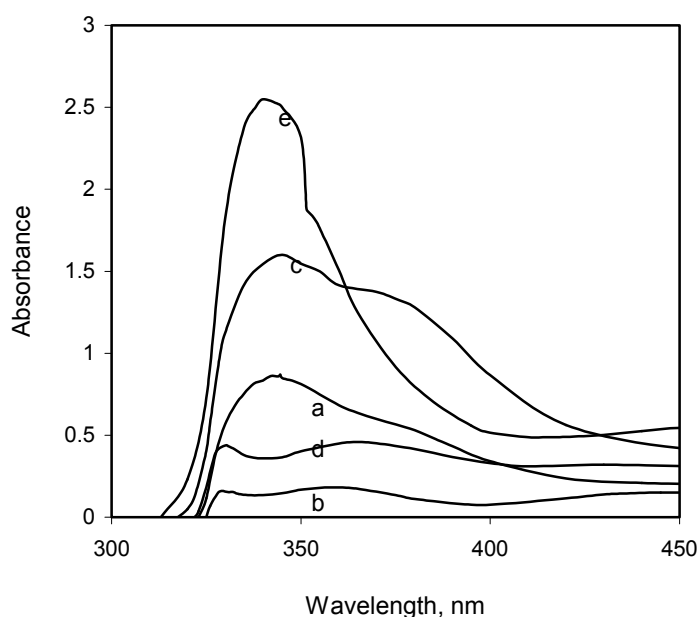
Figure 2.16. UV-vis spectroscopic analysis of Pd-catalysts in MEK at room temperature

a: *0.1 M palladium solution using the isolated complex, $(PPh_3CH_3)_2Pd_2I_6$ in MEK;* **b**: *CO was bubbled for 5 min. in the solution* **a**; **c**: *0.2 M palladium solution using $Pd(OAc)_2$ in MEK with 4 equiv. of HI per Pd;* **d**: *CO was bubbled for 5 min. in the solution* **c**; **e**: *0.3 M palladium solution using $Pd(OAc)_2$ in MEK with 4 equiv. of NaI and TsOH each per Pd.*

All of the catalyst systems studied ($Pd(OAc)_2$-TsOH-alkali metal iodide,

Pd(OAc)$_2$-HI and Pd(OAc)$_2$-HI-PPh$_3$) were tested for UV-vis spectroscopic analysis and it was found that all of the systems formed Pd$_2$I$_6$$^{2-}$ species prior to carbonylation. The isolated complex (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$, when dissolved in MEK and analyzed for UV-vis spectroscopy, it showed the characteristic absorption at 342 nm (Fig. 2.16; *a*), which was assigned to Pd$_2$I$_6$$^{2-}$ species[21]. Similar UV-vis spectroscopic observations were recorded for the solutions containing Pd(OAc)$_2$-HI in MEK and Pd(OAc)$_2$-TsOH-NaI in MEK (Fig. 2.16; *c* and *e*) and it was observed that the formation of the species Pd$_2$I$_6$$^{2-}$ was consistent in all the cases. Olsson[22] has already reported the formation of dimeric palladium species in organic solvents. The catalysts (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ and Pd(OAc)$_2$-HI were carbonylated by bubbling CO through their solutions in MEK and tested for UV-vis spectroscopy (Fig. 2.16; *b* and *d*). It was observed that the characteristic absorption of Pd$_2$I$_6$$^{2-}$ disappeared, indicating that the Pd$_2$I$_6$$^{2-}$ was converted to an active Pd-carbonyl species, after reaction with carbon monoxide at atmospheric pressure and room temperature. Thus the UV-vis spectroscopic analysis confirmed the formation of Pd$_2$I$_6$$^{2-}$ species in the carbonylation reaction mixture, which was speculated to be an insitu generated, active catalyst precursor for this reaction. Maitlis and coworkers[8] have proposed the formation of species PdI$_4$$^{2-}$ in equilibrium with PdI$_6$$^{2-}$ prior to the formation of PdI$_3$CO$^-$ in carbonylation of methyl iodide using PdCl$_2$(PPh$_3$)$_2$ as a catalyst and tetrabutyl ammonium iodide (TBAI) as a promoter, but they have not characterized the proposed species. In the case studied here, palladium species Pd$_2$I$_6$$^{2-}$ was isolated from the reaction mixture for the first time and characterized using single crystal X-ray crystallography and other analytical tools. Further, UV-visible spectroscopic characterizations using all the studied catalyst systems show the formation of Pd$_2$I$_6$$^{2-}$.

2.6.3. FT-IR Spectroscopic Characterizations of PdI$_3$CO$^-$

IR spectroscopic characterizations of carbonylation of (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ were made at room temperature in MEK and MeI solutions (Fig. 2.17). In presence of carbon monoxide, the dimeric anionic species Pd$_2$I$_6$$^{2-}$, was converted to the monomeric palladium species PdI$_3$CO$^-$, as evidenced by IR spectroscopic analysis at room temperature (Fig. 2.17; *b*), which showed a strong carbonyl frequency at 2094 cm^{-1}, consistent with the literature[23]. Maitlis and coworkers[8] also have proposed the formation

of PdI$_3$CO$^-$, as an active catalytic species in the carbonylation of methyl iodide, but the direct evidence for this species was not given (Speculation of this species was made on the basis of an analogous study done using platinum catalyst for the carbonylation of methyl iodide, where they found the formation of PtI$_3$CO$^-$ species, which was characterized using FTIR spectroscopy). In order to check the stability of the species at
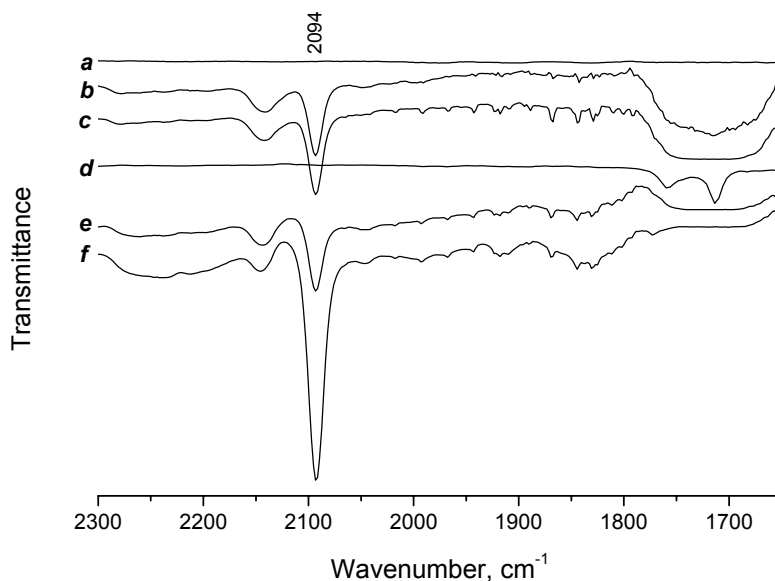
Fig. 2.17. FTIR analysis of (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ at room temperature

a: (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ in MEK; b: CO bubbled to the solution a; c: solution a was heated to 418K for half an hour under stirring at 5.4 MPa CO, the analysis after cooling to room temperature and reducing the pressure to 1 atm.; d: (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ in MeI; e: CO bubbled to the solution d; f: CO was bubbled through a concentrated solution of (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ in MEK and MeI.

the reaction conditions, the isolated complex, (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ was dissolved in MEK, heated at 418 K, pressurized with 5.4 MPa of CO and stirred for 0.5 hour. IR analysis of the reaction mixture after cooling to room temperature and reducing the pressure to 1 atm., showed the characteristic absorption of PdI$_3$CO$^-$ (ν = 2094 cm^{-1}) without any change (Fig. 2.17; *c*). This indicated that the palladium catalyst was stable even at higher temperature. Methyl iodide solution containing (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$, when bubbled with CO at room temperature and analyzed by IR spectroscopy, absorption at 2094 cm^{-1} was the only significant carbonyl frequency observed (no signal for Pd-acyl frequency was

observed). Further, when the solution of $(PPh_3CH_3)_2Pd_2I_6$ in MEK and MeI was concentrated and CO was bubbled through it, the only observation was increase in the intensity of PdI_3CO^-. This may be due to the reversibility of the oxidative addition and methyl migration steps. Dekleva et al.[24] have proved similar reversibility in case of rhodium catalyst. Thus, the FTIR spectroscopic analysis concluded that $Pd_2I_6^{2-}$ species insitu generated in the carbonylation reaction mixtures (containing $Pd(OAc)_2$-HI and other catalyst systems) underwent carbonylation to give the monomeric active catalytic species, PdI_3CO^-. Also, the oxidative addition of methyl iodide and methyl migration steps were speculated to be reversible similar to that for rhodium catalyst.

2.6.4. ^{31}P NMR Spectroscopic Characterizations
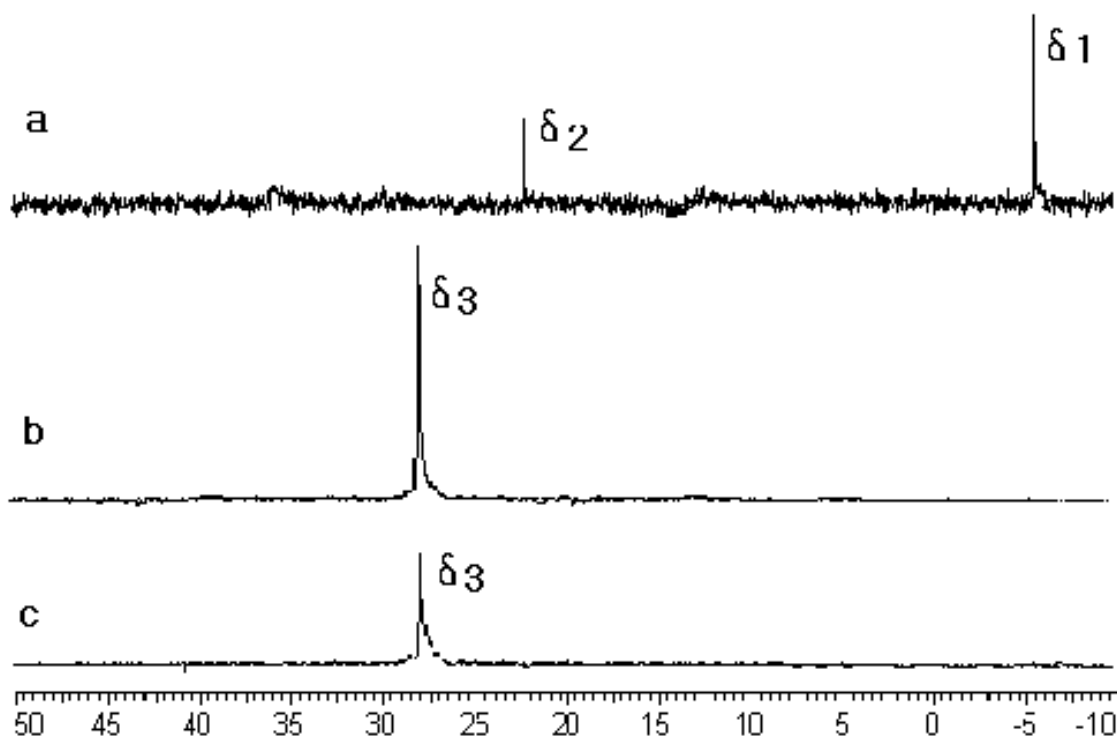
Fig. 2.18. ^{31}P NMR spectroscopic characterization at room temperature in acetone d_6

*a: Reaction mixture after carbonylation reaction at 418K ($Pd(OAc)_2$-HI-PPh_3) was evaporated and dissolved in acetone d_6; **b:** $(PPh_3CH_3)_2Pd_2I_6$ in acetone d_6; **c:** CO was bubbled in the solution **b** for 5 minutes*

When the carbonylation reaction mixture using $Pd(OAc)_2$-HI catalyst system in

presence of PPh$_3$ (20 equivalents to Pd) was analyzed by ^{31}P NMR spectroscopy, free PPh$_3$ ($\delta 1 = -5.6$ ppm) was traced along with PPh$_3$CH$_3$I at $\delta 2 = 22.18$ ppm (Fig. 2.18a). The quaternization of PPh$_3$ from the catalyst PdCl$_2$(PPh$_3$)$_2$ was also reported using ^{31}P-NMR spectroscopy by Maitlis and coworkers[8] in carbonylation of methyl iodide. When the acetone d$_6$ solution of the authentic compound (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ was analyzed by ^{31}P NMR, the only signal observed was at $\delta 27.62$ ppm showing the presence of $^+$PPh$_3$CH$_3$ cations (Fig. 2.18b), which appeared without any change even after bubbling carbon monoxide in it, as shown in Figure 2.18c (species formed was (PPh$_3$CH$_3$)(PdI$_3$CO) as shown by IR spectroscopy; Section 2.7.3). Thus ^{31}P NMR spectroscopic characterizations showed the signal of quaternized phosphines both in (PPh$_3$CH$_3$)$_2$Pd$_2$I$_6$ and (PPh$_3$CH$_3$)(PdI$_3$CO).

2.6.5. Reaction Mechanism

Mechanism for palladium-catalyzed carbonylation of methanol was speculated considering the experimental results and spectroscopic characterizations. The catalytic cycle shows a trend similar to that known for Rh-catalyzed[24] carbonylation of methanol. Though, the presence of different catalytic species was possible under the reaction conditions (Scheme 2.3), the reaction pathway discussed here is primarily based on the spectroscopic characterizations discussed in the previous sections.

Pd$_2$I$_6^{2-}$ (I) species generated insitu undergoes carbonylation to form the species II prior to oxidative addition of methyl iodide to the palladium center. Pd-methyl species III, thus formed undergoes CO addition and methyl migration to generate Pd-acyl species IV. The species IV then reductively eliminates acyl iodide regenerating the active catalytic species II to continue the catalytic cycle. Oxidative addition of methyl iodide and methyl migration steps were found to be reversible. Acyl iodide forms the product acetic acid in the presence of water thus regenerating HI promoter. The speculated mechanism is shown in Figure 2.19.

$Pd_2I_6{}^{2-}$

I

$-CO \quad\| \quad CO$

CH_3COOH
$+ HI$

I
CO � -
I—Pd—
I   I

II

$CH_3OH + HI$

$CH_3I + H_2O$

H_2O

$COCH_3$ ⌐-
I   CO
I—Pd—
I   I
I

IV

CH_3 ⌐-
I   CO
I—Pd—
I   I
I

III

CO
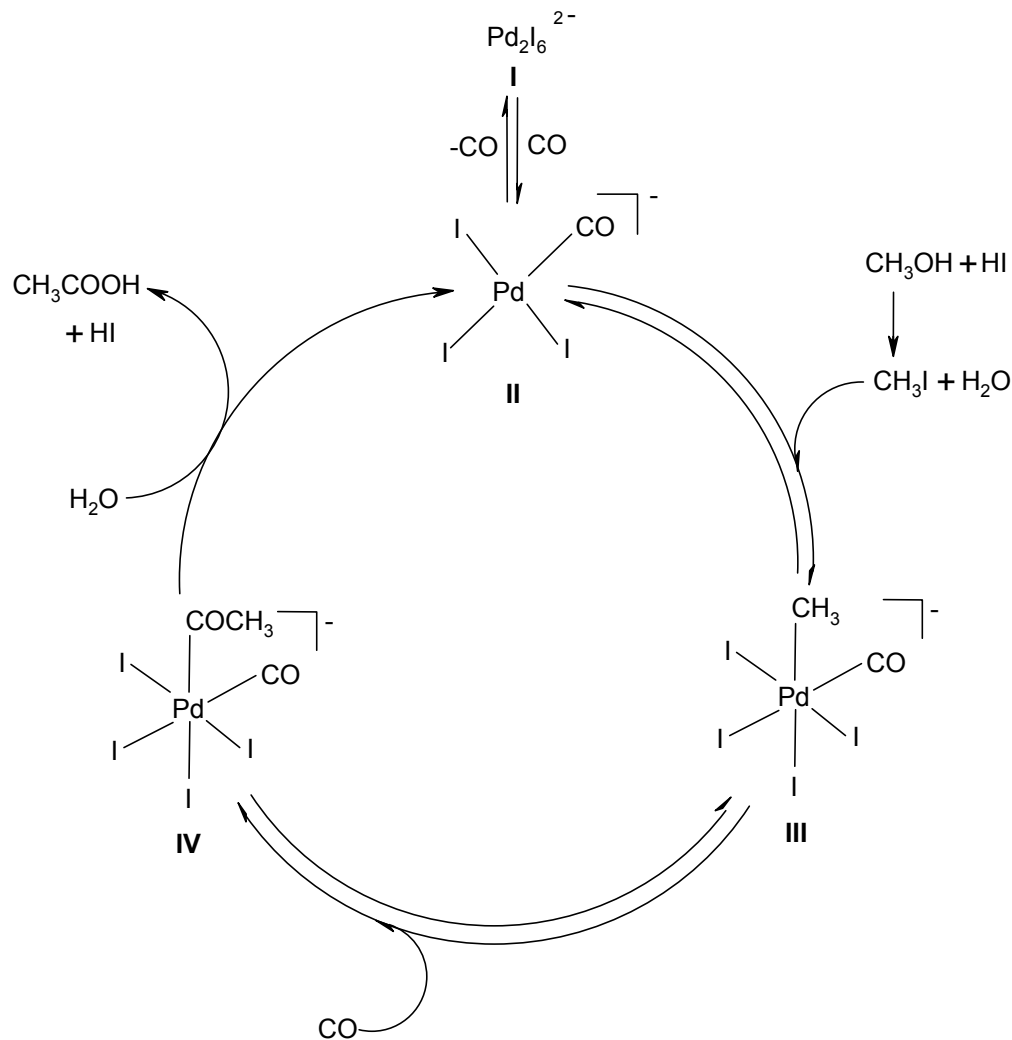
Fig. 2.19. Mechanism of palladium-catalyzed carbonylation of methanol

2.7. Conclusions

Methanol carbonylation reaction was investigated in detail using $Pd(OAc)_2$-TsOH-Alkali metal iodide, $Pd(OAc)_2$-HI and $Pd(OAc)_2$-HI-PPh$_3$ catalyst systems. Effect of different ligands, solvents and catalyst precursors was studied showed following trends:

1) $Pd(OAc)_2$-TsOH-Alkali metal iodide catalyst system generated HI in the reaction mixture, which was found to be the effective promoter for carbonylation of methanol.

2) Various palladium catalysts gave the catalytic activity comparable to $Pd(OAc)_2$-

TsOH-LiI catalyst system, when used in presence of TsOH and LiCl as promoters meaning that the palladium catalyst can be charged in any form along with TsOH and iodide promoters.

3) Pd-catalyst systems studied here were found to be resistant to water-gas shift reaction even at higher concentrations of water.

4) Higher concentration of water was found to be beneficial for achieving higher selectivity to acetic acid.

5) At higher temperatures palladium catalysts were found to be deactivated, when used in the absence of a ligand. Use of excess (40 equiv.) PPh_3 as a ligand at 443 K gave highest catalytic activity (TOF 1052 h^{-1}) for this reaction.

6) Increase in polarity of a solvent increased the activity of palladium catalysts.

Parametric effects were studied in the kinetic regime. The parametric studies showed that carbonylation of methanol is first order with respect to catalyst, first order tending to zero order with respect to methanol, 1st order with respect to CO partial pressure and negative order with respect to HI and water.

Iodide bridged dimeric palladium species, $(PPPh_3CH_3)_2Pd_2I_6$ was isolated from the reaction mixture for the first time and characterized by single crystal X-ray crystallography. Based on the various stoichometric reactions with the complex $(PPPh_3CH_3)_2Pd_2I_6$ and characterization of the catalytic species using ^{31}P NMR, FTIR and UV-vis spectroscopy, a mechanism of methanol carbonylation reaction has been proposed. All the catalyst systems studied showed similar active catalytic species.

Considering the industrial significance of methanol carbonylation for acetic acid manufacture, it is always rewarding to search new catalysts as alternatives to existing ones. Pd-catalysts, though well known for a variety of carbonylation reactions, have not been explored for methanol carbonylation. The results presented in this thesis show that Pd-catalysts can give higher rates and selectivities at milder reaction conditions compared to Rh and Ir systems.

The results presented here show a great potential for developing industrially

competitive Pd-catalyst systems. The challenges for future studies are:

1) To develop a catalyst system in order to achieve higher rates at lower HI (or any iodide) and water concentration at still milder operating conditions. For this purpose, a suitable quaternary ammonium or phosphonium salt can be used to stabilize active palladium species in the reaction medium.

2) To develop a heterogeneous catalyst system using quaternizable polymer bound Pd-catalyst for methanol carbonylation reaction.

3) To develop a catalyst system free from iodide promoters, which can reduce the corrosion of reactor and downstream apparatus.

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CHAPTER 3

Carbonylation of Allyl Alcohol

3.1. Introduction

Carbonylation of alcohols has many industrial applications as discussed in Chapter 1. This route can be extended for synthesis of substituted carboxylic acid derivatives. For example, carbonylation of allyl alcohol can give β,γ-unsaturated carboxylic acid derivatives. The relevant literature on this subject is presented in Chapter 1. The published information is very limited and hence there is a need for further development of catalysts and processes in this area. Some important examples of this class of reaction are: synthesis of γ-lactums, synthesis of γ-butyrolactones, vinyl acetate ester synthesis etc.

Initial developments in the carbonylation of allyl alcohol used palladium catalysts (metallic palladium or palladium salts) in presence of alcohol as a solvent and needed severe operating conditions (353-403 K and 1.5-20 MPa) to obtain lower yields of unsaturated carboxylic acid esters of the corresponding alcohol (42-64%)[1]. Use of a ligand such as thiourea along with PdI_2 as a catalyst in methanol or methanol-dimethylacetamide mixture as a solvent was demonstrated to give good yields of β,γ-unsaturated carboxylic acid derivatives (40-88%) at milder reaction conditions (353 K, 5-10 MPa)[2]. Denis *et. al.*[3] have obtained 3-butenoic acid (60%) and allyl 3-butenoate (30%) using $PdCl_2$ as a catalyst along with quaternary ammonium or phosphonium halides at 353 K and 20 MPa. Addition of water to the reaction mixture was noted to be beneficial to achieve 100% yield of 3-butenoic acid.

Thus, the carbonylation of allyl alcohol is a convenient method to prepare 3-butenoic acid. Literature sites a scanty of information on this reaction, where the issues are severe reaction conditions and lack of understanding of the kinetics and mechanism. Under carbonylation conditions, allyl alcohol can also yield GBL as discussed in the Section 1.5.1, but this chapter presents a detail investigation on palladium-catalyzed carbonylation of allyl alcohol, selectively to 3-butenoic acid and allyl-3-butenoate as products, with the aim of improvements in catalytic activity and kinetic studies.

Effect of different solvents and promoters such as HCl, TsOH, LiCl and quaternary ammonium halides was studied including the effect of water. Use of a ligand in PdCl$_2$-BTEACl-TsOH catalyst system was found to decrease the reaction rate. Effect of PPh$_3$ concentration in this system was studied. The effect of reaction parameters, such as concentration of catalyst, BTEACl, TsOH, allyl alcohol and CO partial pressure was studied in a temperature range of 363-383 K in order to investigate the kinetics of this reaction.

3.2. Materials

PdCl$_2$ and Pd(OAc)$_2$ were purchased from Aldrich Chemicals (Milwaukee, WI). 56% Hydroiodic acid (HI) was purchased from Fluka Chemicals. Allyl alcohol, tertabutyl ammonium chloride (TBACl), tetrabutyl ammonium bromide (TBABr), tetrabutyl ammonium iodide (TBAI), TsOH, LiCl, triethyl amine, benzyl chloride, ammonium chloride, 37% HCl, tetrahydrofuran (THF), toluene, chlorobenzene, acetone, acetonitrile and PPh$_3$ were purchased from SD Fine Chemicals (Mumbai, India). Carbon monoxide (99.9% purity) was supplied by Matheson (Montgomeryville, PA). Allyl alcohol and other solvents were distilled prior to use. Water was used after distillation in laboratory.

3.2.1. Synthesis of PdCl$_2$(PPh$_3$)$_2$

PdCl$_2$(PPh$_3$)$_2$ was synthesized with little modifications in the literature procedure[4]. A solution of PdCl$_2$ (1 mmol) in dilute 25 ml of aqueous hydrochloric acid was slowly added to a stirred warm solution of PPh$_3$ (2.1 mmol) in ethanol (20 ml) and was stirred at ~333 K for 2 hrs. The bright yellow complex precipitated was filtered, washed with hot ethanol and dried in vacuum. The complex was re-crystallized from chloroform to obtain 95% yield of PdCl$_2$(PPh$_3$)$_2$ based on PdCl$_2$. Elemental Analysis was (w/w %): Calculated: C, 61.605; H, 4.308; Cl, 10.102. Found: C, 61.58; H, 4.31, Cl, 9.82.

3.2.2. Synthesis of PdBr$_2$(PPh$_3$)$_2$

PdBr$_2$(PPh$_3$)$_2$ was prepared using the procedure similar to PdCl$_2$(PPh$_3$)$_2$, with only difference that hydrobromic acid was used, instead of hydrochloric acid. The complex PdBr$_2$(PPh$_3$)$_2$ was re-crystallized from chloroform to obtain 93% yield. Elemental Analysis (%): Calculated: C, 54.68; H, 3.8; Br, 20.25. Found: C, 54.51; H, 3.53; Br, 21.29.

3.2.3. Synthesis of PdI$_2$(PPh$_3$)$_2$

Pd(OAc)$_2$ (1 mmol) was dissolved in 5 ml of acetone at room temperature to which, HI (0.25 ml of 56% HI in 10 ml of water) was added under stirring. This solution was added to PPh$_3$ (2.1 mmol in 10 ml of hot ethanol) solution at ~333K. Yellow brown precipitate obtained was washed with hot ethanol (50 ml), filtered and dried in vacuum. PdI$_2$(PPh$_3$)$_2$ obtained was re-crystallized in chloroform to obtain 90% yield. During re-crystallization chloroform was found entrapped in the crystal lattice of PdI$_2$(PPh$_3$)$_2$ as evidenced by single crystal X-ray structure, similar to that observed previously[5]. Elemental Analysis (%): Calculated: C, 48.87; H, 3.39; I, 28.73. Found: C, 49.51; H, 3.91; I, 29.21.

3.2.4. Synthesis of Benzyl Triethyl Ammonium Chloride (BTEACl)

Triethyl amine (1.5 mmol) was added to 1 mmol of benzyl chloride. White precipitate was obtained on stirring the reaction mixture at 363 K for 4 hours. 10 ml of THF was added to the reaction mixture and the contents were filtered. The precipitate obtained was washed twice with 10 ml of THF and dried under vacuum to obtain 85% yield (based on benzyl chloride) of pure BTEACl. Elemental Analysis (%): Calculated: C, 68.57; H, 9.67; N, 6.15; Cl, 15.60. Found: C, 68.98; H, 10.05; N, 6.55; Cl, 14.93.

3.2.5. Isolation and Characterization of Carbonylation Products

Reaction mixtures of a series of carbonylation reactions using PdCl$_2$-BTEACl-TsOH catalyst system (details of carbonylation reactions are given in Section 3.5) were

collected. The solvent and other low boiler components were removed on a *rotavac* at 313 K. The liquid obtained was dissolved in diethyl ether, while the catalyst components were extracted in water. The ether layer was treated with saturated Na_2CO_3 solution (till neutral pH). Aqueous layer was separated with a separating funnel and acidified with 0.1 N HCl, after which water was evaporated on a *rotavac* at 313 K leaving behind the liquid product 3-butenoic acid and NaCl. The product 3-butenoic acid was extracted in diethyl ether. The ether layer after Na_2CO_3 treatment was evaporated to obtain allyl 3-butenoate, which was purified by column chromatography with chloroform as a solvent.

3-butenoic acid and allyl-3-butenoate thus obtained were characterized using GCMS (consistent with NIST library), IR (consistent with reported in SDBS spectral library[6]) and ^{1}H NMR spectroscopy (see Appendix 1, Fig. A1.1-A1.6). These compounds were used as standards for quantitative analysis of the carbonylation reaction mixtures.

