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As required by the University Ordinances 770 and 771, I wish to state that the work embodied in this thesis titled "***Studies on Catalysis and Kinetics of Hydroformylation Reactions by Homogeneous Catalysis***" forms my own contribution to the research work carried under guidance of ***Dr. R. V. Chaudhari*** at ***National Chemical Laboratory***, Pune-411008; this work has not been submitted for any other degree of this or any other university. Whenever references have been made to previous works of others it has been clearly indicated as such included in the Bibliography.

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This research work presented in the thesis has been carried out by **Mr. Yogesh Laxman Borole** for his doctoral degree. I certify that it is his bonafide work. The research work is original and has not been submitted for any other degree of this or any other university. Further that he was a regular student and has worked under my guidance as a full time student at NCL until the submission of the thesis to the University of Mumbai.

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STUDIES ON CATALYSIS AND KINETICS OF HYDROFORMYLATION REACTIONS BY HOMOGENEOUS CATALYSIS

A

THESIS

SUBMITTED TO

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IN

CHEMISTRY

BY

YOGESH LAXMAN BOROLE

Homogeneous Catalysis Division

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APRIL 2004

STUDIES ON CATALYSIS AND KINETICS OF HYDROFORMYLATION REACTIONS BY HOMOGENEOUS CATALYSIS

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Dedicated to,

Aai & Baba

…….For the beautiful life they have bestowed on me

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April 2004 *Yogesh Laxman Borole*
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Homogeneous catalysis has wide ranging applications in many industrially important processes involving hydroformylation, carbonylation, oxidation, hydrogenation, polymerization *etc.* Some important commercial applications of homogeneous catalysts are, (a) Hydroformylation of olefins to oxo-alcohols, (b) Carbonylation of methanol to acetic acid, (c) Oxidation of *p*-xylene to terphthalic acid and (d) Hydrocyanation of butadiene to adiponitrile. Hydroformylation of olefins (Oxo Process) is one of the largest scale applications of homogeneous catalysis in industry. Because of the industrial importance of the oxo process, extensive research work has already been published[1-3] on the role of different ligands and catalysts, product distribution, selectivity behavior, catalyst-product separation strategies *etc.* Studies on kinetics and mechanism using different spectroscopic tools are also reported in the literature for both Co and Rh complexes.

After the breakthrough of Low Pressure Oxo (LP Oxo) process using Rh complex catalysts, considerable attention has been devoted to Rh catalyzed hydroformylation reactions. Promising applications of hydroformylation are also emerging in the synthesis of complex organic molecules useful as fine and specialty chemicals with the aim of developing clean catalytic alternative to the stoichiometric routes. Catalyst-product separation techniques such as biphasic catalysis, Supported Aqueous Phase Catalyst (SAPC), polymer anchored and zeolite-encapsulated complexes have been proposed for the Rh catalyzed hydroformylation reaction. Although, Rh catalyzed processes dominate in the industry, especially for propylene hydroformylation, the importance of Co catalyzed processes is still evident. A considerable volume (~30%, ~2.5 million TPA) of oxo products is still produced by the processes using modified or unmodified Co complexes[4]. Hydroformylation of higher olefin is mainly carried out by phosphine modified cobalt complexes. In addition cobalt complexes are also used in newly emerging commercial applications such as ethylene oxide hydroformylation for 1,3-propanediol production [5].

The principal aim of the present work was to study the hydroformylation of higher olefin (1-hexene) and functionalized olefins with modified and unmodified cobalt and rhodium complexes. The higher alcohols produced by olefin hydroformylation are commercially important as plasticizers and are used in the detergent industry as well. Hydroformylation of functionalized olefins such as vinyl acetate monomer (VAM) has industrial importance as a potential route for propylene glycols. The following specific problems were chosen for the present work,

- Hydroformylation of 1-hexene with tri-*n*-butyl phosphine modified cobalt complex
- Cobalt catalyzed hydroformylation of vinyl acetate monomer: Activity and selectivity studies
- Hydroformylation of Vinyl Acetate Monomer as a potential route for propylene glycol: Activity and selectivity studies with Rh-catalysts
- Hydroformylation of isopropenyl acetate: Activity and selectivity studies of rhodium and cobalt catalysts.

The research work carried out for this thesis, has been presented in five chapters, a brief outline of which is given below:

Chapter 1: Introduction and literature review

This chapter presents a detailed literature survey on catalysis in hydroformylation reactions. The complexes of different metals such as Rh, Co, Ru, Ir, Pt *etc* were found to be active for this reaction though, only Rh and Co give higher activity & selectivity, and hence used in industry. This report is focused on the literature on the hydroformylation of higher olefins and functionalized olefins with respect to catalysis, selectivity behavior, and kinetic studies. Since, hydroformylation of higher olefins is mostly carried out with cobalt complexes, more emphasis has been given to cobalt-catalyzed hydroformylation. The role of catalyst precursors, solvents, promoters, reaction conditions on activity and selectivity, and kinetics and mechanism of the reaction has been critically discussed. Cobalt-catalyzed hydroformylation reactions are accompanied by isomerization and hydrogenation. A brief literature survey on these two side reactions is also included.

Hydroformylation of functionalized substrates such as vinyl acetate monomer, allyl acetate, acrylates, *etc.* has been critically reviewed. A special emphasis is given to

the vinyl acetate monomer hydroformylation. A brief summary on catalyst-product separation techniques such as biphasic and interfacial catalysis is also presented.

Chapter 2: Hydroformylation of 1-hexene with tri-*n*-butyl phosphine modified cobalt complex

This chapter presents experimental results on cobalt-catalyzed hydroformylation of 1-hexene. Different aspects such as rates of olefin isomerization, hydroformylation, and aldehyde hydrogenation, regioselectivity for aldehydes as well as alcohols were studied and the performance compared. Study of the concentration-time profile indicated that nearly 80 % of the terminal olefins were isomerized to internal olefins within first few minutes of the reaction, thus showing the high rates of isomerization. The effect of parameters such as 1-hexene concentration, catalyst concentration, and partial pressures of CO and H_2, on the activity-selectivity of the catalyst was studied. Catalyst concentration was found to show negative effect on the hydroformylation activity whereas it enhanced the rate of olefin isomerization and aldehyde hydrogenation. Knowledge of intrinsic kinetics is essential in understanding the reaction mechanism as well as designing of reactors. There is no previous published report present on the kinetics of olefin hydroformylation using phosphine modified cobalt catalyst and hence, in second part of this chapter, the kinetics of hydroformylation of 1-hexene based on the initial rates of hydroformylation, has been presented. The effect of catalyst and 1-hexene concentration and partial pressures of CO and H_2 on the initial rates of hydroformylation was studied. Initial rates from the syngas absorption and concentration time profiles drawn by liquid sample analysis were compared. Based on this data, a semi-empirical kinetic model was developed the rate parameters were determined by regression analysis.

Chapter 3: Cobalt catalyzed hydroformylation of vinyl acetate monomer: activity and selectivity studies

This chapter deals with a detailed study on cobalt-catalyzed hydroformylation of vinyl acetate monomer, with a focus on increasing the activity and selectivity of the catalyst towards more desirable 3-acetoxy propanal (Linear-isomer). Preliminary studies on unmodified and phosphine modified cobalt-catalyzed hydroformylation of vinyl acetate monomer have been conducted and a selectivity of 45 % for 3-acetoxy propanal (*n*-aldehyde) was achieved with toluene as a solvent. This was a significant improvement

over the previous reports[6] (~23% selectivity). Using phosphine ligands with cobalt, the chemoselectivity of the reaction was drastically reduced to ~ 10 %. Various nitrogen-containing ligands, phosphites, and arsine ligands were tested for this purpose. Among the nitrogen-containing ligands, tertiary amines were found to give better selectivity for 3-acetoxy propanal (~ 45 %) as compared to primary and secondary amines (~20%). $Co_2(CO)_8$ modified with pyridine show almost five times rate enhancement over unmodified cobalt catalyzed hydroformylation. The promoters such as quaternary salts, alkali salts, organic acids and alcohols were also tested for vinyl acetate monomer hydroformylation. The quaternary slats didn't show positive impact on the regioselectivity to 3-acetoxy propanal. Increase in the concentration of quaternary salts retarded the reaction. Among the different solvents screened, halogenated solvents such as chlorobenzene was found to increase the selectivity of 3-acetoxy propanal to 56 %. No hydroformylation was observed in presence of strongly coordinating solvents such as acetonitrile, DMF and DMAc. The effect of promoters, ligands, and solvents on side reactions such as hydrogenation of acetoxy propanals and the decomposition of vinyl acetate monomer and 3-acetoxy propanal were also studied.

Chapter 4: Hydroformylation of vinyl acetate monomer as a potential route for propylene glycol: activity and selectivity studies with Rh-catalysts

Both 1,2-propanediol and 1,3-propanediol are industrially important chemicals. In this chapter, a process for the synthesis of both these diols from vinyl acetate monomer is reported. All the three steps involved in this process *viz.* (i) Hydroformylation of vinyl acetate monomer to acetoxy propanals (2- and 3-acetoxy propanals), (ii) Hydrogenation of acetoxy propanals to acetoxy propanols (2- and 3-acetoxy propanols), and (iii) Hydrolysis of acetoxy propanols to propanediols (1,2-propanediol and 1,3-propanediol), were studied. For the first step, the effect of different catalyst precursors, ligands, and solvents on the activity and selectivity of Rh-catalyst was studied and a maximum selectivity of only 11 % for 3-acetoxy propanal (*n*-aldehyde) was observed. A brief study on rhodium-catalyzed hydroformylation under reverse biphasic conditions, including four recycles of the catalyst-containing organic phase was also carried out.

For the second step of hydrogenation of acetoxy propanals, screening of various hydrogenation catalysts based on Ru, Pd and Ni in solvents such as toluene, cyclohexane

and water was carried out. Ru/Al_2O_3 gave better activity in water as a solvent whereas Raney Ni was found to be very active in organic solvents with ~ 94 % yield for acetoxy propanols in toluene. Different reagents (acids & bases) and catalysts (acidic resins) were tested for the third step of hydrolysis of the acetoxy propanols to propylene glycols, among which Amberlite IR-120 resin was found to give better results in achieving higher yields (91%) of propylene glycols. Optimization of parameters for all the three reactions with an aim to improve the yield of 1,3-propanediol has been done. Thus, hydroformylation of vinyl acetate as a potential route for propenyl glycols is established with development of recyclable catalysts for all the three steps.

Chapter 5: Hydroformylation of isopropenyl acetate: activity and selectivity studies of rhodium and cobalt catalysts

In comparison to linear olefins, hydroformylation of functionalized olefins is not very well studied in the literature. In this chapter, a brief study on activity and selectivity in hydroformylation of other acetate-functionalized olefins such as isopropenyl acetate was carried out and the results were compared with vinyl acetate hydroformylation. Rhodium complexes were generally found to be inactive for the hydroformylation of isopropenyl acetate however, cobalt was found to be active. The effect of ligands, solvents, and parameters such as CO / H_2 partial pressures, substrate and catalyst concentration on rates and linear / branched ratio was studied. Under identical conditions, the linear / branched ratios of isopropenyl acetate hydroformylation (~8) and vinyl acetate monomer hydroformylation (~1.5) were found to be strikingly different. Thus, isopropenyl acetate was found to follow the Keulemans rule giving the 3-acetoxy butanal selectively and forming 2-acetoxy -2-methyl propanal (branched aldehyde containing quaternary carbon atom) in very less quantity. Probable reasons for this difference have been discussed, and the co-ordination of carbonyl group, forming a ring with metal was found to be the most convincing one[6].

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Chapter 1

INTRODUCTION
AND
LITERATURE REVIEW

1.1. INTRODUCTION

"Never in the field of human conflict has so much been owed by so many to so few" -W. Churchill.

These are the famous words used by Mr. Churchill to express his gratitude towards Royal Air-Force's team, which included a group of chemists who developed a new *petroleum reforming* ***catalyst*** capable of producing 100-octane fuel from the distillate produced in the oil refinery. The new fuel helped allies' planes in the World War –II, to perform far better than before. The second example highlighting the exceedingly high significance of the catalytic processes is the ammonia synthesis, which was ranked as the most valuable invention of the 20th century[i]. Such is an impact of catalysis on the modern society that there is virtually no area in which human being don't use products synthesized by catalytic reactions. There are nearly 30,000 chemicals produced worldwide and production of most of the chemicals involves catalysis in at least some of the steps[ii]. It is estimated that 85 % of all chemical processes are run catalytically.[iii]

Catalysis is generally classified into two types depending on the physical nature of the catalyst employed: (a) heterogeneous in which the catalyst is immiscible with the reaction medium or present as a separate phase, and (b) homogeneous, in which the catalyst is soluble in the reaction medium. Some of the general features of heterogeneous catalysts are, generally severe temperature and pressure conditions, mostly continuous mode of operation, long catalyst life, easy catalyst-product separation *etc*. Therefore, almost all important areas, such as mineral oil processing, *e. g.* catalytic reforming, catalytic cracking, hydrogenation, hydro-desulfurization *etc*. and other bulk chemical's processes such as ammonia synthesis, sulfuric acid synthesis *etc*. involve use of heterogeneous catalysts. Thus, fuels (for transports, energy *etc*.) and feed stock generation (for further consumption by chemical industry) from mineral oil and other natural resources is mostly taken care of by heterogeneous catalysts. Compared to heterogeneous catalysis, industrial applications of the homogeneous catalysis are less. Some general features of homogeneous catalysts are: mild reaction conditions, high activity and selectivity, difficult and expensive catalyst-product separation, better

mechanistic understanding *etc*. Most of the processes involving homogeneous catalysis *e.g.* carbonylation, hydroformylation, oxidation, telomerization, co-polymerization, metathesis *etc*. utilize cheap feed stocks available from mineral oil processing and produce important bulk and fine chemicals for polymer, pharmaceutical, paints, and fertilizer industries[iv]. The main drawback of homogeneous catalysis is the separation of the catalyst and products, which is often a tedious task involving precipitation of the catalyst by adding non-polar solvents, high vacuum distillation or extraction of products into a second phase, *etc*. In spite of this situation, about 25% of the industrial catalytic reactions involve homogenous catalysis, and 75% employing the heterogeneous catalysis. More over, the attractive feature of homogeneous catalysis in better mechanistic understanding of its micro 'processes' (catalytic cycles), with the possibility of influencing steric and electronic properties of these molecularly defined catalysts, is highly promising to innovate new chemistry. This is doubtlessly a clear advantage over heterogeneous catalysis, which is said to be an alchemist's 'black art' because of poor mechanistic understanding[v]. This is clearly exemplified by comparing the examples of hydroformylation on one hand and Fischer-Tropsch reaction on the other. While, both represent catalytic carbon monoxide chemistry, the molecular structure of the homogeneous catalyst is precisely known to be trigonal-bipyramidal, *d8*-Rh-I, whereas for Fischer-Tropsch reaction occurring on solid surfaces, no clear molecular level mechanism is known[vi]. The progress of homogeneous catalysis is also significant in the area of fine chemicals, to achieve high atom economics or *E* factors. Thus, the goal of 'green chemistry' as a synonym to environmentally benign chemicals and processes, including sustainable development, are afforded by homogeneous catalysis rather than heterogeneous catalysis.[iii]

The performance of homogeneous catalysts depends not only on the physical conditions of the reaction but also on type of the metal, ligands, promoters and co-catalysts. In most cases the selectivity is one of the most important issues. Generally transition metal complexes are used as catalysts because of their stability in varying oxidation states. Systematic progress in the field of co-ordination chemistry with improved techniques of catalyst characterization helped many homogeneous catalytic processes to achieve higher selectivities at milder reaction conditions. At least in some of

the processes like hydroformylation, the tedious problem of catalyst-product separation is also effectively tackled with the development of biphasic catalysis. Being highly selective, homogeneous catalysis is assuming increasingly important role in highly efficient processes. List of some of the important homogeneous catalytic processes in industry is presented in Table 1.1.

Table 1.1. Applications of homogeneous catalysis: industrial processes

No.	Process	Catalyst	Company
1	Oxidation of ethylene to acetaldehyde	$PdCl_2/CuCl_2$	Wacker-Werke[vii]
2	Oxidation of p-xylene to terephthalic acid/ester	Co/Mn-salts	Du Pont[viii]
3	Polymerisation of ethylene to HDPE/LDPE	Ni-complex	Shell[ix]
4	Hydrocyanation of butadiene to adipic acid	Ni-complex	Du Pont[x]
5	Asymmetric hydrogenation of acetamido cinnamic acid (3-methoxy-4-acetoxy derivative) (l-dopa process)	$Rh(diene)(solvent)]^+$ /DIPAMP	Monsanto[xi]
6	Hydroformylation of propene to butyraldehyde	$NaCo(CO)_4$	BASF[xii]
		$HCo(CO)_3PBu_3$	Shell[xiii]
		$HRh(CO)(PPh_3)_3$	Union Carbide[xiv]
		Rh/TPPTS	Ruhrchemie-Rhone-Poulenc[xv]
7	Hydroformylation of higher olefins to oxo alcohols	$HCo(CO)_3PBu_3$	Shell[xvi]
8	Hydroformylation of diacetoxy butene to 1-methyl-4-acetoxy butanal (Vitamin A intermediate)	$HRh(CO)(PPh_3)_3$	Hoffmann-La Roche [xvii]
		Rh catalyst	BASF[xviii]
9	Carbonylation of methanol to acetic acid	Rh/ Iodide	Monsanto [xix]
		$Co_2(CO)_8$	BASF [xx]
		Ir/Iodide	BP chemicals[xxi]
10	Carbonylation of methyl acetate to acetic anhydride	Rh/MeI	Halcon [xxii]
		Rh/MeI	Eastman Chemical[xxiii]
11	Carbonylation of ethylene to propionic acid	$Ni(OCOC_2H_5)_2$	BASF[xxiv]
12	Carbonylation of acetylene to acrylic acid	Ni-salts or carbonyls	BASF[xxv]
13	Carbonylation of benzyl chloride to phenyl acetic acid	$Co_2(CO)_8$	Montedison[xxvi]
14	Carbonylation of 1-(4-isobutylphenyl)ethanol to Ibuprofen	$PdCl_2(PPh_3)_2/HCl$	Hoechst-Celanese[xxvii]
15	Oxidative carbonylation of methanol to dimethyl carbonate	$PdCl_2$-$CuCl_2$	Assoreni [xxviii]
16	Hydroformylation of Ethylene oxide to 2-hydroxy propanal	$Co_2(CO)_8$	Shell[xxix]

The need of catalytic technologies, for conversion of cheaper feedstock to chemicals, new routes for fine chemicals, pharmaceuticals and specialties, removal of

pollutants, waste minimization and global supply and preservation of energy, is thus obvious. Greater mechanistic understanding is an important reason behind academician's ever-enthusiastic affinity for homogeneous catalysis, especially hydroformylation, reaction and so hydroformylation is acting as a model for other homogeneous catalytic reactions. Hydroformylation is now being viewed as a convenient way to produce fine chemicals from laboratory scale to industrial scale.

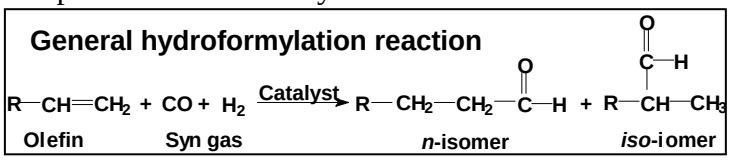
Consequently, the aim of this thesis is to investigate catalysis and kinetics of the transition metal catalyzed hydroformylation reactions. Both rhodium and cobalt complexes are studied with more focus on cobalt catalysts and among substrates, linear olefins like 1-hexene, and acetate-fictionalized olefins are chosen. Because of the importance of the phosphine modified cobalt catalyst to produce higher alcohols, kinetics of 1-hexene hydroformylation with tributyl phosphine modified cobalt catalyst is studied in detail. The next part of the thesis contains work on, hydroformylation of Vinyl Acetate Monomer (VAM). For the first time, cobalt-catalyzed VAM hydroformylation is studied thoroughly and a new route for propylene glycol synthesis is developed. Finally, hydroformylation of isopropenyl acetate is studied and the effect of the substitution on olefinic carbon atoms is demonstrated.

The next section of this chapter is devoted to the literature survey on hydroformylation reaction in accordance with the above said topics.

1.2. LITERATURE SURVEY ON HYDROFORMYLATION

In 1938, while working on Fischer Tropsch Synthesis, Otto Roelen accidentally discovered Oxo synthesis or hydroformylation[xxx]. This reaction was first termed as oxo synthesis because Roelen observed diethyl ketone along with propanal (oxo compounds) as products from ethylene. Later on Adkins introduced the correct expression 'hydroformylation' because of addition of formyl group to one carbon atom and hydrogen to the other carbon atom of the double bond. Despite the chemical versatility of the aldehydes, hydroformylation gained little importance in the first few years of its

General hydroformylation reaction



discovery. Adkins and Krsek[cxcvi], Martin[xxxi], Marko[ciii,cxxx], and Natta[cxxviii,cxxix,ciii] in their pioneering work showed applicability of hydroformylation to a wide spectrum of olefin-substrates and also confirmed the homogeneous nature of hydroformylation catalyst. First commercial application of hydroformylation was by BASF in 1948[xxxii] and since then hydroformylation reaction has steadily increased in importance, mainly because of contributions of two major developments. The first was the rapid growth of the petrochemical industry, which switched the olefin raw material basis away from the natural or FT-olefins to a broad variety of cheap and pure petroleum-based olefins, thus presenting improved feedstock availability and quality. The second factor was the emergence of at least two markets, the PVC and the detergent industries (Even today these sectors have remained the most significant customers for the alcohols produced via hydroformylation-hydrogenation)[ivd]. Beside these two applications, the aldehydes formed in the oxo reaction serve as a turntable in the bulk and specialty chemical business.

Hydroformylation reaction was discovered on cobalt catalyst, which later on was found to be homogeneous hydrido cobalt carbonyl catalyst. The first generation of the hydroformylation processes (*e. g.* by BASF[xxxiii], ICI[xxxiv], Kuhlmann[xxxv], Ruhrchemie[xxxvi] *etc*.) was exclusively based on cobalt as catalyst metal. The reaction conditions were rather harsh: the syngas pressure ranged between 20 and 35 MPa to avoid decomposition of the catalyst and deposition of metallic cobalt and the temperature was adjusted according to the pressure and concentration of the catalyst between 323 K and 353 K to ensure an acceptable rate of reaction. As the reaction conditions were quite similar, the processes differed only in the solution to the problem of how to separate product and catalyst, in order to recover and to recycle the catalyst. Shell Researchers made significant development in the first generation catalyst.[xxxvii] The discovery that phosphines (or arsines) were able to replace carbon monoxide as electron donating ligand was a fundamental step in the metal-carbonyl-catalyzed reactions, which gave accesses, to a certain extent, to tailor made catalysts via the electronic and steric properties of the ligands. The Shell process using cobalt-phosphines catalysts, enhanced the regio-selectivity towards n-isomer, mostly gave alcohol as an end product, and reduced the carbon monoxide pressure by markedly enhancing the stability of the metal carbonyls. But, because of this stability, the temperature required for the Shell process was very high

(in the range of 353 K to 473 K), and the reaction rates were low (forcing the use of larger reactor size). Besides this the side reaction of hydrogenation of olefins to paraffins was a major problem.

The second-generation processes combined the advantages of ligand modification with the transition from cobalt to rhodium as a catalyst metal. The rhodium-phosphine catalysts achieved very high chemo-, regio-selectivity towards n-aldehydes, that too under very mild reaction conditions[xxxviii] (so termed as LPO- Low Pressure Oxo Process). Owing to these advantages of LPO and the mineral-oil supply crises in 1983 (favoring process with high raw material utilization) most of the cobalt-based hydroformylation processes were transferred to LPO, especially the picture of propylene hydroformylation changed drastically. His pioneering work in the organometallic chemistry, especially with rhodium and ruthenium complexes, won Sir Geoffrey Wilkinson a Nobel Prize for Chemistry in 1973. The catalyst $HRh(CO)(PPh_3)_3$ is also popularly known as Wilkinson catalyst. Compared with the cobalt processes, considerable advances had been established in the second-generation rhodium processes, especially with respect to material and energy utilization. After the invention of hydroformylation activity of phosphine modified rhodium catalyst, much attention was paid to development of different phosphine, phosphites, N-containing, and P-N containing ligands.

Further innovation in the hydroformylation processes took place in the reaction-engineering field through development of biphasic reaction system. The basic idea was to immobilize the catalyst molecules with an aid of a *liquid support*.[xxxix] It was achieved in the best way by applying water-soluble phosphines as ligands and thus transferring the hydroformylation in the aqueous phase. Best example of the biphasic catalysis is the hydroformylation of propene using Rh-TPPTS (Triphenyl phosphine trisulfonated), which has been commercialized by Ruhrchemie AG with a 300 MTPA plant. The novel feature of this catalyst system is the high solubility of Rh-TPPTS complex in water such that the catalyst essentially remains in the aqueous phase with reactants and products (being insoluble in water) in the organic phase. While, the appreciable solubility of reactants in aqueous phase is adequate for obtaining reasonable reaction rates, the almost negligible leaching of Rh in the organic phase facilitates easy separation and efficient

reuse of this expensive hydroformylation catalyst. An interesting feature of the process is that, if the heat formed in the exothermic oxo reaction is recovered, the process in contrast to all other processes becomes a net steam exporter.[50] The success of biphasic catalysis on large industrial scale has triggered off excessive research developments in designing novel biphasic systems. The challenges remain in improving reaction rates for higher olefins feed stocks and also the substituted olefinic substrates.

Other than cobalt and rhodium, almost all carbonyl forming metals have been claimed to be active in the oxo reaction *e. g.* Ru, Os, Ir, Pt, Mn, Re, Cr, Cu, Mo, and even Na and Ca. Ru and Pt f*etc*hed some attention but were mostly of academic interest as their activity and selectivity were not even comparable to cobalt and rhodium. Different hydroformylation processes are compared in the Table 1.2.

Table 1.2. Comparison of different hydroformylation processes

Catalyst metal	**Cobalt**		**Rhodium**		
Variant	**Unmodified**	**Modified**	**Unmodified**	**Modified**	
Ligand	None	Phosphines	None	Phosphines	
Process [a]	1	2	3	4	5
Active catalyst species	$HCo(CO)_4$	$HCo(CO)_3L$	$HRh(CO)_4$	$HRh(CO)L_3$	$HRh(CO)L_3$
Temperature (K)	423-453	433-473	373-413	333-393	383-403
Pressure (MPa)	20-30	5-15	20-30	1-5	4-6
Catalyst concn. (rel. to olefin (%)	0.1-1	0.6	10^{-4}-0.01	0.01-0.1	0.001-1
LHSV [b]	0.5-2	0.1-0.2	0.3-0.6	0.1-0.2	>0.2
Products	Aldehydes	Alcohols	Aldehydes	Aldehydes	Aldehydes
Amount of by-product	High	High	Low	Low	Low
N/i ratio	80:20[c]	88:12	50:50	92:8	>95:<5
Sensitivity to poison	No	No	No	Yes	No

[a] Key: 1 = (e. g.) BASF, Ruhrchemie; 2= Shell; 3= Ruhrchemie; 4= Union Carbide; (LPO); 5= Ruhrchchemie / Rhone-Poulenc. [b]LHSV= liquid hourly space velocity. [c] 65:35 at an early stage of development.