3.3. General Procedure for Carbonylation Reactions

All carbonylation reactions were carried out in a 50 ml Parr Autoclave made of Hastelloy-C-276. The reactor setup used is shown in Figure 2.1. In a typical experiment, weighed quantities of $PdCl_2$, BTEACl, TsOH and allyl alcohol were added to THF (solvent) so as to make the total volume 25 ml and charged in the autoclave. The autoclave was then purged once with nitrogen and thrice with carbon monoxide from individual reservoirs at room temperature and the contents were heated to 373 K, after which the autoclave was pressurized with carbon monoxide to 5.4 MPa with CO and the reaction was started at 16.66 Hz by switching on the stirrer. The reaction was carried out at constant pressure by feeding CO from the reservoir with the help of a constant pressure regulator. The progress of the reaction was monitored by CO consumption indicated by depletion of pressure in the reservoir of CO. Intermediate sampling was also done if required. The reaction was continued for a specific time, the contents cooled to room temperature and the gas vented off. The reactor was opened and a small amount of liquid phase was withdrawn for quantitative analysis for reactant and products using GC. Details of liquid phase analysis are given in the following section.

3.4. Analytical Methods

IR analysis was obtained on Bio Rad FTS 175C spectrophotometer. NMR was obtained from a Brucker- MSL300 and Brucker-AC200 machines. Elemental analysis of the synthesized compounds was carried out on a CHNS-O EA1108, Elemental analyzer of Carlo Erba Instruments, and the ion chromatography on a Waters Ion Chromatograph, having Waters 432 Conductivity detector, Waters 600S Controller and Waters 626 Pump. Liquid samples were analyzed on HP 6890 GC using HP-FFAP capillary column (Free fatty acid-modified polyethylene glycol phase, length 50 m, inner diameter 0.2 mm, film thickness 0.3 μm). Conditions of the quantitative analysis of liquid phase are given in Table 3.1. The quantitative analysis was obtained through a calibration curve. Conversion of allyl alcohol, selectivity to 3-butenoic acid and allyl-3-butenoate, TON and TOF were calculated according to the formulae given in equations 3.1-3.5.

$$\%\text{Conversion} = \frac{100 \times [(\text{Initial Mol}_{\text{allyl alc.}})-(\text{Final Mol}_{\text{allyl alc.}})]}{(\text{Initial Mol}_{\text{allyl alc.}})} \qquad (3.1)$$

$$\%\text{Selectivity}_{\text{3-butenoic acid}} = \frac{100 \times (\text{Final Mol}_{\text{3-butenoic acid}})}{[(\text{Initial Mol}_{\text{allyl alc.}})-(\text{Final Mol}_{\text{allyl alc.}})]} \qquad (3.2)$$

$$\%\text{Selectivity}_{\text{allyl-3-butenoate}} = \frac{100 \times 2(\text{Final Mol}_{\text{allyl-3-butenoate}})}{[(\text{Initial Mol}_{\text{allyl alc.}})-(\text{Final Mol}_{\text{allyl alc.}})]} \qquad (3.3)$$

$$\text{TON} = \frac{\text{Moles of carbonylation products formed}}{\text{Moles of catalyst charged}} \qquad (3.4)$$

$$\text{TOF} = \frac{\text{Moles of carbonylation products formed}}{\text{Moles of catalyst charged} \times \text{time}} \qquad (3.5)$$

Table 3.1. Conditions used for liquid phase GC analysis

	Conditions
Inlet (split)	Split ratio = 1:100, 523 K
Column (FFAP)	323-483K (programmed), 0.02-0.2 MPa (programmed)
Detector (FID)	523K
Carrier gas (He)	25 ml/min

3.5. Results and Discussion

Results obtained in allyl alcohol carbonylation reaction using palladium catalysts are discussed in this section. Effect of different solvents, catalyst precursors and promoters was studied in order to improve the catalytic activity. Effect of different reaction parameters on the rate of reaction was investigated at three different temperatures in the range of 363-393 K. Kinetics of this reaction has been investigated and mechanism proposed.
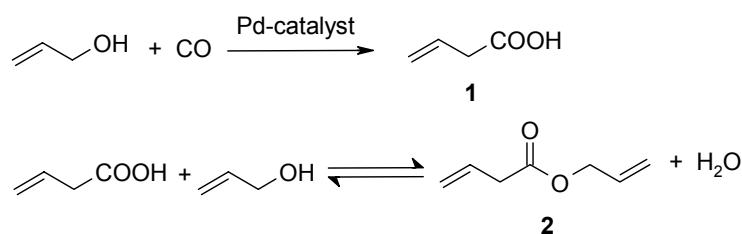
Scheme 3.1. Carbonylation of allyl alcohol to 3-butenoic acid and allyl-3-butenoate

For this purpose, initial experiments were carried out using PdCl$_2$-BTEACl-TsOH catalyst system to identify the products formed. A typical concentration-time profile for 373 K is shown in Fig. 3.1. The main products formed were 3-butenoic acid (**1**) and allyl-3-butenoate (**2**) (Scheme 3.1) as identified by GC and GCMS. GC analysis of the intermediate samples withdrawn from the specific reaction (reaction as presented in Fig. 3.1) showed the mass balance of liquid components, in the range of 93-99%. The consumption of CO was also found to be in good agreement with the carbonylation products formed according to the stoichiometric reaction as shown in Scheme 3.1, giving the balance of CO, in the range of 94-100%. These products (**1** and **2**) were separated and characterized as described in Section 3.2.5 to obtain pure standards. With this experiment

as a benchmark, the effect of different parameters was investigated.
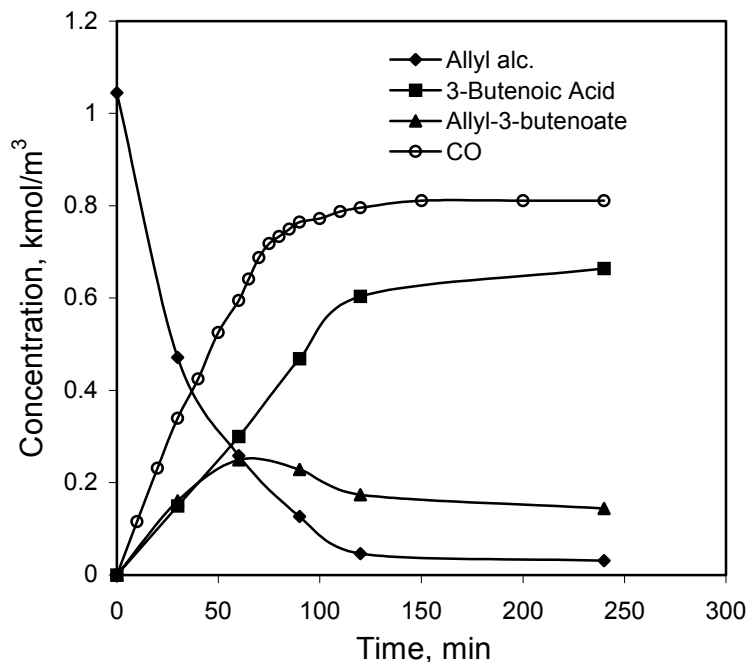
Fig. 3.1. Concentration-time Profile for allyl alcohol carbonylation reaction

Reaction Conditions: PdCl$_2$, 2 × 10^{-3} kmol/m^3; BTEACl, 4 × 10^{-2} kmol/m^3; TsOH, 4×10^{-2} kmol/m^3; Allyl alcohol, 1 kmol/m^3; Solvent, THF; Total Volume, 2.5 × 10^{-5} m^3; Temperature, 373K; P$_{CO}$, 5.4 MPa; Agitation speed, 16.66 Hz

3.5.1. Effect of Chloride Promoters

PdCl$_2$-BTEACl-TsOH catalyst system (benchmark reaction Table 3.2, Run # 10) gave 97% conversion of allyl alcohol with the selectivities of 65.52% and 28.48% to 3-butenoic acid and allyl-3-butenaote respectively. Different other chloride promoters were screened along with palladium catalysts for carbonylation of allyl alcohol in presence and absence of TsOH as a promoter. Addition of water was found to have substantial effect on the catalyst activity (Table 3.2). When 37%HCl was used as a promoter along with PdCl$_2$ as a catalyst, it gave only 61.97% conversion of allyl alcohol in 5.5 hours with a TOF of 46 h^{-1}, whereas TBACl as a promoter increased the conversion (71.57%) level as well as TOF (Table 3.2, run # 1 and 3). Addition of TsOH to PdCl$_2$-TBACl system increased the activity giving a TOF of 90 h^{-1}, which was further increased by addition of

4% of water achieving the TOF as high as 114 h^{-1} (Fig. 3.2). Thus, PdCl$_2$-LiCl-TsOH catalyst system was found to be more active than PdCl$_2$-HCl system (Table 3.2, run # 1 and 3). Increase in conversion levels was found to increase the selectivity to 3-butenoic acid, as per the equilibrium reaction:

$$\text{\ \ \ \ \ \ COOH} + \text{\ \ \ \ \ OH} \rightleftharpoons \text{(allyl 3-butenoate)} + H_2O \qquad (3.6)$$
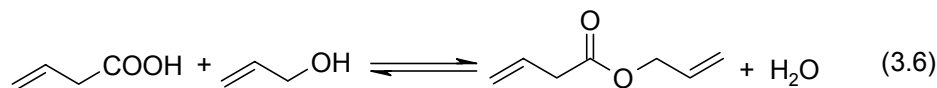
Similarly, the reactions with addition of water to PdCl$_2$-TBACl and PdCl$_2$-TBACl-TsOH systems showed higher selectivity to 3-butenoic acid than allyl-3-

Table 3.2. Effect of chloride promoters and water in allyl alcohol carbonylation reaction[a]

No.	Promoters	Time, h	Conversion, %	Selectivity, % A	B	TOF, h^{-1}
1	HCl	5.5	61.97	48.01	41.90	46
[b]2	LiCl	4	74.42	21.14	73.81	55
3	TBACl	4.5	71.57	44.70	42.69	58
[c]4	TBACl	4	52.22	61.37	35.23	77
[b]5	TBACl	4	80.61	45.58	50.38	90
[bc]6	TBACl	4	91.24	86.35	10.74	114
[bd]7	TBACl	4	81.33	44.58	49.35	88
[be]8	TBACl	4	77.80	41.41	52.66	86
[bf]9	TBACl	4	77.30	43.88	50.87	85
[b]10	BTEACl	4	97.99	65.52	28.48	99

[a]*Reaction Conditions: PdCl$_2$, 2 × 10^{-3} kmol/m^3; Promoter, 4 × 10^{-2} kmol/m^3; Allyl alcohol, 1 kmol/m^3; Solvent, THF; Total Volume, 2.5 × 10^{-5} m^3; Temperature, 373K; P$_{CO}$, 5.54 MPa; A, 3-butenoic acid; B, Allyl-3-butenoate;* [b]*TsOH, 4 × 10^{-2} kmol/m^3;* [c]*H$_2$O, 4% (V/V);* [d]*PdCl$_2$(PPh$_3$)$_2$ instead of PdCl$_2$;* [e]*PdBr$_2$(PPh$_3$)$_2$ instead of PdCl$_2$;* [f]*PdI$_2$(PPh$_3$)$_2$ instead of PdCl$_2$*

butenoate (Table 3.2, run # 3, 4 and 6). Other catalyst precursors such as PdCl$_2$(PPh$_3$)$_2$, PdBr$_2$(PPh$_3$)$_2$, PdI$_2$(PPh$_3$)$_2$ were tested for this reaction, which showed a comparable activity for carbonylation of allyl alcohol, when used in presence of TBACl and TsOH as

promoters (Table 3.2, run # 7, 8 and 9 respectively). The chloride promoters (in presence of TsOH) varied the activity of $PdCl_2$ showing a trend as: BTEACl>TBACl>LiCl>HCl. As bulky quaternary ammonium ion ($BTEA^+$) stabilizes the active palladium species ($PdCl_3CO^-$) formed at carbonylation reaction conditions, higher activity of palladium catalyst in presence of BTEACl promoter was achieved (see Sections 3.5.6.2.3 and 3.5.6.3.2). Thus, a palladium catalyst, in presence of a quaternary ammonium chloride and TsOH as promoters gave high activity for carbonylation of allyl alcohol. Further, the addition of water to this catalyst system increased the selectivity to 3-butenoic acid. The highest activity (91.24% conversion with TOF of 114 h^{-1}) was achieved using the catalyst system, $PdCl_2$-TBACl-TsOH-H_2O.
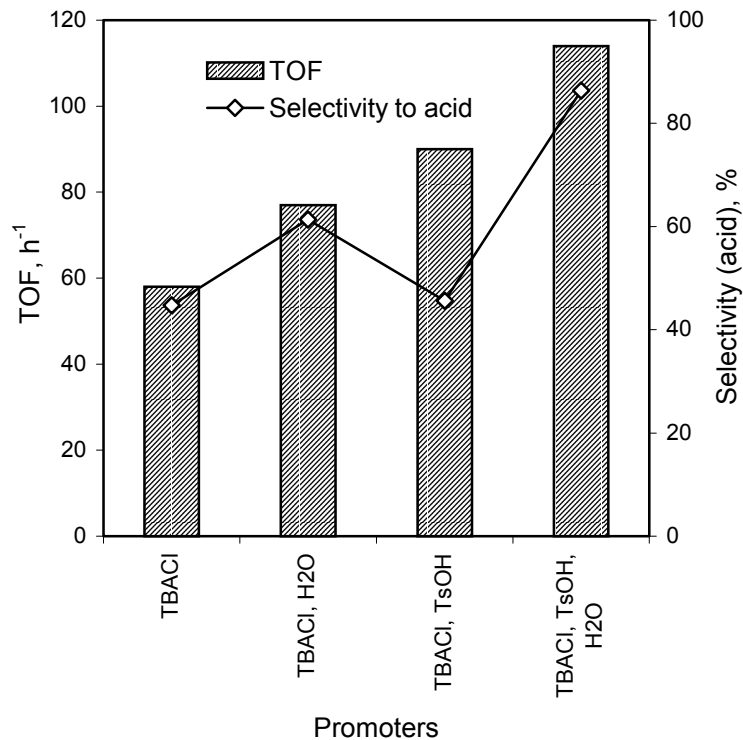
Fig. 3.2. Effect of water and TsOH in TBACl promoted $PdCl_2$ catalyzed carbonylation of allyl alcohol

Reaction Conditions: $PdCl_2$, 2×10^{-3} kmol/m^3; TBACl, 4×10^{-2} kmol/m^3; TsOH, 4×10^{-2} kmol/m^3 (if specified); H_2O, 4% (V/V) (if specified); Allyl alcohol, 1 kmol/m^3; Solvent, THF; Total Volume, 2.5×10^{-5} m^3; Temperature, 373 K; P_{CO}, 5.54 MPa; Agitation Speed, 16.66 Hz

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3.5.2. Effect of Quaternary Halide Promoters in Presence of TsOH

Though, quaternary ammonium chloride and TsOH formed a good combination, as promoters to give high activity, when used in the presence of $PdCl_2$, other quaternary ammonium halides were comparatively less active. It was also observed that the quaternary ammonium chloride promoters are better than alkali metal chloride (LiCl) promoter (Fig. 3.3). Using different quaternary ammonium halide (TBAX with X = Cl, Br or I) promoters, the catalytic activity varied with a trend as: Cl>Br>>I (Table 3.3, run # 1, 2 and 3). TBAI as a promoter along with TsOH and $PdCl_2$ showed no activity in carbonylation of allyl alcohol at the given reaction conditions. This trend in activity of halide promoters was found in reverse order to that observed in the carbonylation of other alcohols (methanol, ethanol etc). This contradictory observation shows that the mechanism of carbonylation of allyl alcohol follows a path, which is different than observed for the carbonylation of other alcohols. The presence of $PdCl_2$ and quaternary ammonium halide in the reaction mixture forms $Pd_2X_6^{2-}$ species, which subsequently forms $PdCl_3CO^-$ in presence of CO, which can be proposed to be an active catalytic species for carbonylation of allyl alcohol (see Section 3.5.6.3.2)[7]. The trend observed with variation of quaternary ammonium halide promoters (TBAX) shows the ease of formation of $PdCl_3CO^- > PdBr_3CO^- > PdI_3CO^-$, which is consistent with the earlier observations[7]. Further, this trend in the catalytic activity can be correlated to the bond strength of Pd-X. Increase in the catalytic activity was observed with a decrease in bond strength of Pd-X in PdX_3CO^- formed. Mechanism of carbonylation of allyl alcohol proceeds through hydroxy-palladium intermediate (see Section 3.5.6.3.2), formation of which involves dissociation of halide from palladium center of PdX_3CO^-. Lower bond strength of Pd-Cl in $PdCl_3CO^-$ allows the dissociation of Cl from palladium center, which favors the formation hydroxy-palladium species. Thus, the trend in catalytic activity with various quaternary ammonium halide promoters suggests that the mechanism in carbonylation of allyl alcohol proceeds through hydroxy-palladium intermediate, which follows a different path than the carbonylation of other alcohols. Further, the stability of $PdCl_3CO^-$ species also decides the activity of the catalyst. Bulky quaternary ammonium ion stabilizes the palladium cation ($PdCl_3CO^-$) in the reaction medium to give better

activity, explaining the activity trend: BTEACl>TBACl>NH$_4$Cl (Table 3.3, run # 1, 4 and 5).

Table 3.3. Effect of quaternary halides and alkali metal halides in presence of TsOH in allyl alcohol carbonylation reaction[a]

No.	Promoters	Conversion, %	Selectivity, %		TOF, h^{-1}
			A	B	
1	TBACl	80.61	45.58	50.38	90
2	TBABr	39.25	5.21	0	3
3	TBAI	4.00	0	0	[b]0
4	NH$_4$Cl	17.25	16.76	0	3
5	BTEACl	97.99	65.52	28.48	99
6	LiCl	74.42	21.14	73.81	55

[a]Reaction Conditions: PdCl$_2$, 2 × 10^{-3} kmol/m^3; Promoter, 4 × 10^{-2} kmol/m^3; TsOH, 4 × 10^{-2} kmol/m^3; Allyl alcohol, 1 kmol/m^3; Solvent, THF; Total Volume, 2.5 × 10^{-5} m^3; Temperature, 373K; P$_{CO}$, 5.54 MPa; Time, 4 h; Agitation Speed, 16.66 Hz; [b]No CO absorption was observed, no carbonylation product was detected in GC
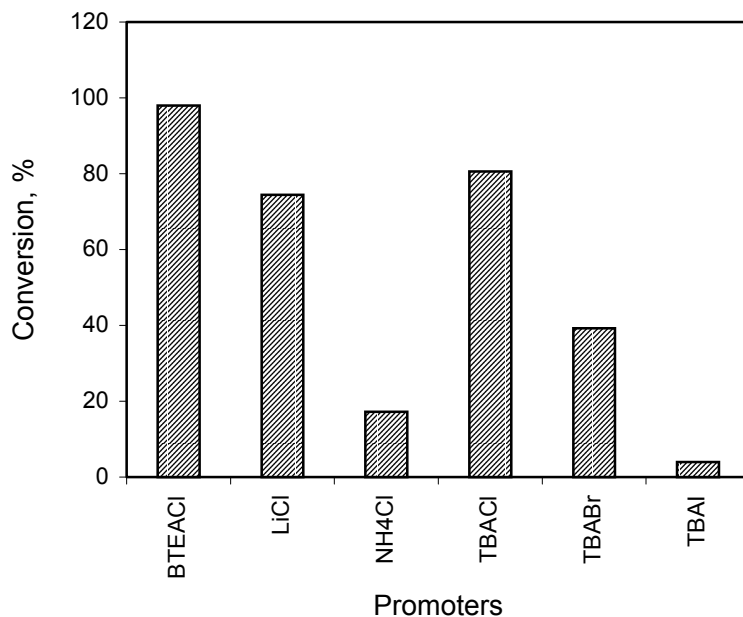
Fig. 3.3. Effect of promoters

Reaction Conditions: As in Table 3.3

3.5.3. Effect of Temperature

Increase in temperature in the carbonylation of allyl alcohol using $PdCl_2$-BTEACl-TsOH catalyst system increased the catalytic activity and conversion level. Maximum conversion (99%) was obtained in 1.5 hours with a high TOF (256 h^{-1}) at 393 K (Table 3.4). Increase in the conversion was again found to be beneficial for higher selectivity to 3-butenoic acid according to equation 3.6 (Fig. 3.4).

Table 3.4. Effect of temperature in $PdCl_2$-BTEACl-TsOH catalyzed carbonylation of allyl alcohol^a

Run No.	Temperature, K	Conversion, %	Selectivity, %		TOF, h^{-1}
			A	B	
1	373	84.66	49.91	47.01	229
2	383	95.61	54.09	42.76	240
3	393	99.00	61.79	28.12	256

^{a}*Reaction Conditions*: *PdCl$_2$, 2 × 10^{-3} kmol/m^3; TEBACl, 4 × 10^{-2} kmol/m^3; TsOH, 4 × 10^{-2} kmol/m^3; Allyl alcohol, 1 kmol/m^3; Solvent, THF; Total Volume, 2.5 × 10^{-5} m^3; Time, 1.5 hr; P$_{CO}$, 5.51 MPa; A, 3-butenoic acid; B, allyl-3-butenoate*
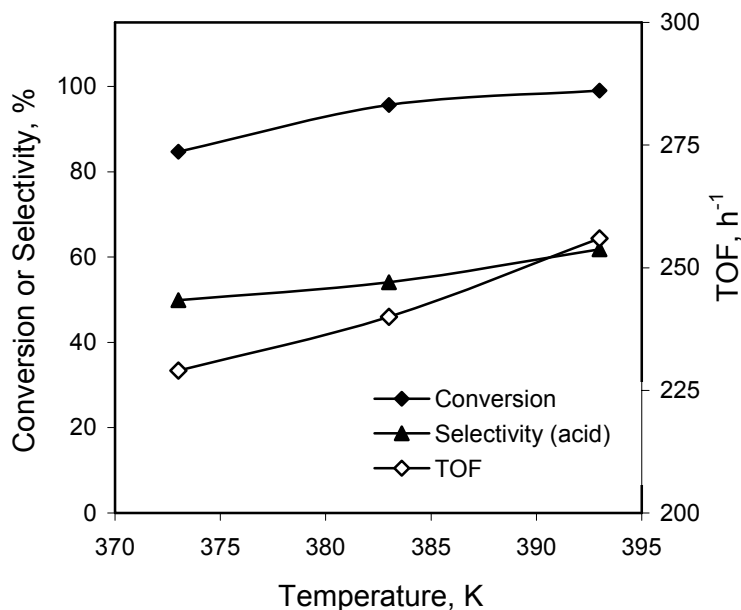
Fig. 3.4. Effect of temperature on conversion, selectivity and activity of $PdCl_2$-BTEACl-TsOH catalyst system
Reaction conditions: *As in Table 3.4*

3.5.4. Effect of PPh$_3$ Concentration in PdCl$_2$-TEBACl-TsOH Catalyst System

To examine the effect of a ligand in the carbonylation of allyl alcohol, a few reactions were carried out with various concentrations of PPh$_3$ using PdCl$_2$-BTEACl-TsOH catalyst system (Table 3.5). The use of PPh$_3$ as a ligand in PdCl$_2$-BTEACl-TsOH catalyst system showed negative effect on the catalytic activity. The use of PPh$_3$ up to 2 equivalents to palladium showed a marginal decrease in the catalytic activity (TOF decreased from 99 to 87 h^{-1}), whereas the effect was much significant at higher PPh$_3$ concentration. As the ratio of PPh$_3$ to Pd concentration was increased to 4, the catalytic activity was decreased to a TOF of 26 h^{-1} with decrease in conversion level from 97.99 to 43%. This effect was due to the strong coordinating PPh$_3$ ligand, blocking active sites of palladium center, making it inactive for the carbonylation reaction. As weakly coordinating ligand favors the formation of hydroxy-palladium species (an active catalytic intermediate for carbonylation of allyl alcohol) (see Section 3.5.2), strong coordinating ligand (PPh$_3$) perhaps prevents the formation of hydroxy-palladium intermediate and decreases the catalytic activity. Thus, the use of a ligand (PPh$_3$) for allyl alcohol carbonylation reaction along with PdCl$_2$-BTEACl-TsOH catalyst system showed significant decrease in the catalytic activity even at a PPh$_3$:Pd ratio of 4.

Table 3.5. Effect of PPh$_3$ concentration in allyl alcohol carbonylation using PdCl$_2$-BTEACl-TsOH catalyst system[a]

Run No.	PPh$_3$/Pd ratio	Conversion, %	Selectivity, %		TOF, h^{-1}
			A	B	
1	—	97.99	65.52	28.48	99
2	1	95.09	50.84	44.53	88
3	2	95.10	49.80	46.55	87
4	4	43.00	18.11	68.43	26

[a]*Reaction conditions: PdCl$_2$, 2 × 10^{-3} kmol/m^3; TEBACl, 4 × 10^{-2} kmol/m^3; TsOH, 4 × 10^{-2} kmol/m^3; Allyl alcohol, 1 kmol/m^3; Solvent, THF; Total Volume, 2.5 × 10^{-5} m^3; Time, 4 hr, Temperature, 373K; P$_{CO}$, 5.4 MPa; Agitation Speed, 16.66 Hz; A, 3-butenoic acid; B, allyl-3-butenoate*

3.5.5. Effect of Solvents

Solvents with various polarities were tested for carbonylation of allyl alcohol using PdCl$_2$-BTEACl-TsOH catalyst system. Dielectric constant of a solvent was

Table 3.6. Effect of dielectric constants of solvents on the rate of allyl alcohol carbonylation reaction[a]

Run No.	Solvent (Dielectric constant)	Conversion, %	Selectivity, %		TOF, h^{-1}
			A	B	
1	Toluene (2.4)	74.93	25.01	70.49	56
2	Chlorobenzene (5.6)	78.28	29.80	61.01	60
3	THF (7.5)	97.99	65.52	28.48	99
4	Acetone (20.7)	99.19	68.86	20.45	98
5	Acetonitrile (36.6)	79.44	23.56	71.69	58

[a]*Reaction conditions: PdCl$_2$, 2 × 10^{-3} kmol/m^3; TEBACl, 4 × 10^{-2} kmol/m^3; TsOH, 4 × 10^{-2} kmol/m^3; Allyl alcohol, 1 kmol/m^3; Total Volume, 2.5 × 10^{-5} m^3; Temperature, 373K; P$_{CO}$, 54 MPa; Agitation Speed, 16.66 Hz; A, 3-butenoic acid; B, allyl-3-butenoate*
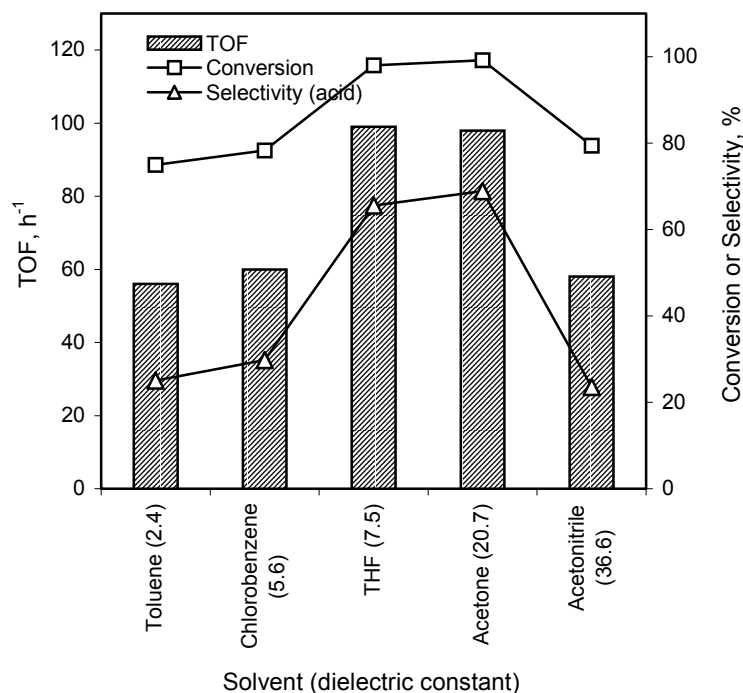

Fig. 3.5. Effect of solvent polarity on catalyst activity
Reaction conditions: As in table 3.6

considered as a measure of polarity. Increase in catalytic activity was observed with increasing polarity of a solvent. This trend in activity can be explained on the basis of stability of active cationic palladium species, $PdCl_3CO^-$ formed in the reaction mixture as discussed in the Sections 3.5.1 and 3.5.2. The polarity of a solvent plays an important role in stabilizing the active Pd-species in the reaction medium, thus increasing the catalytic activity in more polar solvents. According to this analogy, acetonitrile should give higher activity than acetone, as it is more polar than acetone, but the activity of $PdCl_2$-BTEACl-TsOH catalyst system was observed to be lower than acetone at the same reaction conditions. Although, acetonitrile is more polar than acetone, coordinating ability and high concentration of acetonitrile dominate the effect of its polarity, which decreases the catalytic activity. Thus, acetonitrile can act as a ligand to palladium, which decreases the catalytic activity as described in Section 3.5.4. Maximum conversion (99.19%) of allyl alcohol with maximum activity (98 h^{-1} TOF) was obtained, when polar solvent (acetone) was used, whereas less polar solvent (toluene) gave lesser activity (56 h^{-1} TOF). Effect of different solvents on allyl alcohol conversion, selectivity to 3-butenoic acid and catalytic activity is summarized in Table 3.6 and Figure 3.5.