Besides the catalyst metal, ligands used, and application phase, hydroformylation reactions can also be categorized based on substrates employed (Figure 1.1). Even though majority of the hydroformylation applications utilizes linear hydrocarbon olefins (especially α - olefins), there are many reports on hydroformylation of functionalized olefins *e. g.* acetates, alcohols, halides, ethers *etc*., and substrates other than olefins *e. g.* epoxides, alcohols, halides *etc*. Most of the lower olefins feedstock for

hydroformylation is made available from the mineral oil processing units such as cracking processes, especially thermal cracking[xl] whereas higher olefins are mostly produced either by ethylene oligomerization, paraffins dehydrogenation, or SHOP process.[xl] Even though, hydroformylation of functionalized olefins and substrates other than olefins are mostly of academic interest, hydroformylation of diacetoxy butenes, allyl alcohol and ethylene oxide have found industrial applications. Thus, functionalized olefins, as substrates are useful, especially for the fine chemicals and pharmaceutical industries.

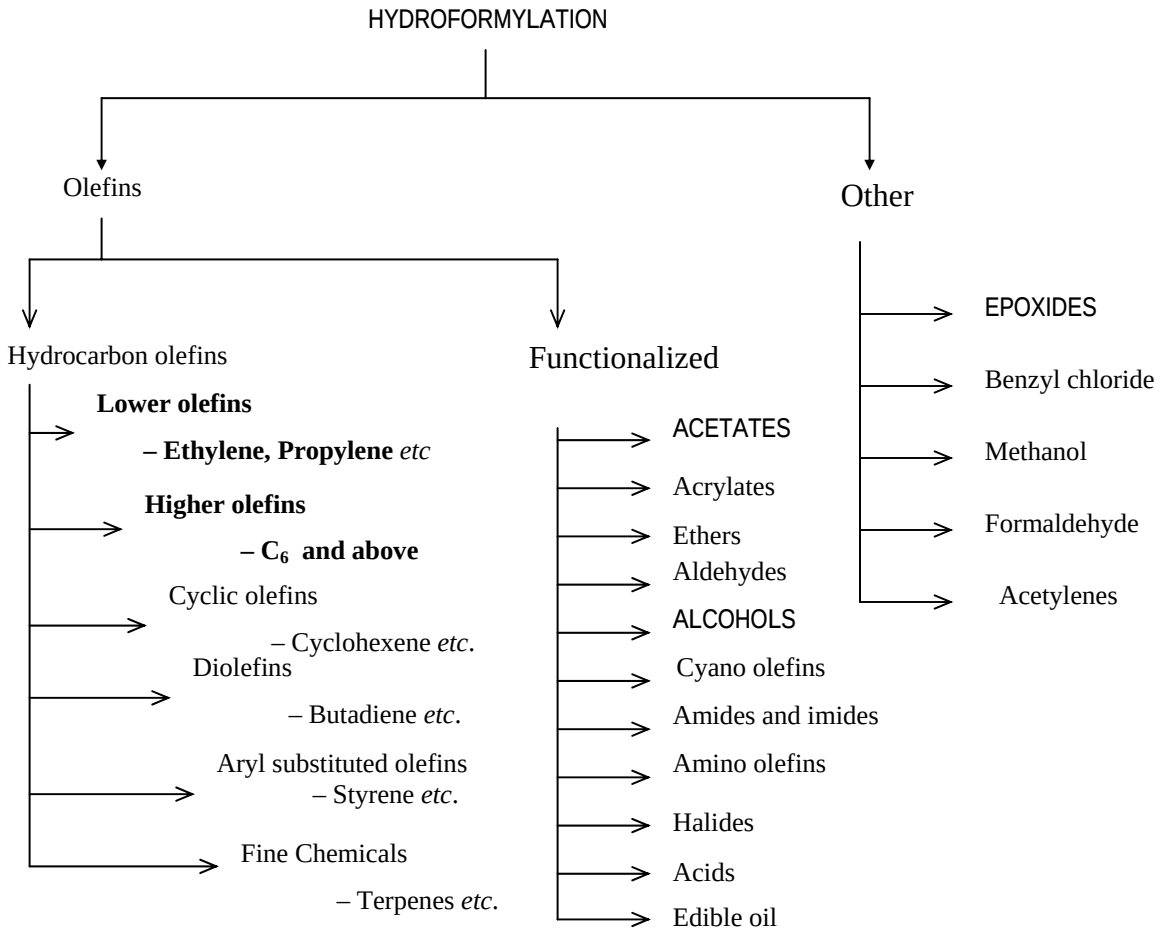


Figure 1.1. Classification of hydroformylation based on the substrates employed. (Commercial applications: Bold font)

Indeed, tremendous efforts are already put into the development of hydroformylation chemistry and processes and the end result is the activity of the oxo catalysis has improved in the past 50 years by a factor of 10,000.[iii] Presently the research in the hydroformylation reaction and technology is focused on three main areas,

(a) *Hydroformylation for synthesis of fine chemicals*. This includes hydroformylation of epoxides, functionalized olefins, asymmetric hydroformylation[xli], tandem reactions[xlii] *e. g.* Shell process of Ethylene Oxide hydroformylation to 2-hydroxy propanal, which on further hydrogenation, gives 1,3-propanediol.[xliii] Shell has recently commercialized this process.

(b) *Development of heterogeneous or heterogenised-homogeneous catalysts for hydroformylation*. Aqueous, interfacial, encapsulated, supported, anchored, SAP / SLP *etc*. catalysts are the ones, which are being probed extensively[xliv].

(c) *Hydroformylation of higher olefins and internal olefins e. g.* Utilization of cheaper feed stocks such as 'Rafinate-*II*' (mixed butenes), which on sequential hydroformylation, aldol condensation, and hydrogenation can give a C_{10} alcohol (possible replacement to 2-ethyl hexanol in PVC), puts before the challenge of efficiently hydroformylating internal olefins[lxxviii]. Recently there is a flood of patents and papers on rhodium-catalyzed hydroformylation of higher olefins in biphasic mode.[xlv]

The current state of developments on the catalysis and chemistry of hydroformylation is briefly reviewed in the following sections.

1.2.1. Hydroformylation of lower olefins

Among various substrates, simple hydrocarbon olefins are the most important for commercial applications of hydroformylation, and so are the most studied substrates. Generally olefins with 2 to 5 carbon atoms (C_2 to C_5) are considered to be lower olefins and olefins with 6 or more carbon atoms (C_6 onwards) are considered to be higher olefins[xlvi]. Thus, in lower olefins ethylene, propylene and butenes (1-butene, 2-butenes and *iso*-butenes, Raffinate-*II*) are included. Some reports classify olefins from C_2 to C_4 carbon atoms into lower olefins and C_5-C_8 as middle range olefins and C_9 onwards into higher olefins. One more terminology frequently used by some reports is, olefins of 'medium chain length', for diisobutene and tripropene[xlvii]. While ethylene

hydroformylation accounts for 2 % of the total industrial hydroformylation capacity, hydroformylation of propene accounts for nearly 73 %, thus the economic importance of hydroformylation is mainly based on the hydroformylation of propene.

The key issues in the lower-olefin's hydroformylation are:

Regioselectivity – Regioselective synthesis of *n*-aldehydes is the key issue in lower olefins hydroformylation. *n*-aldehydes have more applications compared to their branched isomers.

Chemoselectivity – Chemoselectivity to the oxo-aldehydes and alcohols is an important factor, since side reactions like hydrogenation results in significant loss of olefins, the cost of which is the most important contributor in the process. *e. g.* in case of n-butanal production, about 64 % of the product value is contributed by the costs of propene[xlviii],

Catalyst-product-separation – the commercial success of homogeneous reactions is dependent on the efficient recycle and reuse of not only the catalyst metal but also the ligands and promoters. So, catalyst-product separation has been one of the most critical issues limiting applications of hydroformylation in spite of several achievements in chemistry.

Mechanistic understanding – The understanding of the catalytic chemistry is an important issue not only for improvement of catalyst activity, selectivity, and stability but also for applying the catalyst system to different substrates. While the hydroformylation reaction mechanism is generally well understood, specific understanding of the nature of active species is limited for various cases.

In this section, literature on hydroformylation of lower olefins: with cobalt, with rhodium, and the heterogenization attempts are discussed.

1.2.1.1. Cobalt catalyzed hydroformylation of lower olefins

~ 20 % of the total lower olefin hydroformylation capacity is produced with Co-based processes, by companies like BASF, Shell *etc*.[ivd]. In spite of breakthroughs of Wilkinson's catalyst and biphasic hydroformylation, the production capacity of cobalt-based processes has remained at a constant level over the years albeit without any technological development as the focus was always on rhodium catalyst.

Slaugh *et al.*[xlix], in 1966, have carried out hydroformylation of propene with $Co_2(CO)_8$-TBP system for the first time and demonstrated that direct alcohols, with n-regioselectivity higher than unmodified cobalt catalyst, can be synthesized from propene or even from propyne. Slaugh could obtain 100 % conversion with *n/iso* ratio of 9 at 443 K temperature, 3.5 MPa 1:2 $CO:H_2$ pressure. Latter on Tucci[l] has studied the effects of different phosphine ligands on the modified cobalt catalyst system and found out that, among various cyclic, bicyclic, alkyl, and aryl phosphines, alkyl phosphines are the best ligands for Co catalysts. Tucci[li] has also studied the effect of various parameters on alcohol distribution and regioselectivity and concluded that catalyst concentration, H_2:CO ratio, and temperature have positive effect on alcohol formation. One of the major drawbacks of the Tucci's work was use of very high catalyst concentration (Substrate/Catalyst = 16.2) and so the parametric effects are not very reliable. Murata *et al.*[lii] coupled the Water Gas Shift Reaction with Co-catalyzed hydroformylation. He obtained 100 % conversion of propene in ether + water solvent system, with $Co_2(CO)_8$-DPPE catalyst at 400 K and 1.2 MPa CO. Even though Murata's system doesn't use any H_2 the drawbacks like low rates so high contact time of 17-20 h., and catalyst decomposition didn't attract much attention.

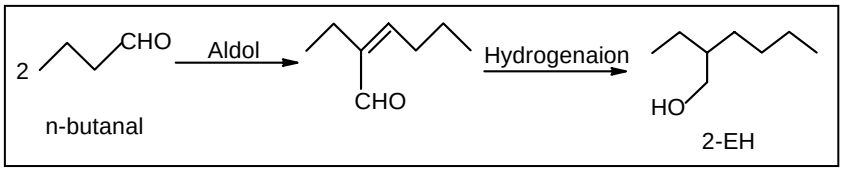
1.2.1.2. Rhodium catalyzed hydroformylation of lower olefins

The rhodium-based processes dominate in the industrial applications of lower olefin hydroformylation. ~ 80 % of the total propene hydroformylation capacity is processed by companies like UCC, BASF, Hoechst-Celanese *etc.*, with LPO and Ruhrchemie / Rhône Poulenc processes. All lower olefins *i. e.* ethene, propene and butenes are very well hydroformylated with Rh complexes with high activity, chemoselectivity and regioselectivity.

Even though ethylene hydroformylation is not highly important from commercial point of view, it is most of the time studied as a standard substrate for hydroformylation, mainly because of simplicity, as the question of substrate-isomerization doesn't arise and it gives only one product on hydroformylation[liii]. Ethylene hydroformylation reaction is mainly studied to know the mechanistic aspects of the hydroformylation reaction, to test different ligands and catalysts, and for theoretical studies in hydroformylation

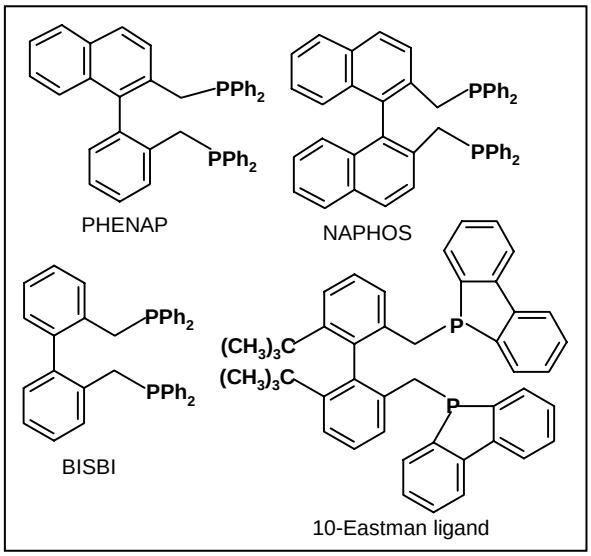
King *et al.*[liv] have studied ethylene hydroformylation in 1979 to have an in site in to the mechanism of the reaction. They studied the Rh-catalyzed hydroformylation of C_2H_4 in *n*-tetradecane solution. by IR spectroscopy using diverse Rh(I) carbonyl derivatives, including $[Rh(CO)_2Cl]_2$, (pyridine) $Rh(CO)_2Cl$, $[AcRh(CO)_2]_2$, and $(MeCO)_2CHRh(CO)_2$ to generate systems that catalyze the hydroformylation under mild conditions, *e. g.*, 308 K and 5.0-10.0 MPa. In each of these systems absorption bands, which occur at the n(CO) frequencies 2115 w, 2019 s cm^{-1}, were attributed to an unstable Rh alkyl, presumably $C_2H_5Rh(CO)_4$. Later, in 1989 Chuang *et al.*[lv]. have used an *in situ* IR technique to study the selective S-poisoning in the heterogeneous hydroformylation on Rh/SiO_2 catalysts and compare the FT Synthesis and Hydroformylation mechanistically. *In situ* IR observation provided evidence for adsorbed acyl species on the Rh/SiO_2 catalyst indicating that CO insertion steps take place on the catalyst during hydroformylation. The CO insertion step in hydroformylation was concluded to be less structure-sensitive than the hydrocarbon synthesis reaction of CO hydrogenation (FT Synthesis).

Recently, Garland *et. al*[lvi]. have studied $Rh_4(CO)_{12}$ catalyzed hydroformylation of ethylene. The homogeneous rhodium catalyzed hydroformylation of ethylene was studied, starting with $Rh_4(CO)_{12}$ in n-hexane solvent, at 293 K. *In situ* high-pressure IR spectroscopy was used for mechanistic explorations. Two different metal carbonyl spectra appeared during the course of active hydroformylations. One spectrum, primarily at high CO partial pressures, corresponds exactly to the well-documented mononuclear acyl-rhodium tetracarbonyl (2112, 2068, 2038, 2020 cm^{-1}). The other spectrum, observed primarily at low CO partial pressures, has absorbance maxima at 2089, 2038 and 2017 cm^{-1}. It was tentatively suggested that the latter spectrum may belong to the elusive ethyl-rhodium tetracarbonyl.

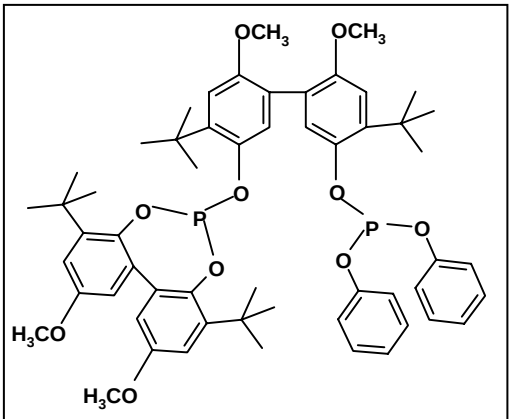


Most of the work on propene hydroformylation is excellently reviewed in the literature [ive]. Propene hydroformylation is important for production of 2-ethylhexanol (2-EH) by aldol condensation of n-butanal followed by hydrogenation. About 52% of the n-butanal produced from propene hydroformylation is used to prepare 2-EH and majority of the rest goes to n-butanol[xlviii]. Dioctyl phthalate (DOP) produced from 2-EH, is a plasticizer useful for wide range of PVC applications and n-butanol is either used as a direct solvent or is converted into acrylate esters, glycol esters and acetate esters for further use.

Unlike ethylene, propene hydroformylation has regioselectivity problems. So, a lot of attention was paid on increasing the selectivity of the n-butanal (n-aldehyde) and suppressing the formation of iso-butanal. $HRh(CO)(PPh_3)_3$ catalyst offered very good regioselectivity (n:iso = 95:5) compared to other rhodium and cobalt catalysts, and most of the propylene hydroformylation research after invention of Wilkinson catalyst was focused on the development of different ligands especially arylphosphines, diphosphines, phosphites *etc*.[lvii] Recently, diphosphines with bulky aryl groups showed considerably high activity and selectivities. Eastman Kodak developed a series of diphosphines such as NAPHOS, BISBI, PHENAP *etc*.[lviii] These ligands showed considerable activity and very high regioselectivity for hydroformylation reactions. Normal-to-branched ratios of 96:4 were observed at very low phosphine : rhodium ratios (4-8:1).[lix] The best ligand in this series of ligands by Eastman Kodak is 2,2'-bis (dibenzophospholylmethyl)-5,5'-di-tert-butyl-1,1'-biphenyl which gives the best regioselectivity with *n/iso* ratio of 99.6/0.4 This means exclusive formation of n-butanal at attractive TOF of 1.2 kg aldehyde / g $Rh.h^{-1}$.[lx]



Among the lower olefins, butenes are next to propene in importance. Hydroformylation of butenes gained importance in 1990s mainly because of three reasons, a requirement of plasticizers based on C_{10} alcohols, increased demand of isononanol (INA) and the third being availability of Raffinate-*II* as a cheap source of butenes. The requirement for C_{10} alcohol-plasticizer aroused because of some concerns about the DOP (a plasticizer based on C_8 alcohol- 2-EH). The concerns emerged from three types of exposure and emission: plasticizer migration into food from plasticized packaging; plasticizer evaporation from indoor floor tiles and wall coverings; and plasticizer migration into blood plasma or medicine from plasticized medical equipment.



UCC -Diphosphite ligand for Raffinate-II Hydroformylation

The pressure to minimize exposure was felt and so the large manufacturers started looking for plasticizers with less volatility, C_{10} alcohols were looked at as a probable solution. The best starting material for the production of C_{10} alcohols is the above-mentioned Raffinate-2, a C_4 feedstock derived from the mixed C_4 streams of steam crackers. Raffinate-2 as a raw material, is converted to C_5 aldehydes and finally to C_{10} alcohols by sequential hydroformylation, aldol condensation, and hydrogenation[lxi]. Raffinate-2 contains 50-65 % of *n*-1-butene, the remainder consisting of *cis* / *trans* / *n*-2-butene and saturated butanes. The presence of internal olefins poses a problem as their hydroformylation give a poor selectivity to *n*-pentanal, which is of importance. Union Carbide and Davy Process Technology have developed a hydroformylation process based on mixed butenes and a rhodium / diphosphine catalyst to produce 2-propylheptanol (2-PH) as the C_{10} analog to 2-EH. The catalyst converts Raffinate-2 with 94 % yield to n-propanal, whereas only 5 % 2-methylbutanal and 1 % 3-methyl butanal (from isobutene) are formed as isomeric products[lxii]. This mixture is further reacted to get the final C_{10} alcohol.

Further developments in the Rh-catalyzed hydroformylation of lower olefins occurred in biphasic hydroformylation and are discussed in the heterogenization attempts of hydroformylation catalysts.

1.2.1.3. Heterogenization attempts for hydroformylation catalyst for lower olefins

Since catalyst-product separation is a major problem for the homogeneous reactions, heterogenization of the catalyst is in vogue for last couple of decades. For lower olefins the requirement of heterogenization is more felt because of large production volumes and costly catalyst and ligands. Various ways such as use of supported catalyst, polymer anchored catalysts, biphasic and SAPC techniques, and encapsulation in zeolite cages *etc*. have been attempted for heterogenization.

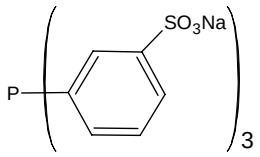
Initially, a major emphasis was given on developing a supported catalyst for gas phase continuous hydroformylation of lower olefins *e. g.* Ichikawa[lxiiia], Takeuchi *et al.*[lxiiib,c], Huang *et al.*[lxiiid] *etc*. have carried out extensive work in this area. Various monometallic and bimetallic catalysts based on Co, Rh and Ru supported on Al_2O_3, SiO_2, zeolites *etc*. were tested for ethylene hydroformylation. Major drawback of all these catalysts was poor selectivity to hydroformylation, hydrogenation being a prominent side reaction. Recently nano-fiber supported Rh-catalysts was used for ethylene hydroformylation by Gao *et al.*[lxiv]. Several different types of graphite nanofibers (GNFs) were used as supports, among the various rhodium/GNF catalysts, ribbon type nanofibers appeared to give the highest selectivity to the desired product. High partial pressures of CO and C_2H_4, and a concomitant low partial pressure of H_2 gave the best results. The optimum temp. for the hydroformylation reaction was found to be 513 K, which is very high compared to the conventional homogeneous reaction. Overall it can be concluded that the heterogeneous (supported metal) catalysts are in no way comparable to the homogeneous catalysts as far as hydroformylation is concerned.

The failure of the inorganic supported catalysts for hydroformylation lead to an idea of using liquid supports and the field of biphasic catalysis emerged. The basic principle of biphasic catalysis is to keep catalyst and products in separate immiscible phases. In order to have an efficient catalyst separation, it is essential that the solubility of the catalyst in the reactant phase should be negligible and the substrate, while being immiscible with catalyst phase should have minimum solubility in the catalyst phase to obtain reasonable reaction rates. Lower olefins like propene have better solubility in the aqueous phase compared to higher olefins and so aqueous biphasic catalysis is applied

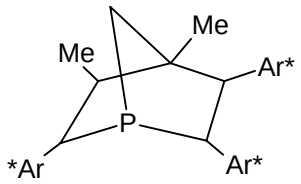
extensively for propene hydroformylation. In recent years, aqueous biphasic catalysis using water-soluble catalysts have been studied to develop new routes and efficient process for a variety of products and the subject has been repeatedly reviewed by researchers like, Kalck and Monteil[lxv]; Herrmann and Kohlpainter[lxvi]; Beller *et al.*[lxvii]; Joó and Kathó[lxviii], Joó *et al.*[lxix] and Cornils and Herrmann[lxx].

In some cases whereby the substrate and products have greater solubility in water, reverse biphasic systems are used where catalyst is kept in the organic phase and products are extracted *in situ* in the aqueous phase. Deshpande *et al.* [lxxi] have studied the reverse biphasic system for allyl alcohol hydroformylation. The second phase of water minimizes catalyst contact with substrate as well as products, thus avoiding side reactions and catalyst poisoning.

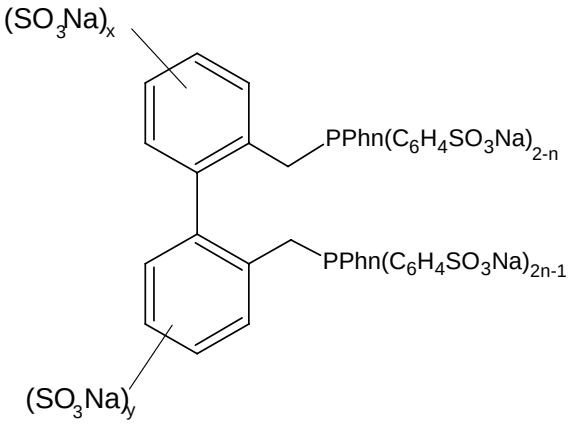
Water-soluble ligands play a major role in the aqueous biphasic catalysis for lower olefins. The water-solubility of the catalysts used in the aqueous two-phase catalysis can be achieved by appropriate modification of the phosphine ligands with polar groups such as SO_3^-, COO^-, NMe_3^+, OH *etc*. Majorities of the water-soluble ligands reported are based on the sulfonated phosphines. Even though the monosulfonated derivative of phosphine was synthesized as early as 1958 by Aharland *et al.*[lxxii], it was only after the synthesis of trisulfonated triphenylphosphine *i.e.* Tris(sodium-m-sulfonatophenyl) phosphine (TPPTS),) by Kuntz[lxxiii], that the research on water-soluble lignads was initiated as major activity in the field of biphasic catalysis. In several reports sulfonation was extended to new sophisticated bidentate ligands. Herrmann's group has developed a number of sulfonated bisphosphines such as BINAS[lxxiv], BISBIS[lxxv], which in combination with rhodium are used as propene hydroformylation catalysis and found to exhibit higher activities and higher *l/b* ratios than TPPTS. Furthermore, it was shown that displacement of the biphenyl unit of BISBIS by a binapthyl unit in BINAS leads to an increase of the catalytic activity, which was ascribed to electronic effects and large bite angle of the ligand. In addition, the steric effect of the binapthyl unit was believed to cause higher *l/b* selectivities than TPPTS.



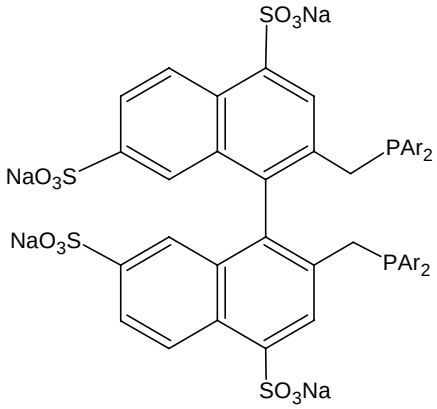
(**TPPTS**)



Ar* = 4-SO_3Na-C_6H_4 (**NORBOS**)



(**BISBIS**)



Ar = C6H4-*m*-SO3Na **(BINAS)**

Systematic studies on the oxo process in particular have significantly improved activities through variation of ligands. The comparison of the standard ligand triphenylphosphino trisulfonate (TPPTS) of aqueous biphasic technology with new ligands such as BISBIS, NORBOS, or BINAS shows distinct differences (Figure 1.2). The hydroformylation results so far demonstrate that different requirements such as highest possible activity, highest *n/iso* ratio or lower excess of ligands (in all cases BINAS » TPPTS) can be achieved by different ligands.

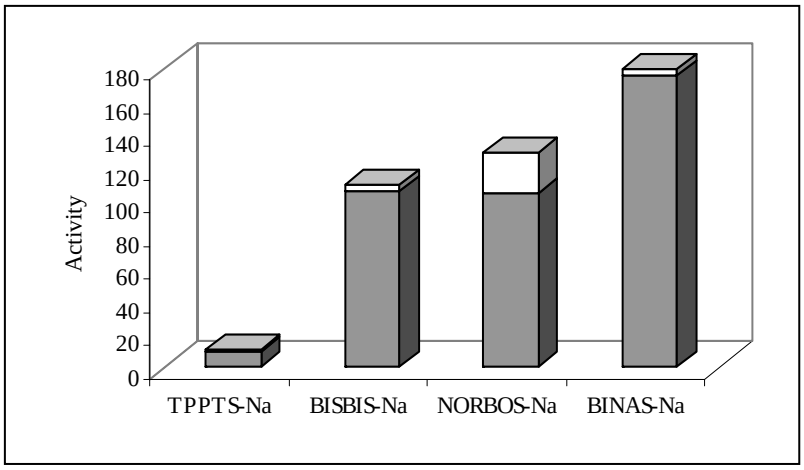


Figure 1.2. Comparison of oxo catalyst $HRh(CO)L_3$, with L is either of TPPTS, BISBIS, NORBOS and BINAS

Although, sulfonated aryl phosphine catalysts synthesis is the central activity of the research carried out in the area of aqueous catalysis, other types of water-soluble ligands based on quaternary ammonium salts[lxxvi], N-containing ligands, carboxylic acid functional groups[lxxvii] *etc* have also been reported.

Aqueous biphasic hydroformylation is also applied to other substrates like Raffinate-*II*, in the lower olefins category, Hoechst has recently patented a process for the hydroformylation of Raffinate-*II* using a water-soluble rhodium catalyst; a plant is on stream[lxxviii]. Surprisingly, there are almost no reports on application of biphasic hydroformylation to the cobalt catalysts. The reason may be the high temperatures required for phosphine modified cobalt catalysts, as sulfonated phosphines are generally not stable at temperatures above 413 K. Beller *et al*[xlivC]. have studied the hydroformylation of internal pentenes in biphasic mode with Co-TPPTS complexes. The aim of the study was to apply the biphasic catalyst system to internal olefins such as Raffinate-2 fraction. He found the typical problems of Co-leaching in the organic phase, low rates, and alcohol formation. A reasonable *n/iso* ratio of 70:30 is obtained in some cases and up to four recycles without the loss of activity has been demonstrated.

1.2.2. Hydroformylation of higher olefins

Higher olefins (C_5 onwards) account for more than 20 % of the commercial hydroformylation capacity and completely reverse situation (compared to C_2-C_3) is encountered in this area of hydroformylation: cobalt dominates rhodium by far, the 9:1 ratio being in favor of cobalt[xlviii]. Almost all the products of higher olefins hydroformylation plants are converted to either plasticizer or detergent grade oxo alcohols. SHELL and BASF are the largest producers of oxo alcohols in the world. If compared with lower olefins higher olefins hydroformylation is more complicated in many ways.

1.2.2.1. Complications involved in the higher olefins hydroformylation

A general reaction scheme for 1-hexene hydroformylation with all side reactions is presented in Scheme 1.1. The essential distinctions of higher olefins hydroformylation compared to propene hydroformylation are as follows,

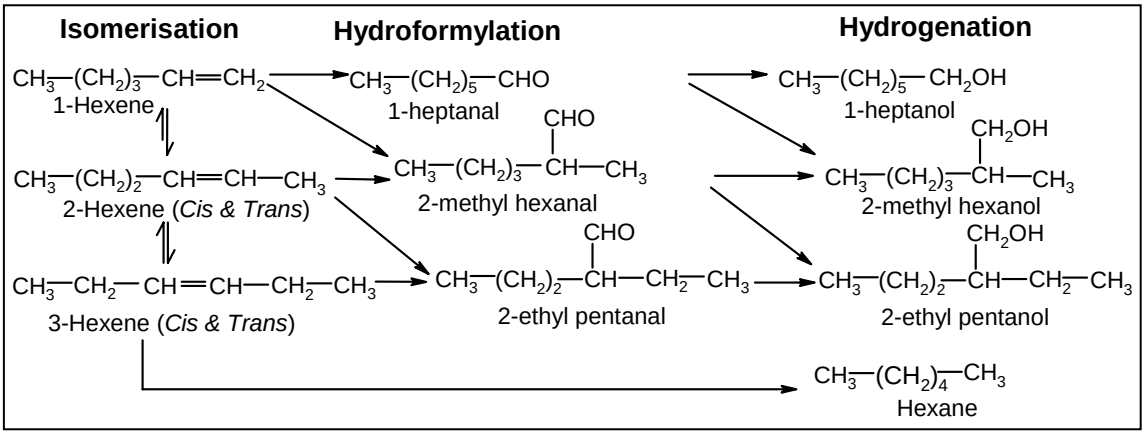
I) Isomerization of higher olefins is a prominent side reaction under hydroformylation conditions. Isomerization affects the regioselectivity and rates of the hydroformylation reaction. Isomerization also affects the TON of the hydroformylation reaction as a part of active hydroformylation catalyst is always involved in the catalytic isomerization cycle (in which all the steps are reversible).

II) There are chances of hydrogenation of the olefins, which enhances under certain conditions.

III) At higher temperatures heavy ends formation is more compared to lower olefins

IV) Catalyst-product separation is a problem. As the aldehydes of higher olefins are generally unstable at higher temperatures, distillative separation of the aldehydes from reaction mixture is difficult. Also, due to the high boiling points of the aldehydes, catalyst stability becomes an issue for distillative separation.

V) Aqueous biphasic hydroformylation is either slow or impossible with higher olefins as substrates because of less solubility of the higher olefins in water.



Scheme 1.1. Simultaneous isomerization, hydroformylation and hydrogenation of 1-hexene

On the above listed problems, cobalt catalysts (especially phosphine modified) offers better solutions compared to rhodium catalysts. Even though, phosphine-modified cobalt complexes (Shell catalyst) catalyze the side reactions (isomerization and hydrogenation), they give high selectivities to n-aldehydes at better rates. Shell catalyst is stable even at higher temperatures and it generally gives alcohols as end products and so the problem of aldehyde decomposition and catalyst instability at higher temperatures, is taken care of. Drawbacks of the Shell catalyst are, high reaction temperatures (> 433 K),

low rates, and low chemoselectivity to oxo products because of side reactions like hydrogenation of olefins. Rh-catalysts are not used for higher olefins hydroformylation because of low regioselectivities and their inability to hydroformylate internal olefins. Also, with rhodium catalyst/product separation is more tedious as the product aldehydes and Rh-catalyst both are unstable at higher temperatures. Still, frantic efforts to find out an isomerizing-hydroformylation catalyst based on Rh are on.[iii] It is said that the forth generation hydroformylation catalyst will concern higher alkenes only, since for propene hydroformylation there are hardly any wishes left.[lxxix]

Since isomerization, hydrogenation and heavy-ends formation are such major and important side-reactions accompanying hydroformylation, a brief study of these three reactions under hydroformylation conditions is given below. Higher olefins hydroformylation is studied under two categories, Rh-catalyzed, and Co-catalyzed hydroformylation.

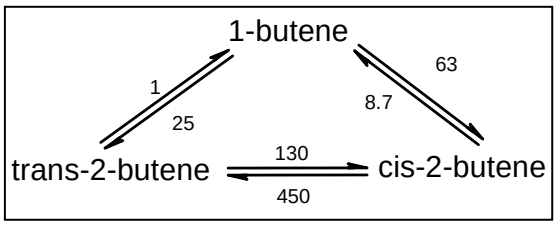
1.2.2.2 Isomerization under hydroformylation conditions:

Isomerization during hydroformylation, as stated above, is an unwanted side reaction but sometimes act in the favor of commercial interest *e. g.* shell catalyst's ability to hydroformulate the internal olefins to terminal alcohols (high *n/iso* selectivity) helps companies to use mixture of internal and terminal olefins as hydroformylation feed sock.

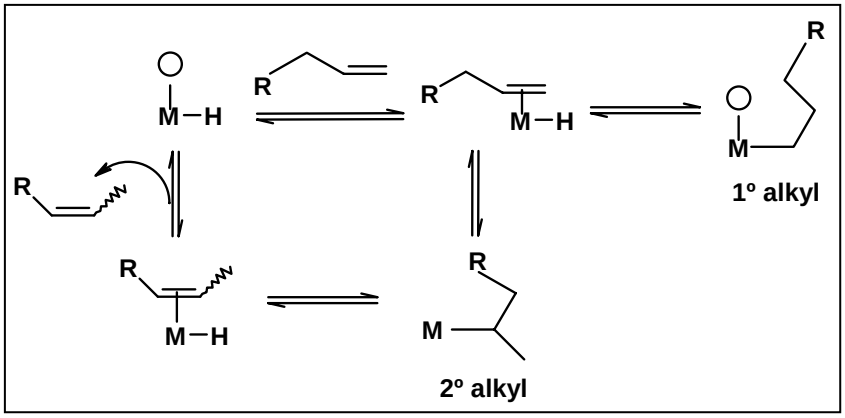
It was know for a long time that Co-catalysts promotes isomerization of olefins. Heck and Breslow[lxxx] studied isomerization of olefins under hydroformylation conditions and even proposed mechanism for olefin isomerization. Schultz *et. al*[lxxxi]., while studying olefins dimerization have found that with Co/C catalysts, extensive isomerization of terminal olefins to internal olefins takes place but surprisingly the dimerization products of only terminal olefins are obtained in the product profile. Fell et al. proved the same thing for hydroformylation[lxxxii]. They have shown that with tricyclohexyl phosphine modified cobalt catalyst; nearly same product composition is obtained with both 1-octene and *trans*-4-octene as hydroformylation substrates. The works of Fell, Piacenti[lxxxiii], Hershman[lxxxiv] *etc*. gave conclusive support to the rapid isomerization of olefins with both modified as well as unmodified cobalt carbonyl catalysts.

Cobalt carbonyl complexes not only catalyze the linear olefin's isomerization but also carry out *cis-trans* isomerization, allyl alcohol-propanal isomerization *etc*. Roos *et al.*[lxxxv] have carried out stoichiometric isomerization of allyl benzene to *trans*-1-phenyl propene with the help of $HCo(CO)_4$ catalyst. Similar treatment with $DCo(CO)_4$ gave the same results but only about 5 % deuterium was incorporated into the isomerized olefin and so the intramolecular 1,3-hydride shift mechanism is proposed to explain the results. Contrary to allyl benzene, when allyl alcohol was isomerized with $DCo(CO)_4$, the only product observed was 3-D-propanal and the authors proposed 1,3-allylic exchange mechanism[lxxxvi]. $DCo(CO)_4$ readily isomerises dimethyl maleate to dimethyl fumarate (*cis*-trans isomerization) under mild conditions[lxxxvii].

The driving force for isomerization is the formation of thermodynamically more stable isomers[lxxxviii]. In case of hydrocarbon olefins, thermodynamically the internal olefins are more stable compared to terminal olefins also highly branched alkenes are more stable compared to less branched alkenes.



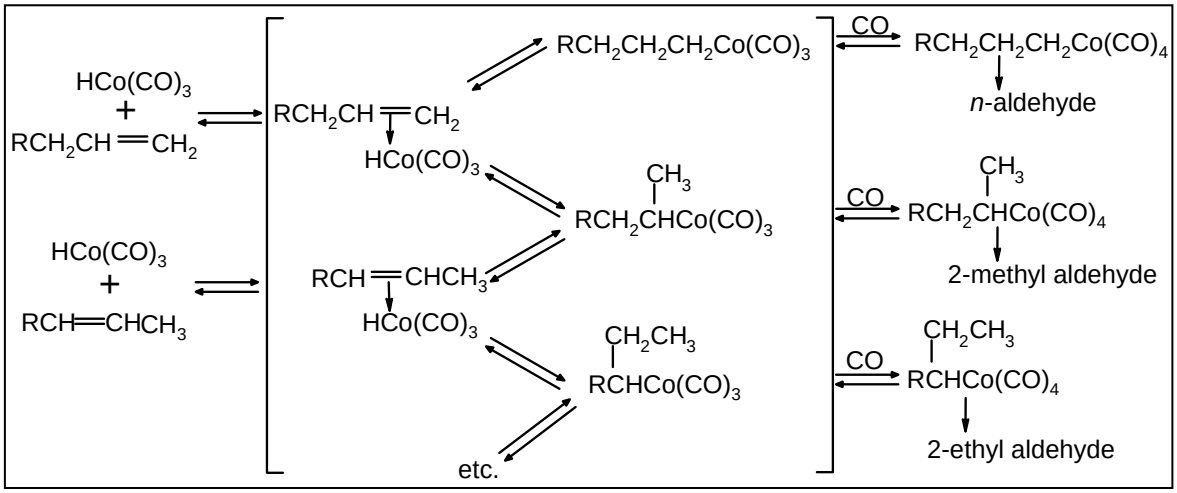
The popular equilibrium triangle for butene isomers with $Ni(P(OEt)_3)_4$ –H_2SO_4 catalyst, at 298 K is shown in the adjacent figure[lxxxix]. Because of this thermodynamic constraint, in presence of isomerization catalyst and suitable conditions, most of the substrate tends to form a mixture of olefins in which the internal olefins dominate. Among the internal olefins the *cis*-isomers are favored initially but the final ratio depends on thermodynamics and the *trans*-isomers are favored. There are different mechanisms proposed for olefin-isomerization with hydroformylation catalysts *e. g.* alkyl mechanism, 1,3-hydride shift, allyl mechanism



(1,3-allylic exchange), and 1,2-hydrogen shift (1,2-addition-elimination or metal migration along the skeleton of the substrate)[xc,xci,lxxx]. Out of these, alkyl mechanism and 1,2-hydrogen shift explains most of the olefin isomerization experiments.

Metal-hydrogen bond is required for alkyl mechanism to operate. Metal hydride complex first forms a π-bond with the olefin and then an alkyl species is formed. According to the regiochemistry of insertion, two different alkyl species (1º alkyl and 2º alkyl) can be formed as shown in the adjacent figure. 1º alkyl species on *β*-elimination gives back the original olefin, however, 2º alkyl species on *β*-elimination, either gives back original olefin or an internal isomer (*cis*- or *trans-)*[xc]. Because of the thermodynamic stability of the internal olefins the equilibriums of this isomerization cycles are shifted more towards formation of internal olefins and very soon a thermodynamic equilibrium is attained.

1,2-hydrogen shift (metal migration along the carbon chain) is actually the



Scheme 1.2. Isomerization mechanism

mechanism of the metal alkyl species (or metal-olefin complex) isomerization without formation of free isomerized olefins as shown in the Scheme 1.2)[xcii].

According to this mechanism, the metal-alkyl species of terminal and internal olefins are in equilibrium with each other while the metal-olefin-π-complexes working as intermediates. Heck and Breslow made a hypothesis that the metal-olefin-π-complex of the terminal olefins is more stable compared to that of the internal olefins and its

formation is rapid compared with aldehyde formation or with return to olefin and hydridocarbonyl species.[lxxx] So the metal-π-complex of the terminal olefin is formed predominantly even from internal olefins and it leads to the formation of linear aldehydes. Heck and Breslow have also demonstrated that CO inhibits olefin isomerization and so they assume that the active species for olefin isomerization is hydridocobalt tricarbonyl and not the tetracarbonyl complex. Takegami *et al.* have supported Heck and Breslow in their assumption of isomerization of the alkyl cobalt species [xciii] however Piacenti *et al.* have apposed the idea of isomerization of the alkyl or acyl species[lxxxiii]. They have experimentally shown that isomerization occurs at lower CO pressures only whereas at higher CO concentrations isomerization is negligible and very slow but they couldn't give an alternate mechanism for internal olefins hydroformylation to linear aldehydes. Isomerization of terminal to internal olefins is a temperature dependant reaction and is faster at higher temperatures. Pregaglia *et al.* [xciv] have studied isomerization with Shell-type catalysts in more details. They have shown that with $HCo(CO)_2(PBu_3)_2$, in 240 minutes, not even 1 % internal pentenes are formed from 1-pentene, under 3 MPa H_2 pressure and 333 K, whereas at 388 K extensive isomerization occurs. The authors have also concluded that at lower temperatures, $HCo(CO)(PBu_3)_3$ is more active for isomerization as compared to $HCo(CO)_2(PBu_3)_2$ and presence of free phosphines drastically lowers the catalytic activity. One more interesting finding by Pregaglia is that $HCo(CO)(PBu_3)_3$ catalyses the isomerization of internal olefins more than that of the terminal olefins.

Stefani *et al.* [xcii] have postulated that, the alkyl mechanism of isomerization, must be operating during the Rh-catalyzed hydroformylation and 1,2-hydrogen shift, to be operational during cobalt catalyzed hydroformylation. The Rh-catalysts catalyses isomerization of terminal higher olefins, but contrary to cobalt, Rh-catalysts especially the triphenyl phosphine modified rhodium (Wilkinson catalyst) gives predominantly linear aldehydes with terminal alkenes and branched aldehydes (at much slower rates compared to those of terminal olefins) with internal olefins (*cis* or *trans*)[xcv]. Thus, question of getting linear aldehydes from internal olefins doesn't arise in case of Wilkinson catalyst. Also, Rh catalysts-unmodified or modified by phosphines, do not

promote the conversion (hydroformylation, hydrogenation, isomerization *etc*.) of internal double bonds[iii,xcix].

From the literature survey it can be concluded that (a) the effect of parameters such as *P*CO, *P*H_2, temperature, free ligand *etc*. on isomerization is similar to hydroformylation. (b) Different mechanisms are proposed but there are still doubts about mechanisms operating with different catalysts and more study is needed. (c) Cobalt catalysts outweigh Rh catalysts in the reactions of internal olefins.

The higher *internal* alkenes are available in considerable amounts from some of the petrochemical processes and efforts are on to develop a Rh based 'isomerising hydroformylation' catalyst so as to utilize these feedstocks[iii].

1.2.2.3. Hydrogenation under hydroformylation conditions

Because of the presence of reducing environment (syngas) in the hydroformylation reactions and also because many of the hydroformylation catalysts are active for hydrogenation, it is an important side reaction involved along with hydroformylation. Weinder *et al.*[xcvi] in 1950 have found that when catalytic hydroformylation of alkenes is conducted at about 458 K, with unmodified Co catalyst, the product consists principally of alcohols. With unmodified Co carbonyls aldehydes are reduced under stoichiometric conditions also, albeit slowly.[xcvii] Phosphine modified cobalt catalyst (Shell catalyst), under hydroformylation conditions, is known to hydrogenate the olefins along with aldehydes formed after hydroformylation of olefins[xcviii], where as under hydroformylation conditions, Rh catalysts are not as active as Co catalysts for hydrogenation[xcv]. There are reports of exclusive hydrogenation being carried out with active hydroformylation catalysts *e. g.* $HRh(CO)(PPh_3)_3$ under H_2 pressure gives fast hydrogenation of 1-alkenes[xcix,c], $HCo(CO)(PPh_3)_3$ under 5 MPa H_2 pressure and 423 K, hydrogenates cyclohexene to cyclohexane[ci]. Pregaglia *et al.* have prepared and characterized $[Co(CO)_2PR_3]_n$ complex. This deep green complex is formed by stoicheiometric hydroformylation of olefins (under H_2 atmosphere). The trimeric complex (n=3) is used for hydrogenation of olefins (conditions are 339 K, 1.5 MPa H_2). With butadiene, this complex selectively hydrogenates one double bond giving butenes[cii].

Like isomerization, hydrogenation as a side reaction, also have some advantages from commercial point of view. Hydrogenation of aldehydes to alcohols is sometimes a useful side reaction as alcohols are the end products required in the detergents as well as

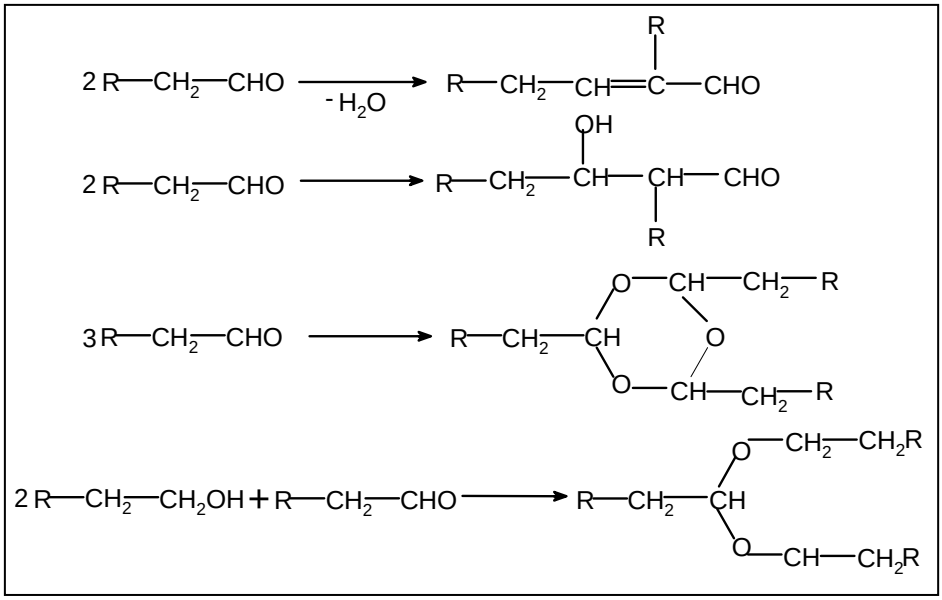
$$RCHO + HCo(CO)_4 \longrightarrow RCH_2OCo(CO)_4 \xrightarrow[HCo(CO)_4]{H_2 \text{ or}} RCH_2OH$$

plasticizer market. But of course, olefin hydrogenation is an unwanted side reaction, which consumes the substrate. There is not much study done on the hydrogenation reactions under hydroformylation conditions. Marko, in 1962, has proposed speculative mechanism with an intermediate possessing a O-Co bond, for stoichiometric as well as catalytic hydrogenation.[ciii] Pregaglia *et al.* have studied hydrogenation and isomerization of alkynes, alkenes and aldehydes by TBP-Co-hydride complexes. With $HCo(CO)(PBu_3)_3$ alkynes hydrogenates to alkenes but alkenes hydrogenation to paraffins is much slower. 1-pentyne hydrogenates faster than 2-pentyne, the same is applicable to 1- and 2- pentene. In case of butanal hydrogenation with $HCo(CO)_4$ and TBP, at *P*CO lower than 1 MPa, increasing phosphine concentration reduces the aldehyde hydrogenation whereas at higher *P*CO, the increase in phosphine concentration doesn't affect the aldehyde hydrogenation. This is postulated to be due to the higher concentrations of more phosphinated (*e. g.* $HCo(CO)_2(PBu_3)_2$, $HCo(CO)(PBu_3)_3$) species at lower *P*CO and higher phosphine concentration. Such species may be less active in aldehyde hydrogenation due to their higher steric hindrance. $HCo(CO)_4$ alone hydrogenates butanal, the hydrogenation activity increases initially for 0.2-0.6 MPa CO and then reduces as the CO pressure is increased further, the reason may be a problem in formation of unsaturated species for aldehyde hydrogenation. The dissociative mechanism of the catalyst is proposed.[xciv]

Generally, olefin hydrogenation under hydroformylation conditions is slow and stops earlier than aldehyde hydrogenation. There is no study explaining reasons behind this fact. Certain olefin substrates react by hydrogenation rather than hydroformylation under catalytic hydroformylation conditions *e. g.* α,β-unsaturated aldehydes/ketones are reduced to saturated aldehydes, or ketones at about 398 K. However, α,β-unsaturated esters undergo hydroformylation under similar conditions.[civ] Thus, sometimes a small structural change in a substrate can steer reactions with $HCo(CO)_4$ from complete hydroformylation to complete hydrogenation.

1.2.2.4. Heavy ends formation

Heavy ends – the byproducts of the oxo synthesis- can result in various ways; via condensation, trimerization, aldolization, acetaliazation *etc*. Unlike isomerization and hydrogenation, all these reactions originates from the product oxo aldehydes. Some of the general reactions are given in Scheme 1.3. Heavy end formation is more common for Co-catalyzed hydroformylation as the conditions (especially temperature) are rather harsh and Co is active for hydrogenation. For different reasons, phosphine modification helps in reduction of the heavy ends. Co-phosphine complexes convert aldehydes into alcohols and so aldehyde side reactions are reduced whereas Rh-phosphine systems operates at low reaction temperatures and so heave end formation is less.



Scheme 1.3. Heavy end formation during hydroformylation reaction

1.2.2.5. Cobalt catalyzed hydroformylation of higher olefins

Both modified and non-modified cobalt catalysts are commercially used for hydroformylation of higher olefins. Processes of BASF, Kuhlmann and Exxon utilizes unmodified cobalt carbonyl as catalyst and Shell uses phosphine modified cobalt catalyst for hydroformylation. The literature reports of progress in hydroformylation are dominated by publications from industry (mainly patients) and the open literature in journals, *etc* about the industries using cobalt-catalyzed processes discloses only minor secrets[xlviii]. A brief literature survey on the modified and unmodified cobalt catalyzed hydroformylation in Table 1.3**.**

Table 1.3. Literature table for hydroformylation of higher olefins

No.	Catalyst system	Substrates	Reaction conditions		Conv. %	*n* / *iso*	Other features	Reference
			Temp K	MPa $CO:H_2$,				
1	$Co_2(CO)_8$, TBP	Propene, isobutyne	443	3.5, 1:2	100	8-9	Alkenes and alkynes are hydroformylated to aldehyde and alcohols.	Slaugh *et al.* (1966)[cv]
2	$[Co(CO)_3(PBu_3)]_2$, other ligands	1-pentene	468	3.0, 1:2	100	10	First elaborate paper on hydroformylation with modified Co.	Slaugh *et al.* (1968)[xcviii]
3	$[Co(CO)_3(PBu_3)]_2$	1-hexene, propene	433	6.66, 1:1.2	100	9	Effects of parameter on P-modified Co catalyst.	Tucci (1968)[cvi]
4	$Co_2(CO)_8$, PCy_3, And Rh_2O_3, PBu_3	Internal olefins.	423	20.0, 1:1	100	4	With Co-P *trans*-4-octene give nearly same regioselectivity as 1-octene	Fell *et al.* (1968)[cvii]
5	$Co_2(CO)_8$, PBu_3	1-hexene, 2-hexene	468	3.5, 1:1	96	4-5.5	Both 1-and 2-hexene gives same products with Co-P system	Hershman *et al.* (1968)[cviii]
6	$Co_2(CO)_8$, PBu_3	1-hexene, 2-hexene	443	23.0, 1:1.2	96	4-5.5	Both 1-and 2-hexene give same products	Tucci *et al.* (1968)[cix]
7	$Co_2(CO)_8$, PBu_3	Internal octenes	463	20.0, 1:1	100	4-4.1	1-octene and *trans*-4-octene give nearly the same *n/iso*.	Asinger *et al.* (1969)[cx]
8	$Co_2(CO)_8$, PBu_3	1-octene, 2-octene	463	8.0, 1:2	~60	5.5	CT profiles of 1- and 2-octene hydroformylation are given	Kniese *et al.* (1969)[cxi]
9	$Co_2(CO)_8$, PBu_3	1-hexene	433	6.6, 1:1	-	-	Ligand basicity is related to rates	Tucci (1970)[cxii]
10	$Co_2(CO)_8$, PBu_3 or PPh_3	1-pentene, 1-hexene	443	~10, 1:1	90	5.5	Alcohol formation decreases with increase in temperature, P_{CO} and dilution.	Rupilius *et al.* (1971)[cxiii]

No.	Catalyst system	Substrates	Reaction conditions		Conv. %	*n / iso*	Other features	Reference
			Temp K	MPa $CO:H_2$,				
11	$HCo(CO)_4$, $Co_2(CO)_8$	1-heptene, 1-octene	288	0.05 CO	Dicobalt octacarbonyl catalyzes the formation of acylcobalt tetracarbonyls and paraffins from olefins			Ugvary *et al.* (1981)[cxiv]
12	$Co_2(CO)_8$	1-octene	-	-	-	-	Photocatalytic hydroformylation	Mirbach *et al.* (1981)[cxv]
13	$Co_2(CO)_8$, Diphos	*trans*-6-dodende	473	20,1:1	35	-	DPPE showed more branched products.	B. Fell (1982)[cxvi]
14	HCo(CO)4 and poly-anchored Co	2-pentene	413	7.5, 1:1	97	4.6	Polymer anchored cobalt shows heavy leaching, *n/iso* is higher because of cobalt.	De-An *et al.* (1983)[cxvii]
15	$Co_2(CO)_8$, PBu_3, water	1-octene	463	5.5, 1:1	70	-	Effect of water on TBP-Co system is studied.	Bartik *et al.* (1993)[cxviii]
16	$PhCCo_3(CO)_9$	1-pentene	403	4, 1:1	-	-	CIR data on $Co_2(CO)_8$.	Jaw-Don *et al.*(1994)[cxix]
17	$Co_2(CO)_6(TBP)_2$	1-hexene	423	4.5,1:8	96	1.5	Different alkyl phosphine ligands used	Rosi *et al.* (1996)[cxx]
18	Rh- -xanthene	1-, 2-, 4-octenes	393	0.2, 1:1	54-67	4.4-6	Very poor conversion	Van Leeuwen *et al.* (1999)[cxxi]
19	Rh- xanthene	1-, 2-, 4-octenes	393	0.2, 1:1	54-67	4.4-6	Very poor conversion,	Van Leeuwen *et al.* (1999)[cxxii]
20	Rh- Phosphonite ligands.	Internal – n-octenes	413	2, 1:1	93% yield	0.4	Very high TOFs (83600 h^{-1} max) are claimed for 1-octene hydroformylation	Detlef Selent *et al.* (2000)[cxxiii]
21	Rh-substituted Naphos	1- and 2-pentenes	393	1, 1:1	61	93 / 7	High temperatures used	Beller *et al.* (2001)[cxxiv]

No.	Catalyst system	Substrates	Reaction conditions		Conv. %	*n* / *iso*	Other features	Reference
			Temp K	MPa $CO:H_2$,				
22	Co/ SiO_2, Pt, Pd, Ru promoters	1-hexene	403	5, 1:1	90 5	-	Leaching observed. Pd acted as better promoter.	Qiu *et al.* (2001)[cxxv]
23	Rh – pyrrolyl phosphine,	2-pentene	393	0.5, 1:1	11	1.5	Pyrrolyl, Indolyl, carbazolylphosphanes as ligands with Rh	Jackstell *et al.* (2001)[cxxvi]
24	Rh-Phosphine oxide	Isomeric octenes	413	10.2, 1:1	87	~ 0.2	Rh-TP phosphine oxide hydroformylate the internal olefins	He *et al.* (2001)[cxxvii]

1.2.2.6. Unmodified cobalt catalyzed hydroformylation

Plain hydridocobalt carbonyl [$HCo(CO)_n$] is generally known as unmodified cobalt catalyst and the most common precursors for it are dicobalt octacarbonyl and cobalt octanoate. These precursors, under hydroformylation conditions, readily form hydridocobalt carbonyl catalysts [$HCo(CO)_4$ and $HCo(CO)_3$]. Hydridocobalt carbonyl catalysts can also be prepared in-situ from any cobalt salt or complexes *e. g.* $CoCl_4$, CoO, CoO_2, $Co(acetate)_2$, Co-carbonate, $Co(OH)_2$ *etc.* under high temperature – high pressure conditions.