3.5.6. Kinetics of Allyl Alcohol Carbonylation Reaction

A kinetic study is important in optimising the reaction conditions and reaction parameters. As a very scanty of information is available on carbonylation of allyl alcohol, kinetic study is useful to understand the behaviour of the components present in the reaction system. Further, it is useful to understand the mechanism of a reaction. Kinetics of allyl alcohol carbonylation reaction was investigated using $PdCl_2$-BTEACl-TsOH catalyst system. Effect of various reaction parameters such as concentration of catalyst, allyl alcohol, BTEACl, TsOH and CO partial pressure was studied at three different temperatures, in the range of 363 to 383K. The range of conditions used for this study is tabulated in Table 3.7. Different empirical rate models were considered and a suitable rate equation was proposed for carbonylation of allyl alcohol. Different kinetic parameters were evaluated. Reaction mechanism was also proposed.

Table 3.7. Range of conditions used for kinetic study

No.	Parameter	Range of conditions
1	PdCl$_2$, kmol/m^3	$(1 \times 10^{-3}) - (6 \times 10^{-3})$
2	BTEACl, kmol/m^3	$(20 \times 10^{-3}) - (80 \times 10^{-3})$
3	TsOH, kmol/m^3	$(10 \times 10^{-3}) - (80 \times 10^{-3})$
4	Allyl alcohol, kmol/m^3	$0.3 - 1.4$
6	P$_{CO}$, MPa	$1.37 - 9.65$
7	Temperature, K	$363 - 383$
8	Agitation speed, Hz	$6.66 - 20$

3.5.6.1. Solubility Data

Concentration of a reactive component plays an important role in the kinetics of a reaction. For interpretation of kinetic data of a gas-liquid reaction, knowledge of concentration of the gaseous reactants in the reaction solvent or reaction mixture is essential, which can be achieved by solubility measurements at the reaction conditions. All of the kinetic runs (except allyl alcohol concentration effect) were started with 7% allyl alcohol in THF. Solubility of CO in 7 weight % of allyl alcohol in THF was determined experimentally at 363, 373 and 383 K using a method described by Purwanto et. al.[8] The solubility measurements were done in the same 50 ml Parr autoclave used for kinetic study, as shown in Fig. 2.1, except that the deep tube was removed prior to these measurements.

In a typical experiment of CO solubility measurement, a known volume of 7% allyl alcohol in THF was charged in the reactor. The contents were flushed with nitrogen and were heated to the desired temperature. After the thermal equilibrium was attained, the void space in the reactor was pressurised with CO to the required level. The contents were then stirred for about ten minutes at 16.66 Hz to equilibrate the liquid phase with the solute gas. The change in pressure in the autoclave was recorded as a function of time till it remained constant, indicating saturation of the liquid phase with the solute gas at that set of conditions. From the initial and final pressure readings, the solubility was calculated in mole fraction as per equation 3.7.

$$X_a = \frac{(P_i - P_f)V_g M_s}{RTV_L \rho_s} \qquad (3.7)$$

Where P_i and P_f are the initial and final pressure readings, X_a represents the mole fraction of CO in the liquid phase at the partial pressure of the solute gas prevailing at P_f (final pressure reading), V_g and V_L are the volumes of the gas and liquid phases respectively, R is the gas constant, T is the temperature, M_s is the molecular weight of the solvent and ρ_s is the molar density of the liquid.

The Henry's constant, H_e was calculated according to the equation 3.8. Henry's constant calculated for 363, 373 and 383K are given in Table 3.8.

$$H_e = \frac{X_a}{P_f} \qquad (3.8)$$

Table 3.8. Henry's constant for 7% allyl alcohol in THF at different temperatures

Temperature, K	363	373	383
Henry's constant $\times 10^3$, kmol/m^3/MPa	6.207	6.742	7.345

The saturation solubility (concentration) of CO in liquid phase (A*) was calculated using the equation:

$$A^* = P_{CO} \times H_e \qquad (3.9)$$

3.5.6.2. Parametric Effects

The effect of different parameters such as catalyst loading, allyl alcohol, BTEACl, TsOH concentrations and CO partial pressure was carried out at three different temperatures in the range of 363-383 K and discussed in this section.

In order to investigate the mass balance of all the components, a reaction was carried out with intermediate sampling. A typical concentration-time profile of this reaction at 373 K is shown in Fig. 3.1. It was observed that allyl alcohol concentration was decreased as a function of time, whereas 3-butenoic acid was increased. As allyl

alcohol concentration was decreased to 0.25 kmol/m^3, the concentration of allyl-3-butenoate started decreasing, which can be explained by the equilibrium reaction as shown in equation 3.6.

In the concentration-time profile, analysis of liquid phase samples showed the balance of liquid components in the range of 93-99%. Carbonylation products formed, accounted the total CO consumed with 94-100% balance at the respective time meaning that the CO absorbed in the reaction doesn't form any byproduct. So for the kinetic studies, the initial rates were calculated based on CO consumption. The rates obtained were preferentially initial rates for 15-20% conversion allyl alcohol.
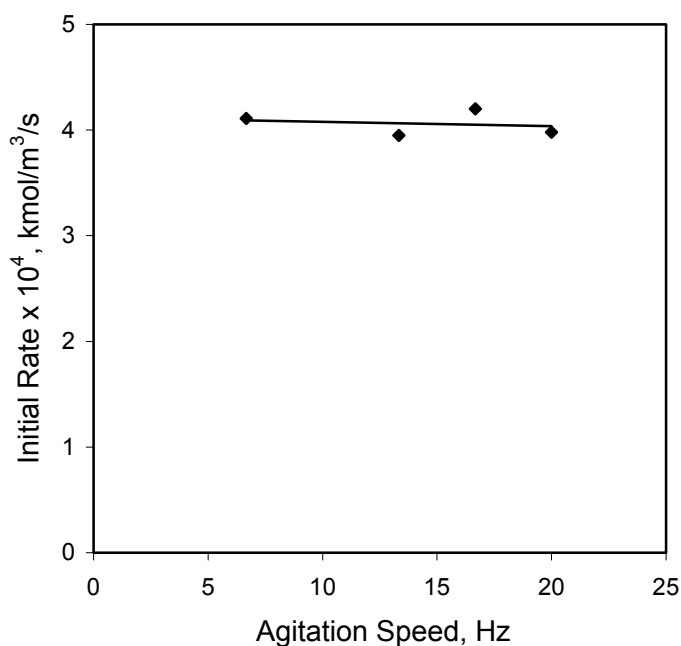
3.5.6.2.1. Effect of Agitation Speed

Fig. 3.6. Effect agitation speed on the rate of CO absorption in allyl alcohol carbonylation

Reaction Conditions: _PdCl$_2$, 2 × 10^{-3} kmol/m^3; TEBACl, 4 × 10^{-2} kmol/m^3; TsOH, 4 × 10^{-2} kmol/m^3; Allyl alcohol, 1 kmol/m^3; Solvent, THF; Total Volume, 2.5 × 10^{-5} m^3; P$_{CO}$, 5.4 MPa_

Few experiments were carried out using $PdCl_2$-BTEACl-TsOH catalyst system at various agitation speeds to ensure that the reaction occurs in kinetic regime. Highest catalyst loading at highest temperature (used for kinetic study) was preferred to study this effect, as gas-liquid mass transfer problem generally arises at high catalyst loading in a reaction. Allyl alcohol carbonylation reaction studied here was found to be free from mass transfer barrier achieving the same rates of reaction at various agitation speeds as shown in Figure 3.6. Further parametric effects were carried out at 16.66 Hz where the reaction was perfectly under kinetic control.

3.5.6.2.2. Effect of Catalyst Loading

Effect of catalyst loading was carried at three different temperatures in the range of 363-383K, which is shown in Figure 3.7. Increase in the amount of $PdCl_2$ in the reaction system increased the rate of reaction, with a little deviation from linearity. This is due to the possible formation of different palladium species such as $PdCl_2(CO)_2$[7], $PdCl_4^{2-}$, $Pd_2Cl_6^{2-}$ and $(\eta 3\text{-allyl})_2PdCl_2$,[9] in the reaction mixture (see Sections 3.5.6.2.3, 3.5.6.2.5 and 3.5.6.3.2) under the reaction conditions. As the formation of active palladium-carbonyl species $(PdCl_3CO^-)$[7] is very much favored at the reaction condition, it is proposed to be an active catalytic intermediate for the carbonylation of allyl alcohol (also see Sections 3.5.2 and 3.5.6.3.2). Andreine *et. al.*[7] have observed the equilibrium between the species $PdCl_4^{2-}$, $PdCl_2(CO)_2$ and $PdCl_3CO^-$. So the species $PdCl_4^{2-}$ and $PdCl_2(CO)_2$ formed in the reaction mixture may be considered as active catalysts. Synthesis of $(\eta 3\text{-allyl})_2PdCl_2$ involves allyl chloride and CO atmosphere as reported elsewhere[9], which doesn't produce any Pd-carbonyl species even in presence of CO. So the species can be considered as an inactive for the carbonylation of allyl alcohol. Thus the formation of different palladium species in the reaction mixture under the reaction condition gives rates of the reaction in variable magnitude, which deviates the linearity of the rate of reaction with catalyst concentration.
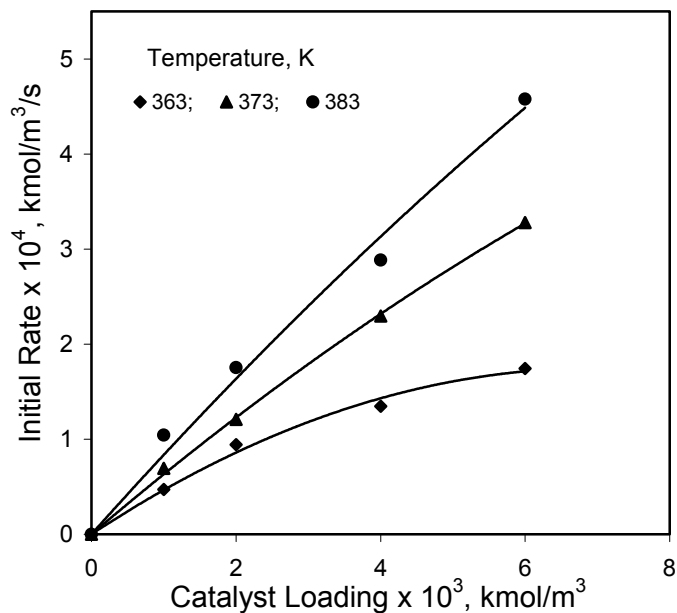
Fig. 3.7. Effect of catalyst loading on the rate of CO absorption in allyl alcohol carbonylation

Reaction Conditions: TEBACl, 4 × 10⁻² kmol/m³; TsOH, 4 × 10⁻² kmol/m³; Allyl alcohol, 1 kmol/m³; Solvent, THF; Total Volume, 2.5 × 10⁻⁵ m³; P_{CO}, 5.4 MPa; Agitation Speed, 16.66 Hz.

3.5.6.2.3. Effect of BTEACl Concentration

Marginal increase in the rate of reaction was noted with increase in temperature, when 2×10^{-2} kmol/m³ of BTEACl were used as a promoter, whereas at higher concentration of BTEACl ($>4 \times 10^{-2}$ kmol/m³), the rise in the reaction rate was much significant. Increase in temperature also showed the increase in reaction rates. BTEACl in presence of $PdCl_2$ formed a chloro-bridged-dimeric palladium species, $(BTEA)_2Pd_2Cl_6$ (this compound was isolated from the carbonylation reaction mixtures and characterized using elemental analysis, %C= 39.00 (38.56), %H= 5.56 (5.44), %N= 3.21 (3.46), %Cl= 26.53 (26.33)). $Pd_2Cl_6^{2-}$ thus formed, can generate catalytically active species $PdCl_3CO^-$, in presence of CO, at reaction conditions[7]. Thus, increase in BTEACl concentration helps to stabilize the active catalytic species $PdCl_3CO^-$ (see Section 3.5.2), in the reaction mixture, which increases the reaction rate. Effect of BTEACl concentration on the
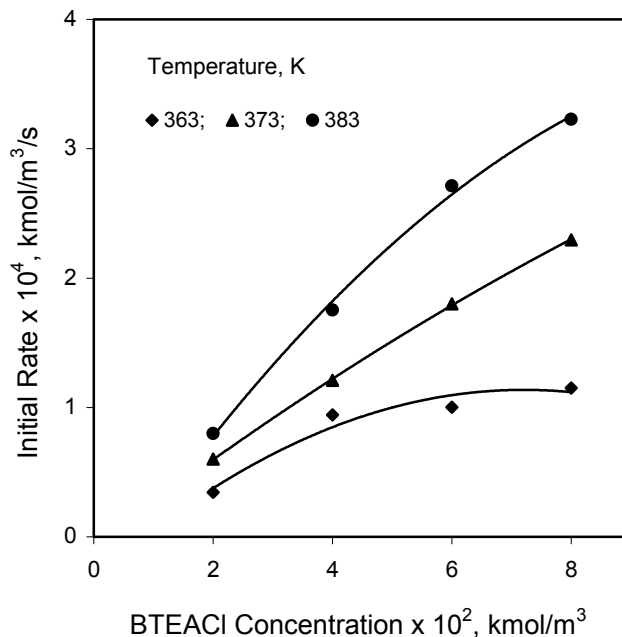
reaction rate is shown in Figure 3.8.

Fig. 3.8. Effect of promoter (BTEACl) concentration on the rate of CO absorption in allyl alcohol carbonylation

Reaction Conditions: $PdCl_2$, 2×10^{-3} kmol/m³; TsOH, 4×10^{-2} kmol/m³; Allyl alcohol, 1 kmol/m³; Solvent, THF; Total Volume, 2.5×10^{-5} m³; P_{CO}, 5.4 MPa; Agitation Speed: 16.66 Hz

3.5.6.2.4. Effect of Allyl Alcohol Concentration

Initial rates were obtained for various allyl concentrations in carbonylation reaction in the range of 0.3 to 1.4 kmol/m³. Increase in the concentration of allyl alcohol increased the rate of reaction linearly at low concentration (1 kmol/m³), beyond which it was found to be independent of allyl alcohol concentration. Increase in temperature also increased the rate of reaction. The effect of allyl alcohol concentration on initial rate of carbonylation reaction is shown in Figure 3.9.
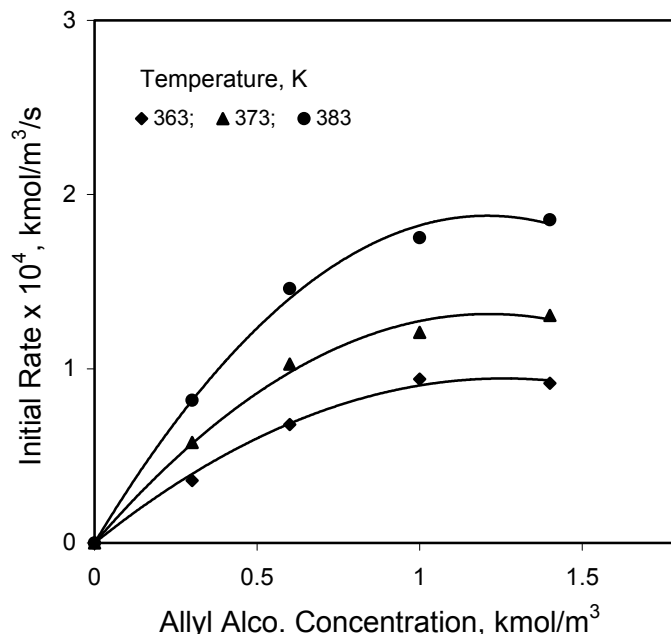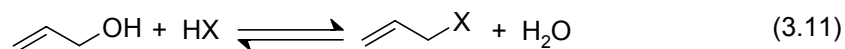
Fig. 3.9. Effect of allyl alcohol concentration on the rate of CO absorption in allyl alcohol carbonylation

Reaction Conditions: PdCl$_2$, 2 × 10^{-3} kmol/m^3; TEBACl, 4 × 10^{-2} kmol/m^3; TsOH, 4×10^{-2} kmol/m^3; Solvent, THF; Total Volume, 2.5 × 10^{-5} m^3; P$_{CO}$, 5.4 MPa; Agitation Speed, 16.66 Hz

3.5.6.2.5. Effect of TsOH Concentration

Increase in the TsOH concentration showed increase in the reaction rates at lower concentration (< 0.02 kmol/m^3), beyond which decrease in the reaction rate was observed

$$NR_4X + TsOH \rightleftharpoons NR_4OTs + HX \qquad (3.10)$$

$$\diagup\!\!\!\diagdown OH + HX \rightleftharpoons \diagup\!\!\!\diagdown X + H_2O \qquad (3.11)$$

with increasing concentration of TsOH. Such a trend in the rae variation was consistent at all temperatures studied (Fig. 3.10). TsOH in presence of BTEACl forms HCl in the reaction medium as per equilibrium reaction shown in equation 3.10. HCl thus formed, generates allyl chloride by reaction with allyl alcohol charged, which successively generates an inactive palladium species[9] (η3-allyl)$_2$PdCl$_2$ in presence of CO and PdCl$_2$. Increase in the concentration of TsOH showed increase in the formation of allyl chloride

in the reaction mixtures, as evidenced by GC analysis of the set of reactions with various TsOH concentrations. For example, increasing the TsOH concentration from 0.01 to 0.02 kmol/m^3 increased the formation of allyl chloride from 2.33% to 5.98%. Thus, higher concentration of TsOH increased the formation of allyl chloride, which successively generated higher amount of inactive palladium species, (η3-allyl)$_2$PdCl$_2$. This observation also suggests that the reaction doesn't proceed through allyl chloride oxidative addition at the reaction conditions used. Gupte et. al[10] have also reported that the carbonylation of allyl chloride to 3-butenoic acid proceeds smoothly in highly basic medium. Further the authors have reported that in the absence of any base, no carbonylation of allyl chloride was observed. Thus, the acidic conditions (as used here) do not favor the carbonylation of allyl chloride, indicating that the carbonylation of allyl alcohol doesn't proceed through allyl chloride oxidative addition, particularly under acidic conditions.
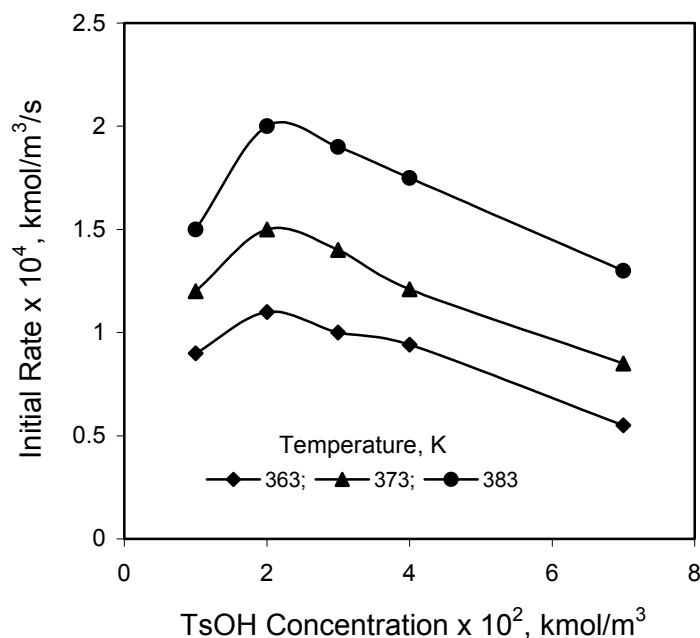

Fig. 3.10. Effect of TsOH concentration on the rate of CO absorption in allyl alcohol carbonylation

Reaction Conditions: PdCl$_2$, 2 × 10^{-3} kmol/m^3; TEBACl, 4 × 10^{-2} kmol/m^3; Allyl alcohol, 1 kmol/m^3; Solvent, THF; Total Volume, 2.5 × 10^{-5} m^3; P$_{CO}$, 5.4 MPa; Agitation Speed, 16.66 Hz

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3.5.6.2.6. Effect of CO Partial Pressure
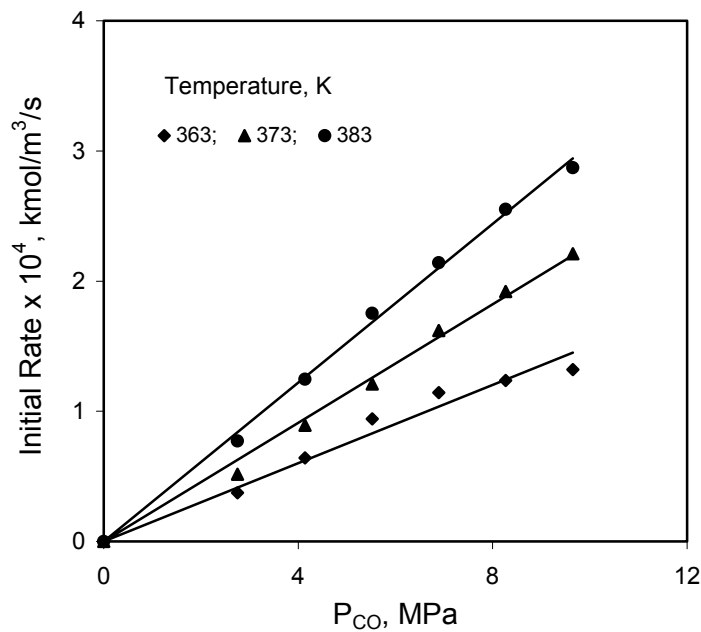
Fig. 3.11. Effect of CO partial pressure on the rate of CO absorption in allyl alcohol carbonylation

Reaction Conditions: PdCl$_2$, 2 × 10^{-3} kmol/m^3; TEBACl, 4 × 10^{-2} kmol/m^3; TsOH, 4×10^{-2} kmol/m^3; Allyl alcohol, 1 kmol/m^3; Solvent, THF; Total Volume, 2.5 × 10^{-5} m^3; Agitation Speed, 16.66 Hz

The results in Figure 3.11 show a linear dependence of rate on CO partial pressure at all temperatures.

3.5.6.3. Kinetic Model

The kinetic data were used to develop a rate equation for carbonylation of allyl alcohol. Based on the observed trends, three different forms of rate equations were evaluated, which are given in equations 3.12-3.14.

$$R_{exp} = \frac{k(A)\ (B)\ (C)\ (Q)\ (Ts)}{[1 + K_B(B)]\ [1 + K_T(Ts)]^3} \qquad (3.12)$$

$$R_{exp} = \frac{k(A)\ (B)^{0.5}\ (C)^{0.8}\ (Q)^{0.8}\ (Ts)}{[1 + K_T(Ts)]^3} \qquad (3.13)$$

$$R_{exp} = \frac{k(A)\ (B)\ (C)^{0.8}\ (Q)^{0.8}\ (Ts)}{[1 + K_B(B)]\ [1 + K_T(Ts)]^3} \qquad (3.14)$$

Where R_{exp} is the rate of reaction expressed in kmol/m^3/s, *(A)* is the concentration of dissolved CO in liquid phase (kmol/m^3), *(B)* is the concentration of allyl alcohol (kmol/m^3), *(C)* is the concentration of catalyst (PdCl$_2$), in kmol/m^3, *(Q)* is the concentration of quaternary salt promoter (BTEACl) in kmol/m^3 and *(Ts)* is the concentration of TsOH promoter (kmol/m^3); k is rate constant, and K_B and K_T are the equilibrium constants for allyl alcohol and TsOH respectively.

3.5.6.3.1. Estimation of Kinetic Parameters and Model Discrimination

The rate parameters k, K_B and K_T were evaluated at 363, 373 and 383 K by fitting the observed experimental rate data with equations 3.12 to 3.14 using nonlinear regression analysis and an optimization routine based on Marquard's method[11]. The values of rate parameters at different temperatures are presented in Table 3.9. The values of Φ_{min} suggest the extent of fit of the kinetic models used (least value of Φ_{min} shows the best fit), which is defined:

$$\phi_{min} = \sum_{i=1}^{n} \left(R_{exp} - R_{pre} \right)^2 \qquad (3.15)$$

Where R_{exp} is the rate observed experimentally, R_{pre} is the predicted rate using nonlinear regression analysis and n is number of data points.

Table 3.9. Values of kinetic parameters at different temperatures

Model	Temp., K	$k \times 10^{-3}$	$K_T \times 10^{-1}$, m³/kmol	K_B, m³/kmol	Ea, kJ/mol	$\Phi_{min} \times 10^9$
I	363	8.732	3.393	-5.844×10^{-5}		12.53
	373	9.476	2.807	-5.530×10^{-5}		8.357
	383	30.18 (m³/kmol)⁵/s	2.449	-2.449×10^{-5}		10.04
II	363	1.180	3.005			4.181
	373	1.322	2.524		8.94	3.390
	383	1.372 (m³/kmol)⁴·¹/s	2.197			6.882
III	363	1.972	2.954	0.724		6.473
	373	3.565	2.517	1.718	38.72	4.129
	383	3.828 (m³/kmol)⁴·⁶/s	2.192	1.795		6.361

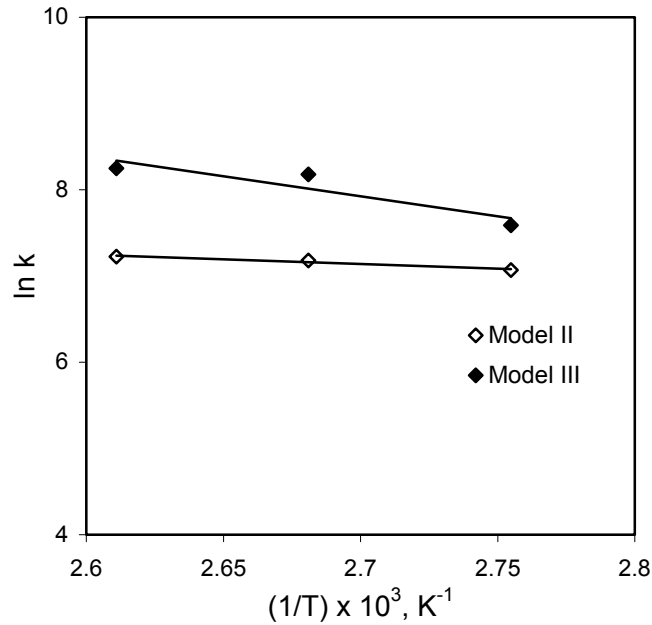Fig. 3.12. Temperature dependence of rate constant (k)

As the analysis of experimental data was performed using nonlinear regression analysis that has purely mathematical basis, further model discrimination was done based on thermodynamic considerations[12,13]. Considering the thermodynamics of any reaction, the values of a kinetic constant should have a positive value (k, K_T or $K_B > 0$ and $E_a > 0$).