Effect of syngas pressure (*P*CO & *P*H_2)

Since, $HCo(CO)_4$ is a highly unstable complex, high pressures of carbon monoxide are required to stabilize it under hydroformylation conditions. In an initial report on kinetics of hydroformylation Natta *et al.* proposed that the rate of hydroformylation is independent of the pressure of the synthesis gas in the range of 12 MPa to 38 MPa[cxxviii]. The same authors latter proposed that the partial pressures of CO and H_2 have nearly equal and apposite effects on the reaction velocity[cxxix] and so increase in total syngas pressure shows negligible effect on rate of reaction. Low CO partial pressures initially increase the rate of reaction before it once again drops off[cxxix,cxxx]

$$HCo(CO)_3 \rightleftharpoons HCo(CO)_4$$

(Wilkinson catalysts also behaves similarly). Apparently, the actual catalyst is initially unsaturated with regard to CO and after certain CO partial pressures (~ 1.5 MPa) the saturated species starts forming. Fivefold saturated coordinate species $HCo(CO)_4$ is correlated with the decreasing reaction rate and $HCo(CO)_3$ is regarded as the more active form of the catalysts[cxxxi]. This interpretation of saturated and unsaturated species is in accordance with the effect of *P*CO on the regioselectivity, the share of unbranched isomer increases with increasing *P*CO.[cxxxii] Increase in H_2 partial pressure raises the reaction velocity and also negligibly increases the linear:branched ratio.[lxxxiii] Thus, the highest possible reaction velocity can be achieved by high *P*H_2 and the highest possible yield of unbranched isomers via high *P*CO, in short high pressures of syngas are required for better results in an unmodified Co catalyzed hydroformylation reaction. In industrial Oxo Processes, total pressures of ~ 30-35 MPa is generally used. Similar reports on the

effects of *P*CO and PH_2 on the reaction rates and regioselectivity for higher olefins (terminal as well as internal) are present in the literature[xcii,cxxxiii]. The *P*CO and PH_2 also have effects on the side reactions. Lower *P*CO generally increases the degree of hydrogenation thereby increasing the alcohol and paraffin formation. As discussed in the section on isomerization, low *P*CO also promotes extensive isomerization of the substrate.

Effect of temperature

While stoichiometric hydroformylation takes place even at room temperature, the catalytic activity requires minimum temperatures between 298 and 303 K depending on the olefin.[cxxxiv] Generally rising temperatures increases the reaction velocity at the same time decreases the selectivity towards favored unbranched aldehydes.[cxxxv] In the temperature range of 353 – 453 K, with α-olefins the n:iso ratio drops from ~ 3 - 5 to 0.8 - 2.[cxxxvi] One of the reasons for low n:iso at very high temperatures, is CO deficiency, which can only be partially balanced- and not eliminated- by extremely good mixing or by special construction features in the oxo reactors.[cxxxvii] Unwanted side reactions such as condensation, aldolization, acetal formation *etc*. also increase with temperatures. Parallel reactions such as isomerization and hydrogenation shows positive effect of temperature and so high temperatures are used only when alcohols (plasticizer or detergent grade) are the desired products.

1.2.2.7. Modified cobalt catalyzed hydroformylation

A modification in plain hydridocobalt carbonyl complexes by replacing one or more carbonyl (CO) ligands with other electron donating ligands alters many properties of the complex. Many monodented or polydented- phosphines, phosphites, amines, arsines, stibanes *etc*. can be used for such modifications. The complex can be prepared *in situ* by treating $Co_2(CO)_8$ with the complementary ligand under 2 to 5.5 MPa syngas pressure and 423-473 K temperature. Cobalt salts such as cobaltous acetate, chloride, oxide, and hydroxide *etc*. can also be used instead of $Co_2(CO)_8$.[xcviii] Phosphine ligands especially trialkyl phosphines are more popular ligands for hydroformylation catalyst.

Depending upon the conditions, the P-modified cobalt complex exists in equilibrium with the unmodified complex through intermediate complexes[xciv] as shown in

$$HCo(CO)(P)_3 \underset{+P}{\overset{+CO}{\rightleftharpoons}} HCo(CO)_2(P)_2 \underset{+P}{\overset{+CO}{\rightleftharpoons}} HCo(CO)_3(P) \underset{+P}{\overset{+CO}{\rightleftharpoons}} HCo(CO)_4 \underset{+P}{\overset{+CO}{\rightleftharpoons}} HCo(CO)_3$$

the adjacent scheme. Slaugh *et al.* have found two species, $[Co(CO)_3(PBu_3)]_2$ and $[Co(CO)_3(PBu)_2]^+[Co(CO)_4]^-$, on treatment of $Co_2(CO)_8$ with PBu_3 (Tri-*n*-butyl phosphine) under syngas pressure and 423 K. The authors concluded that under high temperature and syngas pressure the active hydroformylation catalyst is $HCo(CO)_3(PBu_3)$.[xcviii] The effect of modification on different aspects is discussed below.

Stability: Compared to CO, phosphine ligands possess better σ-donor and poorer π-acceptor property. As a consequence, in P-modified cobalt complexes, electron density on the Co increases and the remaining CO ligands gets more strongly bonded to the metal via stronger electron back donation, increasing the stability of the complex.[cxxxviii] This leads to greater resistance of such catalysts with regard to thermal strain at lower CO partial pressures. Because of the increased thermal stability, distillative separation of the hydroformylation products poses less threat to the catalyst.[cxxxix]

Activity: Increased stability reduces the activity of the catalysts. The necessary dissociation of CO ligand in the catalytic cycle is impeded by strong Co-CO bonds. This effect is more noticeable at higher ligand: metal ratios[cxl] Lower activity makes higher temperature and greater reactor volume necessary to achieve the same productivity. In fact, the $HCo(CO)_3(PBu_3)$ catalyst is not active below 413 K for hydroformylation of course for better rates and yields, temperatures in the range of 453 to 473 K are required.

Hydrogenation activity: Increased electron density on Co result in the H atom of the hydrido complex possessing a stronger hydride character, increasing the hydrogenation activity of the catalyst. Since, hydroformylation with modified Co catalyst is carried out at higher temperatures, the hydrogenation activity also increases, and generally alcohols are obtained as the end products. However, the hydrogenation tendency of the modified catalysts depends strongly on the type of ligands present.

Selectivity: Higher regioselectivities are obtained with $HCo(CO)_3(PBu_3)$ catalysts. Various interpretations have been presented involving steric and electronic effects of the ligand, cone angle of the ligand[cxli], ligand basicity[cxii] *etc* however, the actual reason must

be a combination of the above factors. Chemoselectivity depends on the reaction conditions but generally alcohols are obtained along with the aldehydes as end products, thus hampering the aldehyde selectivity. Only alcohols are obtained at higher temperatures. Rapid isomerization also takes place, so the unreacted olefin is always in the isomeric-mixture form.[cx]

Because of the above aspects, the reaction conditions required for hydroformylation with modified Co catalysts are much different as compared to unmodified Co catalyst. Also, various parameters have different effects on the activity-selectivity of the unmodified Co catalysts. The work done in this area is summarized below.

Effect of syngas pressure (*P*Co & *P*H_2)

Piaenti *et al.*[cxxxiia] have studied the effects of both *P*CO and *P*H_2 on $Co_2(CO)_6(PBu_3)_2$ catalyzed hydroformylation of propene. The authors have observed that, on increasing *P*CO, *n*-selectivity passes through minima whereas *P*H_2 has a positive effect on *n*-selectivity. On increasing *P*H_2 from 1 to 4 MPa, *n*-selectivity increases from 58 % to 68 % and remains constant on further increase. Under *P*H_2 of 2 MPa, as the *P*CO increased, the straight chain isomers (82.2 % at 0.35 MPa PCO) decreases, reaches a minimum of 55 % at 1 MPa *P*CO, again increases up to 61.5 % at 3 MPa *P*CO and shows no effect on further increase. Whereas, on addition of extra phosphine, no change in the percentage of straight chain isomers is observed, in the *P*CO range of 0.35 to 5 MPa. *P*CO has a negative effect on hydrogenation activity. The yield of alcohol decreases from 29.2 % to 1%, olefin hydrogenation is also reduced from 6.1 to 1% as *P*CO is increased from 0.35 to 10 MPa. In case of unmodified catalyst *i. e.* $Co_2(CO)_8$ the influence of *P*CO on *n*-selectivity is exactly in the other direction when varied from 0.35 to 1 MPa, straight chain isomer increases. Author has concluded that the ligand displacement by CO is the main reason behind similar trends for both modified and non-modified catalyst after 1 MPa of CO pressure. He has put before a hypothesis that as CO pressure is increased from 0.35 to 1 MPa, CO is progressively displacing phosphine and after 1 MPa it is the non-modified catalyst, which gives the effect. When Phosphine is added in excess, author observed that the phosphine displacement is minimum or negligible. Tucci's study

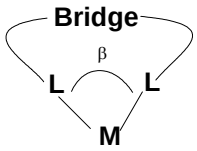
supports Piacenti's conclusion. He has studied pressure effects on hydroformylation of propene with $Co_2(CO)_8$-PBu_3 system[cxlii] and found that when P:Co is 4, as the total pressure is increased from 6.6 to 23.1 MPa, the olefin conversion decreases slightly from 85 % to 78 % and selectivity remains constant. In an another study, where P:Co ratio is only 1, Rupilius *et al.* have found a decrease in n-selectivity on increasing the *P*CO from 4.9 to 14.7 MPa[cxiii]. Thus, the effect of *P*CO on reaction rate and regioselectivity varies depending on the phosphine concentration. Tucci has also found a drop in alcohol concentration from ~ 40 % to ~ 28% on increasing the total pressure from 3.6 to 25.2 MPa. In an another effect of PH_2:*P*CO ratio, Tucci has found that as the ratio increases alcohol formation increases.

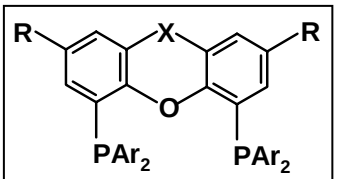
All these studies are carried out at high pressures and very high catalyst concentrations (Sub.: catalyst = ~32 for Tucci's studies) and so the results are misleading. Effect of partial pressures on reaction rates is not studied. Also, there is no report on proper study of the effect of *P*CO and PH_2 variation on isomerization and hydrogenation in the case of terminal olefins with carbon chain > C_5.

1.2.2.8. Rhodium catalyzed hydroformylation of higher olefins

In this area, major emphasis in the last few years is given on developing different phosphine/phosphite ligands, which can isomerize and hydroformylate higher olefins. Van Leeuwen, Beller, Selent *etc*. have been very active in synthesizing and applying different lignads to achieve high *n/iso* ratios at high rates.

Van Leeuwen *et al.*[cxliii] have worked extensively with Xanthene-based ligands with specific bite angles. The bite angle (ligand-metal-ligand angle, '*β*') depends upon the bridge between the two ligands. Metal complexes with chelating ligands prefer certain bite angles for stability *e. g.* bite angle of 90º stabilize square planar geometry. Ligands that maintain well-defined bite angle can be used to induce distortions of certain geometries and, as a result, destabilize them. This not only affects the activity and selectivity of a catalytic reaction but it can also make alternative reaction pathways

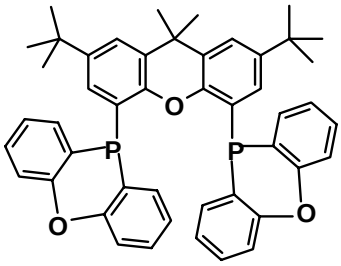




Xantphos
X= CH_2CH_2, RP, R_2Si, R_2C, RN,S
Ar = Ph, cyclic rings etc.
R = H, *t*-C_4H_9

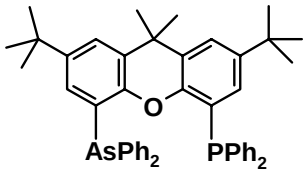
accessible. By altering the X, Ar and R groups on the basic xantphos skeleton, Van Leeuwen's group has prepared a series of ligands of various bite-angles and used them for rhodium catalyzed hydroformylation reactions.

Phosphacyclic xantphos derivatives show a high activity for hydroformylation of terminal and internal octenes than their non-cyclic parent ligand.[cxliv] *e. g.* For 4-octene hydroformylation at 393 K and 2 MPa syngas pressure, POP-xantphos is shown to obtain 67 % conversion with *l:b* (linear : branched) ratio of 4.4, in 17 hours. This result is a significant improvement if compared with conventional PPh_3 ligand which gives only 9 % conversion with *l:b* ratio of 0.3 under similar conditions.

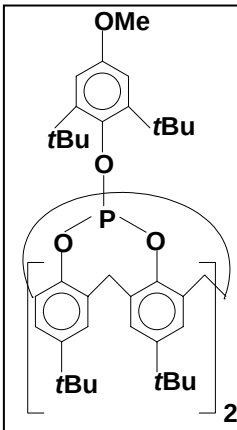


Phosphocyclic, POP-xantphos

With the xanthene backbone, mixed arsine-phosphine ligands were also prepared by van der Veen *et al.*[cxlv]. These ligands, with the Pt-Sn system give unprecedented high selectivity of 96 % to *n*-nonanal at 333 K and 4 MPa syngas pressure. Only 3.1 % isomerized olefins are obtained and the TOF calculated was 350 h^{-1}.

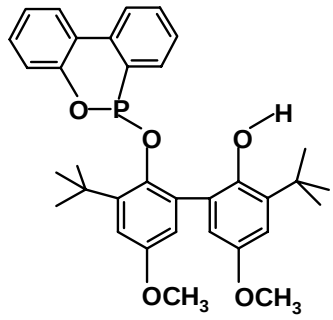


Xantphosarsine



Calixarene bisphosphite

Like xanthene backbone, Paciello *et al.*[cxlvi] used Calix [4] arene backbone for synthesizing various phosphine ligands. The *t*-Bu substituted arene ligand of this type, the authors have shown to get 63 % conversion of 1-octene with 99.5 % nonanal regioselectivity. The selectivity to internal octenes is only 12 % but octane formation is very high at 27 %. Beller *et. al*[cxlvii]. have used various NAPHOS derivatives for hydroformylation of internal pentenes and octenes. The best result obtained shows, *n:iso* ratio of 91:9, 48 % yield and 300 h^{-1} TOF, for 2-octene hydroformylation. The contact times however are very high in the range of 56-96 h. With NAPHOS ligands, Rh catalyst shows good thermal stability, as the reaction temperature is 413 K. Yields are poor and still drops down for internal olefins like 4-octene.



Phosphonite ether

Selent *et al*[cxlviii]. have used oxyfunctionalized Phosphonite ligands for hydroformylation of mixture of octenes. For Rh-catalyzed 1-octene hydroformylation, these phosphonite ethers have reported to give TOF of the order of 83000 h^{-1} with 94 % yield and n:iso ratio of 1.03.With internal octenes, TOF drops down at 7390 h^{-1}, with *n:iso* ratio of ~ 1.7. He *et al*[cxlix]. have used various phosphine oxide ligands for hydroformylation of mixture of octenes. Surprisingly Rh-TPP system gives only 20 % yield for internal octene hydroformylation whereas Rh-TPPO catalyst carries out the reaction at 413 K and give 90 % yield of C_9 aldehydes, albeit with very poor regioselectivity (<1). The authors have tested various alkyl and aryl phosphine oxide ligands and parametric effects are studied.

Thus, it can be concluded that frantic efforts to get regioselective catalyst system for internal olefins hydroformylation are on. The trend is to synthesize ligands with varying steric-electronic properties for hydroformylation. Still, for Rh-catalyst system, the problems of, catalyst-product separation, higher-aldehyde instability *etc*., are not particularly looked into.

1.2.2.9. Heterogenization techniques for higher olefin hydroformylation catalysts

The reaction rates in aqueous biphasic hydroformylation depend upon solubility of substrate in the aqueous phase. Naturally, aqueous biphasic technique if applied for reactions of higher olefins, the rates decrease as the number of carbon atom increases. Various techniques such as Soluble Aqueous Phase Catalysis (SAPC), use of co-solvents, use of tensile ligands are used to enhance the rates.

Not many reports are available on application of biphasic catalysis to the cobalt catalysts.[cl]

1.2.3. Hydroformylation of functionalized olefins

Functionalized olefins are important substrates for hydroformylation as they produce dual functional organic compounds, which are very useful fine chemicals for organic synthesis. The commercial utility of fictionalized olefins category is very well

demonstrated by various processes like, Ajinomoto process for acrylonitrile hydroformylation to L-glutamic acid (Na-salt)[cli], Vit. A synthesis from diacetoxy butenes[clxxxii,clxxxiii], Shell process for 1,3-propanediol from ethylene oxide[xxix] *etc*. In spite of the importance, functionalized olefins are somewhat ignored by the hydroformylation researchers mainly because of the following limitations,

1) Because of two functional groups, chemoselectivities regioselectivities are often low.
2) Substrates sometimes are unstable under hydroformylation conditions.
3) Products formed, sometimes acts as a catalyst poison
4) In general reaction rates are lower than those found for hydrocarbon olefins.

As shown in Figure 1.1, various compounds such as olefinic alcohols, ethers, acetals, halo compounds, cyano compounds, esters, amino compounds, nitro compounds *etc*. can be used as hydroformylation substrates. Table 1.4 enlists references for some important functionalized olefin hydroformylation papers.

The work presented in this thesis deals mainly with olefinic esters and so they are reviewed in more detail in the following sections.

1.2.3.1. Hydroformylation of olefinic esters (Substrates other than VAM)

Olefinic ester is the most studied substrate-group in functionalized olefins category. The motivation in studying hydroformylation of olefinic esters is prompted by, the commercial interests in products, varying (*challenging!*) regioselectivity patterns and as convenient prochiral substrates for asymmetric hydroformylation. Easy availability, in bulk quantities, of some of the olefinic esters such as allyl acetate, vinyl acetate and methyl acrylate (which gives economically important hydroformylation products), also aroused the commercial interests.

Olefinic esters can be differentiated in two groups, esters of unsaturated alcohols (acetates), and esters of unsaturated acids (acrylates). In the present section the literature survey on the hydroformylation of esters of unsaturated alcohols is discussed in detail (Table 1.5).

Table 1.4. Literature table for hydroformylation of functionalized olefins (other than acetates)

No.	Catalyst system	Substrates	Reaction conditions		Conv. %	n / iso	Other features	Reference
			Temp, K	*P*CO : pH_2, atm				
1	$HRh(CO)(PPh_3)_3$ + Diphos	Allyl alcohol	65	1:2 , 3	95	6.5	Continuous reactor	US 4215077[clii]
2	$PdCl_2(PPh_3)_2$ - $Co_2(CO)_8$ + NEt_3	Internal alkynes	150	1:1, 50-70	100	-	Described the synergy of Pd-Co bimetallic cata.	Youichi Ishii (2001)[cliii]
3	$Co_2(CO)_8$, P-O ligands	Epoxides	100	1:1, 100	-	-	-	Weber *et al.* (2000)[cliv]
4	$HCo(CO)_4$	Phenyl acetylene	RT	CO, atm	-	-	Stoichiometric.	Bockman *et al.*(1999)[clv]
5	$HRh(CO)(PNS)_3$ Aq.	Unsat. C_4 alcohols	50-80	300, 1:1	100	~ 9	Biphasic hydroformylation and hydrogenation.	Mieczynska *et al.* (1999)[clvi]
6	MeNpy-Ru	Diphenyl acetylene	70	20, 1:3	20	~ 100	α-phenyl cinnamaldehyde is prepared by hydroformylation	Nombel *et al.* (1999)[clvii]
7	$Co_2(CO)_8$	Fun. Olefins	125	1:1, 235	-	-	First report on hydroformylation of many functionalized olefins.	Adkins *et al.* (1949).[clviii]
8	$Co(CO)_3(PBu_3)$, other ligands	Isobutylene	195	30, 1:2	100	24	Isobutylene gives very high *n/iso* compared to 1-pentene.	Slaugh *et al.* (1968)[clix]
9	$Co_2(CO)_8$	Dienes	145-175	200-275, 1:1	30	-	Substituted and unsubstituted dienes	Adkins *et al.* (1952)[clx]
10	$Co_2(CO)_8$, Rh-complexes	All fun. Olefins	-	-	-	-	Review on work done in the hydroformylation of functionalized olefins till 1987.	Botteghi *et al.* (1987)[clxi]

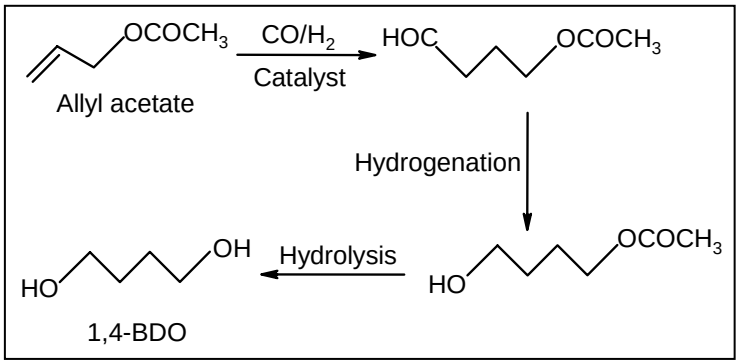
11	$HRh(CO)(PPh_3)_3$ / Xantphos	ω-vinylaldehyde acetals	40-60	20, 1:1	~99	68 /32	With Xanthphos ligands ~99 % linear dialdehydes are obtained	Botteghi *et al.* (2001)[clxii]

Table 1.5. Literature table for hydroformylation of acetate-functionalized olefins (other than VAM)

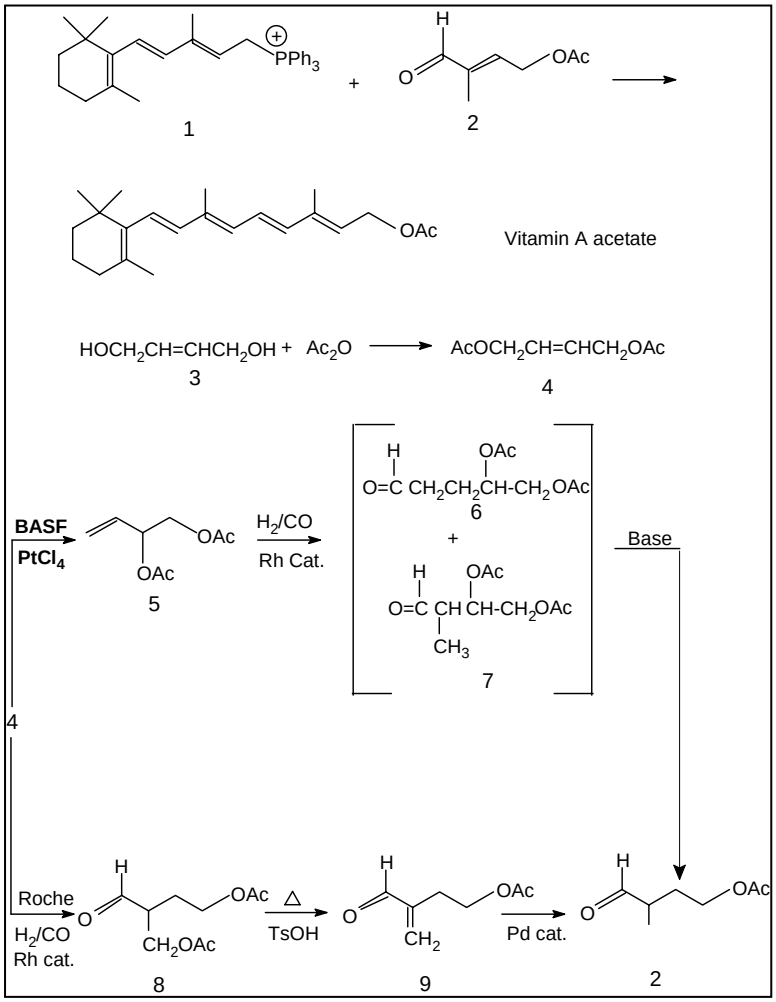
No.	Substrate	Catalyst system	Reaction conditions			Conv./ Yield %	Selectivity, %		Remarks	Reference
			T, K	Syn gas, MPa	Others		branched	linear		
1	3,4-diacetoxy-1-butene	Rh-carbonyl	373	4.8	Xylene solvent	-	-	-	Preparation of C_5 --acetate for Vit. A	Rheude *et al.* (2002)[clxiii]
2	3-pentenoic methyl ester	Rh-phosphite	373	0.61	Contact time = 8h	52	24	76	Chilating biphosphites ligands	Tsai *et al.* (2000)[clxiv]
3	Methallyl acetate	Rh- phosphite	383	8.1	Contact time = 6 h	93	-	100	-	Omatsu *et al.* (1998)[clxv]
4	Allyl acetate	$Rh(Ph_3P)_2(NO)$	373	3.9	Contact time = 2 h	33	70	30	Isoaldehyde formed preferentially.	Hayashi *et al.* (1976)[clxvi]
5	Allyl acetate	$Co_2(CO)_8$	-	-	-	98	30	70		Smith (1974)[clxvii]
6	Allyl acetate, allyl formate	$Co_2(CO)_8$-diphosphine	-	-	-	98	20	80	Total three isomeric aldehydes	Murata *et al.* (1981)[clxviii]
7	Allyl acetate	$Co_2(CO)_8$	-	-	-	-	-	-	Propylene to butanediol	Smith *et al.* (1977)[clxix]
8	Allyl acetate	$Co_2(CO)_8$	-	-	-	-	-	-	Dehydroformylation of isoaldehyde	Smith (1977)[clxx]

No.	Substrate	Catalyst system	Reaction conditions			Conv./ Yield %	Selectivity, %		Remarks	Reference
			T, K	Syn gas, MPa	Others		branched	linear		
9	Allyl acetate	Rh4(CO)12 – Pyridine	383-403	14.2	Toluene / Dioxane	-	-	-	Reduced Fe is also used as promoter.	Lapidus *et al.* (1981)[clxxi]
10	Mercapto-propene	$HRh(CO)(PPh_3)_3$, PPh_3	383	7-8	Solvent = Benzene	-	-	-	High selectivities to linear products.	Kleemann *et al.* (1982)[clxxii]
11	Allyl acetate	$Rh_4(CO)_{12}$ / Silicate	383-403	14.2	Toluene / Dioxane	-	-	-	Aluminosillicate are used as supports	Lapidus *et al.* (1981)[clxxiii]
12	Allyl acetate	Rh – Phosphine	--	-	Mechanistic hypothesis	-	-	-	Chelation of acetate functionality	Drenth (1984)[clxxiv]
13	Vinyl propionate	$HRh(CO)(PPh_3)_3$, PPh_3	343	2.9	Contact time = 3 h	88	94	6	Products extraction, catalyst recycled.	Kitamura *et al.* (1981)[clxxv]
14	Allyl acetate	$Co_2(CO)_8$, Ph_2S	402	6.9	Diphenyl ether	90	11	57	Ph_4Ge, Ph_3GeH, used as ligands	Lin *et al.* (1989)[clxxvi]
15	Allyl acetate	$Rh(CO)_2$acac-$(PhO)_3P$	333	6	Contact time = 0.5 h	98	73	-	More selectivity to branched aldehyde	Drent (1989)[clxxvii]
16	Allyl acetate	$[Rh(cod)(PhBPH_3)]$, dppb	353	4	Contact time = 12 h	56	5	95	Less yield and high contact time.	Alper *et al.* (1993)[clxxviii]
17	Allyl acetate	$[Rh(cod)Cl]_2$ - dppb / Montmorilonite -	303	7.6	Contact time = 24 h	85	23	77	L/b depend heavily on temperature	Lee *et al.* (1996)[clxxix]
18	Allyl acetate	Rh(Ph3P)(NO), PPh_3	373	3.9	Contact time = 2 h	33	70	30	More Branched aldehyde obtained.	Hayashi *et al.* (1978)[clxxx]

The hydroformylation of esters formed from saturated carboxylic acids and unsaturated alcohols has been studied intensively, as the resulting acylated hydroaldehydes represents a valuable starting material for the production of commercially interesting diols.