The analysis of Model-I gave negative values of equilibrium constant K_B. Also magnitude of Φ_{min} for model-I was higher than for other models, suggesting lack of fit of the model-I. So model-I was rejected. The model-II and model-III have positive values of all of the kinetic parameters estimated and therefore they need to be discriminated further. Comparison of the values of Φ_{min} obtained for model-II and III shows that model-III is superior for carbonylation of allyl alcohol and hence is recommended. Activation energies for model-II and model-III were calculated using Arrhenius plots (Fig. 3.12 and Table 3.9). Activation energy for model –III was 38.72 kJ/mol. According to the model III, the allyl alcohol carbonylation reaction followed 0.8^{th} order with respect to palladium, 0.8^{th} order with respect to TBACl and first order with respect to CO. A comparison of the experimental rates with the predicted rates using model III is shown in Fig. 3.13, which also indicates a good agreement between experiments and prediction.
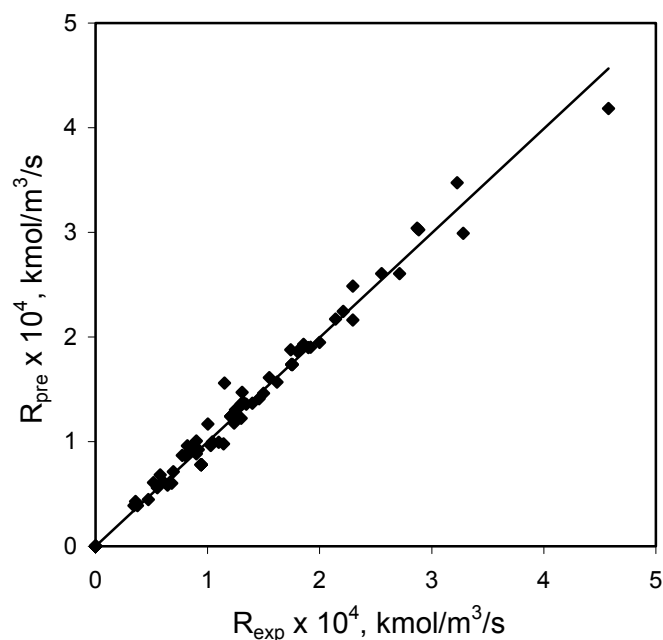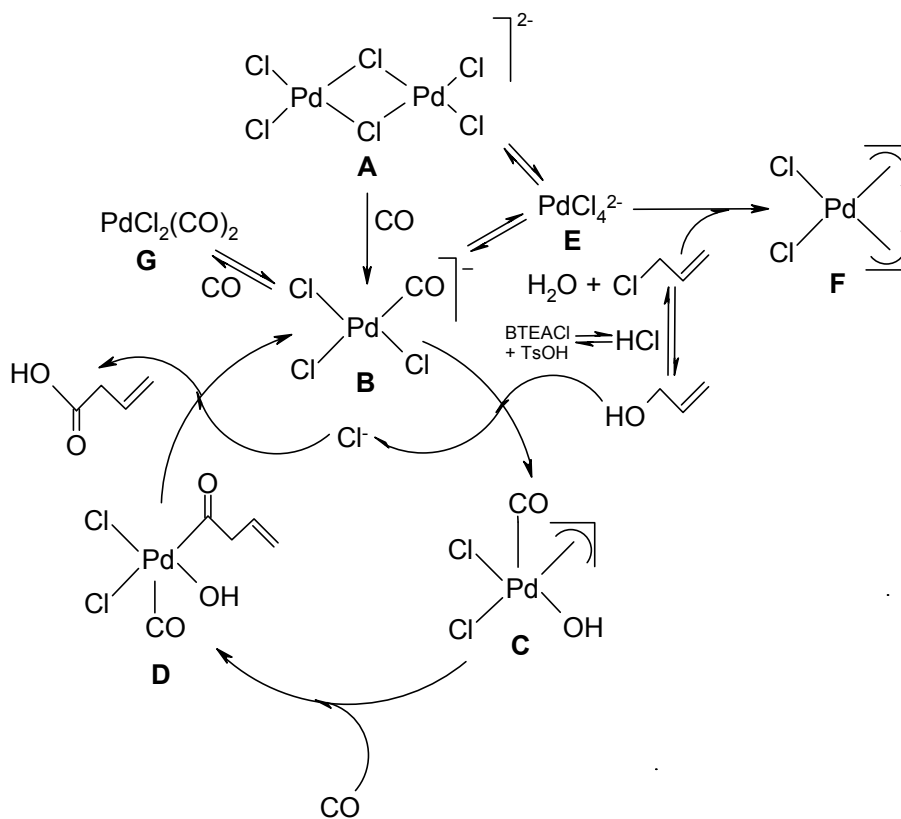

Fig. 3.13. Comparison of experimental rates and rates predicted using model III

3.5.6.3.2. Reaction Mechanism:

Scheme 3.2. Mechanism of palladium catalyzed carbonylation of allyl alcohol

Based on the trends observed in the rate of palladium-catalyzed carbonylation of allyl alcohol, reaction mechanism was proposed, which is given in Scheme 3.2. $Pd_2Cl_6^{2-}$ species **A**, formed in the reaction mixture due to the presence of TBEACl and PdCl$_2$ undergoes carbonylation yielding an active Palladium-carbonyl species **B**[7], PdCl$_3$CO⁻. The species **B** can form hydroxy-palladium species **C**, which further forms species **D** by carbonylation. The species **D** reductively eliminates the product 3-butenoic acid and the active Pd-carbonyl species, **B** to continue the catalytic cycle. Thus, the carbonylation of allyl alcohol proceeds through hydroxy-palladium intermediate species at the given reaction conditions. Such hydroxy-palladiium species formation has been reported by Zau *et. al.*[14] and Wan *et. al.*[15] in aqueous acidic medium, when they carried out oxidation of allyl alcohol using PdCl$_2$ as catalyst. Apart from the main catalytic cycle few more reactions are involved, yielding different forms of catalytically active and inactive species. The species **E** and **G** are in equilibrium with the active catalytic species **B**[7].

Presence of BTEACl, TsOH, CO and **E** in the reaction mixture can also generate species **F** [9] as discussed in Section 3.5.6.2.2.

3.7. Conclusions

Carbonylation of allyl alcohol using soluble $PdCl_2$-BTEACl-TsOH catalyst system provides useful route for synthesis of unsaturated carboxylic acid (3-butenoic acid) and its ester (allyl-3-butenoate). The experimental study on the effect of catalyst and reaction parameters showed the following trends:

1) Quaternary ammonium halide promoters showed the decreasing trend in catalytic activity as Cl> Br >>I.
2) Presence of water in the reaction system increased the catalytic activity and selectivity to 3-butenoic acid.
3) Increase in the polarity of a solvent decreased the catalytic activity
4) Use of a strongly coordinating ligand along with $PdCl_2$-BTEACl-TsOH catalyst system showed substantial decrease in the catalytic activity

The kinetic study of carbonylation of allyl alcohol revealed that the reaction is 0.8^{th} order with respect to $PdCl_2$ (catalyst) and BTEACl (promoter), first order with respect to CO, first order tending to zero order with respect to allyl alcohol and negative order with respect to TsOH promoter. The activation energy of the reaction was found to be 38.72 kJ/mol. Mechanism of carbonylation of allyl alcohol was found to proceed through hydroxy-palladium species.

Notations:

(A)	=	Concentration of CO in the reaction mixture, $kmol/m^3$
(B)	=	Concentration of allyl alcohol, $kmol/m^3$
(C)	=	Catalyst concentration, $kmol/m^3$
H_e	=	Henry's constant, $kmol/m^3/MPa$
k	=	Reaction rate constant, $(m^3/kmol)^n.s^{-1}$
K_B, K_T	=	Equilibrium constants for allyl alcohol and TsOH, $m^3/kmol$
M_s	=	Molecular weight of the solvent
P_i	=	Initial pressure reading, MPa
P_f	=	Final pressure reading, MPa
(Q)	=	Concentration of BTEACl promoter, $kmol/m^3$
R	=	Gas constant, J/K.mol
R_{exp}	=	Experimental rate, $kmol/m^3/s$
R_{pre}	=	Predicted rate, $kmol/m^3/s$
T	=	Temperature, K
(Ts)	=	Concentration of TsOH promoter, $kmol/m^3$
V_g	=	Volume of the gas phase, m^3
V_L	=	Volume of liquid phase, m^3
X_a	=	Mole fraction of the solute gas in the liquid phase
ρ_s	=	Molar density of the liquid, $kmol/m^3$

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CHAPTER 4

Carbonylation of Vinyl Acetate (VAM)

4.1. Introduction

Lactic acid, known for almost 2000 years, has been produced for only a century on an industrial scale. Lactic acid is important commercially in baking industry, cheese industry, pharmaceutical industry, cosmetic industry, in dying wool, to make plasticisers for resin, etc. Lactic acid has become increasingly important especially as a preservative and stabilizer in fat reduced food products. One of the first commercial applications in biodegradable polymers has appeared recently using polylactide polymer obtained from lactic acid[1]. There are two commercial methods for the production of lactic acid, a) fermentation of molasses, and b) Hydrocyanation of acetaldehyde followed by hydrolysis of cyanohydrin produced. Both commercial processes produce racemic lactic acid, while the resolution is carried out separately since only L-lactic acid is useful in polylactide synthesis.

a) Fermentation of molasses: Today major quantity of lactic acid is produced from molasses from sugar production. The fermentation is achieved on industrial scale in stirred tank bioreactors with low productivities. Lactic acid is separated from the lactate salts by addition of sulfuric acid and subsequent separation of the emerging gypsum. The gypsum has no further use and is an environmental threat to dispose off.

b) Hydrocyanation of acetaldehyde followed by hydrolysis of cyanohydrin produced: This route produces cyanohydrin upon hydrocyanation of acetaldehyde using toxic HCN. The cyanohydrin produced is hydrolyzed with corrosive sulfuric acid. In addition to lactic acid, this process generates stoichometric amount of ammonium sulfate, which is undesirable from environmental point of view. Thus, a need for a clean atom efficient and environmentally competitive alternative route exists even today for lactic acid synthesis.

A novel catalytic route via vinyl acetate (which is industrially produced in large volumes from ethylene) has been proposed for lactic acid, which deserves consideration. The first report describing lactic acid synthesis by a three steps route via VAM appeared in 1978[2], in which VAM was hydroformylated to yield 2-acetoxy propanal using

Rh(COD)(PPh$_3$)$_2$ as a catalyst at 373 K and 3.33 MPa syn gas pressure. The intermediate aldehyde was then oxidized using cobalt or manganese catalysts with 0.2 MPa air pressure to yield 2-acetoxypropionic acid that was hydrolyzed to lactic acid in 75% yield using acidic catalysts such as TsOH or H$_2$SO$_4$. In another report, hydrocarbonylation of VAM to yield 2-acetoxypropionic acid using Pd-complex catalysts (373-473K, 0.6-6.9 MPa CO) was reported using [(allyl)PdCl$_2$]$_2$ or Pd(OAc)$_2$ as a catalyst to achieve 96% conversion and 67% selectivity along with VAM hydrolysis products such as acetaldehyde and acetic acid[3]. During hydrocarbonylation reaction, hydrolysis of VAM was predominant side reaction especially at higher ligand (PPh$_3$/Pd ratio > 20) and water concentrations (> 0.9 wt%). A process for *dl*-lactic acid via alkoxycarbonylation of VAM has been patented by Mark-Clark[4] to achieve methyl-2-acetoxypropionate using Pd, Rh and Ni catalysts at 373 K and 6.9 MPa CO pressure. PdCl$_2$(PPh$_3$)$_2$ was found to give the maximum yield (81.6%) of methyl-2-acetoxypropionate (catalytic activity was: TON = 20 in 10 hours), whereas Rh and Ni catalysts were less active for alkoxycarbonylation. Methoxycarbonylation of VAM to yield methyl-2-acetoxypropionate in 62% yield with very low catalytic activity (2.5 h^{-1} TOF) using palladium catalysts in presence of a base such as pyridine or pyridine derivatives was reported at severe operating conditions (373-423K, 15-25 MPa.)[5]. Mechanistic investigations by the authors[5] suggested that the alkoxycarbonylation reaction proceeded through the hydride mechanism as discussed in Chapter 1. A schematic representation of VAM carbonylation reaction yielding methyl-2-acetoxypropionate (**2**), methyl lactate (**3**) is represented in Scheme 4.1.
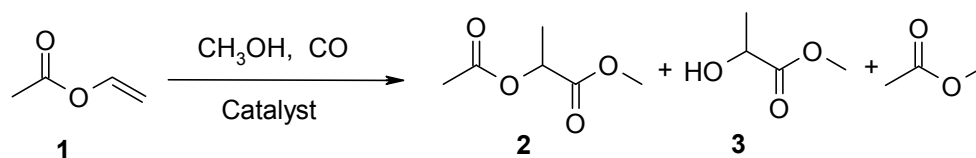
Scheme 4.1. Methoxycarbonylation of VAM

Thus, the methoxycarbonylation or hydroxycarbonylation of VAM provides an economic and environmentally benign catalytic method for synthesis of a precursor (methyl-2-acetoxypropionate or 2-acetoxypropionic acid) to lactic acid, which can be easily converted to lactic acid by hydrolysis. Literature sites very limited published

information for this route. The literature on methoxycarbonylation of VAM shows that with $PdCl_2(PPh_3)_2$ or $PdCl_2(PPh_3)_2$-Pyridine as a catalyst only 2.5 h^{-1} TOF was obtained at severe operating conditions (373-423K, 15-25 MPa.). Thus, the lower catalytic activity, severe reaction conditions and lack of understanding of the kinetics were the issues in alkoxycarbonylation of VAM, which was the motivation of the present work. In this work, methoxycarbonylation of VAM using different catalyst precursors, promoters and solvents were studied in order to improve the catalyst activity. Effect of various reaction parameters were studied at three different temperatures using $PdCl_2(PPh_3)_2$ as a catalyst in order to understand the kinetics of this reaction. An empirical rate model has been proposed. Hydrolysis of VAM alkoxycarbonylation products was carried out using various acidic catalysts to yield *dl*-lactic acid.

4.2. Materials

$PdCl_2$, $Pd(OAc)_2$, $Pd(acac)_2$, 2,2'-bipyridine, 2,2',2''-terpyridine, 1, 10-phenanthroline, pyridine-2-carboxylic acid, acetyl acetone (acac) and vinyl acetate (VAM) were purchased from Aldrich Chemicals (Milwaukee, WI). Acetonitrile, methanol, chlorobenzene, toluene, THF, TsOH, PPh_3, TBACl, TBABr, TBAI, anthranilic acid, nicotinic acid and pyridine (Py) were purchased from SD Fine Chemicals (Mumbai, India). $PdCl_2(PPh_3)_2$, $PdBr_2(PPh_3)_2$ and $PdI_2(PPh_3)_2$ were synthesized as described in Chapter 3. Carbon monoxide (99.9% purity) was supplied by Matheson (Montgomeryville, PA).

4.2.1. Synthesis of PdCl₂(Py)₂

A solution of $PdCl_2$ (1 mmol) in dilute 20 ml aqueous hydrochloric acid was slowly added to a stirred warm solution of pyridine (2.2 mmol) in water (100 ml) at ~333 K for 1 hr. The yellow complex was precipitated, which was filtered, washed with water and dried in vacuum. The complex was re-crystallized from chloroform to obtain 96% yield of $PdCl_2(Py)_2$ based on $PdCl_2$. Elemental Analysis (%): Calculated: C, 35.82; H, 2.98; N, 8.35; Cl, 21.19. Found: C, 36.01; H, 2.85; N, 8.42; Cl, 21.15.

4.2.2. Synthesis of PdCl₂(AsPh₃)₂

A solution of $PdCl_2$ (1 mmol) in dilute 25 ml aqueous hydrochloric acid was slowly added to a stirred warm solution of $AsPh_3$ (2.1 mmol) in ethanol (200 ml) at ~333 K for 2 hrs. The bright yellow complex precipitated was filtered, washed with hot ethanol and dried in vacuum. The complex was re-crystallized from chloroform to obtain 90% yield of $PdCl_2(AsPh_3)_2$ based on $PdCl_2$. Elemental Analysis (%): Calculated: C, 54.75; H, 3.80; Cl, 8.99. Found: C, 54.80; H, 3.83; Cl, 8.90.

4.2.3. Synthesis of Methyl Lactate

50 ml methanol and TsOH (1 mmol) were added to 88% lactic acid (20 g) and the reaction mixture was refluxed under stirring for 2 hours. The reaction mixture was cooled to room temperature to which 100 ml of chloroform was added. Water in the reaction mixture (from the source lactic acid and formed by esterification reaction as shown in equation 4.1) was removed by azeotropic distillation with chloroform at 325 K[6]. The distillation was continued to remove methanol at 338 K. The last fraction of distillation was collected as methyl lactate at 386 K.

$$\underset{OH}{\overset{COOH}{\diagup}} + CH_3OH \rightleftharpoons \underset{OH}{\overset{COOCH_3}{\diagup}} + H_2O \qquad (4.1)$$
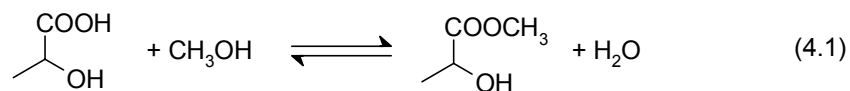
The methyl lactate thus synthesized was characterized using IR, ^{1}H NMR [δ = 4.22 (q, 1H), 3.68 (s, 3H), 3.32 (s, 1H), 1.31 (d, 3H)] and GCMS (consistent with NIST library), which are shown in Appendix-II, Fig. A2.1, A2.3 and A2.5. The compound was used as a standard for quantitative analysis of carbonylation reaction mixtures using GC.

4.2.4. Isolation and Characterization of Carbonylation Product, Methyl-2-Acetoxypropionate

A series of VAM carbonylation reactions were carried out at 373 K, using $PdCl_2(PPh_3)_2$ as a catalyst (see experimental section for the details of carbonylation reactions) and the reaction mixtures were collected together to isolate the carbonylation products. Toluene (solvent), unreacted components (methanol and VAM) and methyl lactate formed were removed using a *rotavac* at 313 K, which left behind the liquid methyl-2-acetoxypropionate and the precipitated catalyst $PdCl_2(PPh_3)_2$. The catalyst was filtered off; product was passed through a silica column and eluted with hexane as a solvent to remove any trace of impurities. The isolated product was characterized using IR, ^{1}H NMR [δ 5.01 (q, 1H), 3.67 (s, 3H), 2.06 (s, 3H), 1.43 (d, 3H)] (consistent with the literature[5]), and GCMS, which are shown in Appendix II, Fig. A2.2, A2.4 and A2.6 respectively. The compound was used as a standard for quantitative analysis of carbonylation reaction mixtures using GC.

4.2.5. Extraction of Methyl Lactate from Carbonylation Reaction Mixtures

Carbonylation reaction mixtures containing solvent (toluene), methyl-2-acetoxypropionate, methyl lactate, methyl acetate and unreacted VAM were collected together. Methanol, methyl acetate and VAM were removed using a *rotavac* at 310 K. Methyl lactate was extracted in water. GC analysis of the aqueous fraction showed methyl lactate concentration to be 0.5%. This fraction containing methyl lactate was used for hydrolysis (see Section 4.6.2).

4.3. General Procedure

4.3.1. Carbonylation Reaction

VAM carbonylation reactions were carried out in a 50 ml Parr Autoclave made of Hastelloy-C-276. The reactor setup is shown in Figure 2.1. In a typical VAM carbonylation reaction, toluene (solvent) was added to a known amount VAM and methanol so as to make the volume to 25 ml and was charged to the reactor. Weighed quantities of $PdCl_2(PPh_3)_2$ and

other promoters (if specified) were also charged and the reactor was closed. Thereafter, the contents were purged once with nitrogen and thrice with carbon monoxide. The reactor was heated to the desired temperature, which was then pressurized with CO to a desired pressure. The reaction was started at 16.66 Hz and reaction carried out at a constant pressure by feeding CO from a reservoir with the help of a constant pressure regulator. The progress of the reaction was monitored by the CO consumption as a function of time. After specific time intervals, intermediate samples were taken out for analysis if required. The reaction was continued at a constant pressure for the specific time and was then cooled to room temperature. The gas was vented off and the reactor flushed with N_2 and the contents removed. Small amount of liquid sample was taken out and analyzed quantitatively with GC. The details of the quantitative GC analysis are discussed in the Section 4.4.

4.3.2. Hydrolysis of Carbonylation Products

A known amount of methyl-2-acetoxypropionate (isolated from carbonylation reactions as described in Section 4.2.4) was taken in a 50 ml round bottom flask containing 15 ml of distilled water (methyl-2-acetoxypropionate was insoluble in water). A known amount of catalyst was added to it and heated at 353 K under stirring. After a specific reaction time, the contents were cooled to room temperature. Unreacted methyl-2-acetoxypropionate was extracted in toluene and quantified using GC. While analyzing toluene extract, no product other than methyl-2-acetoxypropionate and trace lactic acid was found. Aqueous phase was found to contain lactic acid, which was characterized using GCMS (Appendix-II, Fig. A2.7).

25 ml of aqueous fraction containing methyl lactate, extracted as in Section 4.2.5 was taken in a 50 ml round bottom flask. A known amount of catalyst was added to it and heated at 353 K under stirring. After specific reaction time, the contents were cooled to room temperature and quantitatively analyzed using GC for methyl lactate.

4.4. Analytical Methods

IR analysis was done on Bio Rad FTS 175C spectrophotometer. NMR was obtained from a Brucker- MSL300 and Brucker-AC200 machines. Elemental analysis

was carried out on a CHNS-O EA1108, Elemental analyzer of Carlo Erba Instruments, and the ion chromatography on a Waters Ion Chromatograph, having Waters 432 Conductivity detector, Waters 600S Controller and Waters 626 Pump. Liquid samples of carbonylation reactions were quantitatively analyzed with HP 6890 GC using HP1 methyl siloxane capillary column (length 30 m, diameter 30 μm, film thickness 0.25 μm). Conditions of quantitative analysis are shown in Table 4.1. The quantitative analysis was obtained through a calibration curve. Conversion of VAM, selectivities to methyl-2-acetoxypropionate, methyl lactate and methyl acetate, TON and TOF were calculated according to the formulae as shown in equations 4.2-4.7.

Table 4.1. Conditions used for liquid phase GC analysis

	Conditions
Inlet (split)	Split ratio = 50:1, 523 K
Column (HP1)	303 – 523 K (programmed), 0.02 – 0.2 MPa (programmed)
Detector (FID)	523 K
Carrier gas (He)	20 ml/min

$$\%\text{Conversion} = \frac{100 \times [(\text{Initial Mol}_{VAM})-(\text{Final Mol}_{VAM})]}{(\text{Initial Mol}_{VAM})} \qquad (4.2)$$

$$\%\text{Selectivity}_{\text{methyl-2-acetoxy propionate}} = \frac{100 \times (\text{Final Mol}_{\text{methyl-2-acetoxy propionate}})}{[(\text{Initial Mol}_{VAM})-(\text{Final Mol}_{VAM})]} \qquad (4.3)$$

$$\%\text{Selectivity}_{\text{methyl lactate}} = \frac{100 \times (\text{Final Mol}_{\text{methyl lactate}})}{[(\text{Initial Mol}_{VAM})-(\text{Final Mol}_{VAM})]} \qquad (4.4)$$

$$\%\text{Selectivity}_{\text{methyl acetate}} = \frac{100 \times (\text{Final Mol}_{\text{methyl acetate}})}{[(\text{Initial Mol}_{VAM})-(\text{Final Mol}_{VAM})]} \qquad (4.5)$$

$$\text{TON} = \frac{\text{Moles of carbonylation products formed}}{\text{Moles of catalyst charged}} \qquad (4.6)$$

$$\text{TOF} = \frac{\text{Moles of carbonylation products formed}}{\text{Moles of catalyst charged} \times \text{time}} \qquad (4.7)$$

4.5. Results and Discussion

The experimental results on methoxycarbonylation of VAM using different palladium precursors, and promoters such as quaternary ammonium halides, TsOH and ligands are discussed in this section. Effect of different solvents was studied using $PdCl_2(PPh_3)_2$ as a catalyst and acetyl acetone as a ligand. Effect of reaction parameters such as catalyst, VAM, methanol concentrations and CO partial pressure on activity selectivity behavior was studied over a temperature range of 363-383K.
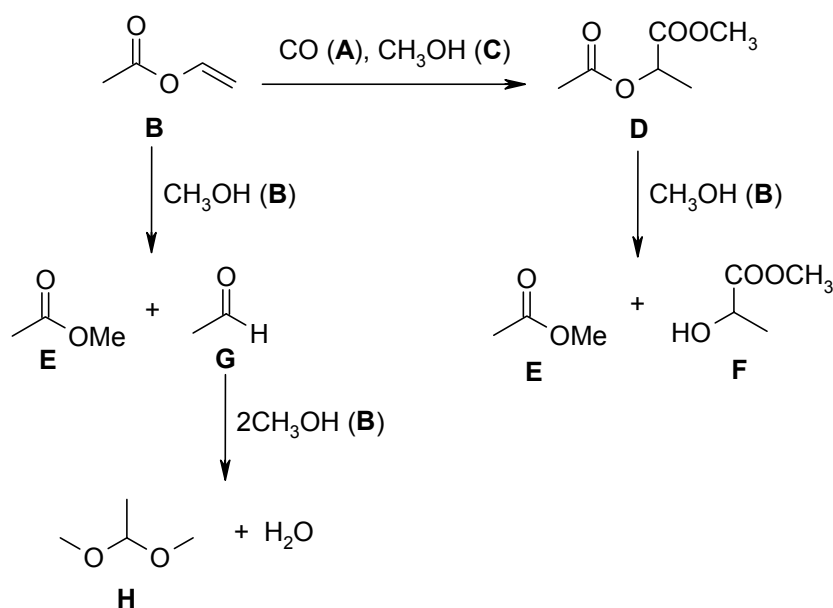
Scheme 4.2. Schematic of reactions involved in methoxycarbonylation of VAM

For this purpose, initial experiments were carried out using $PdCl_2(PPh_3)_2$ as a catalyst to identify and characterize the products formed. A typical concentration-time profile for 373 K is shown in Fig. 4.1. The main products formed were methyl-2-acetoxypropionate, methyl lactate, methyl acetate and dimethyl acetal as identified by GC and GCMS (see Appendix-II). Out of these products, methyl-2-acetoxypropionate (**D**) and methyl lactate (**F**) were generated through the carbonylation reaction whereas methyl acetate (**E**) and dimethyl acetal (**H**) were formed as side reactions as shown in Scheme 4.2. Molar stoichometry of VAM conversion generates methyl-2-acetoxypropionate (**D**),

methyl lactate (**F**), methyl acetate (**E**) and acetaldehyde (**G**). Acetaldehyde further reacts with methanol to form dimethyl acetal (**H**). The balance of VAM converted was observed to be in the range of 91-99% with respect to the products, whereas the balance of methanol was in the range of 96-98%. The balance of CO consumed was observed to be in the range of 80-95%. The carbonylation product, methyl-2-acetoxypropionate was isolated from the reaction mixture in pure form as described in Section 4.2.4, characterized (see Appendix-II) and used as a standard for quantitative analysis of carbonylation reactions using GC. Methyl lactate was synthesized as described in Section 4.2.3 and used as a standard for GC analysis. Methyl lactate was also isolated from carbonylation reaction mixtures (in the form of aqueous solution) for its hydrolysis to lactic acid.
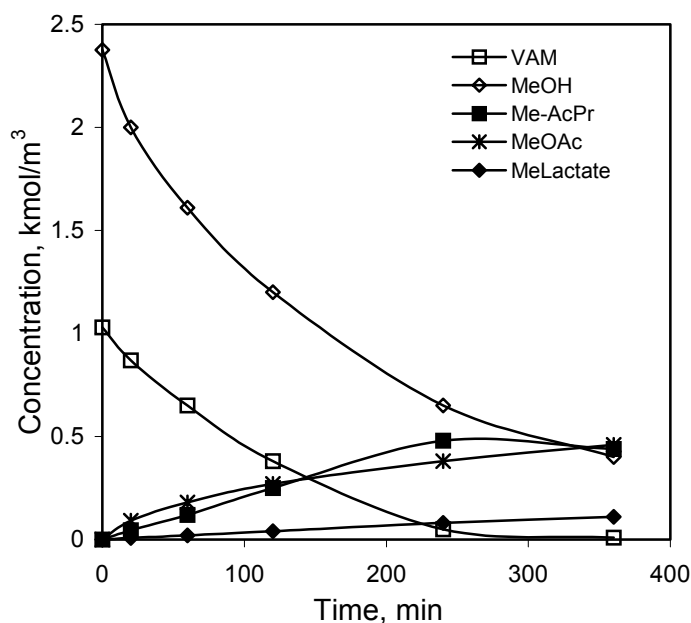

Fig. 4.1. Concentration-time profile at 373 K in VAM methoxycarbonylation reaction

Reaction conditions: PdCl$_2$(PPh$_3$)$_2$, 2 × 10^{-3} kmol/m^3; VAM, 1 kmol/m^3; CH$_3$OH, 2.4 kmol/m^3; Solvent, Toluene; Total Volume, 2.5 × 10^{-5} m^3; Temperature, 373K; P$_{CO}$, 5.4 MPa; Agitation Speed, 16.66 Hz

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4.5.1. Screening of Catalyst Precursors

Table 4.2. Effect of palladium precursors in the carbonylation of VAM[a]