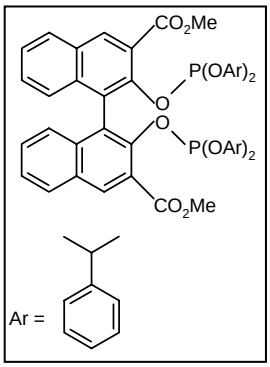
Most research on this topic is carried out with three substrates, vinyl acetate, allyl acetate, and diacetoxy butenes. Allyl acetate hydroformylation is studied mainly as a potential route for the synthesis of commercially important 1,4-butanediol. (See adjacent scheme). Latter on allyl alcohol is found to be more suitable than allyl acetate and in 1990, ARCO launched a production plant based on the technology developed by Kuraray with a 30,000 tons/annum 1,4-BDO capacity.[clxxxi]



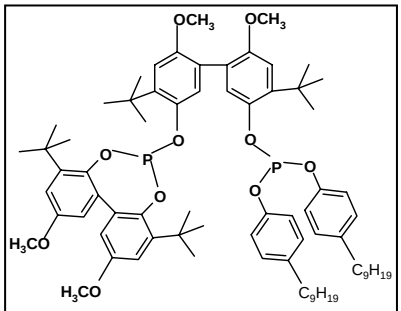
The commercial interests also prompted work on hydroformylation of diacetoxy butenes. It is studied mainly as a route for an intermediate precursor for the synthesis of Vit. A. (See adjacent scheme). Both BASF[clxxxii] and Hoffmann-LA Roche[clxxxiii] uses hydroformylation step to produce an intermediate 2 starting from 1,2-diacetoxy-3-butene and 1,4-diacetoxy-2-butene

respectively. 1,2-diacetoxy-3-butene is one of the rare hydroformylation substrates, branched aldehydes of which are commercially more important. BASF achieves that by using unmodified rhodium catalyst.

Fatty acid esters containing additional functional group are important high-value-added oleochemicals.[clxxxiv] Therefore, hydroformylation of unsaturated fatty acids and their esters are important hydroformylation substrates. Not much work is done with these substrates as mostly they contain internal olefinic groups and in bulk quantities they contain impurities, which can retard catalytic reactions. Muilwijk *et al.* have studied hydroformylation of pure and technical grade methyl oleate using rhodium bulky phosphite catalysts and could obtain good selectivities for methyl formylstearate only with pure methyl oleate.[clxxxv]



Methyl-3-pentenoate is another potentially important hydroformylation substrate, which gives useful intermediate to nylon-6 feedstock. Again, It contains internal olefin and the linear aldehyde is the desired one. Du Pont and DSM have used ligand along with rhodium and could obtain very high selectivity towards the desired product.[clxxxvi] The same catalyst system gives selectivity up to 97 % with 2-hexene as a substrate. BASF reported hydroformylation of methyl-3-pentene carboxylate with $Rh(CO)_2(acac)$ and a ligand. Methyl-5-valerate was formed with 72 % selectivity. [clxxxvii]



BASF - Diphosphite ligand for methyl-3-pentene carboxylate

Since vinyl acetate hydroformylation is one of the important topics of this thesis, it is discussed in more detail in the following sections.

1.2.3.2. Vinyl acetate monomer carbonylation and hydroformylation

VAM is an important commodity chemical with wide applications in the polymer industry. Most of the commercial production of VAM is carried out by reaction of ethylene with acetic acid and oxygen in the presence of a palladium catalyst. Nearly 50 % of the VAM produced is used to prepare polyvinyl acetate.

Chemically VAM, with its double functionality viz. olefinic and acetate group, is an interesting substrate for carbonylation reactions. The acetate group exerts both steric as well as electronic effects on the double bond reactions and so largely varying regio- and chemoselectivity patterns are obtained on reaction. To understand the reactivity of VAM double bond, literature on VAM carbonylation and hydroformylation is briefly reviewed.

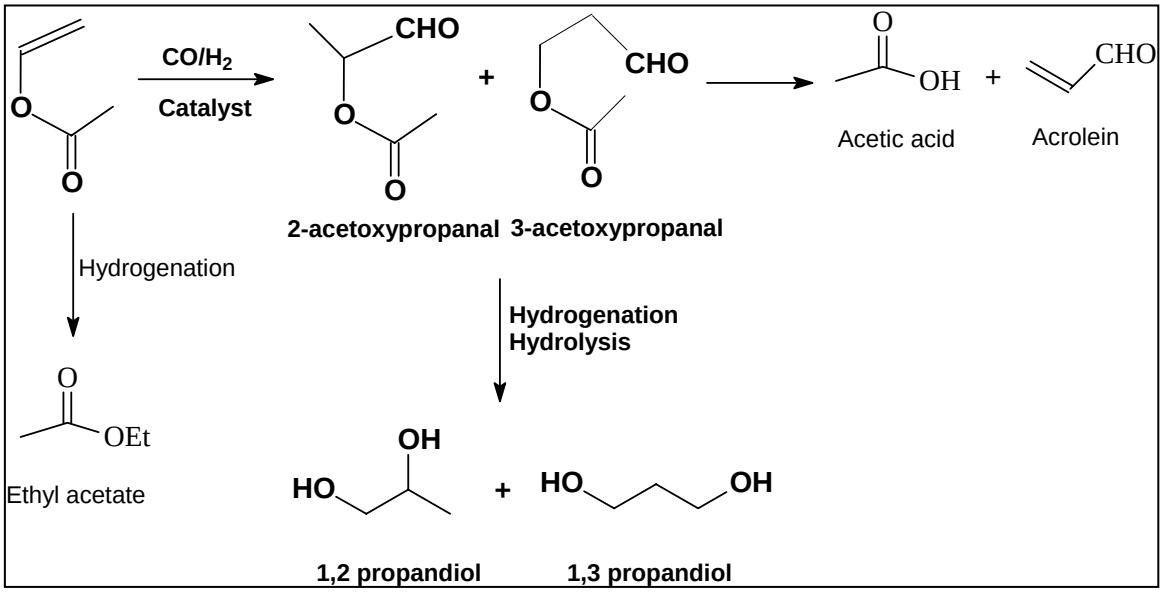
VAM carbonylation:

VAM carbonylation is mainly studied as a probable route for lactic acid synthesis. Morris *et al.* provides a process for hydrocarbonylation of VAM using water with an aim to produce lactic acid. The catalyst used by authors is $PdCl_2(PPh_3)_3$, 96 % conversion with total selectivity to α-esterification is obtained. Cesa *et al.* studied alkoxycarbonylation of VAM with hydroxy compounds using Pd, Rh and Ni catalysts, and further hydrolysis of 2-acetoxy propionic acid ester obtained, leads to lactic acid. Pd catalyzed alkoxycarbonylation of VAM with methanol is reported also by Kudo *et al.* in which high pressures of carbon monoxide (15-20 MPa) and a base such as pyridine or its derivative are used. Authors observed a peculiar thing that with $PdCl_2(PPh_3)_3$ as a catalyst only methyl-2-acetoxypropionate (branched isomer) is obtained with 71 % conversion in 5 h, whereas with $PdBr_2(PPh_3)_3$, 3 % of methyl-3-acetoxypropionate (normal isomer) along with methyl-2-acetoxypropionate is obtained with 66 % conversion in the same period. The authors have suggested a correlation of the order of the bond strength of Pd(II)─X (X = I > Br > Cl) with the above results and concluded that an electron-deficient, poorly coordinated Pd (II) center favors α-esterification (giving branched isomer), whereas a strongly coordinated palladium retards the reaction and gives β-esterification (normal isomer) to some extent. All the VAM carbonylation studies revel selective α-esterification to produce a branched isomer *i.e.* 2-acetoxy propionic acid or ester.

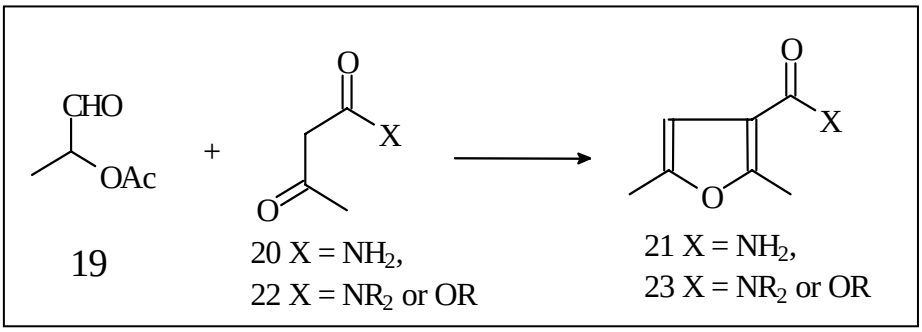
VAM hydroformylation:

VAM is an important substrate for hydroformylation because of the possibility of obtaining propanediols through VAM hydroformylation followed by hydrogenation and hydrolysis (adjacent Scheme). Both 1,3- and 1,2-propanediols (1,3-PDO and 1,2-PDO)

are commercially important products, 1,3-PDO has many applications in polymer industry and 1,2-PDO is mainly used as an antifreeze agent.



Prochiral nature is yet another reason for the continued interest of researchers in VAM hydroformylation. Most of the reports on VAM hydroformylation consist of asymmetric synthesis to obtain optically pure 2-acetoxypropanal and 1,2-propanediol. Majority of the reports uses Rhodium complexes as catalysts and like α-esterification dominance in VAM carbonylation, in VAM hydroformylation α-formylation is predominant, thus always giving 2-acetoxy propanal (branched isomer) as a major product.



2-acetoxy propanal is a valued fine chemical with some commercial applications, *e. g.* 2-acetoxy propanal (19), and also other 2-alkoxypropanals, are important intermediates for a novel one step synthesis of furan carboxylic acid derivatives, which

are of great industrial importance in seed-disinfection[clxxxviii] and in wood preservation[clxxxix]. Reaction of (19) with acetoacetamides (20) or acetoacetates (22) leads to 2,5-dimethyl-3-furancarboxamides (21) or the corresponding esters (23), in high selectivity.

Adkins *et al.* reported VAM hydroformylation for the first time in their survey of usefulness and limitations of the hydroformylation. The authors have studied dicobalt-octacarbonyl catalyzed hydroformylation of many olefinic substrates and in that they have reported one reaction with VAM. With 31.5 MPa syngas pressure, at 398 K they obtained 70 % conversion of VAM. The selectivity to 2-acetoxypropanal (branched isomer) was 65 % whereas 3-acetoxy propanal (normal isomer) selectivity was 35 %. Pressure used by Adkins *et al.* was very high. The VAM hydroformylation was not explored further by Adkins *et al.*. In their patent titled 'a process for preparing α- acetoxy propanal, Ajinomoto Co. Inc. have prepared 2-acetoxy propanal by VAM hydroformylation with rhodium tricarbonyl as a catalyst. With 16.4 MPa, 1:1 syngas pressure at 353 K, they obtained 96 % conversion with 72 % selectivity to 2-acetoxypropanal and < 2 % selectivity to 3-acetoxypropanal. Watanabe *et al.* studied hydrido cobalt carbonyl catalyzed hydroformylation of VAM in some detail with temperature and carbon monoxide & hydrogen partial pressure effects. They could obtain 100 % conversion of VAM in 1 h at 393 K and 12.3 MPa 1:1 syngas pressure. Watanabe *et al.* observed that with 1:3 = $CO:H_2$ at 373 K, the VAM conversion stops at 18 %. Contradictory to Adkins *et al.*, Watanabe didn't find any 3-acetoxypropanal in his studies on the hydrido cobalt carbonyl catalyzed VAM hydroformylation.

Tinkar *et al.* have studied VAM hydroformylation as a potential route for lactic acid production. In acetic acid solvent they have taken Rh-phosphine complexes and hydroformylation is carried out at 398 K with 3.7 MPa, 1:1 syngas pressure. The products were subjected to oxidation with 0.2 MPa air and 298 K temperature. After oxidation, hydrolysis was carried out with water at 423 K for 2 hours. 60 % yield of lactic acid yield (based on VAM reacted) was obtained along with 22 % propionic acid. No β-hydroxy propionic acid was observed indicating that 3-acetoxypropanal was not formed during VAM hydroformylation. Different rhodium precursors and phosphine ligands for VAM

hydroformylation were tested by the authors and observed that 3-acetoxypropanal doesn't form during Rh catalyzed VAM hydroformylation.

Detailed study on rhodium catalyzed VAM hydroformylation was carried out by Abatjoglou *et al.* Authors studied the effect of different phosphines at various temperatures on the decomposition of 3-acetoxypropanal and found that in presence of triphenyl phosphine or tri-*n*-butyl phosphine all the 3-acetoxypropanal is decomposed to acetic acid and acrolein at 333 K within an hour. Effect of different phosphines on the regioselectivity of rhodium catalyzed VAM hydroformylation is also studied but none of the phosphine ligand could improve the selectivity of 3-acetoxypropanal beyond 20 %. A side reaction of catalytic decomposition of vinyl acetate with $HRh(CO)(PPh_3)_3$ to yield ethylene and $Rh(CO)(OCOCH_3)(PPh_3)_2$ was observed and this rhodium complex was isolated and characterized by elemental analysis. Different vinyl carboxylates other than VAM were also hydroformylated but 3-acetoxypropanal formed was always < 10 %. Presence of acetic acid was found to retard the hydroformylation of vinyl acetate. Abatjoglou *et al.*, also speculated formation of species responsible for higher selectivity to 2-acetoxypropanal (branched isomer) and lower selectivity to 3-acetoxypropanal (n-isomer). Two alkyl species formed after the hydride additions differ in their stability and five-member ring chelate predominates thus giving more branched aldehyde. Thus, in the entire literature on VAM hydroformylation, only Abatjoglou *et al.* have studied the reaction in some detail.

Two reports on kinetics of VAM hydroformylation catalyzed by $HRh(CO)(PPh_3)_3$ and $[Rh(CO)Cl]_2$ catalyst complexes are available in the literature (Deshpande *et al.*). With $HRh(CO)(PPh_3)_3$ the kinetics of hydroformylation of vinyl acetate has been investigated in the temperature range 323 – 343 K. It was observed that certain minima of concentration of and H_2 partial pressure are necessary for the reaction to proceed. Beyond such critical concentrations, the rate was found to be first order with H_2 and catalyst. With increasing CO and vinyl acetate concentrations, the rates passed through maxima, indicating substrate inhibition at higher concentrations. The observed kinetics has been discussed on reaction mechanism. Several rate equations were examined and the activation energy was found to be 17.86 kcal / mol.

With $[Rh(CO)Cl]_2$ catalyst the trends were found to be quite different from those observed for the $HRh(CO)(PPh_3)_3$ catalyzed system. The dependence of the rate on *P*(H2) and *P*(CO) was reported to be linear, whereas the dependence of the rate on VAM concentration was found to be first order, followed by substrate-inhibited kinetics at higher olefin concentrations. The rate dependence on the catalyst concentration was fractional order. The hydrogen addition to rhodium acyl species was considered to be the rate-determining step. The following rate model was reported to fit the data satisfactorily:

Guan *et al.* studied hydroformylation of vinyl acetate to α-acetoxy propanal catalyzed by a recyclable, silica supported, polyalumazane-rhodium complex. $Rh_2(CO)_4Cl_2$ was complexed with silica-supported polyalumazane and used for VAM hydroformylation in the temperature range between 363 and 393 K at syngas (1:1) pressure range between 4.9 to 9.5 MPa. The authors obtained only α-acetoxy propanal, up to 90 % and no β-acetoxy propanal was observed. Five recycles of the catalyst, without loss of any activity was shown.

1.2.4. Asymmetric hydroformylation

First report on asymmetric hydroformylation of VAM was by Watanabe *et al.*, with $Rh_2(CO)_4Cl_2$-(-) DIOP catalyst to yield (*S*)-2-acetoxypropanal in 10-24 % optical yields. Formation of 3-acetoxypropanl was not mentioned. The authors have also hydrogenated and hydrolyzed the optical active 2-acetoxypropanal with lithium aluminium hydride and 1 M HCl respectively. The product (S)-1,2-propanediol showed specific rotation $[\alpha]_D$ + 2.35º with optical yield 14.4%. The (-) DIOP / Rh ratio was shown to have a great effect on the stereoselectivity, with highest optical yield obtained with the ratio of 2.

Hobbs *et al.* studied the asymmetric hydroformylation of VAM with DIOP-type ligands, in more detail. Different ligands were synthesized and studied for VAM hydroformylation at different temperatures, in the range of 333 to 373 K and syngas ($CO:H_2$ = 44:56) pressures in the range of 1.7 to 6.7 MPa. 3-acetoxypropanal in very minor quantity was observed and regioselectivity up to 95 % towards 2-acetoxypropanal was obtained. The highest asymmetric induction of 51 % *ee* was obtained with the 5*H*-dibenzophospholyl derivative of DIOP.

Tinkar *et al*. of Monsanto Company have studied asymmetric hydroformylation of large number of olefinic substrates with different optically active ligands. With Vinyl acetate they claim to achieve 100 % selectivity for 2-acetoxy propanal.

Sakai *et al.* have studied asymmetric hydroformylation of VAM with chiral *bis* (triarylphosphite)-rhodium (I) complexes. Many such complexes were synthesized and used for hydroformylation in the temperature range of 303 – 333 K at syngas (1:1) pressure of 10 MPa. 2-acetoxypropanal was obtained in up to 95 % regioselectivity and 49 % *ee*. The contact times were very high (40-50 h), partly because of lower temperatures.

Kadyrov *et al.* used carbohydrate biphosphites as chiral ligands for asymmetric hydroformylation of VAM, allyl acetate and *p*-methoxystyrene. Though the ligands showed chiral activity for allyl acetate and *p*-methoxystyrene hydroformylation, in VAM hydroformylation no optical rotation was observed. 2-acetoxypropanal was obtained with 97 % regioselectivity.

Recently, Clark *et al.* have studied asymmetric hydroformylation of substituted-unsubstituted styrenes and vinyl carboxylates with Rh-phosphine oxide ligands. With vinyl benzoate regioselectivity of 97 % for branched aldehyde with 52 % ee was achieved. With vinyl acetate 97 % 2-acetoxypropanal was obtained at 313 K and 4.1 MPa of syngas (1:1) pressure. The conversions of VAM were very low, in the range of 7 – 31. Literature on VAM hydroformylation in a condensed form is given in Table 1.6.

1.2.5. Kinetics and mechanism of Hydroformylation reaction

Compared to the large volume of literature on catalysis of hydroformylation, there are only a few reports on kinetics of this important reaction. Study of kinetics of reaction is essential in understanding the catalyst and molecular process occurring around it. In the present section a brief survey of the kinetic studies on hydroformylation reactions is presented with emphasis on the unmodified and phosphine modified catalyzed reactions.

For the catalysts $Co_2(CO)_8$ and $Rh_4(CO)_{12}$ the rate of reaction is positively influenced by increase in the concentration of catalyst, olefin and hydrogen[cxc]. While increasing the carbon monoxide partial pressure, the rate passes through a maximum. At

lower partial pressures (1 MPa) an increasing concentration of carbon monoxide enhances the overall reaction rate, indicating the necessity of carbon monoxide to generate hydridocobalt carbonyls, namely the $16e^-$ species $HCo(CO)_3$. At higher CO partial pressures the less reactive $HCo(CO)_4$ is formed and the reaction rate decreases. Unmodified rhodium catalyst also behaves in the same way. The equation derived by Natta and Ercoli is generally accepted [cxxviii,cxxix] (eq. 1)

$$R = k \times [\text{substrate}] \times [\text{catalyst}] \times [P_{H_2}]/[P_{CO}] \qquad 1.1$$

Gholap *et al.*[cxci] reported a detailed study on the kinetics of hydroformylation of propene under industrial hydroformylation conditions (temperature range 383-423 K and syngas pressures of up to 10 MPa. A rate equation was derived, which was found to explain the observed kinetic data satisfactorily. The rate of reaction was found to be linearly dependent on the propene concentration and fractional order with respect to catalyst and hydrogen. With carbon monoxide partial pressure, the rate showed a positive dependence up to a CO partial pressure of 1 MPa and negative order beyond 1 MPa. The trends observed were almost similar to that observed by Natta although they were not obtained under industrial conditions. By analysis of the Arrhenius plot the activation energy was determined to be 77 kJ/mol. In another study Gholap *et al.*[cxcii] studied the kinetics of isomeric aldehyde formation in hydroformylation of propene. The activation energies required for the formation of n- and isobutanal were determined to be 54 and 82 kJ/mol respectively.

Brown and Wilkinson[cxciii] studied the kinetics of hydroformylation of 1-hexene using $HRh(CO)(PPh_3)_3$ complex catalyst at 298 K. The rate of hydroformylation was first order with respect to catalyst, hexene concentration and hydrogen partial pressure and negative order with respect to partial pressure of carbon monoxide and concentration of excess PPh_3. The negative-order dependence of the reaction rate at higher carbon monoxide pressures is mainly due to the formation of *di*- and *tri*-carbonyl rhodium complexes $RCORh(CO)_2(PPh_3)_2$ and $RCORh(CO)_3(PPh_3)$, which are un-reactive toward oxidative addition of hydrogen. At lower carbon monoxide partial pressure, the formation of these species is expected to be negligible. A positive-order dependence of the rate is observed as the monocarbonyl species $RCORh(CO)(PPh_3)_2$ is stabilized.

Chaudhari and co-workers have studied kinetic modeling of hydroformylation extensively for a variety of substrates such as hexene, vinyl acetate, allyl alcohol, decene and dodecene[cxciv]. Kinetics of hydroformylation of hexene was studied using $HRh(CO)(PPh_3)_3$ in temperature range of 303-323 K. The rate was found to be first order with respect to hydrogen and catalyst (beyond a certain critical concentration) whereas, the rate versus partial pressure of CO and 1-hexene concentration passed through a maximum. A rate equation was proposed, which was found to predict the observed trends satisfactorily. The activation energy was found to be 115 kJ/mol.

In general the trends observed for kinetics of hydroformylation using phosphine-modified rhodium catalysts on different parameters can be summarized as follows.[cxcv]

1. First order in catalyst concentration
2. First order in hydrogen partial pressure
3. At lower olefin concentration, positive order, and at high olefin concentration, negative order (substrate inhibition)
4. At lower CO partial pressure (P_{CO} < 1 MPa), positive order and at high CO partial pressure, negative order

1.3. SCOPE AND OBJECTIVE OF THE THESIS

It is evident from the literature review presented here that hydroformylation of higher olefins and acetate-functionalized olefins are industrially important reactions as they provide commercially important products. In the linear hydrocarbon olefins area, extensive work with respect to phosphine modified Rh-catalysts has been done, whereas various aspects of cobalt catalyzed hydroformylation like kinetics, isomerization and hydrogenation activities need investigations. Similarly in functionalized olefins category, establishing hydroformylation, as an important process for fine and specialty chemicals is a challenge in itself. Consequently, the main objective of the present work was to establish acetate-functionalized hydroformylation as an important process to synthesize commercially important products. It was also the aim to investigate the ligand modified cobalt system for detailed kinetics and side reactions accompanying hydroformylation. With these objectives, the following specific problems were chosen for the present work.

- Hydroformylation of 1-hexene with tri-*n*-butyl phosphine modified cobalt complex
- Cobalt catalyzed hydroformylation of vinyl acetate monomer: Activity and Selectivity studies
- Hydroformylation of Vinyl Acetate Monomer as a potential route for propylene glycol: Activity and Selectivity studies with Rh-catalysts
- Hydroformylation of isopropenyl acetate: Activity and selectivity studies of rhodium and cobalt catalysts.

Table 1.6. Literature table on hydroformylation of vinyl acetate

No.	Catalyst system	Reaction conditions			Conv./ Yield %	Selectivity, %		Remarks	Reference
		T, K	Syn gas, MPa	Others		Branched	Linear		
1	**$Co_2(CO)_8$**	398	24.1	VAM/Co = 25	70	**62**	**32**	Only one reaction with VAM, poor selectivity to aldehydes	Adkins *et al.* (1949)[cxcvi]
2	$Rh(CO)_3$	353	16.37	Time = 25 min.	96.4	72	2	Promoters like Cu-powder used	Ajinomoto Co. Inc. (1965)[cxcvii]
3	**$Co_2(CO)_8$**	393	12.41	VAM / Co = 43	100	**77**	**No**	**Results contradicts with Adkin's**	Watanabe *et al.* (1974)[cxcviii]
4	$RhCl_3$	408	18	Time – 40 mins	99.7	85	6	Active catalyst prepared first at 170º C. O-xylenol as a solvent	Rasp *et al.* (1976)[cxcix]
5	Rh_2O_3	363	20	NMP and Water	90	92	8	Optimum conditions for 2-acetoxy propanal	Fell *et al.* (1977)[cc]
6	Rh(COD)(DIOP) BPh_4	253	0.83	Extra (-) DIOP added	-	100	Not obtained	31 % optical purity obtained.	Tinker *et al.* (1978)[cci]
7	$HRh(CO)(PPh_3)_3$, PPh_3	368	3.43	Solvent = Acetic acid	70	100	Not obtained	Lactic acid is prepared (65 % yield) via hydroformylation	Tinker *et al.* (1978)[ccii]
8	$[RhCl(CO)]_2$, (-)-DIOP	393	10.13	Time = 15 hrs	61	100	Not obtained	Optical yield is only 15 %. Poor conversion	Watanabe *et al.* (1979)[cciii]
9	Rh(COD)(CAMP $)_2BPh_4$	373	1.05	Solvent - Benzene	100	100	Not obtained	60 % optical purity obtained	Tinker *et al.* (1981)[cciv]
10	$HRh(CO)(PPh_3)_3$, PPh_3	343	2.94	$CO:H_2$ = 1:2	88-91	94	-	Catalyst recycled and products extracted in water	Kitamura *et al.* (1981)[ccv]
11	Rh(COD)acac, DIOP	363	1.72	L /Rh = 8	95-100	75-95	3-4	Maximum ee obtained is 46 %.	Hobbs *et al.* (1981)[ccvi]

No.	Catalyst system	Reaction conditions			Conv./ Yield %	Selectivity, %		Remarks	Reference
		T, K	Syn gas, MPa	Others		Branched	Linear		
12	$Rh(CO)_2$acac-phosphines	333	0.83	P / Rh = 15	-	-	-	Hydroformylation of VAM is slower than linear α–olefins.	Abatjoglou *et al.* (1981)[ccvii]
13	$HRh(CO)(PPh_3)_3$, PPh_3	343	2.94	Solvent = Toluene	91	90-95	Not obtained	Methyl lactate *via* VAM hydroformylation	Kitamura *et al.* (1982)[ccviii]
14	$HRh(CO)(PPh_3)_3$, PPh_3	353	2.94	$CO:H_2$ = 1:2	-	95	Not obtained	95 % 2-acetoxy propanal obtained	Kuraray Co. Ltd. (1983)[ccix]
15	$Rh(CO)_2$acac-phosphines	333	0.83	P / Rh = 15	-	86	14	Effect of phosphine ligands, solvents studied.	Abatjoglou *et al.* (1983)[ccx]
16	$HRh(CO)(PPh_3)_3$, PPh_3	353	2.94	-	-	> 95	Not obtained	Propylene glycol monoacetate prepared by hydrogenation	Kitamura *et al.* (1984)[ccxi]
17	$HRh(CO)(PPh_3)_3$, PPh_3	353	2.94	Separation-extraction	-	> 95	Not obtained	Extraction of products under syngas reduces Rh losses	Kitamura *et al.* (1984)[ccxii]
18	$HRh(CO)(PPh_3)_3$	323-343	2.4 – 5.47	Kinetic study	-	-	-	Substrate inhibition at higher concentration.	Deshpande *et al.* (1989)[ccxiii]
19	$Rh(CO)_2Cl_2$	353	2.4 – 5.47	Kinetic study	-	-	-	PH_2 and PCO affects linearly on rate.	Deshpande *et al.* (1991)[ccxiv]
20	Rh(I) – chiral phosphite	303-353	10.13		11	94	6	49 % ee obtained, poor conversion	Sakai *et al.* (1992)[ccxv]
21	Polyaluminaze-Rh / Silica	-	-	Catalyst recycled	> 90	100	Not obtained	Exact temp-pressure conditions are not given	Guan *et al.* (1992)[ccxvi]
22	Chiral catalyst	-	-	GC Study	> 95	98.7	Not obtained	Non-polar solvents give better yield, selectivity	Huang *et al.* (1996)[ccxvii]
23	Rh / Inorganic-organic polymers	343	1	Contact time = 24 h	-	-	-	Recyclable catalyst, leaching observed	Kant *et al.* (1997)[ccxviii]

No.	Catalyst system	Reaction conditions			Conv./ Yield %	Selectivity, %		Remarks	Reference
		T, K	Syn gas, MPa	Others		Branc hed	Linear		
24	Rh-chiral phosphinite- *β-cd*	353	7	Contact time = 24 h	-	100	0	27.4 % ee obtained	Xu *et al.* (1997)[ccxix]
25	BINAPHOS-Rh (acac) / Polymer	333	10.13	Sub / Cata = 500	78	90	10	89 % ee obtained	Nozaki *et al.* (1998)[ccxx]
26	Rh-Chiral biphosphites	253	4	Contact time = 24 h	94	97	3	Chirality is not induced in the hydroformylation products	Kadyrov *et al.* (1998)[ccxxi]
27	Rh(I)-chiral binaphthyl	-	-	-	-	-	-	Review on asymmetric hydroformylation	Pittman *et al.* (1999)[ccxxii]
28	Rh-diphos-silenophos-Ti	353	1	Contact time 24 h	19	97	3	Poor yield	Quimbach *et al.* (1999)[ccxxiii]
29	BINAPHOS-Rh (acac) / Polymer	333	10.13	Sub / Cata = 500	78	90	10	Styrene, (Z)-2-2butene, 3,3,3-trifluoropropene *etc*	Nozaki *et al.* (1999)[ccxxiv]
30	Rh(I)- BINAP	333	1	Contact time = 72 h	19	97	3	60 % ee obtained, poor yield.	Hoegaerts *et al.* (1999)[ccxxv]
31	Rh-Diphosphine glucopyranose	353	6	Contact time = 24 h	96	95	5	92 % ee obtained.	Lu *et al.* (2000)[ccxxvi]
32	Rh-PPh_2-Dendrimer-Silika	338	6.89	Solvent = CH_2Cl_2	99	96	4	Contact time = 22 h. Leaching observed.	Bourques *et al.* (2000)[ccxxvii]
33	Rh-PPh_2-Dendrimer-Silika	3118	3.45	Contact time = 5 h	72	95	5	Conversion is less. Catalyst recycled for 5 times.	Arya *et al.* (2001)[ccxxviii]
34	Rh-BINAP	-	-	-	-	Predo-minant	Minor	Homogeneous as well as biphasic medium used.	Kockritz *et al.* (2000)[ccxxix]
35	Rh-Diaza phospholidine	333	8	Contact time = 5 h	98.5	94.5	4.5	89 % ee obtained.	Breeden *et al.* (2000)[ccxxx]

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Chapter 2

HYDROFORMYLATION OF 1-HEXENE WITH TRI-*n*-BUTYL PHOSPHINE- - COBALT COMPLEX

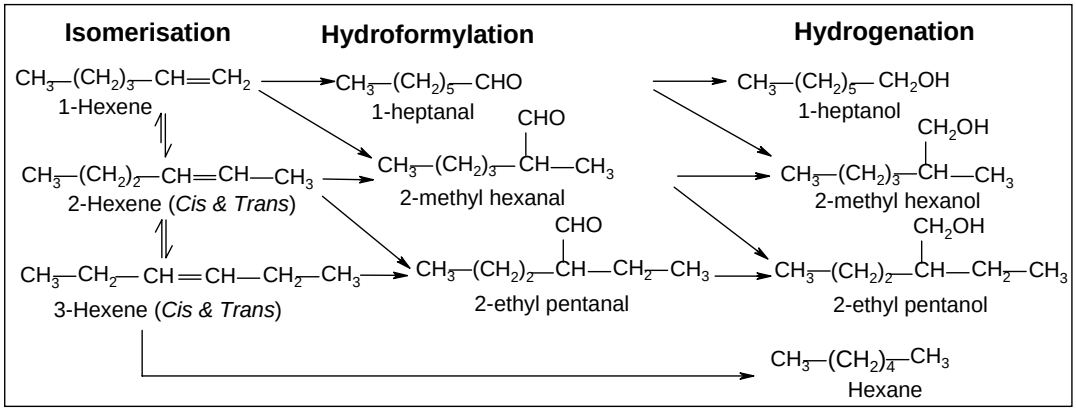
2.1. INTRODUCTION

Hydroformylation of olefins is commercially practiced either using Cobalt (Co) or Rhodium (Rh) complex catalysts, a review of important developments of which is presented in Chapter 1. In spite of the major breakthrough of the low-pressure Rh-catalyzed hydroformylation, even today several processes employ cobalt-complex catalysts. About 90 % of hydroformylation of higher olefins is carried out using trialkyl phosphine modified cobalt catalysts and the hydroformylation of C_5 + olefins account for about 25 % of the worldwide capacity of the oxo products. Thus, a significant quantity of oxo products (ca. 2.5 million tons / annum) are still produced using cobalt catalysts.

Excepting some processes (*e.g.* BASF – non-modified cobalt), most of the cobalt catalyzed hydroformylation processes use trialkyl phosphine modified cobalt catalysts. Trialkyl phosphine modified cobalt catalysts under hydroformylation conditions, simultaneously give isomerization, and hydrogenation as side reactions. In the literature, considerable efforts were made to study the effect of different parameters such as catalyst concentration, partial pressures of CO / H_2, temperature, total pressure, phosphine / cobalt ratio on activity and selectivity of hydroformylation. Tucci[i] has studied the effect of catalyst concentration on propylene hydroformylation and found that activity of hydroformylation and subsequent hydrogenation of aldehyde to alcohol was increased with an increase in the catalyst concentration. Piacenti *et al.*[xv] have studied the effects of CO and H_2 partial pressures on the regioselectivity of propene hydroformylation and found that with increase in CO partial pressure, the selectivity to *n*-butanal was decreased first and then increased slightly before becoming constant. Partial pressure of H_2 was also shown to have a positive effect on the butanal selectivity. *ligand / metal* ratio between 0 to 1 is shown to increase the *linear / branched* ratio of butanal, which remains constant with further increase in ligand / metal ratio.[i] It was found that under identical reaction conditions both 1-hexene and 2-hexene gave nearly same product distribution at essentially the same reaction rate.[ii] It was shown that the high *linear / branched* ratio obtained using modified cobalt catalyst, compared to the unmodified cobalt catalyst, was due to selective addition of olefin to the complex and not due to suppression of isomerization of olefins.[iii] However, all these studies reported in the literature were carried out at very high catalyst concentration with *substrate / Co* ratio of 16-20. Due to the high catalyst concentration, alcohol formation via aldehyde hydrogenation was very prominent. Also, since the focus was always on conversion, chemoselectivity, and

regioselectivity of the hydroformylation reaction, a detailed study of parametric effects on isomerization, and hydrogenation was not found in the literature. Very rare studies reported complete concentration-time profiles involving all the products of 1-hexene hydroformylation with trialkyl modified cobalt catalyst.

Knowledge of kinetics and development of rate equations is important in understanding the mechanistic features of such complex catalytic reactions. Kinetic modeling of hydroformylation of olefins with rhodium complexes is very well studied for variety of substrates such as ethylene, propylene, hexene, decene, dodecene, vinyl acetate, allyl alcohol, styrene *etc*[iv], while there are only a few reports on kinetics of hydroformylation with non-modified cobalt system.[v] Gholap *et al.* studied the kinetics of propylene hydroformylation with non-modified cobalt carbonyl catalysts and proposed empirical rate models for the overall hydroformylation reaction as well as separately for *linear* and *branched aldehyde*s. The authors observed a first order dependence of the rate with respect to propylene concentration, fractional order with respect to hydrogen concentration as well as catalyst concentration, and negative order with respect to CO concentration. However, there is no report on the kinetics of trialkyl phosphine modified cobalt catalyzed hydroformylation. The hydroformylation with trialkyl phosphine modified cobalt catalysts is more complex as the catalyst is active for simultaneous isomerization and hydrogenation reactions (Scheme 2.1). It is a prominent example where a major product is formed from a minor intermediate, as during the reaction, internal olefins dominate over the terminal olefins while the products obtained are of terminal olefins. This is a result of simultaneous isomerization reaction, which is an equilibrium reaction.



Scheme 2.1. Reactions occuring under hydroformylation conditions with 1-hexene

In the present work, the effect of hexene concentration, catalyst concentration, and CO / H_2 partial pressures on the isomerization, hydroformylation and hydrogenation reactions has been studied using cobalt-tributyl phosphine catalyst. Based on these data, activity / selectivity behavior, initial rates and kinetics of hydroformylation have been discussed.

2.2. EXPERIMENTAL

2.2.1. Materials

Cobalt (II) acetate tetrahydrate, DPPB, DPPP, DPPH and 1- hexene (Aldrich, USA) were used as received without further purification. Tri-*n*-butyl phosphine (TBP) (Fluka, Switzerland) was distilled in an inert atmosphere and stored under argon and was used as a dilute stock solution (10 %) in toluene (^{31}P NMR in Annexure II NMR-3). Since, TBP is highly flammable and carcinogenic, it was always handled with safety gloves, and exposure to its fumes was always avoided. CO, 99.9 % purity (Matheson, USA) and H_2 99 % purity (Industrial Oxygen Company, India) were used as received without further purification. Syngas mixture in the required CO : H_2 ratio was first premixed in a reservoir and then used for hydroformylation reactions. All the solvents were distilled and degassed with argon before use.

2.2.2. Experimental procedure for hydroformylation

All the hydroformylation reactions were carried out in a 50 ml Parr Autoclave made of stainless steel (Maximum pressure capacity of 20.7 MPa at 548 K), having facilities for gas inlet, outlet, intermediate sampling, temperature controlled heating (±1K) and variable agitation speed (0 –33.3 Hz). The typical reaction set-up is shown in Figure 2.1. As a safety precaution, a rupture disc (gold faced), which can withstand a maximum pressure of 20.7 MPa was attached to the reactor. Gas was fed through constant pressure regulator attached to the syngas reservoir while for high-pressure experiments. Syngas reservoir was always maintained at a minimum of 1.5 MPa higher pressure compared to the reactor pressure. Ice water-cooled condensers were used for intermediate sampling.

The literature on phosphine modified cobalt catalyst showed two different ways of preparation of the catalyst. Slaugh *et al.*[vi] and Tucci[i] had used $Co_2(CO)_8$ and TBP and allowed the catalyst to be prepared *in situ* whereas Rupilius *et al.*[xvi] and Piacenti *et al.*[xv] have prepared $Co_2(CO)_6(Pbu_3)_2$ before and used the catalyst itself. For the present work

we have used Co(II) acetate as a catalyst precursor instead of $Co_2(CO)_8$. Slaugh *et al.*[vi] have confirmed that under the hydroformylation conditions *i. e.* at 453 K and 4.1 MPa syngas pressure the catalyst $Co_2(CO)_6(PBu_3)_2$ was immediately formed from Co(II) acetate and TBP. Even with Co(II)acetate and TBP, we studied different modes of carrying out 1-hexene hydroformylation. When the catalyst was prepared *in situ*, it was found that the results were not reproducible. The main reasons behind the lack of reproducibility were insolubility of Co(II)acetate in toluene, and slow formation of $HCo(CO)_3(PBu_3)$ at lower temperatures such as 433 K and 453 K. Even when $HCo(CO)_3(PBu_3)$ was prepared separately in batches and used, the reproducibility couldn't be obtained due to rapid decomposition of the catalyst. Therefore for the present study, we have used freshly prepared catalyst for every reaction as explained below.

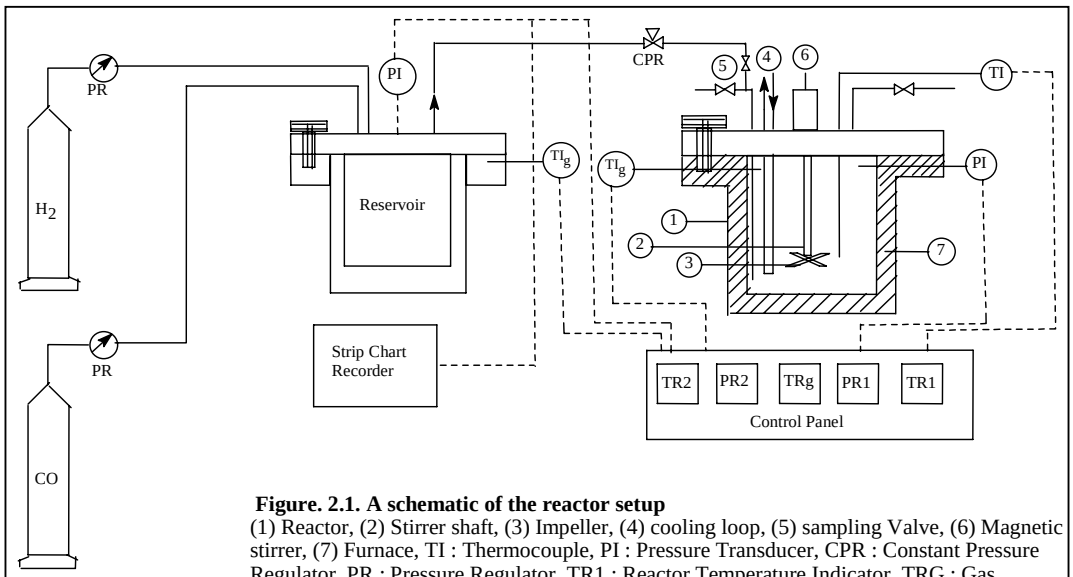


Figure. 2.1. A schematic of the reactor setup
(1) Reactor, (2) Stirrer shaft, (3) Impeller, (4) cooling loop, (5) sampling Valve, (6) Magnetic stirrer, (7) Furnace, TI : Thermocouple, PI : Pressure Transducer, CPR : Constant Pressure Regulator, PR : Pressure Regulator, TR1 : Reactor Temperature Indicator, TRG : Gas Temperature Indicator, PR1: Reactor Pressure Indicator, PR2: Resorvoir Pressure Indicator, TR2 : Reservoir Temperature Indicator

In a typical experiment, tributyl phosphine modified cobalt catalyst was prepared first by charging known quantities of the cobalt acetate tetrahydrate (catalyst precursor) and tri-*n*-butyl phosphine along with the solvent, under inert atmosphere into the autoclave and the reactor was flushed with nitrogen. The contents were then flushed twice with a mixture of CO and H_2 (1:2) and the gas was filled up to 4.1 MPa and heated to 468 K for 45 minutes. The reactor was cooled thoroughly to 288 K, degassed and a known amount of 1- hexene was added to it under inert atmosphere, a sample was taken as an initial sample. A care was taken to maintain totally inert atmosphere during the addition

of 1-hexene and human exposure to the poisonous $HCo(CO)_3PBu_3$ catalyst vapours was strictly avoided. Again the contents were flushed twice with a mixture of CO and H_2 and 1.37 MPa syngas ($CO:H_2$ = 1:2), was introduced into the autoclave to save the catalyst from decomposition. In order to carry out the hydroformylation experiments under constant pressures for this system, it was not enough to use the $CO:H_2$ supply in 1:1 ratio since, the consumption is expected to be more than 1:1 due to simultaneous hydroformylation and hydrogenation reactions. It was observed by some preliminary experiments that by feeding $CO:H_2$ in 1:2 ratio the composition of $CO:H_2$ in the reactor was maintained very close to the initial composition, in most of the cases. However, this aspect was checked by analysis of CO at the end of the reaction. $CO:H_2$ ratio of 1:2 was also helpful to maintain the catalyst in the modified form (Phosphine modified cobalt carbonyl catalysts transforms into unmodified hydridocobalt carbonyl catalysts at higher CO partial pressures).[xv] Addition of more syngas pressure at the room temperature was avoided as it starts the isomerization and hydroformylation reaction even before accomplishment of the required temperature. The contents were heated to the desired temperature under 1.5 Hz stirring, liquid-sample was withdrawn (Time-0 sample), and the reaction started by increasing the agitation to 20 Hz. The reaction was then continued at a constant pressure by intermittent filling of CO + H_2 (1:2) from the reservoir vessel. Since, the major products formed were isomeric aldehydes and alcohols, supply of CO + H_2 at a ratio of 1:2 was adequate to maintain a constant composition of CO and H_2 in the autoclave, as introduced in the beginning. The amount of gas in the reactor was always in large excess compared to the 1-hexene charged, so minor variation in the aldehyde-alcohols ratios didn't show much effect on the overall composition of CO and H_2 in the reactor. This was confirmed in a few cases by analysis of the CO content in the gas phase during the reaction and at the end of the reaction and also by checking the mass balance and the gas balance at different intervals (Section 2.3.5.3).

In each run, samples were withdrawn at regular intervals of time and analysed for reactants and products in order to check the material balance and to get concentration-time profile. Since the reaction temperatures were higher, to avoid the losses of volatile materials and to avoid exposure to the poisonous catalyst vapours, a special ice-water chilled high-pressure sampling condenser was used for sampling. At the end of the required reaction time, the reactor was thoroughly cooled to ~ 288 K, degassed and flushed twice with nitrogen to remove all the catalyst vapours before opening the reactor.

To avoid contamination to the reaction charge, the reactor was given a reflux with acetone-water mixture and a thorough N_2 flushing before every reaction. Reproducibility of the experiments was checked in some representative cases, and the data was found to be matching with an error in a range of 5-7 %.

2.2.3. Analytical methods

Liquid samples were analyzed using a Hewlett Packard 6890 Series GC controlled by the HP Chemstation software and equipped with an auto sampler unit, by using an HP-5 capillary column (60 m x 30 µm x 0.25 µm film thickness with a stationary phase of polymethyl siloxane). The quantitative analysis was carried out by constructing calibration-table in the range of concentrations studied. To avoid the injection error, isooctane was used as an internal standard. The % conversion, % selectivities TON and TOF (hr^{-1}) were calculated using the following formulae given below. The % Conversion was always calculated based on the liquid substrate charged. The standard GC conditions for the analysis of products of different reactions are given in Tables 2.1. Complete mass balance of the liquid phase components were thus obtained from the quantitative GC analysis. The observed syngas absorption was found to match with the products within ~ 5 % error. Thus, the complete mass balance of liquid and gases was established.

Table 2.1. Conditions for GC analysis

Injector (split) Temperature	523 K		
Flame ionization detector Temp	523 K		
Inlet flow – total (He)	32.3 ml/min		
Split ratio for Injector	50:1		
Column Temperature	Rate (K/min)	Temp (K)	Hold time (min)
		308	4
	293	373	2
	313	473	2
Column Pressure	Rate (psi/min)	Pressure (Psi)	Hold time (min)
		3	2
	10	5	3
	10	30	0

$$Conversion, (\%) = \frac{Initial\ concentration\ of\ substrate - Final\ concentration\ of\ substrate}{Initial\ concentration\ of\ substrate} \times 100$$

$$Selectivity, (\%) = \frac{No.\ of\ \ moles\ of\ \ a\ \ product\ \ formed}{No.\ of\ \ moles\ of\ \ substrate\ converted} \times 100$$

$$\text{Regioselectivity to I} = \frac{I}{(I+II)} \times 100$$

$$\text{Regioselectivity to II} = \frac{II}{(I+II)} \times 100$$

CO from the gas phase was analyzed using an Orset Apparatus. Cuprous chloride solutions in 50 % liquor ammonia were used to absorb the carbon monoxide from the gas samples. Effective functioning of the apparatus was ensured by analysis of gas samples with known CO concentrations. Adequate care was taken for effective contact of the gases with liquor ammonia solution and usual safety precautions for CO handling were taken.

The TBP-stock solutions were checked routinely with ^{31}P NMR technique using a Brucker- MSL-300 machine. GC-MS analysis was carried out on an Agilent GC machine of 6890N series equipped with 5973N Mass Selective Detector.

2.3. RESULTS AND DISCUSSION

The results on effect of substrate concentration, catalyst concentration, partial pressures of CO as well as H_2 on the isomerization, hydroformylation and hydrogenation reactions occurring during tri-*n*-butyl modified cobalt-catalyzed hydroformylation of 1-hexene, have been discussed in this part. Initially, to understand the product distribution and the reaction stoichiometry, concentration-time profiles were studied (Section 2.3.1). Separate data, by taking out samples in the first 15 minutes of the reaction were obtained for a study on isomerization of 1-hexene and the results are discussed in Section 2.3.2**.** To know the overall products profile, the parametric effect study of a complete reaction (90 minutes) was carried out again by intermittent sampling (Section 2.3.3 and 2.3.4). The mass balance of gases and liquid reactants / products was checked. Initial rate data were obtained from the syngas absorption profiles, under conditions where only hydroformylation and isomerization reactions were predominant.

2.3.1. Concentration-time profiles

A study of the concentration-time (C-T) profiles is the best way to assess the mass balance, reaction stoichiometry and product distribution at a glance. Here, the aim was to study the simultaneous isomerization-hydroformylation-hydrogenation reactions occurring during tri-*n*-butyl modified cobalt catalyzed hydroformylation of 1-hexene. As shown in Scheme 2.1, internal hexenes *viz* 2- and 3- hexenes; hexane; oxo aldehydes *viz* 1-heptanal, 2-methyl hexanal and 2-ethyl pentanal; and oxo alcohols *viz* 1-heptanol, 2-methyl hexanol were the major products obtained in Co-tri-*n*-butyl phosphine modified catalyzed hydroformylation of 1-hexene.

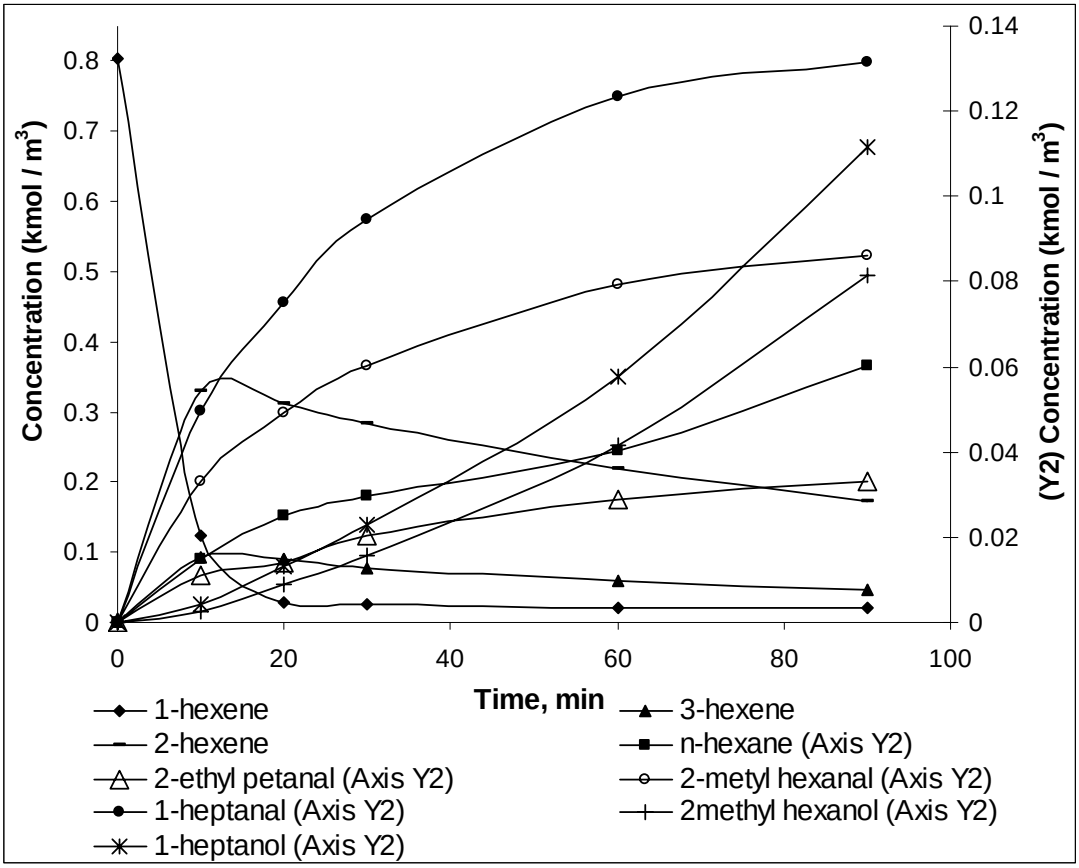


Figure 2.2. Concentration-time profile of 1-hexene hydroformylation

Reaction conditions: 1-hexene, 0.9 kmol/m^3; Co (II) acetate, 0.3 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH$_2$, 2.7 MPa; Agitation 20 Hz

Figure 2.2 shows a C-T profile obtained under a typical set of conditions. In this figure, all the products plotted with the secondary Y-axis (Y2) scale are shown with a bracket containing Y2 tag (This is applicable to all the figures with two Y axis in this

chapter). It was observed that within a few minutes (before 10 minutes) almost 90 % of the 1-hexene was converted to the internal olefins, *cis*- and *trans*- 2-hexenes and 3-hexenes. In all the concentration-time profiles, the *cis*-2-hexene and trans-2-hexene were clubbed together as 2-hexene so also for 3-hexene. Among the *cis*- and *trans* hexenes, the latter was formed predominantly with a *trans : cis* ratio of ~ 3:1. Such rapid isomerization of 1-hexene confirmed the literature reports of higher thermodynamic stability of the internal olefins over the terminal ones (Section 1.2.2.2 in Chapter 1). Over a period, steady increase in the formation of isomeric C-7 aldehydes *i. e.* 1-heptanal, 2-methyl-hexanal, and 3-ethyl pentanal was observed. The alcohol formation was initially (up to ~ 20 minutes) slow but increased as the aldehyde concentrations increased. Among the alcohols, only 1-heptanol and 2-methyl hexanol were detected and no 2-ethyl pentanol was observed. Hexene hydrogenation to hexane was found to be a simultaneous but slow reaction accompanying aldehyde hydrogenation and after 90 minutes, hexane was obtained with ~ 13-14 % selectivity.