No.	Catalyst	Time, h	Conversion, %	Selectivity, %			TOF, h^{-1}
				A	B	C	
[b]1	PdCl$_2$	4	6.13	50.30	0	0	0
[c]2	PdCl$_2$	10	98.76	45.37	44.13	10.67	27
[b]3	PdCl$_2$Py$_2$	4	8.96	49.67	0	0	0
[c]4	PdCl$_2$Py$_2$	10	98.05	47.40	42.35	8.43	28
[b]5	PdCl$_2$(AsPh$_3$)$_2$	4	54.68	46.89	0	0	0
6	PdCl$_2$(PPh$_3$)$_2$	10	99.12	45.09	43.13	10.78	28
7	PdBr$_2$(PPh$_3$)$_2$	4	25.28	51.72	21.54	4.33	9
8	PdI$_2$(PPh$_3$)$_2$	4	12.00	72.47	0	0	0
[b]9	Pd(OAc)$_2$	2	3.67	44.90	0	0	0
[b]10	Pd(acac)$_2$	2	0.98	0	0	0	0

[a]Reaction conditions: Catalyst, 2 × 10^{-3} kmol/m^3; VAM, 1 kmol/m^3; Methanol, 2.4 kmol/m^3; Solvent, Toluene; Total Volume, 2.5 × 10^{-5} m^3; Temperature, 373K; P$_{CO}$, 5.4 MPa; A, Methyl acetate; B, Methyl-2-acetoxypropionate; C, Methyl lactate; [b]Substantial amount of palladium was found precipitated in the reactor when discharged; [c]PPh$_3$: 4 × 10^{-3} kmol/m^3

Results obtained in the screening of catalyst precursors are shown in Table 4.2. PdCl$_2$(PPh$_3$)$_2$ was found to be the most effective catalyst for VAM methoxycarbonylation reaction giving 99.12% conversion of VAM with 53.91% combined selectivity to the carbonylation products (Table 4.2, run # 6). The rest of VAM was converted to methyl acetate. PdCl$_2$ alone gave no reaction whereas addition of 2 equivalents of PPh$_3$ as a ligand to PdCl$_2$ showed the activity similar to PdCl$_2$(PPh$_3$)$_2$ catalyst (Table 4.2, run # 1, 2, 6). Similarly, PdCl$_2$Py$_2$ as a catalyst showed no carbonylation activity, but addition of 2 equivalents of PPh$_3$ to this catalyst showed the activity comparable to PdCl$_2$(PPh$_3$)$_2$ catalyst (Table 4.2, run # 3, 4, 6). These catalysts were found to deactivate without PPh$_3$ ligand, as substantial amount of palladium black was observed in the reaction mixtures, where no PPh$_3$ was used. Thus, palladium was found to be active in the form of PdCl$_2$(PPh$_3$)$_2$ which was either charged as a prepared complex or formed insitu by

addition of PPh$_3$ ligand to a palladium precursor. Other palladium precursors such as PdCl$_2$(AsPh$_3$)$_2$, Pd(OAc)$_2$, Pd(acac)$_2$ were screened for this reaction without PPh$_3$ ligand which showed no carbonylation activity (Table 4.2, run # 5, 9, 10).
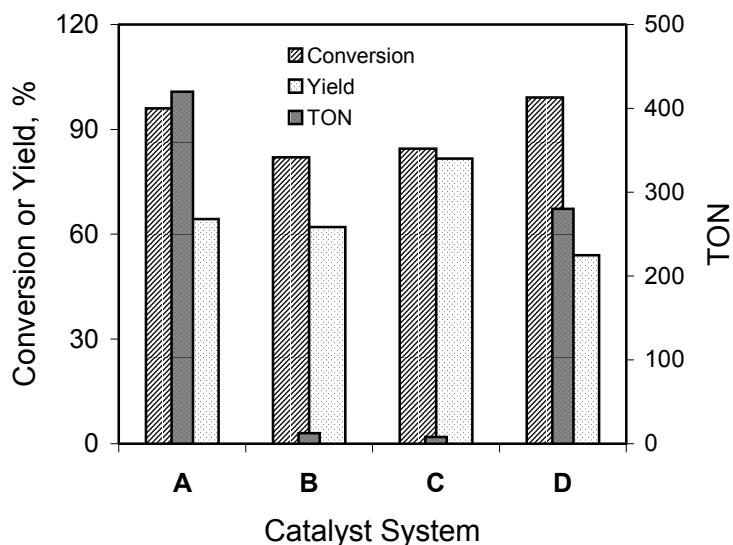

Fig. 4.2. Comparison of catalytic activity with literature[3-5]

Catalyst system A[3] for hydrocarbonylation of VAM: Pd(allyl)Cl$_2$, 5 × 10^{-3} kmol/m^3; PPh$_3$, 0.1 kmol/m^3; VAM, 3.2 kmol/m^3; Water, 0.46 kmol/m^3 (maintained in the reaction mixture by continuous feeding);Solvent, Butyric acid; Total Volume, 1.2 × 10^{-4} m^3; Temperature, 423 K; P$_{CO}$, 4.83 MPa; Time, 3 hr.

Catalyst system B[5] for methoxycarbonylation of VAM: PdCl$_2$(PPh$_3$)$_2$, 1 × 10^{-2} kmol/m^3; Pyridine, 0.1 kmol/m^3; VAM, 0.2 kmol/m^3; Solvent, Benzene (1 × 10^{-5} m^3); Methanol, 0.25 kmol/m^3; Temperature, 373 K; P$_{CO}$, 15.2 MPa; Time, 5 hr.

Catalyst system C[4] for methoxycarbonylation of VAM: PdCl$_2$(PPh$_3$)$_2$, 9.6 × 10^{-3} kmol/m^3; VAM, 9.6 × 10^{-2} kmol/m^3; Methanol, 0.5 kmol/m^3; Solvent, THF, Total Volume, 5 × 10^{-6} m^3; Temperature, 373 K; P$_{CO}$, 6.89 MPa; Time, 44 hr.

Catalyst system D (as studied here) for methoxycarbonylation of VAM: PdCl$_2$(PPh$_3$)$_2$, 2 × 10^{-3} kmol/m^3; VAM, 1 kmol/m^3; Methanol, 2.4 kmol/m^3; Solvent, Toluene; Total Volume, 2.5 × 10^{-5} m^3; Temperature, 373K; P$_{CO}$, 5.4 MPa; Time, 10 hr; Agitation Speed, 16.66 Hz

PdX$_2$(PPh$_3$)$_2$ as catalysts showed a typical trend in the catalytic activity (Table 4.2, run # 6, 7 and 8), which was found to vary in the order: X = Cl > Br >> I in PdX$_2$(PPh$_3$)$_2$. this observation was in the reverse order of Pd-X bond strength; X = I>Br>Cl. Strongly coordinating iodide ligand in PdI$_2$(PPh$_3$)$_2$ showed no carbonylation activity at the reaction conditions used. Similar trend in the catalytic activity was observed by Komatsu and coworkers[5] using PdX$_2$(PPh$_3$)$_2$ as a catalyst in the presence of pyridine as a ligand at severe operating conditions (373-423 K, 15-25 MPa). Though, the authors used severe operating conditions for methoxycarbonylation of VAM, the catalytic activity was very low (TOF = 2.5 h^{-1}). The main reason of such lower catalytic activity was that they used very low concentration of VAM (VAM/Pd ratio = 20). As the rate of VAM methoxycarbonylation reaction is strongly dependant on VAM concentration (see Section 4.5.5.1.2), they obtained such a lower catalytic activity even at severe reaction conditions. In the present case, at higher VAM concentration (VAM/Pd ratio = 500) showed 11 times increase in the catalytic activity (TOF = 28 h^{-1}) compared to the literature[5] even in absence of pyridine ligand at lower reaction conditions. Thus, low bond strength of Pd-X bond, and weakly coordinated palladium center favored the carbonylation of VAM. Also, it is evident from the comparison of present results with the literature (see Fig. 4.2) that the VAM methoxycarbonylation is favored at higher concentration of VAM (> 1 kmol/m^3) in the reaction medium.

4.5.2. Screening of Quaternary Halides as Promoters

Different quaternary ammonium (tetra butyl ammonium) halide salts were screened for VAM methoxycarbonylation reaction as promoters along with PdCl$_2$(PPh$_3$)$_2$ as a catalyst, in which it was observed that TBACl was superior among the other ammonium halides. Addition of 20 equivalents of TBACl to PdCl$_2$(PPh$_3$)$_2$ catalyst showed 63.04% conversion of VAM in four hours with an improvement in selectivity to carbonylation products (from 53.91 to 62.5%) (Table 4.3, run # 1 and 2). Use of TBABr as a promoter decreased the catalyst activity towards carbonylation products (Table 4.3, run # 3), whereas TBAI as a promoter showed only VAM methylation[5] product, methyl acetate without any carbonylation reaction (Table 4.3, run # 4). Using a promoter TBAX with X = Cl, Br or I, in presence of PdCl$_2$(PPh$_3$)$_2$ as a catalyst, a typical trend in the

catalyst activity was observed in the order: Cl > Br >> I in TBAX. Further, when the catalysts from the carbonylation reaction mixtures containing $PdCl_2(PPh_3)_2$ along with TBAX promoters (X= Cl, Br or I) were separated and characterized by elemental analysis, $PdX_2(PPh_3)_2$ was noted to be formed in the reaction mixtures (For this purpose, the solvent and low boiler components such as VAM and methanol were removed using a *rotavac*. TBAX promoter and methyl lactate were extracted in water leaving behind the catalyst and the product methyl-2-acetoxypropionate, which was washed with diethyl ether to obtain the catalyst in the form of $PdX_2(PPh_3)_2$ (Elemental analysis of the isolated compounds: $PdCl_2(PPh_3)_2$: C, 61.68 (61.605); H, 4.39 (4.308); Cl, 9.82 (10.102); $PdBr_2(PPh_3)_2$: C, 55.28 (54.68); H, 4.05 (3.8); Br, 21.53 (20.25); $PdI_2(PPh_3)_2$: C, 49.43 (48.87); H, 3.82 (3.39); I, 29.11 (28.73)), as evidenced by elemental analysis). As the formation of $PdX_2(PPh_3)_2$ was noted in the reaction mixture, the trends observed with the TBAX promoters were representative of the catalyst $PdX_2(PPh_3)_2$ formed in the reaction mixture as discussed in the previous section. Thus, using TBAX promoters along with $PdCl_2(PPh_3)_2$ formed $PdX_2(PPh_3)_2$ in the reaction mixture which showed the above explained trend in activity is summarized in Fig. 4.3. Though, these trends were representative of $PdX_2(PPh_3)_2$ formed, it can be noted that the use of a halide promoter increased the conversion of VAM as well as selectivity to the carbonylation products (Table 4.2, run # 6, 7 and 8; Table 4.3, run # 2, 3 and 4)

Table 4.3. Effect of Quaternary ammonium halides (QX) in the carbonylation of VAM

No.	Promoter	Time, h	Conversion, %	Selectivity, %			TOF, h^{-1}
				A	B	C	
1	–	10	99.12	45.09	43.13	10.78	28
2	TBACl	4	63.04	37.60	50.63	11.87	52
3	TBABr	4	32.05	57.67	20.88	5.86	10
4	TBAI	4	24.02	82.47	0	0	0

Reaction conditions: $PdCl_2(PPh_3)_2$, 2×10^{-3} kmol/m³; VAM, 1 kmol/m³; CH₃OH, 2.4 kmol/m³; Promoter, 4×10^{-2} kmol/m³; Solvent, Toluene; Total Volume, 2.5×10^{-5} m³; Temperature, 373K; P_{CO}, 5.4 MPa; Selectivity: A, methyl acetate; B, methyl-2-acetoxypropionate; C, methyl lactate
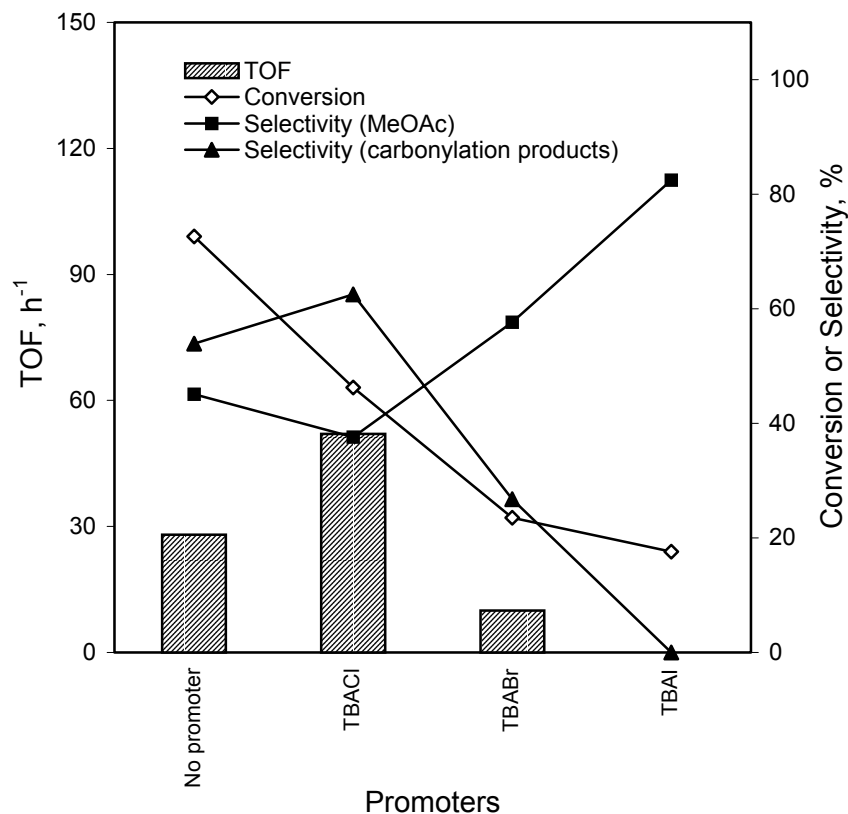
Fig. 4.3. Effect of quaternary ammonium halide promoters in $PdCl_2(PPh_3)_2$ catalyzed carbonylation of VAM.

Reaction Conditions: As in Table. 4.3

4.5.3. Effect of ligands

Various ligands containing N- and O- donor atoms were screened for VAM methoxycarbonylation reaction along with $PdCl_2(PPh_3)_2$ as a catalyst in the presence and absence of TsOH[7]. Addition of 4 equivalents of TsOH to $PdCl_2(PPh_3)_2$ catalyst system helped to increase the conversion of VAM in lesser reaction time (99.89% in 4.5 hours), but the selectivity to carbonylation products was found to be lowered with increase in the selectivity to methyl acetate (Table 4.4, run # 1, 2). Further, the addition of 20 equivalents of N-donor ligand (basic in nature) to $PdCl_2(PPh_3)_2$-TsOH catalyst system was found to enhance the selectivity of carbonylation products at the cost of conversion. Use of acidic ligands (picolinic acid, anthranilic acid) in this catalyst system increased the

conversion level at the cost of selectivity to carbonylation products (Table 4.4, run # 7, 8). Thus, the ligands having basic nature were effective to achieve higher carbonylation selectivity for $PdCl_2(PPh_3)_2$-TsOH catalyst system, whereas the ligands with acidic nature increased the conversion of VAM with decrease in selectivity.

Table 4.4. Effect of ligands in alkoxycarbonylation of VAM using $PdCl_2(PPh_3)_2$ catalyst in presence of TsOH[a]

No.	Ligand	Time, h	Conversion, %	Selectivity, %			TOF, h^{-1}
				A	B	C	
[b]1	—	10	99.12	45.09	43.13	10.78	28
2	—	4.5	99.89	62.18	28.06	1.87	33
3	Pyridine	3.5	90.01	12.91	63.35	12.77	102
4	2,2'-Bipyridine	4.5	88.23	23.24	39.35	20.38	60
5	2,2',2"-terpyridine	4	45.28	24.33	18.09	0	10
6	1,10-Phenanthroline	4	25.01	8.19	2.61	0	1
7	Picolinic acid	2	98.97	33.35	18.01	17.55	93
8	Anthranilic acid	2.5	99.29	34.42	14.54	9.79	49

[a]*Reaction Conditions: $PdCl_2(PPh_3)_2$, 2×10^{-3} kmol/m^3; VAM, 1kmol/m^3; CH_3OH, 2.4 kmol/m^3; Ligand, 4×10^{-2} kmol/m^3; TsOH, 8×10^{-3} kmol/m^3; Solvent, Toluene; Total Volume, 2.5×10^{-5} m^3; Temperature, 373 K; P_{CO}, 5.4 MPa; Selectivity: A, methyl acetate, B, methyl-2-acetoxypropionate, C, methyl lactate;* [b]*No TsOH*

The results in Table 4.4 showed that the acidic ligands generate more methyl acetate (VAM methylation product) in presence of TsOH and $PdCl_2(PPh_3)_2$. So the acidic ligands were screened using $PdCl_2(PPh_3)_2$ as a catalyst in absence of TsOH (Table 4.5). Use of acidic ligands in $PdCl_2(PPh_3)_2$ catalyst system increased the carbonylation selectivity at the cost of conversion over $PdCl_2(PPh_3)_2$-TsOH catalyst system.

Table 4.5. Effect of ligands in absence of TsOH in $PdCl_2(PPh_3)_2$ catalyzed carbonylation of VAM[a]

No.	Ligand	Time, h	Conversion, %	Selectivity, %			TOF, h^{-1}
				A	B	C	
1	–	10	99.12	45.09	43.13	10.78	28
[b]1	Picolinic acid	2	98.97	33.35	18.01	17.55	93
2	Picolinic acid	4	78.41	22.25	43.94	15.57	61
3	Anthranilic acid	10	99.04	25.03	45.04	19.29	34
4	Nicotinic acid	4	60.15	18.75	57.57	16.82	57
5	Acetyl acetone	4	84.09	22.77	46.96	17.88	72

[a]*Reaction Conditions*: $PdCl_2(PPh_3)_2$, 2×10^{-3} kmol/m³; VAM, 1 kmol/m³; CH_3OH, 2.4 kmol/m³; Ligand, 4×10^{-2} kmol/m³; Solvent, Toluene; Total Volume, 2.5×10^{-5} m³; Temperature, 373 K; P_{CO}, 5.4 MPa; Selectivity: A, methyl acetate; B, methyl-2-acetoxypropionate; C, methyl lactate; [b]*TsOH, 8×10^{-3} kmol/m³*

Effect of concentration of phosphine ligand (PPh_3) was studied using $PdCl_2(PPh_3)_2$ as a catalyst (Table 4.6). Marginal increase in the catalytic activity was observed with small amount of increase in PPh_3 concentration in the reaction mixture (0.2 mmol), whereas higher concentration of PPh_3 (0.6 mmol) in $PdCl_2(PPh_3)_2$ catalyst system showed very poor carbonylation activity, yielding more methyl acetate (91.61%), though the maximum conversion could be achieved (99.37%) only in 2 hours (Fig. 4.4)

Table 4.6. Effect of PPh_3 concentration in $PdCl_2(PPh_3)_2$ catalyzed carbonylation of VAM[a]

Run No.	[b]PPh_3/Pd ratio	Time, h	Conversion, %	Selectivity, %			TOF, h^{-1}
				A	B	C	
1	2	10	99.12	45.09	43.13	10.78	28
2	4	4.5	61.58	38.59	31.19	11.29	30
3	12	2	99.37	91.61	1.83	2.06	10

[a]*Reaction Conditions*: $PdCl_2(PPh_3)_2$, 2×10^{-3} kmol/m³; VAM, 1 kmol/m³; CH_3OH, 2.4 kmol/m³; Solvent, Toluene; Total Volume, 2.5×10^{-5} m³; Temperature, 373 K; P_{CO}, 5.4 MPa; Selectivity: A, methyl acetate; B, methyl-2-acetoxypropionate; C, methyl lactate; PPh_3/Pd ratio was maintained by addition of required amount of PPh_3 to the reaction mixture*
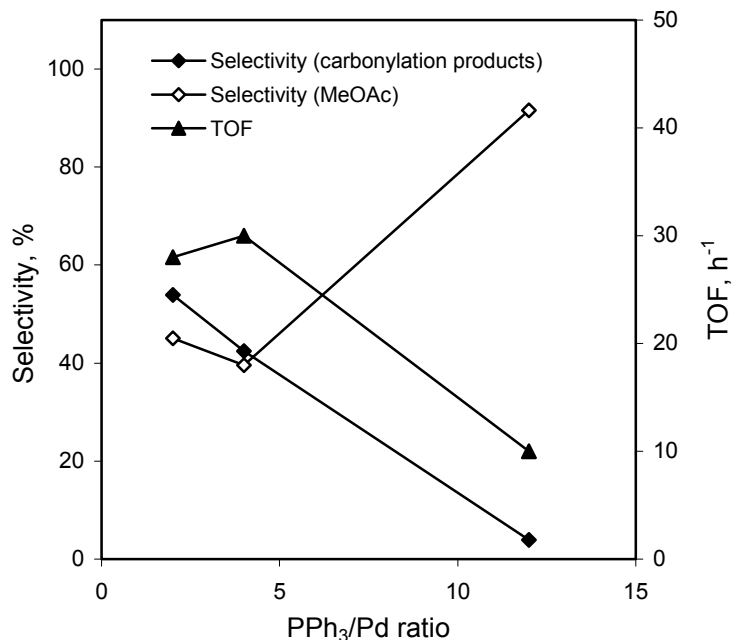
Fig. 4.4. Effect of PPh$_3$ concentration on PdCl$_2$(PPh$_3$)$_2$ catalyst system.

Reaction conditions: As in Table 4.6

4.5.4. Effect of Solvents

Table 4.7. Effect of solvents in PdCl$_2$(PPh$_3$)$_2$ catalyzed carbonylation of VAM.

Run	Solvent	Conversion,	Selectivity, %			TOF,
No.	(dipole moment, debye)	%	A	B	C	h^{-1}
1	Acetonitrile (3.92)	82.65	79.88	3.86	12.87	18
[b]2	Methanol (1.70)	91.56	57.69	22.27	6.70	4
3	THF (1.75)	91.42	46.42	35.67	15.08	61
4	Chlorobenzene (1.54)	97.57	54.13	34.27	9.63	70
5	Toluene (0.37)	84.09	31.41	46.96	17.88	72

[a]*Reaction Conditions: PdCl$_2$(PPh$_3$)$_2$, 2 × 10^{-3} kmol/m^3; VAM, 1 kmol/m^3; CH$_3$OH, 2.4 kmol/m^3; Ligand (acac), 4 × 10^{-2} kmol/m^3; Total Volume, 2.5 × 10^{-5} m^3; Time, 4 hr; Temperature, 373 K; P$_{CO}$, 5.4 MPa; Selectivity: A, methyl acetate; B, methyl-2-acetoxypropionate; C, methyl lactate; [b]Catalyst was found precipitated as Pd-black in the reaction mixture after carbonylation reaction*

Effect of different solvents was carried out at 373 K and 5.4 MPa using PdCl$_2$(PPh$_3$)$_2$ as a catalyst and acetyl acetone as a ligand (Table 4.7). Dipole moment of

solvents was correlated with the catalyst activity and it was observed that the non-polar solvents having less dipole moment were better solvents for VAM methoxycarbonylation reaction. As a trend, the activity was found to increase with decrease in polarity of a solvent (dipole moment). This trend in activity was found inapplicable for methanol as a solvent because substantial amount of palladium catalyst was found precipitated in the reaction mixture, when the reactor was discharged, making it unavailable for the carbonylation reaction (Table 4.7, run # 2). Similarly, increase in the dipole moment of a solvent increased the selectivity to methyl acetate and decreased the selectivity to carbonylation products. The nonpolar solvents probably help to stabilize the neutral catalytic Pd-H species (see Chapter 1, Section 1.4.1.1) in the reaction medium, which increases the catalytic activity. Thus, using toluene as a non-polar solvent, high activity (72 h^{-1} TOF) was obtained with high selectivity to carbonylation products (65%). The results are summarized in Figure 4.5.
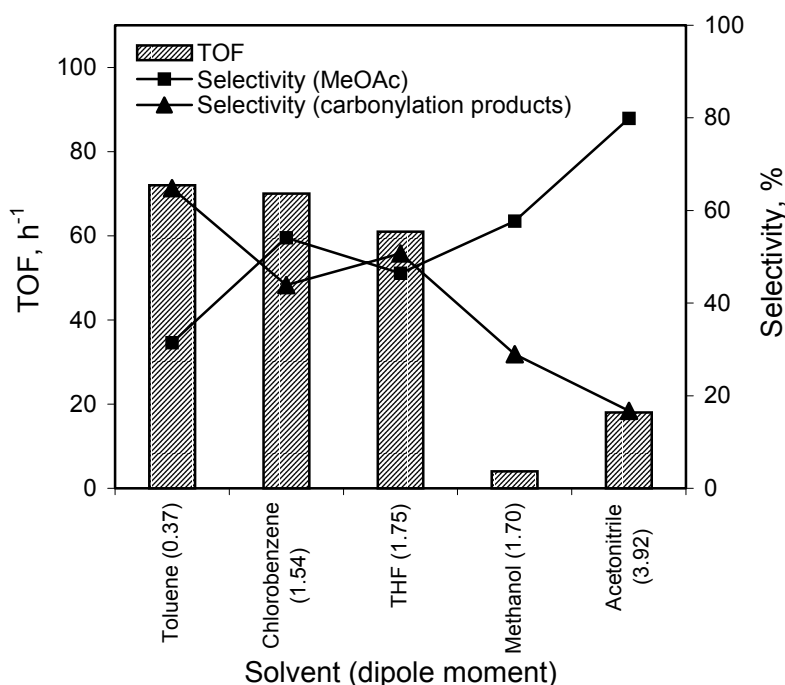
Fig. 4.5. Effect of solvent polarity on the catalytic activity of VAM methoxy-carbonylation reaction

Reaction conditions: As in Table 4.7

4.5.5. Kinetics of VAM Methoxycarbonylation Reaction

Though, methoxycarbonylation of VAM is an important reaction that gives methyl-2-acetoxypropionate (a precursor for industrially important *dl*-lactic acid), very scanty published literature is available on this reaction. Particularly there is no published information on the kinetics of this reaction. This reaction is also a good example to study the kinetics of multi-step homogeneous catalytic reactions, which involve consecutive and parallel reactions (Scheme 4.2). The main objective of this work was to study the kinetics and develop rate equation for methoxycarbonylation of VAM using $PdCl_2(PPh_3)_2$ as a catalyst. The effect of parameters such as concentration of catalyst, methanol, VAM and CO partial pressure on the rate and concentration-time profiles was studied in the temperature range of 363-383 K. The range of concentrations and other parameters used for this study is summarized in Table 4.8. Five different rate models were considered and kinetic parameters evaluated to suggest an appropriate rate model for methoxycarbonylation of VAM.

Table 4.8. Range of conditions used for kinetic study

No.	Component	Range of conditions
1	$PdCl_2(PPh_3)_2$, kmol/m^3	$(1 \times 10^{-3}) - (6 \times 10^{-3})$
2	VAM, kmol/m^3	$0.2 - 2.4$
3	Methanol, kmol/m^3	$1 - 4.8$
4	P_{CO}, MPa	$1.37 - 8.57$
5	Temperature, K	$363 - 383$
6	Agitation speed, Hz	$10 - 20$

In order to establish the mass balance of liquid components at various time intervals, concentration-time profiles were obtained. The GC analysis of all intermediate samples showed the balance of VAM and methanol in the range of 91-99%. A typical concentration time profile of a reaction at 373 K is shown in Figure 4.2. Concentration of VAM decreased as a function of time and was converted to the carbonylation products methyl-2-acetoxypropionate and methyl lactate. A side reaction was also visible yielding methyl acetate (Scheme 4.3) (**4**). This was due to methylation of VAM to acetic acid and

successive esterification, which yields methyl acetate and vinyl alcohol (**5**). Vinyl alcohol always exists in its enol form (acetaldehyde, (**6**)) even below room temperature[8]. The by-product acetaldehyde further reacts with methanol to yield dimethyl acetal (**7**). Thus, during carbonylation methyl-2-acetoxypropionate and methyl lactate were formed as carbonylation products along with methyl acetate and dimethyl acetal as by-products.
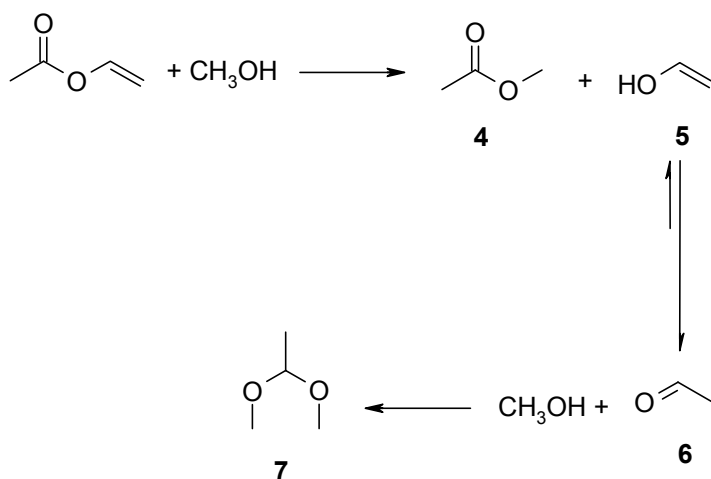
Scheme 4.3. Methylation of VAM

4.5.5.1. Parametric Effects

Effect of different parameters such as catalyst, VAM, methanol concentration and CO partial pressure on concentration-time was studied at three different temperatures using $PdCl_2(PPh_3)_2$ as a catalyst in the range of 363-383 K. The initial rates of reactions r_1 (formation of methyl-2-acetoxypropionate), r_2 (formation of methyl lactate) and r_3 (formation of methyl acetate) (see Scheme 4.4) were evaluated from the data in the range of less than 15 % conversion of VAM, which are presented in Table 4.9. These data represent formation of carbonylation products (methyl-2-acetoxypropionate and methyl lactate) and methyl acetate, which were primarily used to understand the rate dependency on different parameters. For evaluation of rate equations and kinetic parameters estimation, integral concentration-time data were used as discussed later.