Figure 2.3 shows a C-T profile of a reaction for only 15 minutes duration to get an

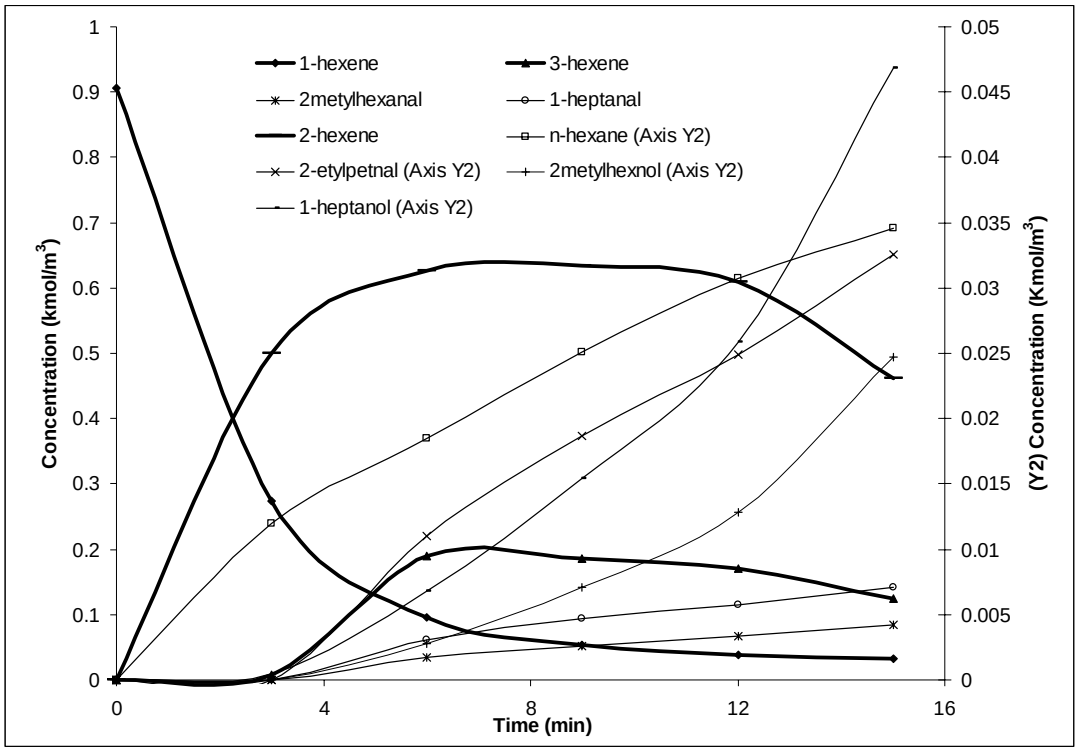
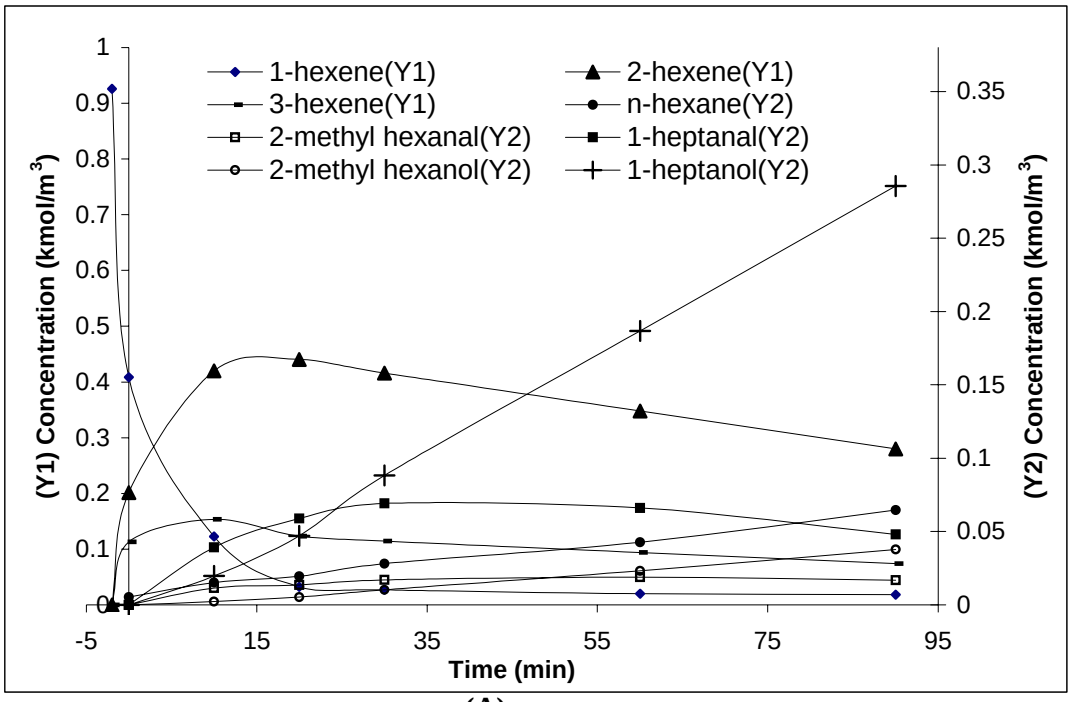


Figure 2.3. Concentration-time profile of initial phase: isomerization reaction
Reaction conditions: 1-hexene, 0.9 kmol/m^3; Co (II) acetate, 1.2 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH$_2$, 2.7 MPa; Agitation 20 Hz

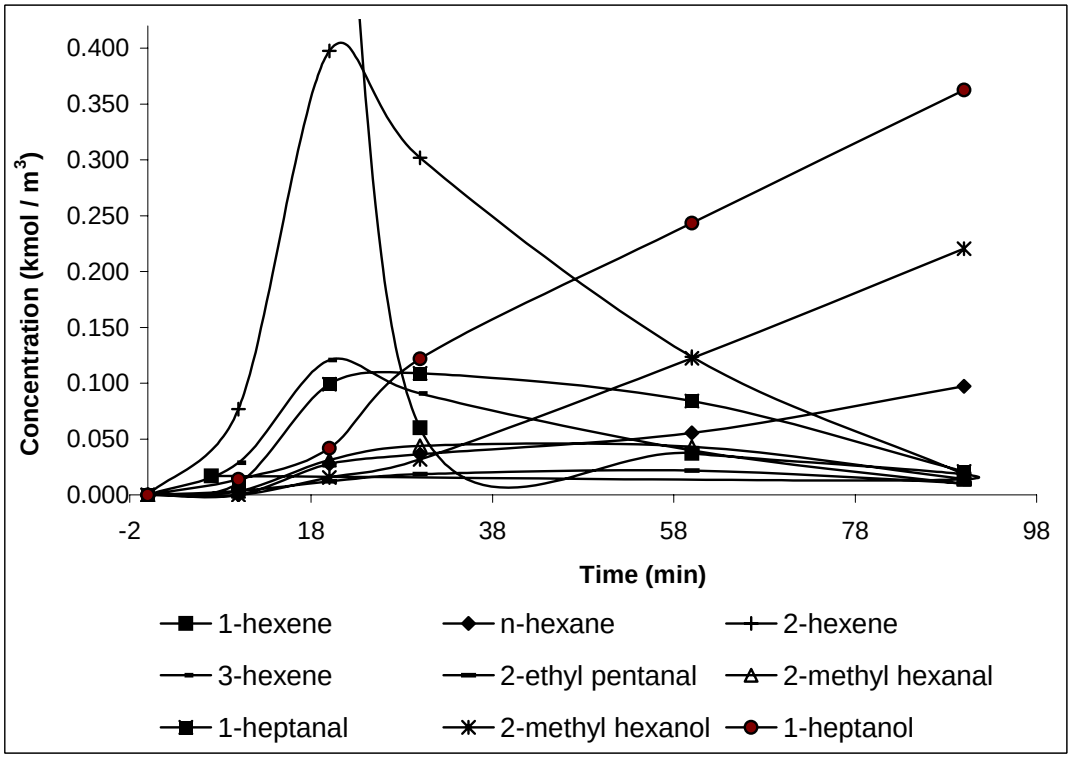
exact picture of the isomerization reaction. In this Figure, hexenes and aldehydes (except 2-ethyl pentanal) were plotted with primary Y-axis scale and alcohols and hexane were plotted with secondary (Y2) Y-axis scale. It was found that, within 4-5 minutes, 1-hexene concentration drops to less than 10 % of the initial charge and 2- and 3- hexenes were formed.

In the first 15 minutes, other than internal hexenes, 1-heptanal and 2-methyl hexanal were observed with a combined selectivity of 16 % for 1-hexene conversion of 97 %. The hydrogenation products were negligible (total below 7 %) in the first 15 minutes of the reaction. Detailed study of isomerization reaction is presented in Section 2.3.2.

Figure 2.4 shows C-T profiles at relatively higher catalyst loading. In Figure 2.4 (A), Co (II) acetate was charged 4 times in excess compared to the standard reaction shown in Figure 2.2. In these figures the 1-hexene concentration reported at time –2 was the actual 1-hexene charged whereas concentrations at time 0 minute are actual concentrations in the liquid phase obtained in the 0 minute sample (This is applicable to all the figures with x-axis starting with –2 or –5 minute). The difference in the hexenes concentrations of –2 or –5 minute sample and the 0 minute sample was due to the isomerization reaction and also due to isomerization of 1-hexene to the internal hexenes. The important features of this C-T profile are; (a) Lower conversion of hexenes compared to the standard reaction with ¼th catalyst concentration (b) Faster hydrogenation reaction indicated by much higher concentrations of 1-heptanol and 2-methyl hexanol compared to 1-heptanal, 2-methyl hexanal and 2-ethyl pentanal and (c) High regioselectivity to 1-heptanol (linear alcohol) with *linear : branched* ratio of 7.5. The reasons behind these results are discussed in a separated section on the effect on catalyst concentration effect (Section 2.3.3).



(A)



(B)

Figure 2.4. Concentration-time profile of 1-hexene hydroformylation at high catalyst concentrations: (A) Co (II) acetate, 12 x 10^{-3} kmol/m^3; (B) Co (II) acetate, 20 x 10^{-3} kmol/m^3;

<u>Reaction conditions:</u> 1-hexene, 0.8 kmol/m^3; Co (II) acetate, 20 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 2; Temperature, 453 K; PCO, 1.37 MPa; PH_2, 2.7 MPa; Agitation 20 Hz

The results obtained under the reaction conditions used in the previous literature by Tucci *et al.*[i] and Slaugh *et al.*[vi] are presented in Figure 2.4 (B). In this reaction, the catalyst concentration is 6.7 times and the TBP / Co ratio is half compared to the standard reaction (Figure 2.2). The important features of this C-T profile are; (a) Faster aldehyde hydrogenation reaction as indicated by much higher concentrations of 1-heptanol and 2-methyl hexanol and maxima in the profiles of 1-heptanal and 2-methyl hexanal (b) Prominent formation of hexane (Selectivity 12 %) indicating enhancement in the olefin hydrogenation (c) Lower regioselectivity to 1-heptanol with linear / branched ratio of 1.6 and (d) Hexenes conversion of 94 %. Higher conversion of hexenes and lower regioselectivity obtained in this reaction can be due to lower TBP/Co ratio of 2. Due to lower TBP/Co ratio formation of highly active unmodified hydrido cobalt carbonyl catalyst would have been enhanced leading to higher conversions and lower regioselectivity. Higher conversion led to higher aldehyde products formation, which, subsequently were hydrogenated to give 1-heptanol and 2-methyl hexanol as major end products.

The key observations made from this study of concentration-time profiles are summarized below.

(a) Isomerization was the most prominent reaction leading to more than 90 % conversion of 1-hexene to *cis*- and *trans*- 2-hexenes and 3-hexenes in initial few minutes. *Trans* isomers of the internal olefins were formed preferentially with *trans* to *cis* ratio of ~3.

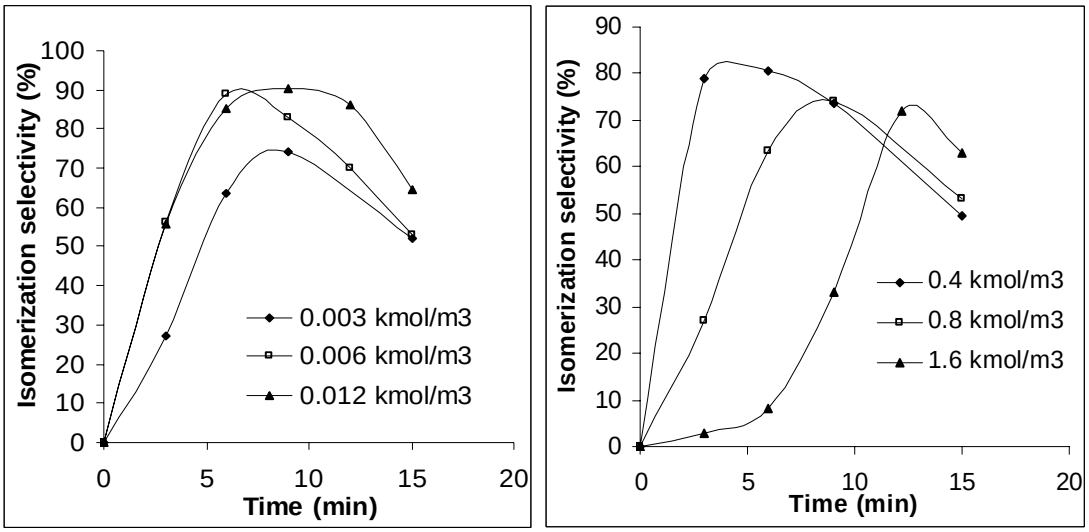
(b) Even though, 2-hexene and 3-hexene were present in much higher concentrations compared to 1-hexene, the hydroformylation products of 1-hexene such as 1-heptanal and 2-methyl hexanal and their respective alcohols were predominant. Thus, it can be concluded that due to thermodynamic stability the internal olefins were formed preferentially but small amount of 1-hexene was always present due to the isomerization equilibrium. Hydroformylation of terminal olefins is much faster compared to the internal ones and hence, 1-hexene even with less concentration compared to 2- and 3-hexenes, reacted faster to give hydroformylation and hydrogenation products. Due to isomerization equilibrium, the steady formation of 1-hexene from 2- and 3-hexenes maintained the required concentration of 1-hexene as it gave the hydroformylation products.

(c) Hydrogenation activity was found to increase with the catalyst concentration. Alcohol formation was dependent on 1-hexene hydroformylation rates *i.e.* aldehyde formation.

2.3.2. Effect of reaction parameters on isomerization reaction

The results on concentration-time profiles clearly showed that isomerization was a rapid catalytic reaction occurring under the hydroformylation conditions. To study the effect of different parameters on isomerization, a set of short time reactions were conducted with samples withdrawn at every three minutes up to 15 minutes. The results are presented in Figure 2.5 A-B and 2.6 A-B.

Figure 2.5 A showed that as the catalyst concentration was increased, the isomerization selectivity was increased initially. In all the cases it was observed that the isomerization selectivity attained maxima at ~ 4-5 minutes and then started dropping due to the conversion of hexenes to aldehyde products. Also, it was observed that at higher catalyst concentrations (0.012 kmol/m^3), the isomerization selectivity didn't show as prominent drop as the reactions with 0.003 and 0.006 kmol/m^3 catalyst concentrations. Thus, it may be concluded from these results, that catalyst concentration has a positive effect on the isomerization of 1-hexene to 2- and 3- hexenes.



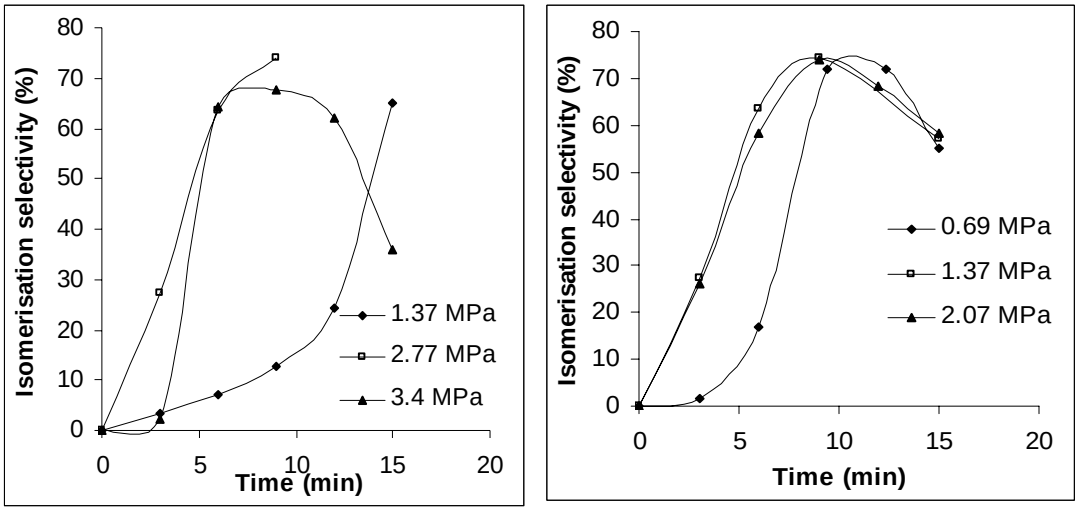
(A) (B)

Figure 2.5. Effect of (A) catalyst concentration and (B) Substrate concentration on the isomerization selectivity

Reaction conditions: Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH$_2$, 2.75 MPa; Agitation 20 Hz; (A) 1-hexene, 0.8 kmol/m^3; (B) Co (II) acetate, 3 x 10^{-3} kmol/m^3

Figure 2.5 B shows the effect of 1-hexene concentration on the isomerization selectivity. 1-hexene concentration showed a negative impact on the isomerization selectivity. The initial isomerization was found to be slower at 1-hexene concentration of 1.6 kmol/m^3. In each case the isomerization selectivity maxima was achieved in the same range (75 - 80 %) but at different times. Thus, 1-hexene concentration showed a negative effect on isomerization reaction.

Figures 2.6 A and B show the effects of H_2 and CO partial pressures respectively on isomerization selectivity. In both the cases isomerization was found to increase with increase in the partial pressures of CO and H_2 individually. For a reaction at highest H_2 partial pressure studied (3.4 MPa), the isomerization selectivity was found to drop drastically after attaining a maxima, which can be attributed to increase in the hydroformylation and hydrogenation reaction rates.



(A) **(B)**

Figure 2. 6. Effect of (A) H_2 partial pressure and (B) CO partial pressure on the isomerization selectivity

Reaction conditions: 1-hexene, 0.8 kmol/m^3; Co (II) acetate, 3 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; Agitation 20 Hz; (A) PCO, 1.37 MPa; (B) PH_2, 2.75 MPa.

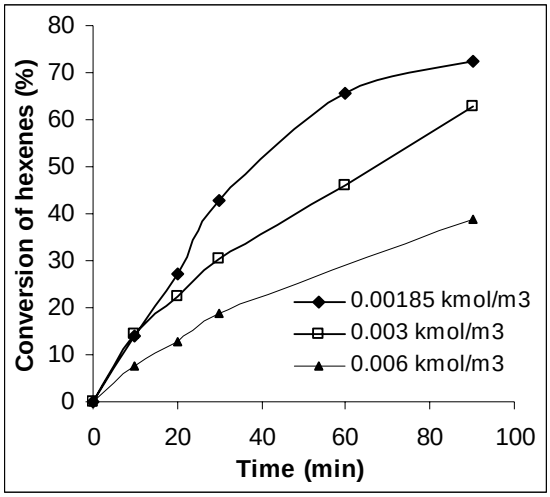
2.3.3. Effect of catalyst concentration on activity-selectivity for hydroformylation and hydrogenation

The effect of catalyst concentration on conversion and selectivities of different components under hydroformylation conditions is presented. Catalyst concentration was varied by keeping the TBP / Cobalt ratio constant (4). In order to study this effect,

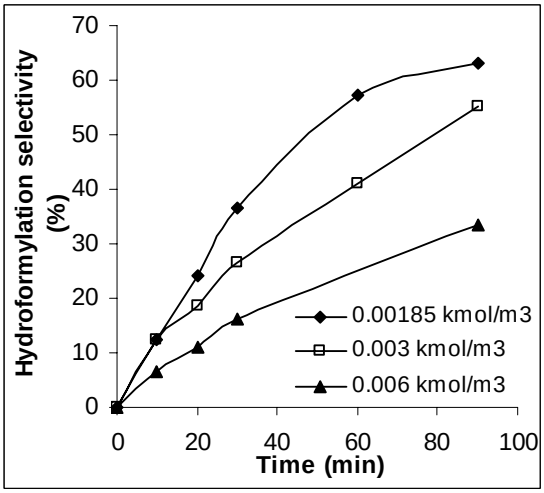
reactions were carried out with intermittent sampling at 10, 20, 30, 60 and 90 minutes. The results are presented in Figures 2.7 A – F.

Figures 2.7 (A) and (B) show the catalyst concentration effect on conversion and hydroformylation selectivity. Conversion was calculated neglecting the isomerization reaction, thus combining the amounts of all the hexenes converted to hydroformylation or hydrogenation products. Hydroformylation selectivity was calculated by addition of all the hydroformylation products like aldehydes and alcohols. Negative impact of catalyst concentration was observed on both conversion as well as hydroformylation selectivity. As catalyst concentration was increased, conversion of hexenes as well as selectivity to hydroformylation products showed almost similar drop.

Figures 2.7 (C) and (D) show the catalyst concentration effect on isomerization and alcohol selectivity. Isomerization selectivity was calculated by adding all the internal hexenes and alcohol selectivity was calculated by adding 1-heptanol and 2-methyl hexanol. The catalyst concentration has shown a positive impact on both these selectivities. Nearly double concentration of internal hexenes with 0.006 kmol/m^3 catalyst compared to 0.003 kmol/m^3 catalyst concentration showed that higher amount of catalyst engages itself in the isomerization cycle on increasing the catalyst concentration. Thus, the catalyst concentration was found to help the isomerization and reducing the conversion to hydroformylation. Figure 2.7 (D) show an a 1.5 times increase in the alcohol selectivity with 4 times rise in the catalyst concentration. Thus, both isomerization and hydrogenation reactions were found to have enhanced with the catalyst concentration whereas as shown in Figure 2. 7 (B), the overall hydroformylation selectivity was reduced.



(A)



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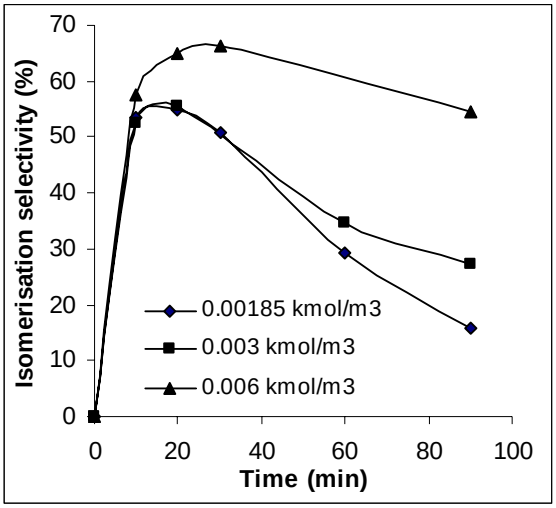
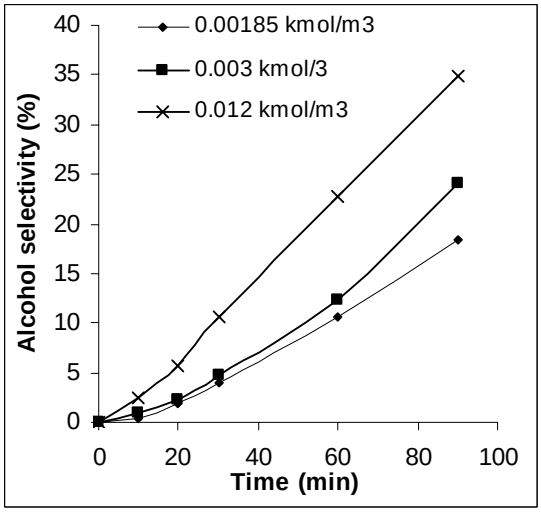
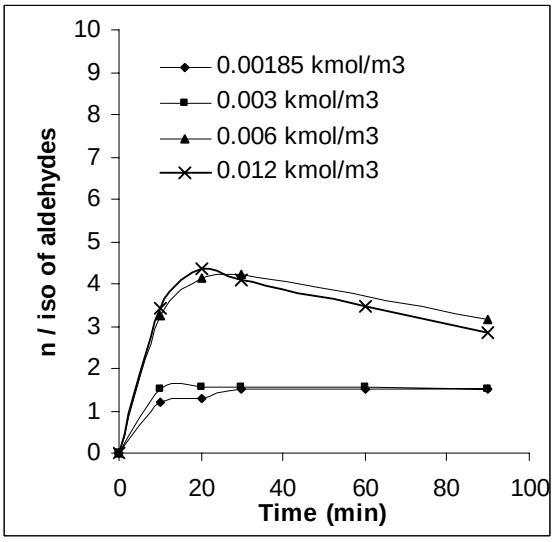


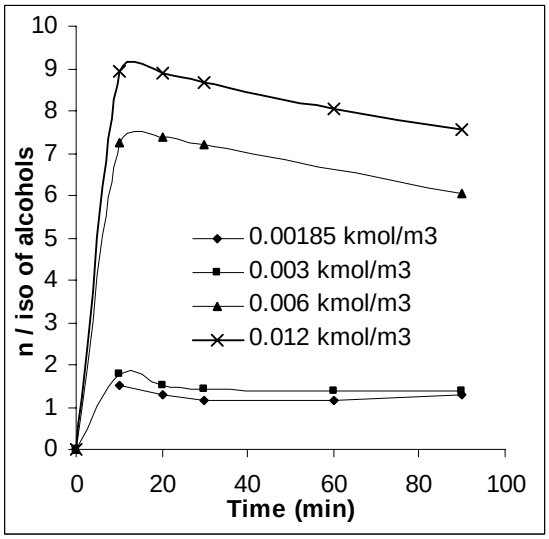
(C)



(D)



(E)



(F)

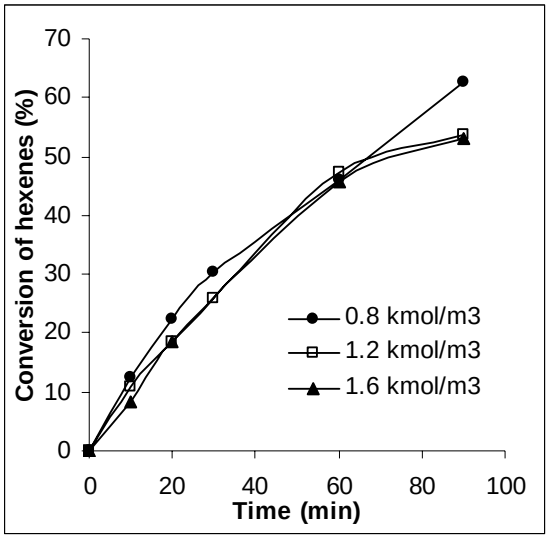
Figure 2.7. Effect of catalyst concentration on (A) Conversion (B) Hydroformylation selectivity (C) Isomerization selectivity (D) Alcohol selectivity (E) Linear / branched ratio of aldehydes (F) Linear / branched ratio of alcohols
Reaction conditions: 1-hexene, 0.8 kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH$_2$, 2.75 MPa Agitation 20 Hz

The most interesting feature of the present study was the effect of catalyst concentration on the regioselectivities of hydroformylation and aldehyde hydrogenation reactions, presented in Figure 2. 7 (E) and (F). The catalyst concentration was found to show a positive effect on the *linear / Branched* ratio, thus favoring the linear products such as 1-heptanal and 1-heptanol. The *linear / Branched* ratio of aldehydes was increased from ~ 1.5 at 0.003 kmol / m^3 to ~ 4 at 0.012 kmol/m^3 catalyst concentration. It was found that, at lower catalyst concentrations of 0.003 kmol / m^3, the aldehyde *linear / branched* ratio was constant over the entire reaction time whereas at higher catalyst

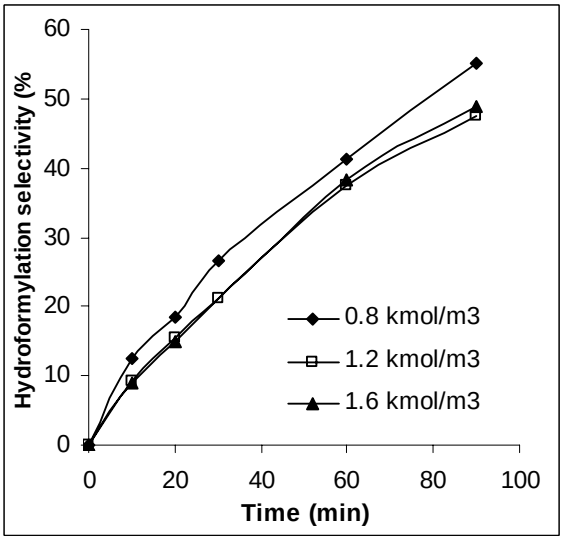
concentrations of 0.012 kmol/m^3, it decreased with time. An interesting observation was, the jump in *linear / branched* ratio of the alcohols which increased from ~ 1.5 at 0.003 kmol / m^3 catalyst concentration to 7 at 0.006 kmol / m^3 and further to 9 at 0.012 kmol/m^3 catalyst concentration. This multiple increase in the regioselectivity coupled with the drop in *linear / branched* ratio of aldehydes indicate preferential hydrogenation of linear aldehyde *i.e.* 1-heptanal over 2-methyl hexanal.