The effect of agitation speed on the rate of reaction was studied at 383 K. In a gas liquid reaction, mass transfer issue becomes important at higher catalyst concentration. Insignificant effect of agitation speed on the reaction rate is one of the criteria to ensure that the reaction is in kinetic regime. As shown in Figure 4.6, the rate of carbonylation was independent of agitation speed indicating that the reaction was not mass transfer controlled. For kinetic study, the effect of various parameters was studied at 16.66 Hz to ensure kinetic regime.
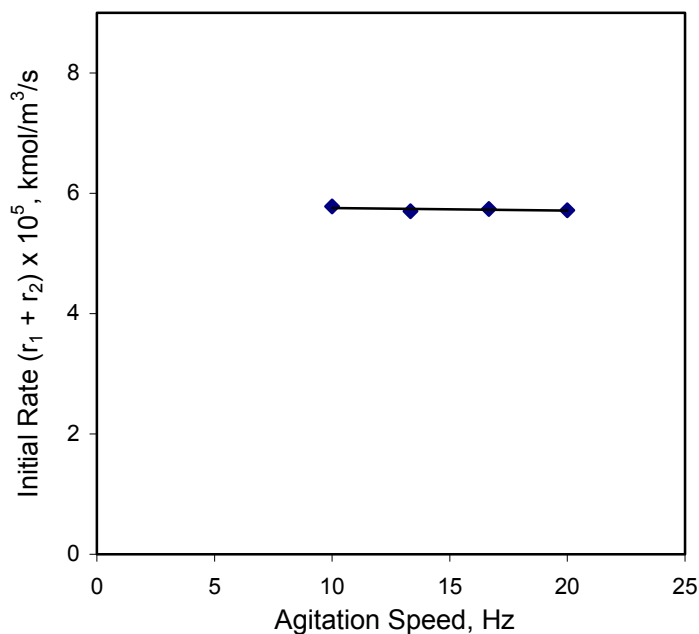
Fig. 4.6. Effect of agitation speed at 383 K

Reaction conditions: *PdCl$_2$(PPh$_3$)$_2$, 2 × 10^{-3} kmol/m^3; VAM, 1 kmol/m^3; CH$_3$OH, 2.4 kmol/m^3; Solvent, Toluene; Total Volume, 2.5 × 10^{-5} m^3; Temperature, 383K; P$_{CO}$, 5.4 MPa*

Table 4.9. Effect of different reaction parameters on initial rate of reactions involved in methoxycarbonylation of VAM

	Conc, kmol/m^3	Rate $\times 10^5$, kmol/m^3/s (363 K)				Rate $\times 10^5$, kmol/m^3/s (373 K)				Rate $\times 10^5$, kmol/m^3/s (383 K)			
		r_1	r_2	r_3	(r_1+r_2)	r_1	r_2	r_3	(r_1+r_2)	r_1	r_2	r_3	(r_1+r_2)
PdCl$_2$(PPh$_3$)$_2$ $\times 10^3$	1	1.41	0.51	2.70	1.90	1.70	0.70	6.27	2.40	2.25	1.00	7.42	3.25
	2	2.80	1.10	3.08	3.90	3.51	1.62	6.65	5.13	4.10	2.22	8.68	6.32
	4	4.5	2.03	4.55	6.53	6.49	2.71	8.63	9.20	8.83	4.40	10.20	13.23
	6	7.22	2.30	5.51	9.52	8.90	3.00	9.17	11.90	11.80	5.00	11.70	16.80
VAM	0.2	0.90	0.40	1.51	1.30	2.25	1.20	5.00	3.45	2.10	1.44	4.83	3.54
	0.4	1.80	0.80	2.20	2.60	3.50	1.60	6.65	5.10	3.35	1.60	7.03	4.95
	1	2.80	1.10	3.08	3.90	3.51	1.62	6.65	5.13	4.10	1.82	8.68	6.32
	2.4	3.30	1.03	4.80	4.13	3.80	1.60	8.27	5.00	4.20	1.79	9.43	5.69
Methanol	1	1.40	0.58	2.15	1.98	2.50	1.00	4.12	3.50	3.30	1.50	4.53	4.80
	2.4	2.80	1.10	3.08	3.90	3.51	1.62	6.65	5.13	4.10	2.22	8.68	6.32
	3.2	3.00	1.20	4.83	4.20	3.55	1.90	6.93	5.45	4.30	2.50	12.95	6.80
	4.8	3.15	1.35	4.47	4.50	3.60	2.10	8.20	5.70	4.35	2.80	14.68	7.15

Table 4.9. Effect of different reaction parameters on initial rate of reactions involved in methoxycarbonylation of VAM (continued)

	MPa	Rate × 10^5, kmol/m^3/s (363 K)				Rate × 10^5, kmol/m^3/s (373 K)				Rate × 10^5, kmol/m^3/s (383 K)			
		r_1	r_2	r_3	(r_1+r_2)	r_1	r_2	r_3	(r_1+r_2)	r_1	r_2	r_3	(r_1+r_2)
	2.76	1.24	0.69	2.08	1.95	1.55	1.00	4.50	2.55	2.11	1.39	7.05	3.50
	4.14	2.01	0.89	2.50	2.90	2.56	1.34	5.81	3.90	3.09	1.90	7.62	5.01
P_{CO}	5.52	2.77	1.13	3.08	3.90	3.51	1.62	6.65	5.13	4.10	2.22	8.68	6.32
	6.89	3.41	1.20	3.40	4.61	4.10	1.71	7.00	5.81	4.71	2.32	8.80	7.03
	8.27	3.82	1.25	3.41	5.07	4.68	1.78	6.80	6.46	5.22	2.38	8.17	7.60

Standard Reaction Conditions: PdCl$_2$(PPh$_3$)$_2$, 2 × 10^{-3} kmol/m^3; VAM, 1 kmol/m^3; CH$_3$OH, 2.4 kmol/m^3; Solvent, Toluene; Total Volume, 2.5 × 10^{-5} m^3; P$_{CO}$, 5.4 MPa; Agitation speed, 16.66 Hz;

Initial Rates: r_1, rate of formation of methyl-2-acetoxypropionate; r_2, rate of formation of methyl lactate; r_3, rate of formation of methyl acetate;(r_1 + r_2), rate of formation of carbonylation products (combined r_1 and r_2)

4.5.5.1.1. Effect of Catalyst Loading

Effect of catalyst loading was investigated in the catalyst concentration range (1×10^{-3}) to (6×10^{-3}) kmol/m^3. Increasing the catalyst concentration was found to increase the reaction rate r_1 linearly at all of the temperatures studied (Fig. 4.7, a). Such a linear increase in the reaction rate with catalyst concentration also suggests that the reaction occurs in kinetic regime. Rate of reaction r_2 varied linearly at lower concentration of catalyst $(< 4 \times 10^{-3}$ kmol/m$^3)$ after which it was found to be independent of catalyst concentration (Fig. 4.7, b). Though, the rate of reaction r_3 increased with catalyst concentration, it can be noted that the reaction occurs even without catalyst (at zero catalyst concentration, $r_3 = 2 \times 10^{-5}$, 5.07×10^{-5} and 6.66×10^{-5} kmol/m^3/s at 363, 373 and 383 K respectively) (Fig. 4.7, c). Thus, the reaction r_3 generates methyl acetate even in absence of catalyst, which increases with catalyst concentration. This increase in reaction rate was because of reaction r_2 generating methyl acetate. Rate of formation of carbonylation products $(r_1 + r_2)$ shows a linear trend with catalyst concentration (Fig. 4.7, d).

4.5.5.1.2. Effect of VAM Concentration

Increase in VAM concentration increased the rate of reaction r_1 linearly in the lower concentration range $(> 0.4$ kmol/m$^3)$. Further increase in concentration showed marginal increase in the rate (up to 1 kmol/m^3) beyond which it became independent of VAM concentration (Fig. 4.8, a). Similar trends in the variation of rates r_2, r_3 and $(r_1 + r_2)$ were observed at all temperatures studied. (Fig. 4.8; b, c and d).

4.5.5.1.3. Effect of Methanol Concentration

Effect of methanol concentration was studied in the range of 1 - 4.8 kmol/m^3 (Fig. 4.9). Rates of the reactions r_1 and r_2 were found to increase with increase in methanol concentration at lower concentration $(<2.4$ kmol/m$^3)$, beyond which the rates were constant showing an independency on methanol concentration at all temperatures studied (Fig. 4.9, a and b). Rate of methyl acetate formation (r_3) was linear at lower methanol concentration $(<3.2$ kmol/m$^3)$, beyond which it was independent of methanol

concentration at 363 and 373 K (Fig. 4.9, c). At 383 K, the rate r_3 showed a linear dependence on methanol concentration. Formation of higher amount of methyl acetate through methylation of VAM has already been reported in literature at higher temperature (> 383 K)[5] (Fig. 4.9, c). The rate of carbonylation reaction ($r_1 + r_2$) showed a linear dependence on methanol concentration at lower concentration range (< 2.4 kmol/m^3), whereas it was independent of methanol concentration at higher methanol concentration (>2.4 kmol/m^3) (Fig. 4.9, d). Though, it has been observed that catalyst precipitation occurs when methanol was used as a solvent as studied in the effect of solvent (Section 4.5.4), parametric effects were done at a maximum of 4.8 kmol/m^3 concentration, where catalyst precipitation was not noted, thus showing that the rates obtained under conditions of homogeneous catalysis.

4.5.5.1.4. Effect of CO Partial Pressure

Effect of CO partial pressure was studied in the range of 2.57 to 8.27 MPa. A linear dependence of the rate of the reaction r_1 on CO partial pressure was observed (Fig. 4.10, a). Rate of reaction r_2 varied linearly at lower CO partial pressure (< 6.9 MPa), beyond which it was independent of CO partial pressure (Fig. 4.10, b). The rate of reaction r_3 showed marginal increase with increase in CO partial pressure (Fig. 4.10, c). The rate of carbonylation ($r_1 + r_2$) varied linearly with CO partial pressure (Fig. 4.10, d).

4.5.5.2. Solubility

Solubility of CO in the reaction medium is necessary for interpretation of the kinetics of VAM methoxycarbonylation reaction. Henry's constants for CO in toluene at 363, 373 and 383 K were achieved by extrapolating the literature values for 333-353 K (Table 4.10)[9], which were calculated as per the formula given in equation 4.8.

$$H_e = {X_a}/{P_f} \qquad (4.8)$$

Where X_a represents the mole fraction of CO in the liquid phase at the pressure P_f
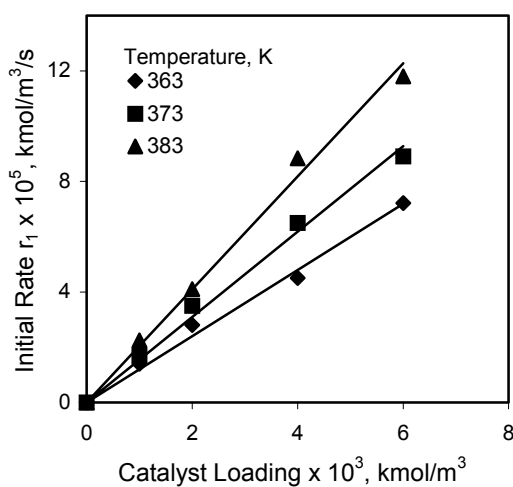
a) Rate dependence of reaction r_1
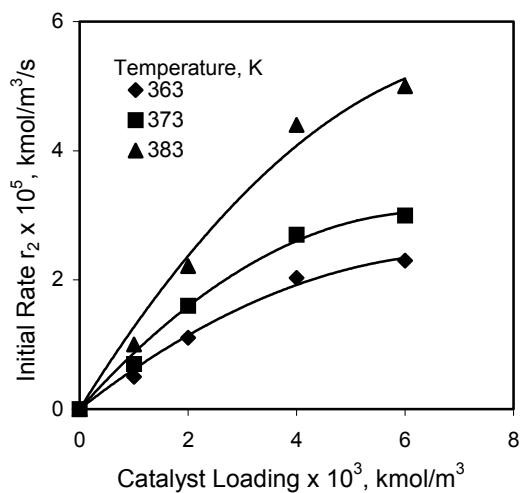
b) Rate dependence of reaction r_2
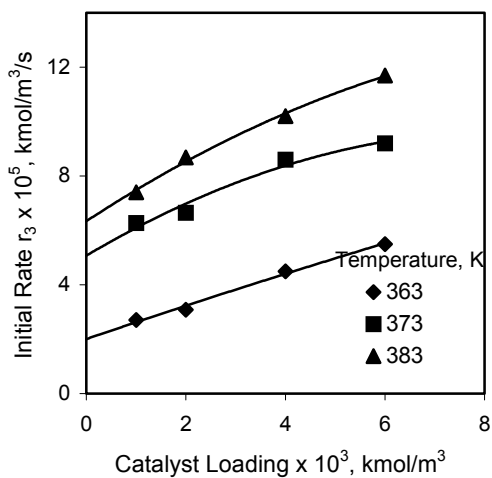
c) Rate dependence of reaction r_3
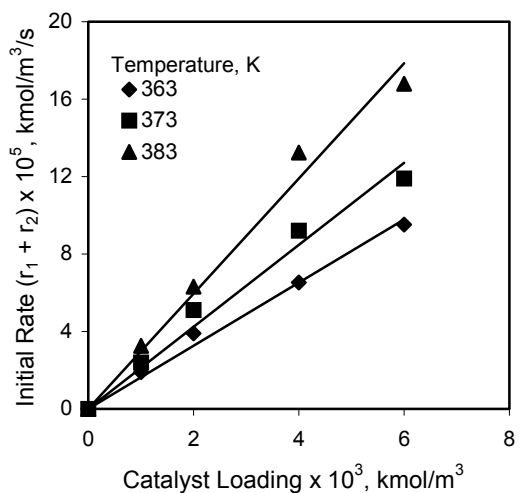
d) Rate dependence of reaction $(r_1 + r_2)$

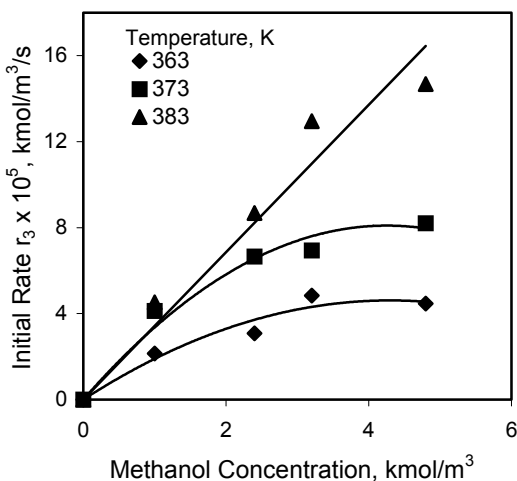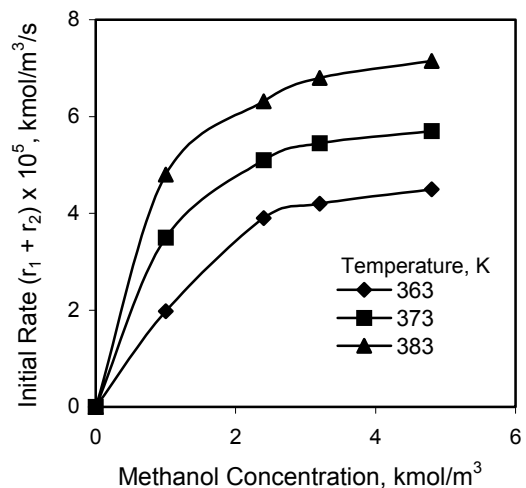Fig. 4.7. Effect of catalyst loading on VAM methoxycarbonylation

Reaction conditions: VAM, 1 kmol/m³; CH₃OH, 2.4 kmol/m³; Solvent, Toluene; Total Volume, 2.5 × 10⁻⁵ m³; P_CO, 5.4 MPa; Agitation Speed, 16.66 Hz

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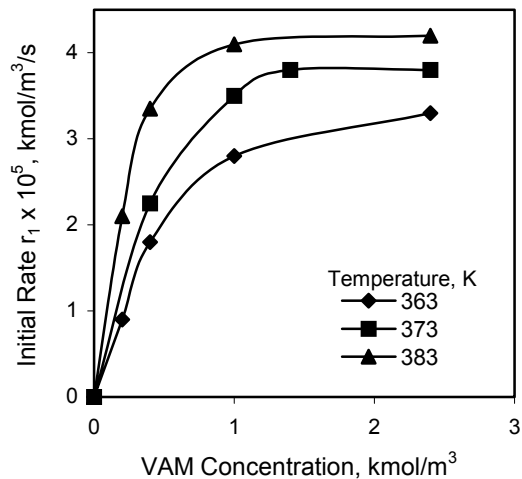
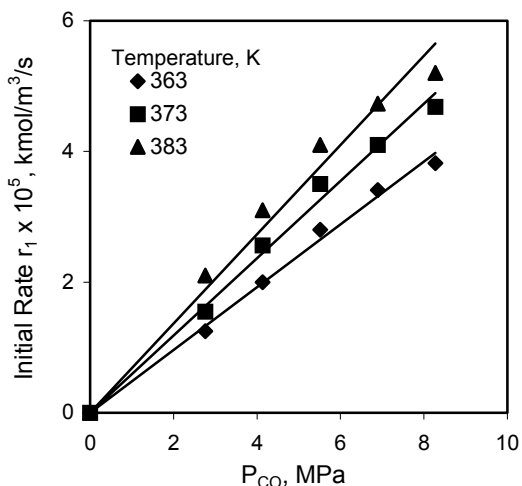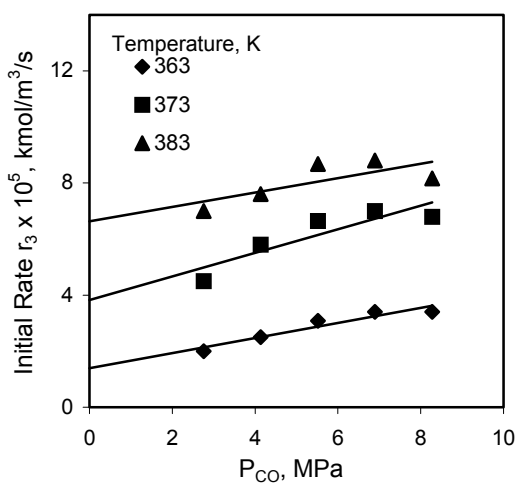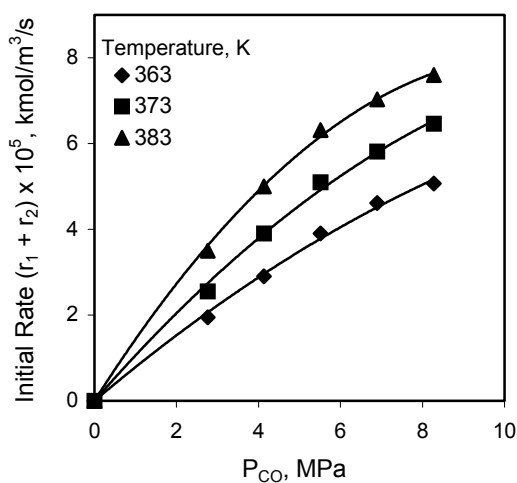a) Rate dependence of reaction r_1
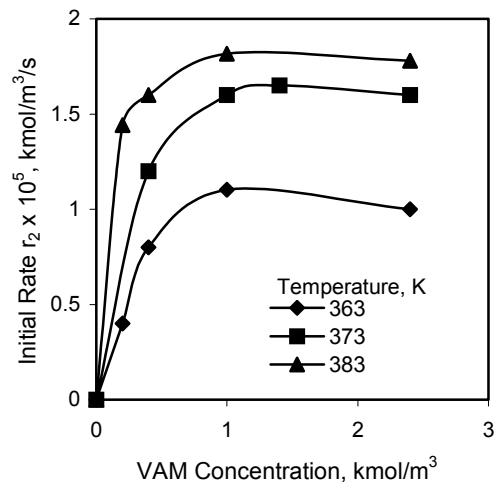
b) Rate dependence of reaction r_2
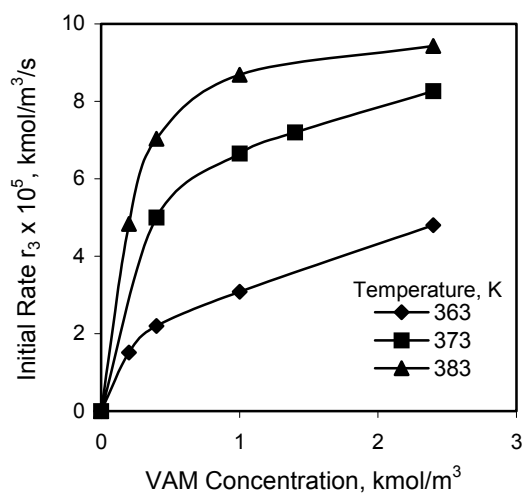
c) Rate dependence of reaction r_3
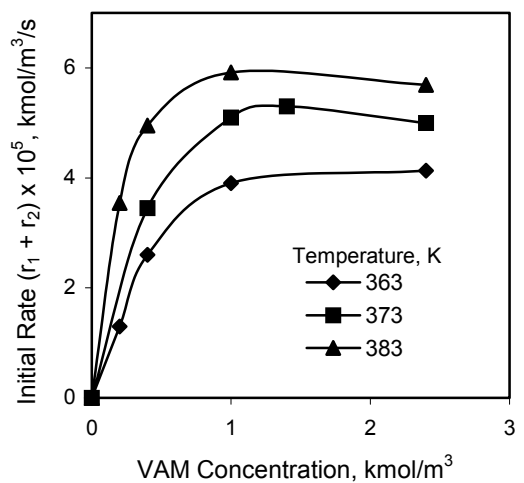
d) Rate dependence of reaction $(r_1 + r_2)$

Fig. 4.8. Effect of substrate concentration in VAM methoxycarbonylation reaction

Reaction conditions: PdCl$_2$(PPh$_3$)$_2$, 2 × 10^{-3} kmol/m^3; CH$_3$OH, 2.4 kmol/m^3; Solvent, Toluene; Total Volume, 2.5 × 10^{-5} m^3; P$_{CO}$, 5.4 MPa; Agitation Speed, 16.66 Hz
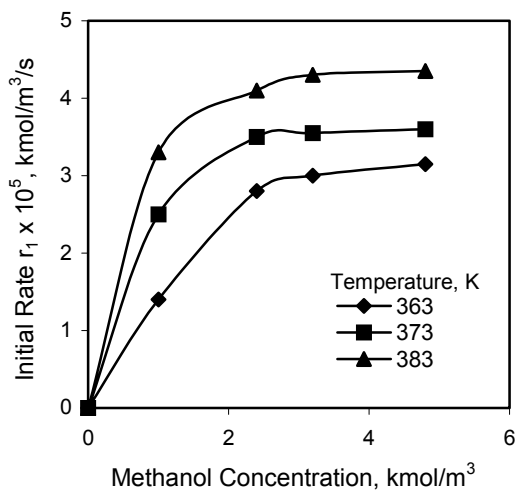
a) Rate dependence of reaction r_1
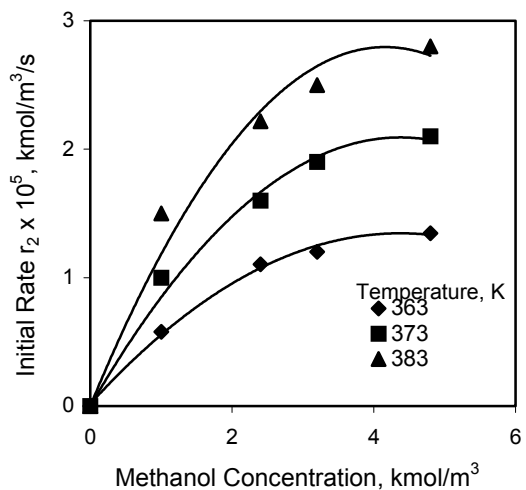
b) Rate dependence of reaction r_2

c) Rate dependence of reaction r_3

d) Rate dependence of reaction $(r_1 + r_2)$

Fig. 4.9. Effect of methanol concentration

Reaction conditions: PdCl$_2$(PPh$_3$)$_2$, 2 × 10^{-3} kmol/m^3; VAM, 1 kmol/m^3; Solvent, Toluene; Total Volume, 2.5 × 10^{-5} m^3; P$_{CO}$, 5.4 MPa; Agitation Speed, 16.66 Hz

a) Rate dependence of reaction r_1
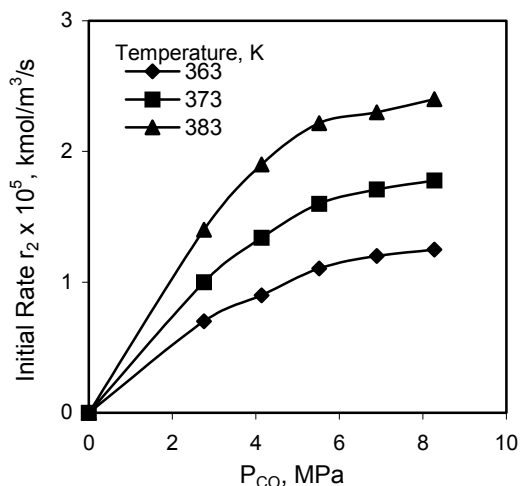
b) Rate dependence of reaction r_2

c) Rate dependence of reaction r_3

d) Rate dependence of reaction $(r_1 + r_2)$

Fig. 4.10. Effect of CO partial pressure

Reaction conditions: $PdCl_2(PPh_3)_2$, 2×10^{-3} kmol/m^3; VAM, 1 kmol/m^3; CH_3OH, 2.4 kmol/m^3; Solvent, Toluene; Total Volume, 2.5×10^{-5} m^3; Agitation Speed, 16.66 Hz

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Table 4.10. Henry's constant for CO in toluene at different temperatures

	Literature[9] Values			Extrapolated Values		
Temperature, K	333	343	353	363	373	383
He $\times 10^2$, kmol/m^3/Mpa	8.403	8.547	8.673	8.816	8.963	9.114

The saturation solubility of CO in liquid phase (A*) was calculated using the following expression,

$$A^* = P_{CO} \times H_e \tag{4.9}$$

4.5.5.3. Kinetic Model

The experimental concentration-time data in the kinetic regime were used to evaluate the different rate equations for methoxycarbonylation of VAM. Methoxycarbonylation of VAM involves different consecutive and parallel reactions as summarized in Scheme 4.2. The reaction Scheme 4.2 was simplified as shown in Scheme 4.4, where it was assumed that formation of methyl acetate (**E'**) by reaction r_3 was in stoichiometric proportion to dimethyl acetal (**H**) formed. Based on the observed trends in methoxycarbonylation of VAM using PdCl$_2$(PPh$_3$)$_2$ as a catalyst, five different rate models were selected to evaluate the most suitable rate model for methoxycarbonylation of VAM.
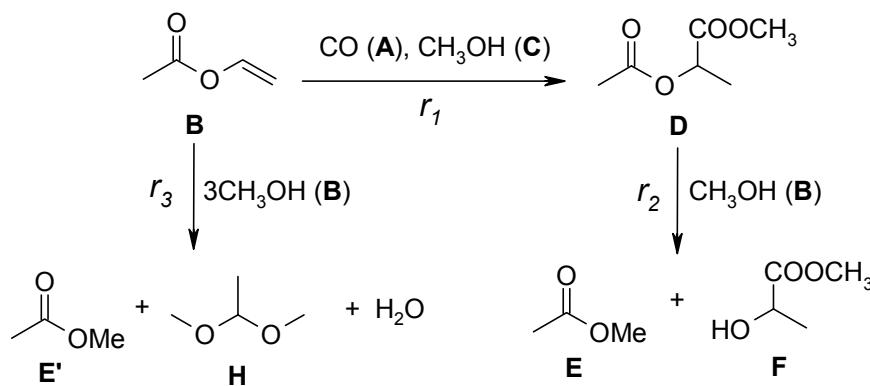
Scheme 4.4. Simplified reaction scheme for methoxycarbonylation of VAM

4.5.5.3.1. Estimation of Kinetic Parameters and Model Discrimination

The integral concentration-time data obtained at 363, 373 and 383 K were used for evaluation of kinetic models, since multistep reactions are involved. A non-linear least square regression analysis was used to obtain the best-fit values of the parameters. For this purpose, an optimization program based on Marquarts method combined with a Runge-Kutta method[10] was used to solve the set of equations shown in Table 4.11. The model parameters were estimated by minimizing the following objective function:

$$\phi_{min} = \sum_{i=1}^{n} \left(R_{exp} - R_{pre} \right)^2 \qquad (4.10)$$

Where R_{exp} is the rate observed experimentally, R_{pre} is the predicted rate using nonlinear regression analysis and n is number of data points.

All five models were thus evaluated for this analysis to obtain the rate parameters. The values of rate parameters at different temperatures are presented in Table 4.11. The values of Φ_{min} indicate the extent of fit of the kinetic models. As five different rate models were considered for the mathematical calculations, few models have to be discriminated in order to get an appropriate model for this reaction. Model I and Model-II gave higher values of the Φ_{min}, suggesting lack of fit of these models. Therefore, the Models I and II were rejected on the basis of their lack of fit. The analysis of experimental data was performed using nonlinear regression analysis that has purely mathematical basis, further model discrimination was done based on thermodynamic considerations[11,12]. Considering the thermodynamics of any reaction, the values of a kinetic constant should have a positive value (k_1, k_2, k_3, K_B or $K_C > 0$ and $E_a > 0$). Model-IV and V gave negative values of k_2 (for Model-V), K_B (for Model-IV) and K_C (for Model IV). Also model-I gave the negative value for its kinetic parameter k_2. So the Models-I, IV and V were rejected based on the thermodynamic constrains. Thus, the discrimination of the proposed models based on the objective function and thermodynamic constrains suggests that the Model-III was found to be the best fit for the methoxycarbonylation reaction.

Table 4.11. Comparison of various models of methoxycarbonylation of VAM at different temperatures

Model No.	Model	Temp, K	$k_1 \times 10^{-3}$, m³/kmol s	$k_2 \times 10^2$, m³/kmol s	$k_3 \times 10^4$, m³/kmol s	$K_B \times 10$, m³/kmol	$K_C \times 10^{-2}$, m³/kmol	$\Phi_{min} \times 10^4$
1	$r_1 = \dfrac{(k_1 C_W C_A C_B C_C)}{(1 + K_B C_B)(1 + K_C C_C)}$	363	0.764	2.578	219	5.486	2.759	15.096
	$r_2 = \dfrac{(k_2 C_C C_D)}{(1 + K_C C_C)}$	373	25.101	-164.0	1987	-169.3	6.043	1.36×10^5
	$r_3 = \dfrac{(k_3 C_B C_C)}{(1 + K_C C_C)}$	383	5.556	18.253	942	14.018	8.949	0.865
2	$r_1 = \dfrac{(k_1 C_W C_A C_B C_C)}{(1 + K_B C_B)(1 + K_C C_C)}$	363	21.350	0.010	2.85×10^5	650.7	70.098	1.58×10^5
	$r_2 = (k_2 C_C C_D)$	373	21.427	0.012	2.19×10^5	84.92	4.762	0.213
	$r_3 = \dfrac{(k_3 C_B C_C)}{(1 + K_B C_B)(1 + K_C C_C)}$	383	6188	0.012	1.11×10^8	169.37	794.7	0.384
3	$r_1 = \dfrac{(k_1 C_W C_A C_B C_C)}{(1 + K_B C_B)(1 + K_C C_C)}$	363	0.911	3.722	12.43	3.566	5.37	15.497
	$r_2 = \dfrac{(k_2 C_C C_D)}{(1 + K_C C_C)}$	373	1.085	12.836	9.76	3.882	4.956	0.265
	$r_3 = \dfrac{(k_3 C_B C_C)}{(1 + K_B C_B)}$	383	3.760	0.378	13.071	2.969	33.91	1.145

		363	3.332	19.062	0.468	-3.687	-27.097	95.568
4	$r_1 = \dfrac{(k_1 C_W C_A C_B C_C)}{(1 + K_B C_B)(1 + K_C C_C)}$ $r_2 = \dfrac{(k_2 C_C C_D)}{(1 + K_C C_C)}$ $r_3 = (k_3 C_B C_C)$	373	10.901	0.843	0.299	-4.775	-50.965	0.803
		383	3.288	46.524	0.607	-1482	-57.955	16.553
5	$r_1 = \dfrac{(k_1 C_W C_A C_B C_C)}{(1 + K_B C_B)(1 + K_C C_C)}$ $r_2 = (k_2 C_C C_D)$ $r_3 = (k_3 C_B C_C)$	363	0.038	-0.004	0.450	6.633	0.137	14.682
		373	0.202	0.018	0.232	4.692	0.660	0.482
		383	0.031	0.008	0.513	5.677	0.123	2.167

Symbols used: r_i is rate of the respective reaction 1, 2 and 3 in Scheme 4.4; k_1, k_2 and k_3 are the rate constants of reactions 1, 2 and 3; K_B and K_C are equilibrium constant for VAM and methanol respectively; C_W is the concentration of catalyst; C_A is the concentration of dissolved CO in liquid phase; C_B is the concentration of VAM; C_C is the concentration of methanol; C_D is the concentration of methyl-2-acetoxypropionate.

According to the suggested model (Model-III), the fit of experimental concentration-time data with the model predictions (predicted) was quite good in the range of conditions used. The concentration-time data of the representative reactions are given in Fig. 4.11-4.17, showing these comparisons.
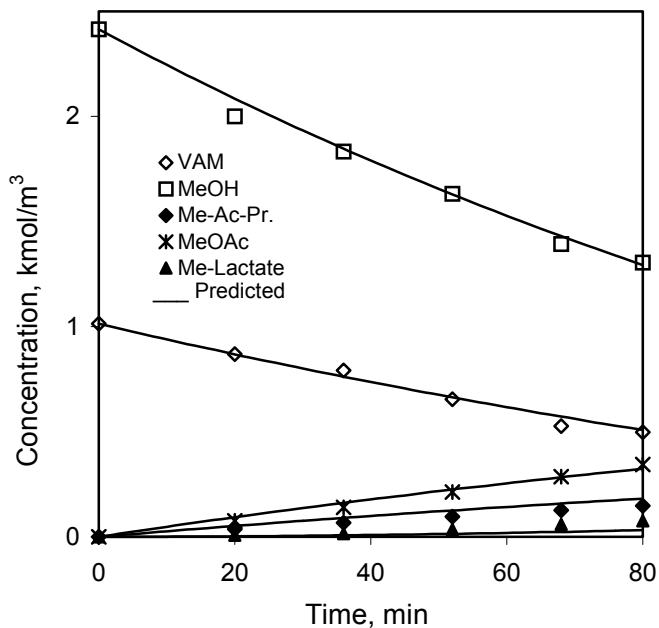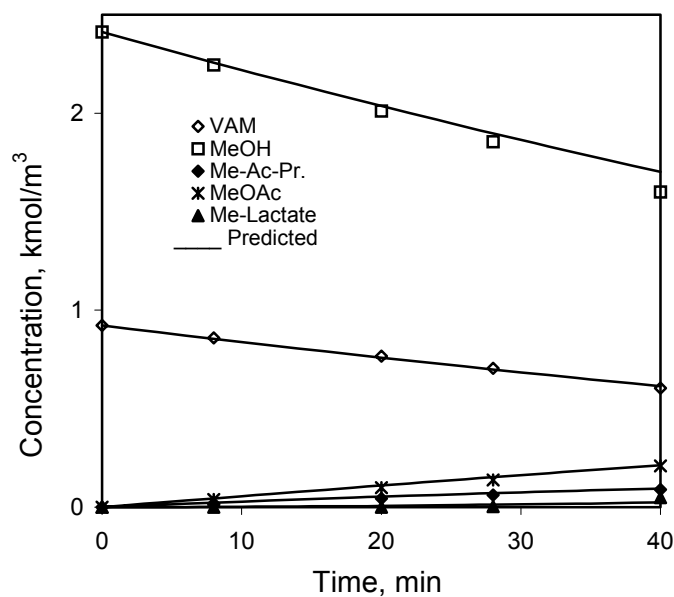

Fig. 4.11. Experimental and predicted concentration-time profile at 363K

Reaction conditions: PdCl$_2$(PPh$_3$)$_2$, 2 × 10^{-3} kmol/m^3; VAM, 1 kmol/m^3; CH$_3$OH, 2.4 kmol/m^3; Solvent, Toluene; Total Volume, 2.5 × 10^{-5} m^3; Temperature, 363K; P$_{CO}$, 5.4 MPa; Agitation Speed, 16.66 Hz
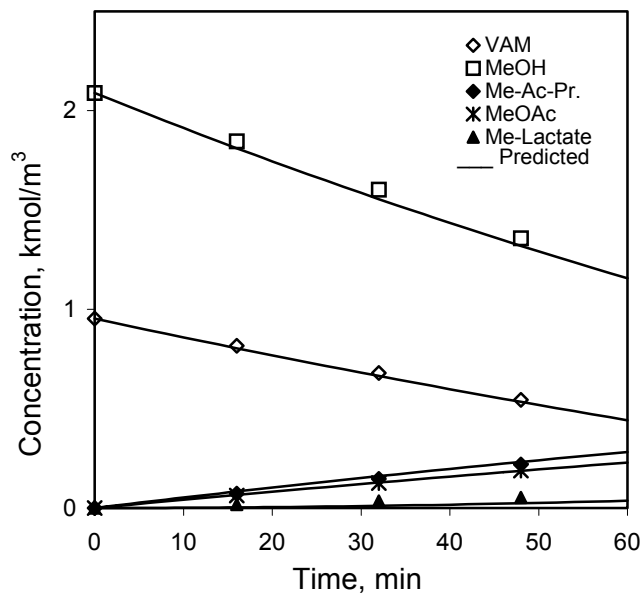
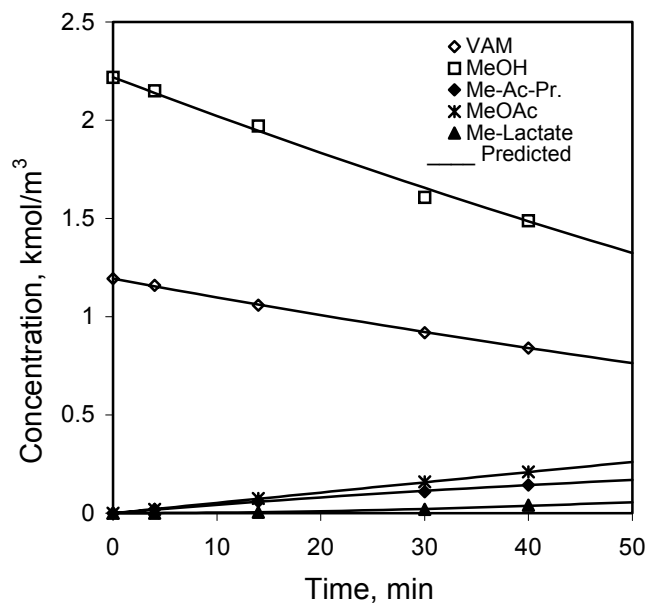Fig. 4.12. Concentration-time profile with higher catalyst loading at 363K

Reaction conditions: $PdCl_2(PPh_3)_2$, 4×10^{-3} *kmol/m³; VAM, 1 kmol/m³; CH₃OH, 2.4 kmol/m³; Solvent, Toluene; Total Volume, 2.5×10^{-5} m³; Temperature, 363K; P_{CO}, 5.4 MPa; Agitation Speed, 16.66 Hz*
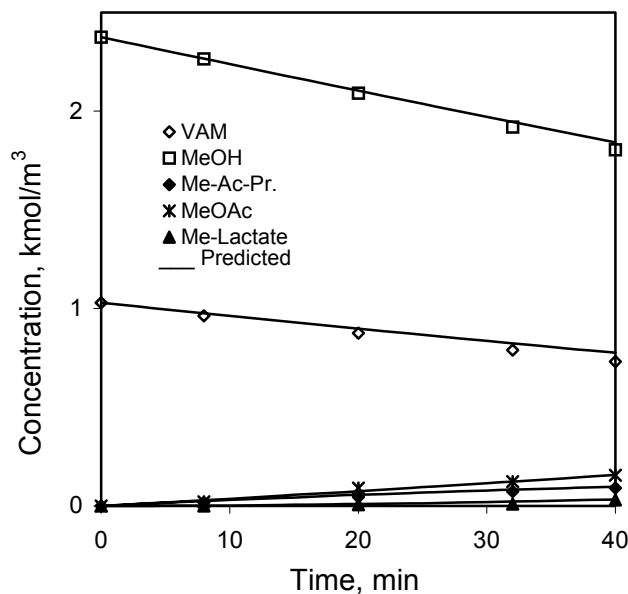
Fig. 4.13. Experimental and predicted concentration-time profile at 373K

Reaction conditions: $PdCl_2(PPh_3)_2$, 4×10^{-3} *kmol/m³; VAM, 1 kmol/m³; CH₃OH, 2.4 kmol/m³; Solvent, Toluene; Total Volume, 2.5×10^{-5} m³; Temperature, 373K; P_{CO}, 5.4 MPa; Agitation Speed, 16.66 Hz*

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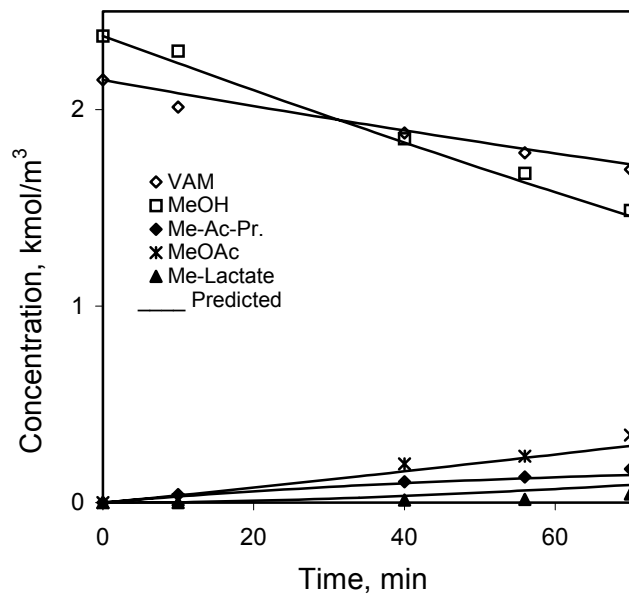
Fig. 4.14. Concentration-time profile with higher VAM concentration at 373K

Reaction conditions: $PdCl_2(PPh_3)_2$, 2×10^{-3} $kmol/m^3$; *VAM, 2.2 $kmol/m^3$; CH_3OH, 2.4 $kmol/m^3$; Solvent, Toluene; Total Volume, 2.5×10^{-5} m^3; Temperature, 373K; P_{CO}, 5.4 MPa; Agitation Speed, 16.66 Hz*

Fig. 4.15. Experimental and predicted concentration-time profile at 383K

Reaction conditions: $PdCl_2(PPh_3)_2$, 2×10^{-3} $kmol/m^3$; *VAM, 1 $kmol/m^3$; CH_3OH, 2.4 $kmol/m^3$; Solvent, Toluene; Total Volume, 2.5×10^{-5} m^3; Temperature, 383K; P_{CO}, 5.4 MPa; Agitation Speed, 16.66 Hz*

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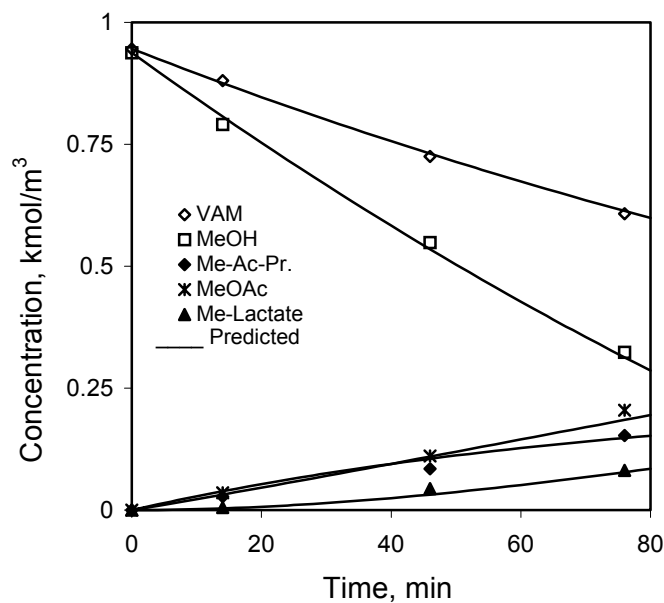
Fig. 4.16. Concentration-time profile with lower methanol concentration at 383K

Reaction conditions: $PdCl_2(PPh_3)_2$, 2×10^{-3} kmol/m³; *VAM, 0.95 kmol/m³; CH₃OH, 0.95 kmol/m³; Solvent, Toluene; Total Volume, 2.5×10^{-5} m³; Temperature, 383K; P_{CO}, 5.4 MPa; Agitation Speed, 16.66 Hz*

Fig. 4.17. Concentration-time profile with higher CO partial pressure at 383K

Reaction conditions: $PdCl_2(PPh_3)_2$, 2×10^{-3} kmol/m³; *VAM, 1.2 kmol/m³; CH₃OH, 2.25 kmol/m³; Solvent, Toluene; Total Volume, 2.5×10^{-5} m³; Temperature, 383K; P_{CO}, 8.27 MPa; Agitation Speed, 16.66 Hz*

Activation energy of the catalytic reaction r_1 was calculated using Arrhenius plot, (Fig 4.18), which was found to be 81.62 kJ/mol. According to the suggested model (Model-III), the methoxycarbonylation of VAM followed first order with respect to catalyst and CO, whereas it was negative order with respect to VAM and methanol.
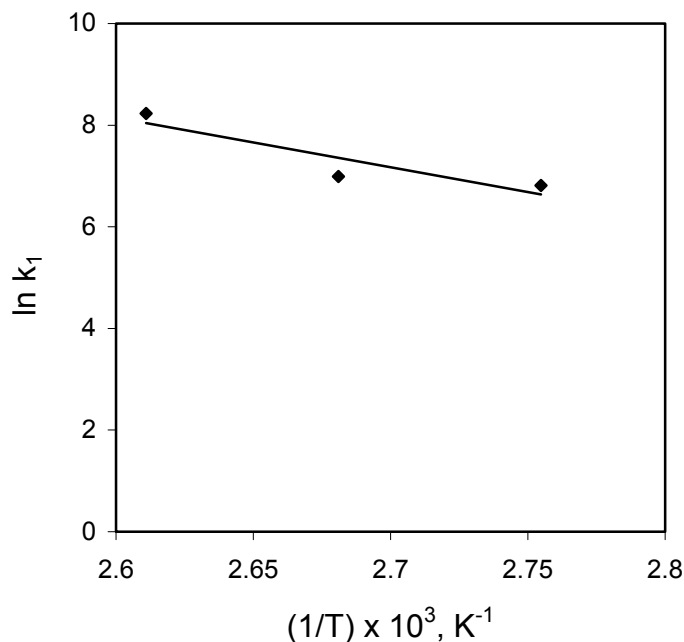
Fig. 4.18. Temperature dependence of rate constant k_1

4.6. Hydrolysis of Carbonylation Products

Carbonylation of VAM yields methyl-2-acetoxypropionate and methyl lactate as products, which are hydrolysable to lactic acid. Hydrolysis can be carried out using acidic catalysts as described in Section 4.3.2. Hydrolysis of methyl-2-acetoxypropionate generated acetic acid in the reaction mixture (Scheme 4.5), which can act as a catalyst due to its acidity that made the hydrolysis of methyl-2-acetoxy propionate faster than that of methyl lactate (Table 4.12 and 4.13).
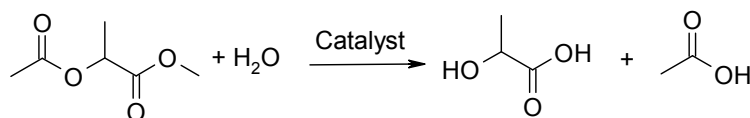
Scheme 4.5. Hydrolysis of methyl-2-acetoxypropionate

4.6.1. Hydrolysis of Methyl-2-Acetoxypropionate

Methyl-2-acetoxypropionate was isolated from the reaction mixtures as in Section 4.2.3 and hydrolyzed to lactic acid using different acidic catalysts. Using TsOH as a catalyst, complete conversion of methyl-2-acetoxypropionate was obtained. Heterogeneous catalyst Amberlite IR-20 resin was used for hydrolysis, which gave 43% conversion in 3 hours and successive recycle maintained the activity (Table 4.11).

Table 4.12. Hydrolysis of methyl-2-acetoxypropionate

Run No.	Catalyst (g or ml)	Time, h	Conversion, %
1	TsOH (0.191 g)	3	100
2	35%HCl (1 ml)	3	95.23
3	Amberlite IR 20 (0.5 g)	3	43.10
4	[b]Amberlite IR 20	3	41.77

[a]*Reaction conditions: Methyl-2-acetoxypropionate, 6.66 × 10^{-1} kmol/m^3; Water, 1.5 ×10^{-5} m^3; Temperature, 353K;* [b]*Catalyst recycled from run no.3*

4.6.2. Hydrolysis of Methyl Lactate

Methyl lactate was extracted from the carbonylation reaction mixture as in section 4.3.5 and hydrolyzed using various acidic catalysts. TsOH was found to be the best catalyst for hydrolysis of methyl lactate. Heterogeneous acidic catalysts also showed comparable activity even in successive recycles (Table 4.13).

Table 4.13. Hydrolysis of methyl lactate

Run No.	Catalyst, (g or ml)	Time, h	Conversion, %
1	TsOH (0.191 g)	3	65.14
2	35%HCl (1 ml)	3	58.05
3	Amberlite IR 20 (0.5 g)	3	38.27
4	[b]Amberlite IR 20	3	37.89

[a]*Reaction conditions*: *Aqueous fraction containing methyl lactate extracted from carbonylation reaction mixtures (section 4.3.5), 2.5×10^{-5} m³; Temperature, 353 K;* [b]*Catalyst recycled from run no.3*

4.7. Conclusions

Lactic acid is commercially important in baking industry, cheese industry, pharmaceutical industry, cosmetic industry, in dying wool, to make plasticisers for resin, etc. The current worldwide production of lactic acid is estimated to be 40,000 TPA. Currently lactic acid is produced industrially by fermentation of molasses, but the process produces large amount of byproducts, making product separation and purification expensive. Any alternative technology yielding lactic acid in lower cost of production using environmentally compatible methods would result in a dramatic increase in the existing market and evolution of a range of new applications.

Methoxycarbonylation of VAM provides an economical and environmentally benign catalytic route for the synthesis of a precursor (methyl-2-acetoxypropionate) to lactic acid. Methoxycarbonylation of VAM using $PdCl_2(PPh_3)$ as a catalyst showed the following trends:

1) Ligands with basic nature enhanced the catalytic activity of $PdCl_2(PPh_3)_2$ when used in presence of TsOH whereas acidic ligands promoted the catalyst activity in absence of TsOH.

2) Polarity of solvents was found to have significant effect on the catalytic activity. Decrease in the catalytic activity was observed with increasing the polarity of solvent.

3) Catalyst precursors $PdX_2(PPh_3)_2$ with X = Cl, Br or I showed the trend in catalytic activity as: X = Cl > Br >> I. Use of quaternary ammonium halide TBAX along

with PdCl$_2$(PPh$_3$)$_2$ as a catalyst increased the conversion of VAM and selectivities to the carbonylation products (methyl-2-acetoxypropionate and methyl lactate).

Methoxycarbonylation of VAM involves consecutive and parallel reactions, which generate carbonylation products (methyl-2-acetoxypropionate and methyl lactate) along with side products (methyl acetate and dimethyl acetal). Kinetics of methoxycarbonylation of VAM was studied using PdCl$_2$(PPh$_3$)$_2$ as a catalyst in a temperature range of 363-383 K. Five different rate models were considered and an appropriate rate model was suggested for this reaction. Kinetic study of methoxycarbonylation of VAM revealed that the reaction was first order with respect to catalyst and CO, whereas it was first order tending to zero order with respect to VAM and methanol. Activation energy of the catalytic reaction was found to be 81.62 kJ/mol.

Lactic acid is industrially important in baking industry, cheese industry, pharmaceutical industry, cosmetic industry, in dying wool, to make plasticisers for resin, etc. Lactic acid is commercially produced by two methods: a) fermentation of molasses and b) Hydrocyanation of acetaldehyde followed by hydrolysis of cyanohydrin produced. Both the processes use toxic and corrosive chemicals and produce stoichiometric amount of byproducts, which is undesirable from environmental point of view. The methoxycarbonylation of VAM provides an economic and environmentally benign catalytic method for synthesis of a precursor (methyl-2-acetoxypropionate) to lactic acid, which can be easily converted to lactic acid by hydrolysis.

Notations:

C_A = Concentration of dissolved CO in the reaction mixture, $kmol/m^3$

C_B = Concentration of VAM, $kmol/m^3$

C_C = Concentration of methanol, $kmol/m^3$

C_D = Concentration of methyl-2-acetoxypropionate, $kmol/m^3$

C_W = Catalyst concentration, $kmol/m^3$

He = Henry's constant, $kmol/m^3/MPa$

k_1, k_2, k_3 = Reaction rate constants, $(m^3/kmol).s^{-1}$

K_B, K_C = Equilibrium constants for VAM and methanol, $m^3/kmol$

R_{exp} = Experimental rate, $kmol/m^3/s$

R_{pre} = Predicted rate, $kmol/m^3/s$

r_1, r_2, r_3 = Rate of respective reactions in Scheme 4.4, $kmol/m^3/s$

T = Temperature, K

X_a = Mole fraction of the solute gas in the liquid phase

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APPENDIX-I

Spectroscopic Characterizations of Allyl Alcohol Carbonylation Products
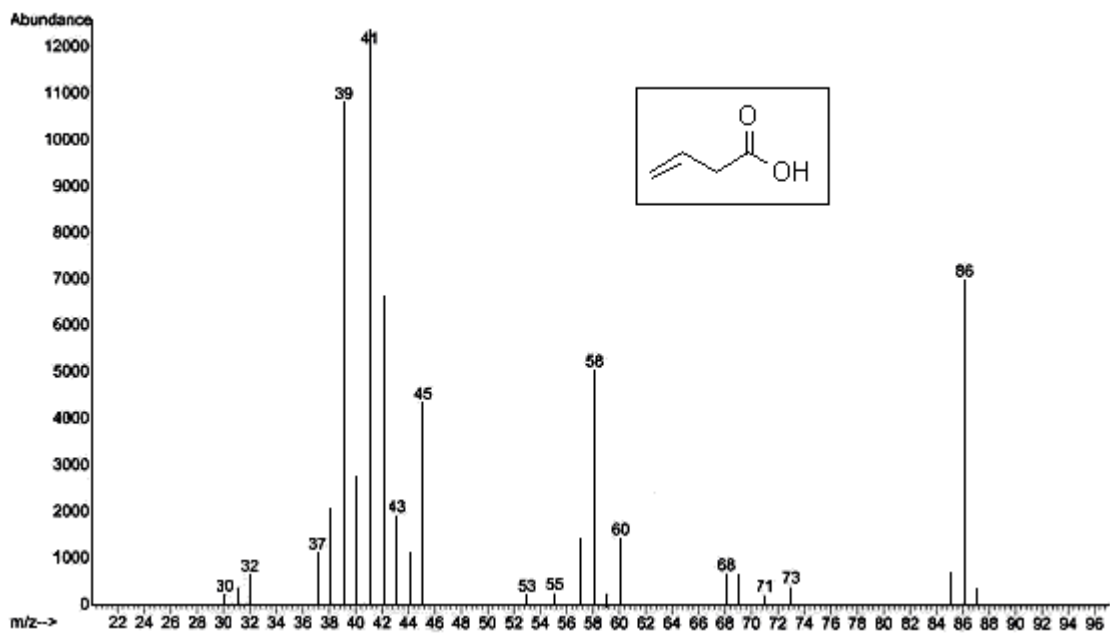
Fig. A1.1. GCMS of the carbonylation product (3-butenoic acid) isolated from the carbonylation reactions
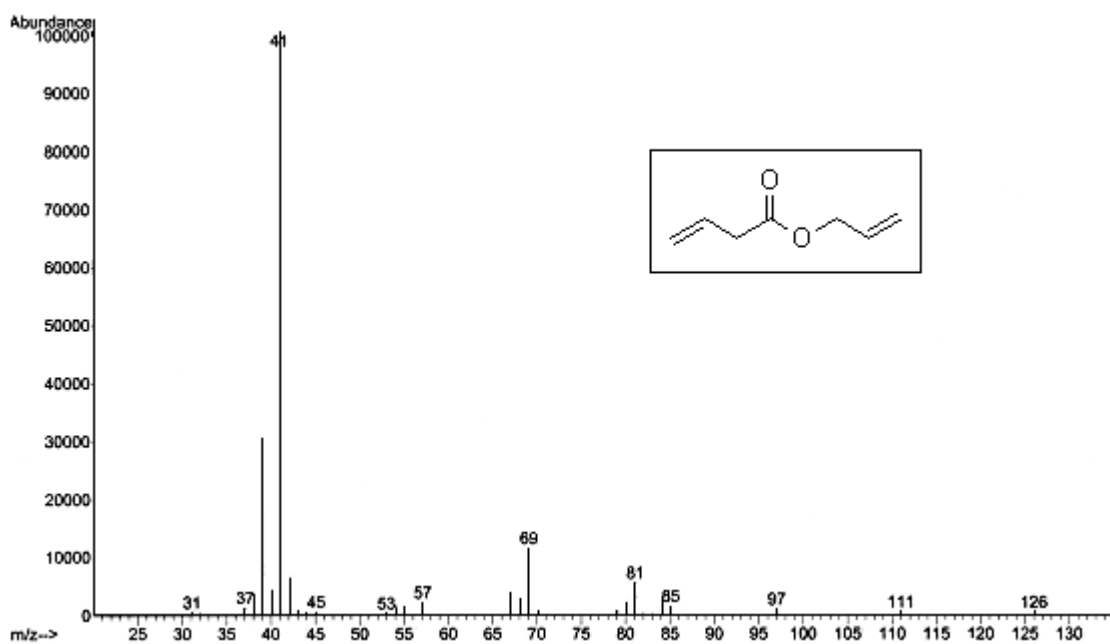
Fig. A1.2. GCMS of the carbonylation product (allyl-3-butenoate) isolated from the carbonylation reactions
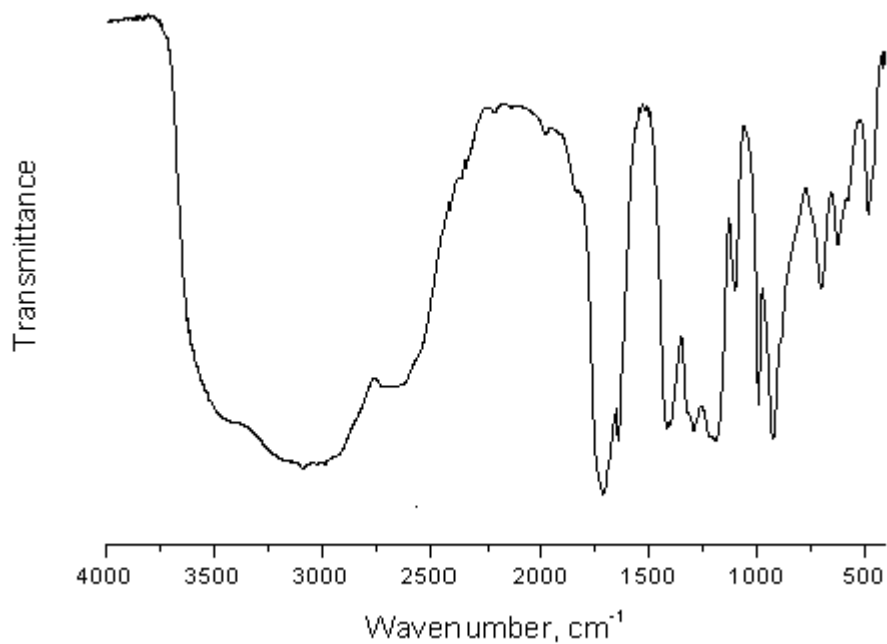
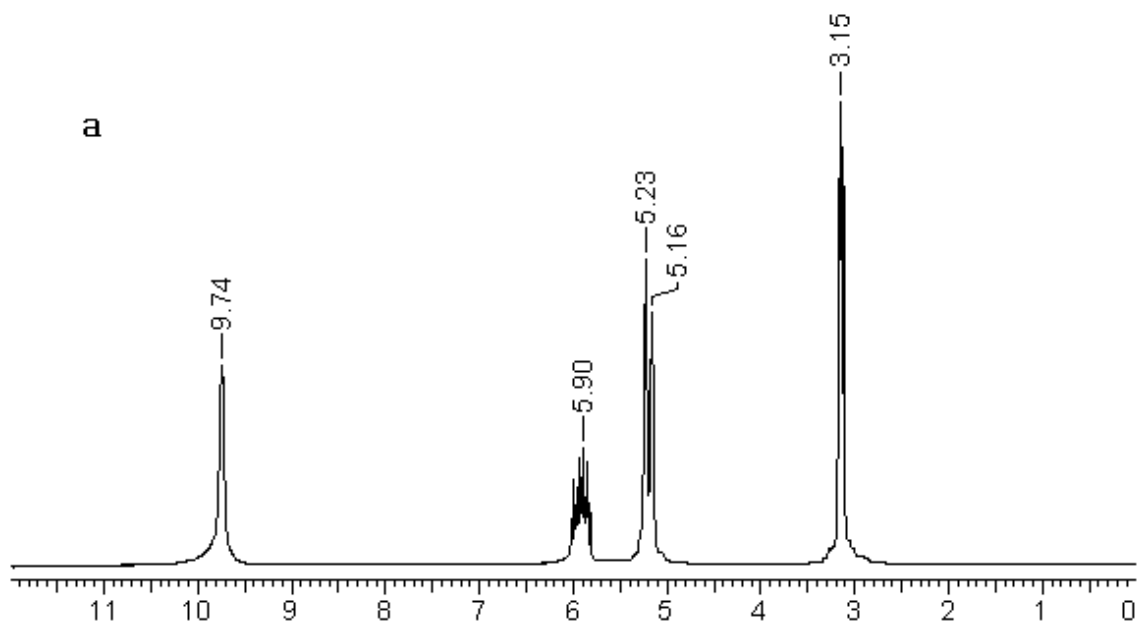Fig. A1.3. FTIR of (3-butenoic acid, ν_{CO}=1716 cm^{-1}) isolated from carbonylation reactions.
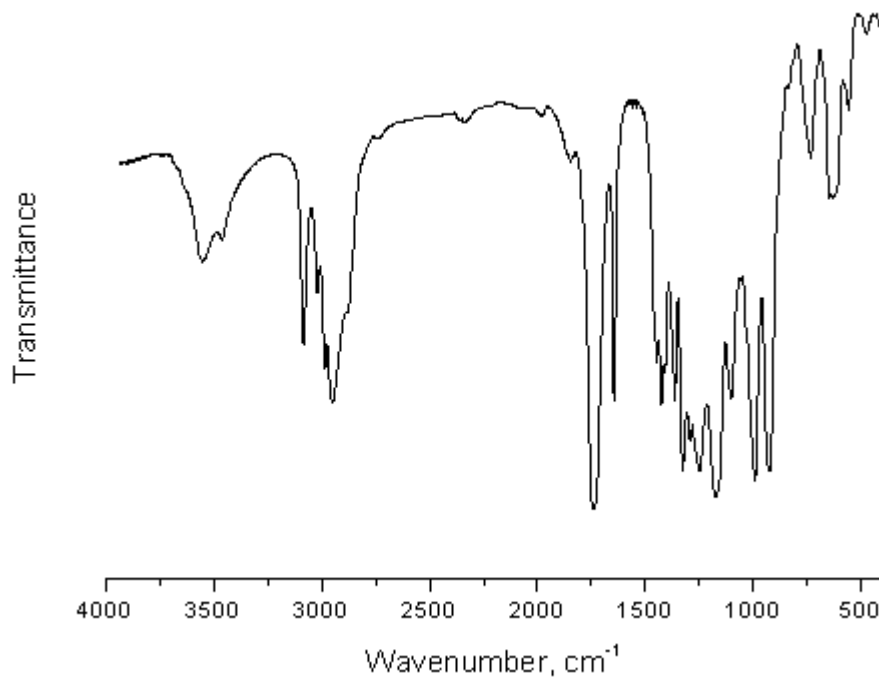
Fig. A1.4. FTIR of (allyl-3-butenoate, ν_{CO}=1739 cm^{-1}) isolated from carbonylation reactions.

Fig. A1.5. ^{1}H NMR of spectra of the carbonylation products isolated from carbonylation reaction mixtures
a: *3-butenoic acid in CDCl₃, [δ 9.74 (s, 1H), δ 5.90 (m, 1H), δ 5.23 (d, 1H), δ 5.16 (d, 1H), δ 3.15 (d, 2H)]*
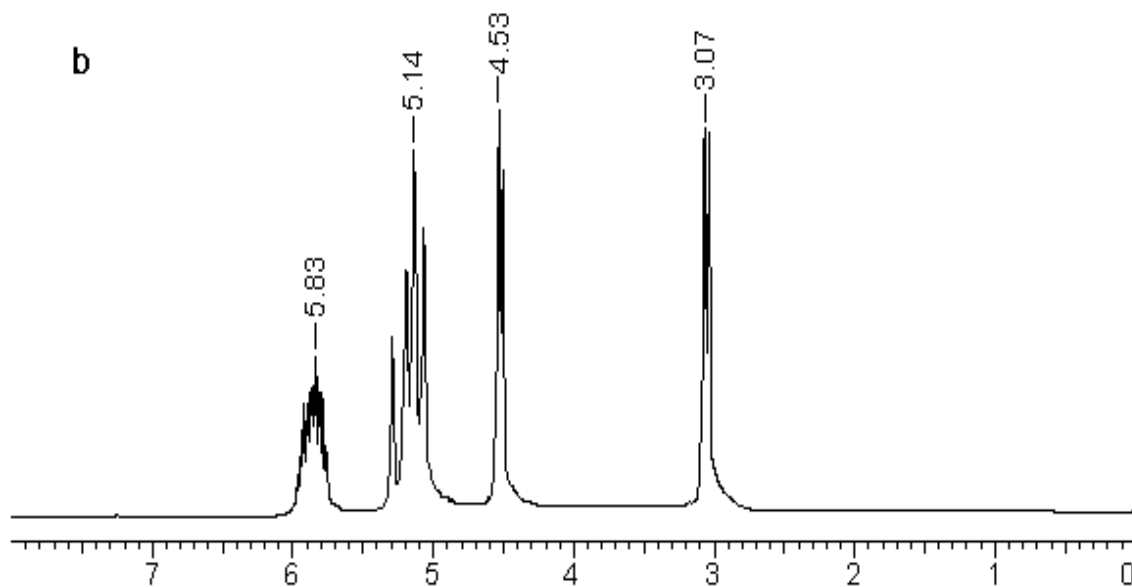
Fig. A1.6. ^{1}H NMR of spectra of the carbonylation products isolated from carbonylation reaction mixture
b: *allyl-3-butenoate in CDCl₃, [δ 5.83 (m, 2H), δ 5.14 (dd, 4H), δ 4.53 (d, 2H), δ 3.07 (d, 2H)]*

APPENDIX-II

Spectroscopic Characterizations of Vinyl Acetate (VAM) Carbonylation Products
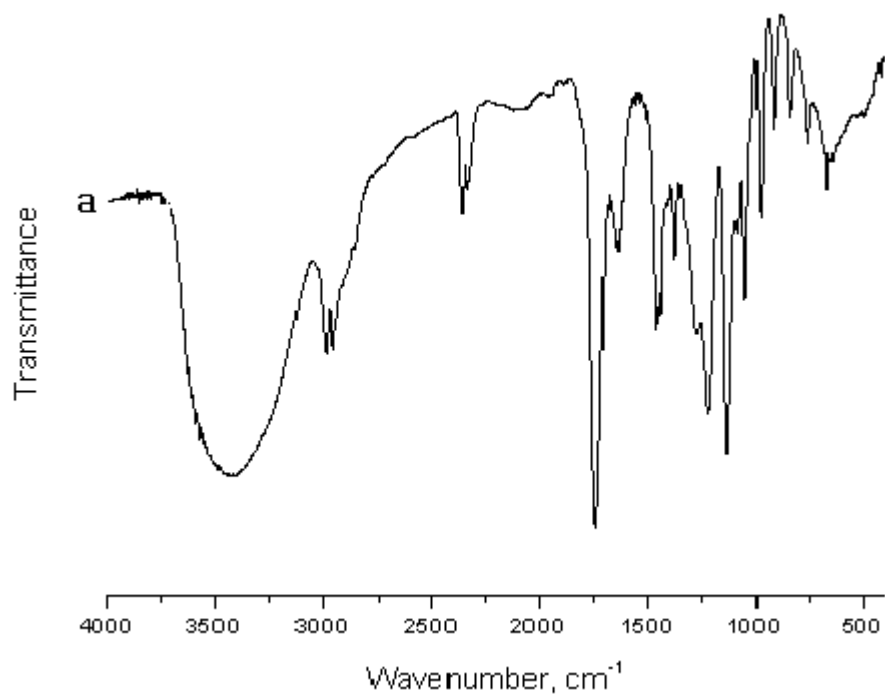
Fig. A2.1. FTIR spectra: *a, methyl lactate; synthesized as in 4.2.3;* v_{CO} *= 1738 cm*[-1]
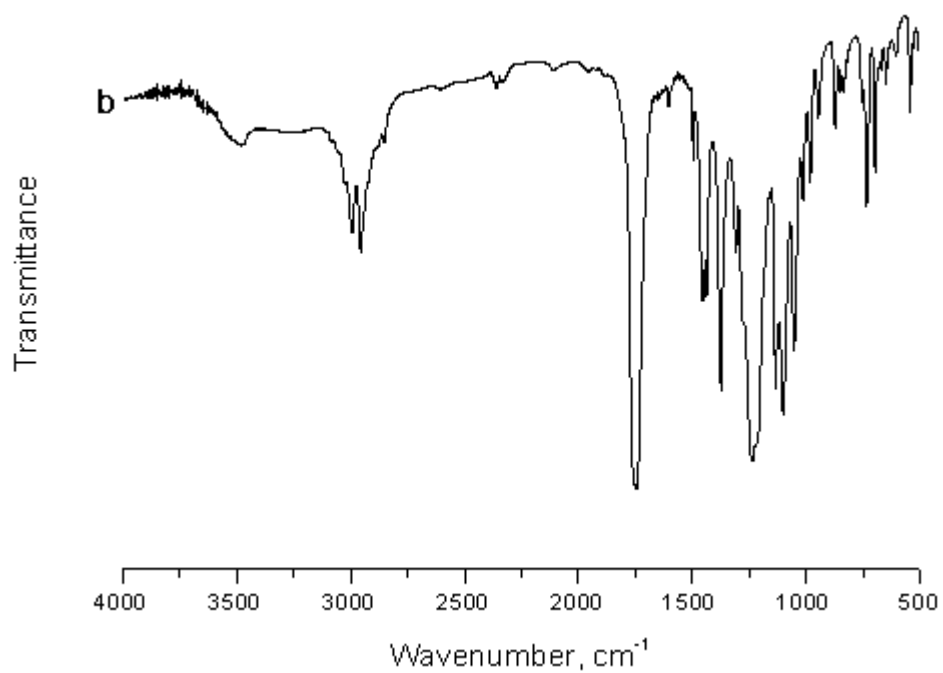
Fig. A2.2. FTIR spectra: *b, methyl-2-acetoxypropionate; isolated from the carbonylation reaction mixtures;* v_{CO} *= 1745 cm*[-1]
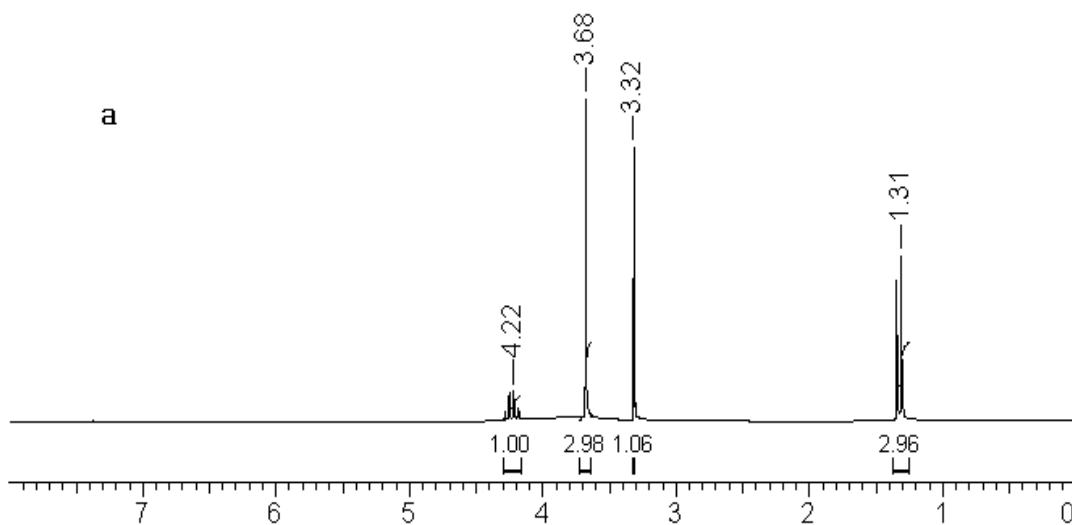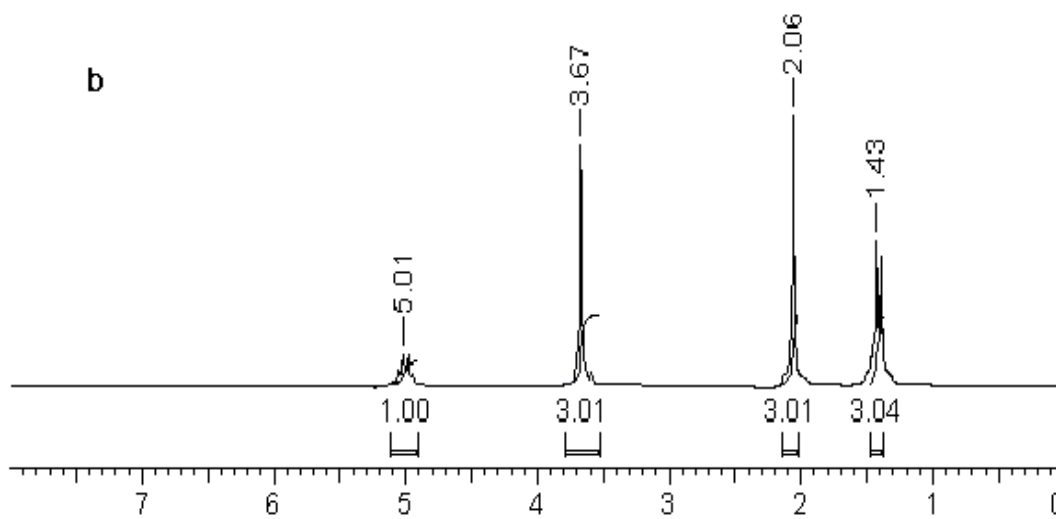
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Fig. A2.3. ^{1}H NMR spectra of (a) methyl lactate

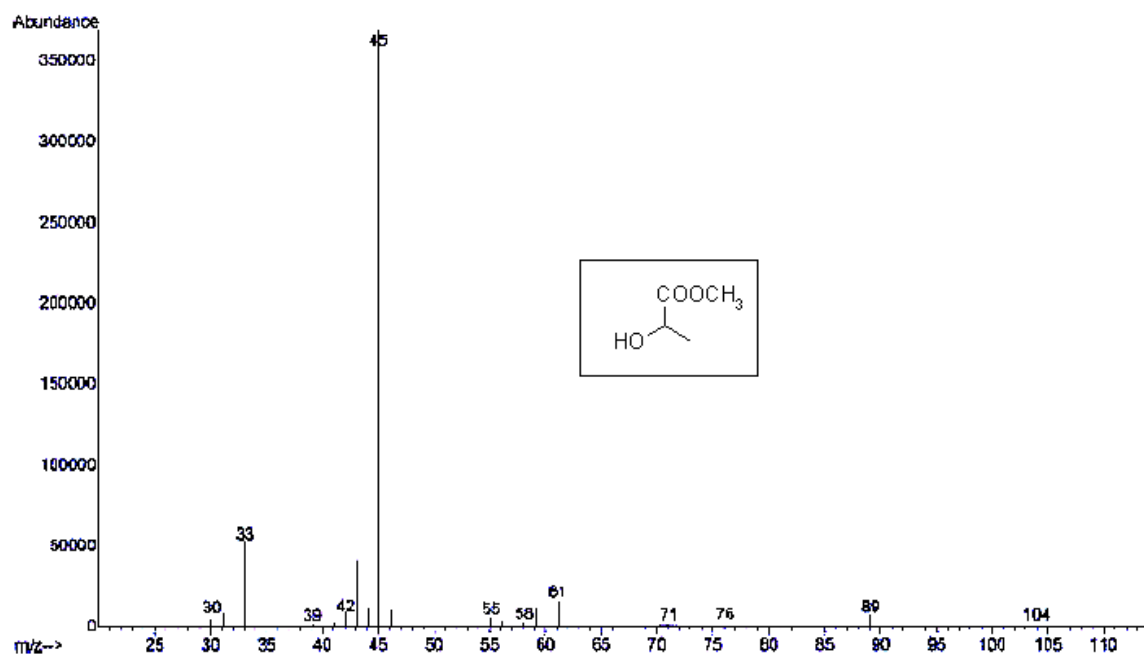Fig. A2.4. ^{1}H NMR spectra of (b) methyl-2-acetoxypropionate

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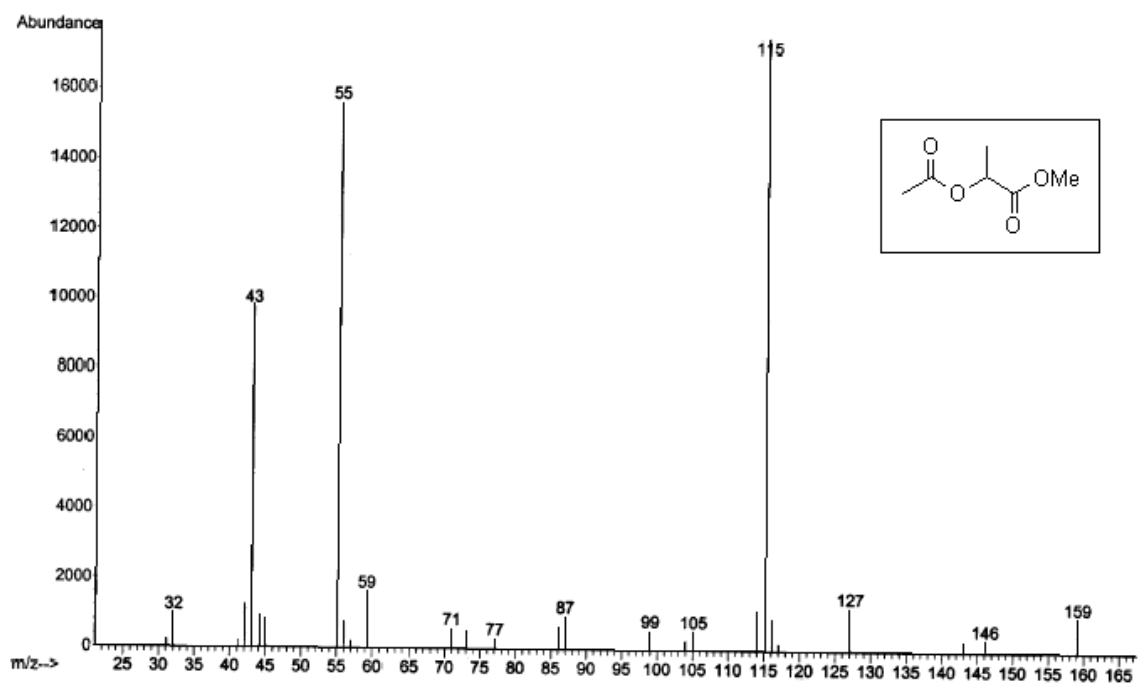Fig. A2.5. MS of methyl lactate synthesized as in Section 4.2.3

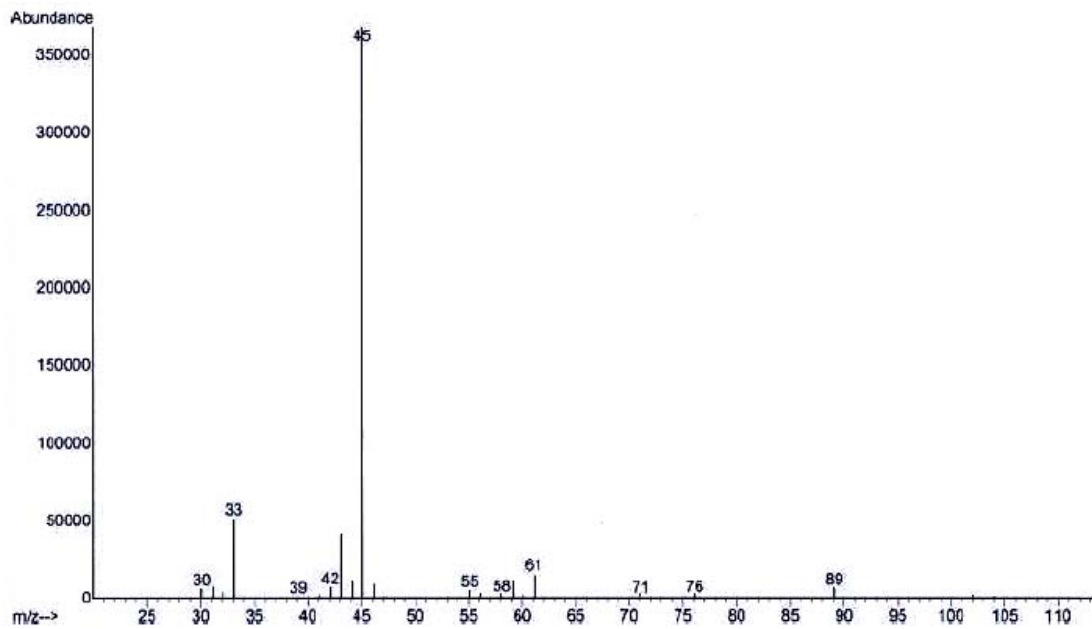Fig. A2.6. MS of methyl-2-acetoxypropionate isolated from carbonylation reaction mixture

Fig. A2.7. MS of lactic acid after hydrolysis of methyl-2-acetoxypropionate

List of Patents

1) Process for the preparation of a carboxylic acid

    Granted: US 6521784, Feb 2003.

    A. A. Kelkar, S. S. Tonde, R. V. Chaudhari

    Also, filed as Indian Patent (Appilcation No. 160/DEL/2001)

2) Process for the preparation of acetic acid or methyl acetate

    Granted: US 6380426, April 2002.

    A. A. Kelkar, S. S. Tonde, S. S. Divekar, R. V. Chaudhari

    Also, filed as Indian Patent (Appilcation No. 893/DEL/2001)

3) Process for the preparation of 2-hydroxy carboxylic acid

    Filed (PTC/IB03/06202, 26th Dec, 2003).

    R. V. Chaudhari, S. S. Tonde