2.3.4. Effect of 1-hexene concentration on activity-selectivity for hydroformylation and hydrogenation

In this section, the effect of 1-hexene concentration on conversion and selectivities of all the three reactions occurring under hydroformylation conditions is presented. 1-hexene concentration was varied by keeping the charge-volume constant. In order to study this effect, reactions at different catalyst concentrations were carried out with intermittent sampling at 10, 20, 30, 60 and 90 minutes. The calculations of conversion and different selectivities were similar to those in Section 2.3.3. The results are presented in Figures 2.8 A – E.



2.8 (A)

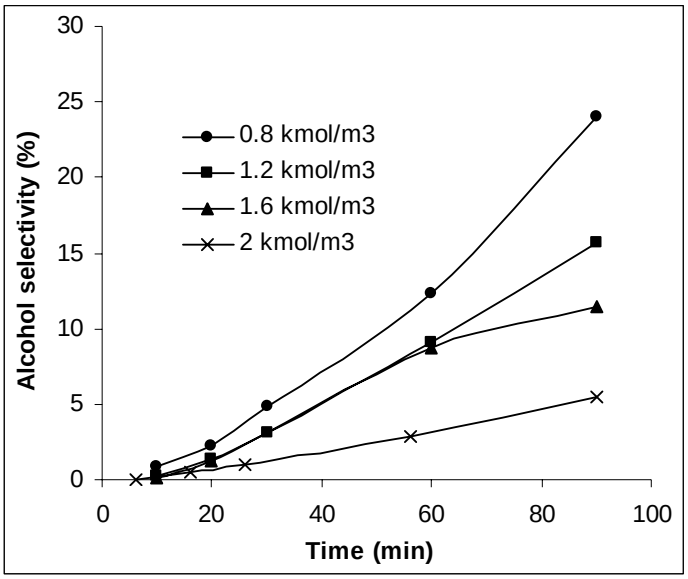


2.8 (B)

Figures 2.8 (A) and (B) shows 1-hexene concentration effect on conversion and hydroformylation selectivity respectively. Both conversion and hydroformylation selectivity were found to be nearly unaffected with 1-hexene concentration.

Figure 2.8 (C) shows the 1-hexene concentration effect on alcohol selectivity. The substrate concentration has shown a negative impact on alcohol selectivity. Figures 2.8

(D) and (E) shows the 1-hexene concentration effect on regioselectivities of aldehydes and alcohols. Unlike the catalyst concentration effect (Section 2.3.3) substrate concentration showed a negative impact on *linear / branched* ratio of aldehydes. Thus, the *linear / branched* ratio of ~ 1.5 at 0.8 kmol / m^3 1-hexene concentration was found to decrease to ~ 1.4 at 1-hexene concentration of 1.6 kmol / m^3. The *linear / branched* ratio of alcohols was nearly unaffected by 1-hexene concentration.



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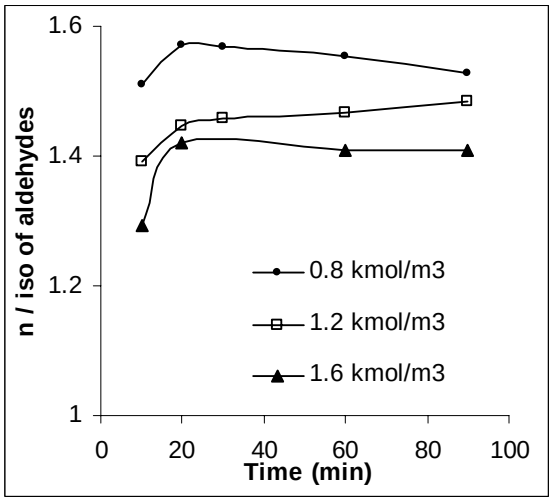
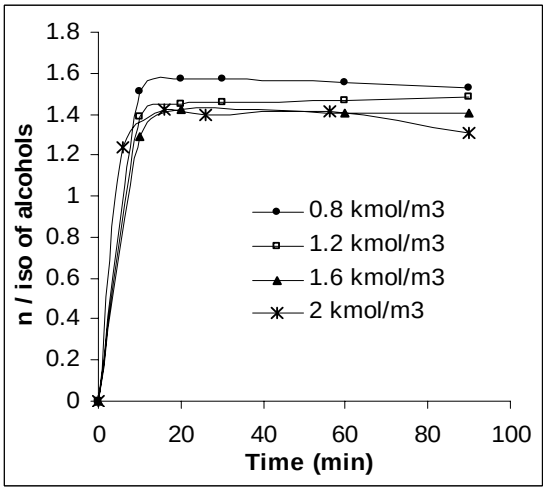


2.8 (D)



2.8 (E)

Figure 2.8. Effect of 1-hexene concentration on (A) Conversion (B) Hydroformylation selectivity (C) Alcohol selectivity (D) Linear / branched of aldehydes (E) Linear / branched of alcohols

<u>Reaction conditions:</u> Co (II) acetate, 3 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH_2, 2.75 MPa. Agitation 20 Hz

2.3.5. Kinetic studies

The initial rates of TBP-modified cobalt catalyzed hydroformylation of 1-hexene were observed under different conditions with systematic variation of the reaction parameters such as cobalt concentration, 1-hexene concentration, and partial pressures of CO / H_2. Initially, the mass balance of liquid and gas phase components was established along with the study of the syngas composition variation in the reactor. A reaction without cobalt-TBP catalyst system was carried out and it didn't yield any products, keeping 1-hexene intact. This confirmed that no non-catalytic reaction was happening under the conditions studied. Initial rates of reaction were calculated from the gas absorption profile and in some cases from the concentration-time profile to show the validity of calculating the initial rates from gas absorption profile. The kinetics of hydroformylation has been discussed and a semi-empirical rate equation explaining the trends of observed rate variation with different parameters has been established.

2.3.5.1. Range of conditions

In order to study the kinetics of the hydroformylation of 1-hexene with TBP-modified cobalt catalyst in toluene, experiments were carried out in the range of conditions given in the Table 2.2.

Table 2. 2. Range of operating conditions for kinetic study

Concentration of Co (II) acetate (catalyst) (kmol/m^3)	$1.8 \times 10^{-3} – 6 \times 10^{-3}$
Concentration of 1-hexene (kmol/m^3)	0.4 - 1.6
Partial pressure of hydrogen, MPa	1.38 - 4.12
Partial pressure of carbon monoxide, MPa	0.69 – 2.76
Temperature, K	453
Solvent	Toluene
Liquid phase volume, m^3	2.5×10^{-5}

2.3.5.2. Solubility data

The hydroformylation of 1-hexene involves two gaseous reactants and one liquid reactant. For interpretation of the kinetic data, knowledge of the concentration of the

gaseous reactants in the liquid phase is essential. The experimental solubility values of CO and H_2 in toluene, at temperatures 333 K, 343 K and 353 K were taken from the earlier work[vii] and extrapolated to 453 K for H_2 as well as CO. Here the solubilities were defined as Henry's constant, which is defined by Equation 2.1. Figure 2.9 represents the graphs of experimental values of Henries constant (H) in the range of 333 K to 353 K and the extrapolated values at 433 to 453 K. These experimental and extrapolated values of the Henrys constant for CO and H_2 are given in Table 2.3.

$$H = P/A \qquad (2.1)$$

Where,

H, represents, Henry's constant (MPa m^3/kmol)

P, represents, Pressure (MPa)

and A, represents, saturation solubility (kmol/m^3)

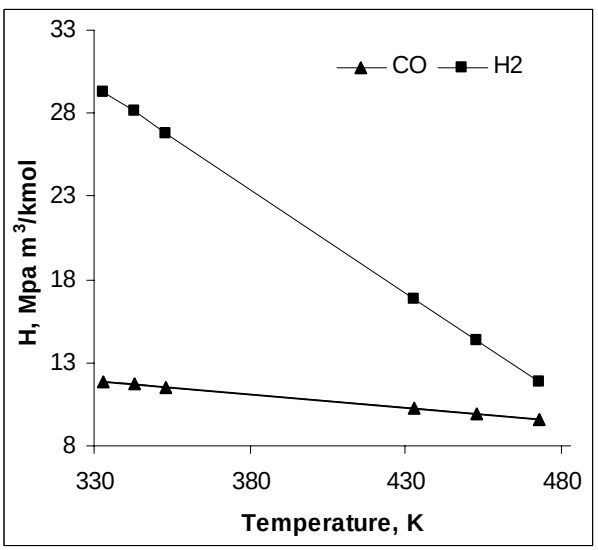


Figure 2. 9. Abstraction of Henrys constant values at higher temperatures from the experimental values at lower temperatures
Reaction conditions: Toluene, 25 x 10^{-6} m^3.

Table 2.3. Henry's constant for CO and H_2 in toluene at different temperatures

Temp	CO	H_2
333	11.9	29.3
343	11.7	28.1
353	11.53	26.8
433	10.262	16.817
453	9.902	14.317
473	9.542	11.817

2.3.5.3. Verification of kinetic regime

To study the kinetics of any homogeneous catalytic gas-liquid reaction it is very important to confirm that the rate data are obtained in a kinetic regime and there is no gas-liquid mass transfer limitation. The effect of agitation on the rate of reactions was

studied at 3:1 of H_2 to CO ratio. The results are presented in Figure 2.10. The rate was calculated from the slope of CO or H_2 absorption vs. time plots. These were essentially initial rates of reaction, calculated under low conversion (<10%) conditions. The results clearly showed that the rate of reaction was constant at 16, 20 and 25 Hz agitation frequencies. Therefore, to ensure the kinetic regime all the reactions were carried out at 20 Hz agitation frequencies.

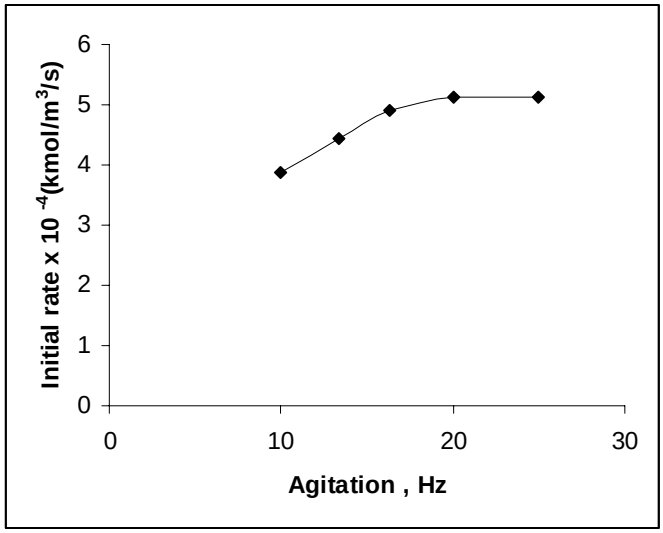


Figure 2. 10. Effect of agitation on the rate of hydroformylation
Reaction conditions: 1-hexene, 0.8 kmol/m^3; Co (II) acetate, 3 x10^{-3} kmol/m3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH$_2$, 4.13 MPa.

In order to further confirm the absence of gas-liquid mass transfer limitations, a quantitative criterion was used in which the ratio of the observed rate to the maximum rate of gas-liquid mass transfer was evaluated. The criteria is[viii],

$$\alpha = \frac{R_a}{k_L a_B A} < 0.1 \qquad (2.2)$$

Where, R_a is the observed rate of hydroformylation, $k_L a_B$ the gas-liquid mass transfer coefficient and A is the saturation solubility of reacting gases *i.e.* CO and H_2 at the reaction temperature. $k_L a_B$ was calculated according to the Equation (2.2) derived by Chaudhari *et al.* ,

$$k_L a_B = 1.48 \times 10^{-3} (N)^{2.18} \times (V_g / V_L)^{1.88} \times (d_I / d_T)^{2.1} \times (h_1 / h_2)^{1.16} \qquad (2.3)$$

The terms involved in Equation (2.2) are described in Table 2.4 along with the respective values obtained from the reactor and charge used in the present case.

The saturation solubility's of CO and H_2 at 453 K in toluene were, calculated from the Henry's constant (Table 2.3) with the Equation 2.1.

Table 2.4. Terms and values involved in $k_L a_B$ calculations (Equation 2.2)

N	Agitation speed (Hz)	20
V_g	Gas volume (m^3)	52×10^{-6}
V_L	Liquid volume (m^3)	25.4×10^{-6}
d_I	Impeller diameter (m)	2×10^{-2}
d_T	Tank diameter (m)	3.3×10^{-2}
h_1	Height of the impeller from the bottom (m)	0.9×10^{-2}
h_2	Liquid height (m)	3.2×10^{-2}

Solving Equation 2.2, the value of $k_L a_B$ obtained was 0.303873 s^{-1}.

The saturation solubilitie's obtained for CO (1.37 MPa) and H_2 (2.75 MPa) at 453 K were 0.1393 kmol/m^3 and 0.1926 kmol/m^3 respectively. With these values of solubility and $k_L a_B$ the α values for CO as well as H_2 were calculated and are presented in Table 2.6.

2.3.5.4. Mass balance and gas balance

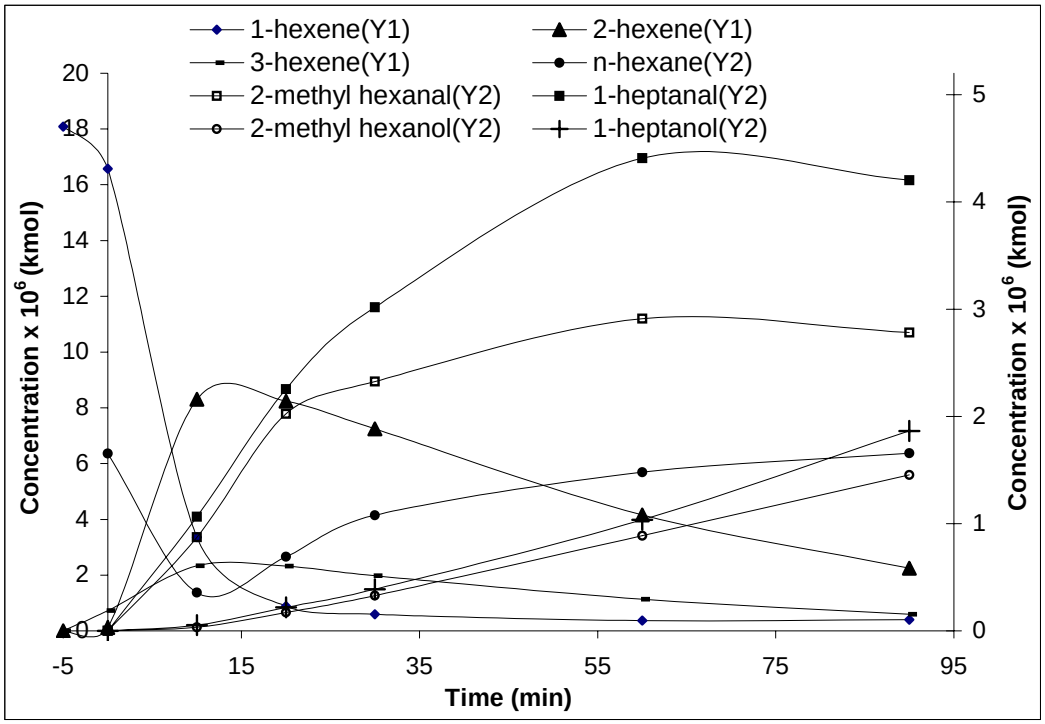
In order to establish that the gas composition of the syngas mixture remains nearly constant in the initial phase of the reaction (< 20 % conversion) and to show mass balance of the reactants and products, intermittent gas sampling was carried out along with liquid sampling. CO analysis was carried out with Orset Appratus as explained in Section 2.2. Data of two such reactions are presented in Tables 2.5 and 2.6 and Figures 2.11 and 2.12. In the reactions, constant pressure was maintained in the reactor by filling the syngas ($CO:H_2$ = 1:2) intermittently. The reactor pressure was adjusted to account for the vapour pressure of the solvent.

In Tables 2.5 and 2.6, requirement of CO and H_2 was calculated from analysis of the liquid sample shown in Figures 2.11 (A) and 2.12 (A) respectively. From the calculated values and actual observed gas absorption, the % of CO and H_2 in the reactor was calculated. Since the reactions were carried out at constant pressure, for these calculations, it was assumed that the gas filled in the reactor was same as the actual gas absorbed. The calculated amount of CO in the reactor was found to match with the CO analysis of the respective sample with an error in the range of 5 %. The calculated amount of required syngas absorption was compared with the actual absorption in Figures 2.12 (B) and 2.12 (B).

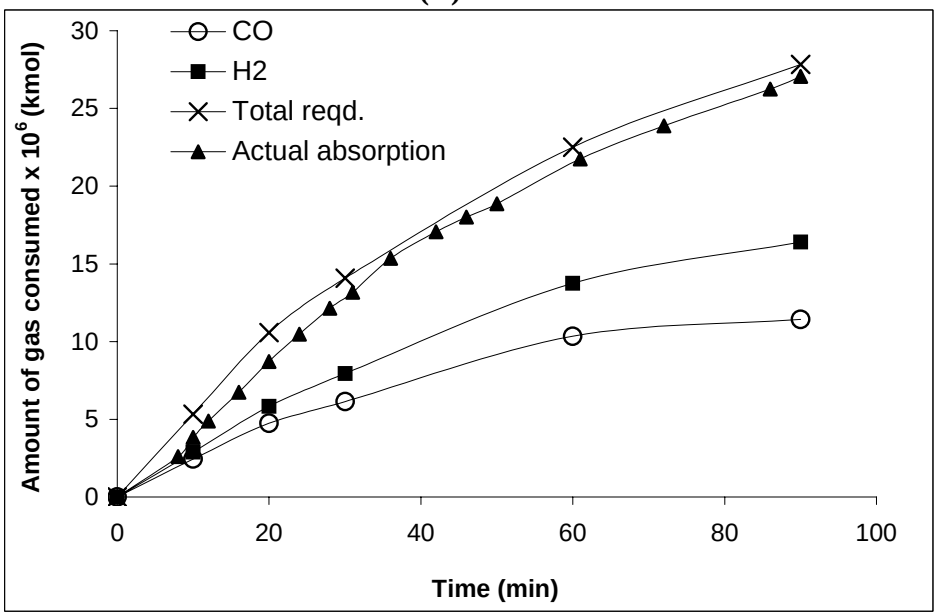
Table 2.5. Gas-liquid balance in the overall reaction

TIME, MIN	10	20	30	60	90
Hexane, x 10^6 (kmol)	0.36	0.69	1.08	1.48	1.66
2-ethyl pentanal, x 10^6 (kmol)	0.42	0.07	0.08	1.10	1.12
2-methyl hexanal, x 10^6 (kmol)	0.87	2.03	2.32	2.91	2.78
Heptanal, x 10^6 (kmol)	1.07	2.26	3.02	4.41	4.20
2-methyl heptanol, x 10^6 (kmol)	0.04	0.17	0.33	0.89	1.46
1-heptanol, x 10^6 (kmol)	0.05	0.22	0.39	1.03	1.87
Total oxo products, x 10^6 (kmol)	2.80	5.44	7.22	11.83	13.08
Amt. of CO required, x 10^6 (kmol)	2.44	4.74	6.14	10.35	11.43
Amt. of H_2 required, x 10^6 (kmol)	2.89	5.82	7.94	13.75	16.40
Amt. of gas required,x 10^6 (kmol)	5.33	10.57	14.08	24.10	27.83
Amt. of gas required,psi	53	105	140	239	276
Co: H_2 consumed,ratio	5/6	4/5	7/9	3/4	2/3
Actual Absorption,psi	42	95	130	228	267
Actual Absorption, x 10^6 (kmol)	0	0	0	0	0
Diffr, observed-reqd, psi	-11	-10	-10	-11	-9
Amt. of CO filled, psi	14	32	43	76	89
Amt. of H_2 filled, psi	28	63	87	152	178
Amt. of CO filled, x 10^6 (kmol)	1.41	3.19	4.36	7.65	8.96
Amt. of H_2 filled, x 10^6 (kmol)	2.82	6.38	8.73	15.30	17.92
Amt. of CO in the reactor, x 10^6 (kmol)	19.93	19.41	19.19	18.27	18.50
Amt. of H_2 in the reactor, x 10^6 (kmol)	41.87	42.49	42.72	43.49	43.45
% of CO in the reactor	**32.26**	**31.36**	**30.99**	**29.58**	**29.86**
% of H_2 in the reactor	**67.74**	**68.64**	**69.01**	**70.42**	**70.14**

<u>Reaction conditions:</u> 1-hexene, 0.8 kmol/m^3; Co(II)acetate, 1.8 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; Temperature, 453 K; PCO, 1.37 MPa; PH2, 2.75 MPa; Agitation, 20 Hz.



(A)



(B)

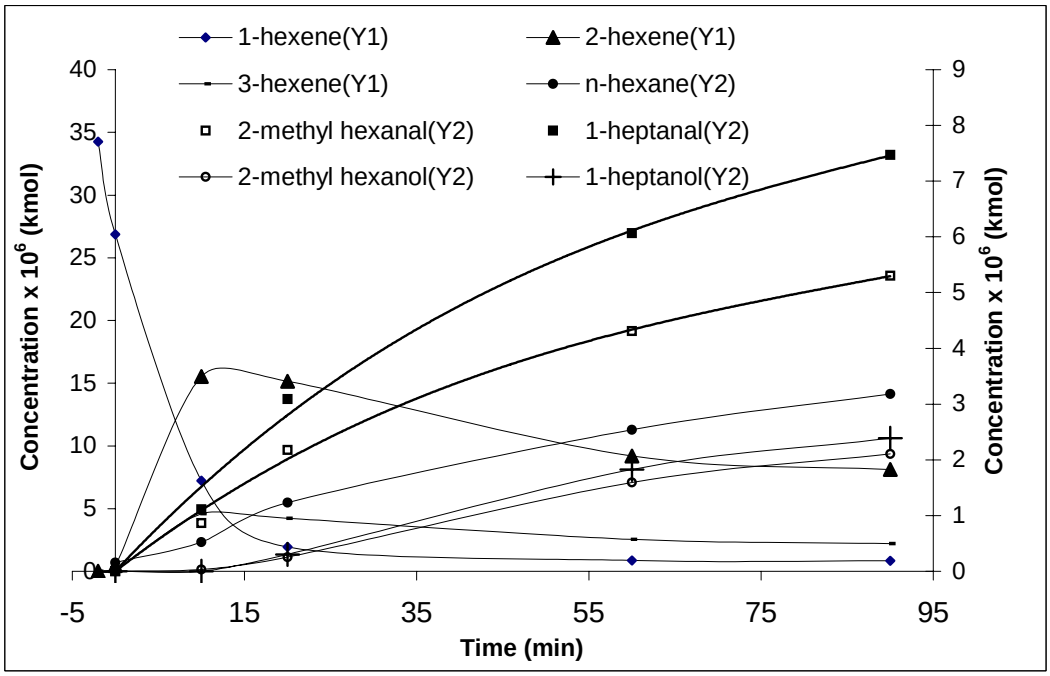
Figure 2.11. Mass balance and gas balance in 1-hexene hydroformylation

Reaction conditions: Same as Table 2.5

Table 2.6. Gas-liquid balance in the overall reaction

TIME, MIN	0	10	20	60	90
Hexane, x 10^6 (kmol)	0.000	0.522	1.232	2.538	3.182
2-ethyl pentanal, x 10^6 (kmol)	0.000	0.167	0.533	1.300	1.942
2-methyl hexanal, x 10^6 (kmol)	0.000	0.863	2.178	4.310	5.302
Heptanal, x 10^6 (kmol)	0.000	1.115	3.092	6.069	7.470
2-methyl heptanol, x 10^6 (kmol)	0.000	0.035	0.251	1.592	2.107
1-heptanol, x 10^6 (kmol)	0.000	0.000	0.304	1.826	2.386
Total oxo products, x 10^6 (kmol)	0.000	2.701	7.590	17.635	22.389
Amt. of CO required, x 10^6 (kmol)	0.000	2.179	6.358	15.097	19.208
Amt. of H_2 required, x 10^6 (kmol)	0.000	2.736	8.145	21.052	26.882
Amt. of gas required,x 10^6 (kmol)	0.000	4.915	14.503	36.149	46.090
Amt. of gas required,psi	0.000	48.818	144.059	359.070	457.811
Co: H_2 consumed,ratio	0.000	4/5	7/9	5/7	5/7
Actual Absorption,psi	0.000	**57**	**158**	**365**	**467**
Actual Absorption, x 10^6 (kmol)	0.000	5.738	15.906	36.746	47.015
Diffr, observed-reqd, psi	0.000	8.182	13.941	5.930	9.189
Amt. of CO filled, psi	0.000	19.000	52.667	121.667	155.667
Amt. of H_2 filled, psi	0.000	38.000	105.333	243.333	311.333
Amt. of CO filled, x 10^6 (kmol)	0.000	1.913	5.302	12.249	15.672
Amt. of H_2 filled, x 10^6 (kmol)	0.000	3.826	10.604	24.497	31.343
Amt. of CO in the reactor, x 10^6 (kmol)	20.135	19.868	19.079	17.287	16.599
Amt. of H_2 in the reactor, x 10^6 (kmol)	40.270	41.360	42.729	43.714	44.731
% of CO in the reactor	**33.333**	**32.450**	**30.868**	**28.339**	**27.065**
% of H_2 in the reactor	**66.667**	**67.550**	**69.132**	**71.661**	**72.935**

<u>Reaction conditions:</u> 1-hexene, 1.6 kmol/m^3; Co(II)acetate, 3 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; Temperature, 453 K; PCO, 1.37 MPa; PH2, 2.75 MPa; Agitation, 20 Hz.



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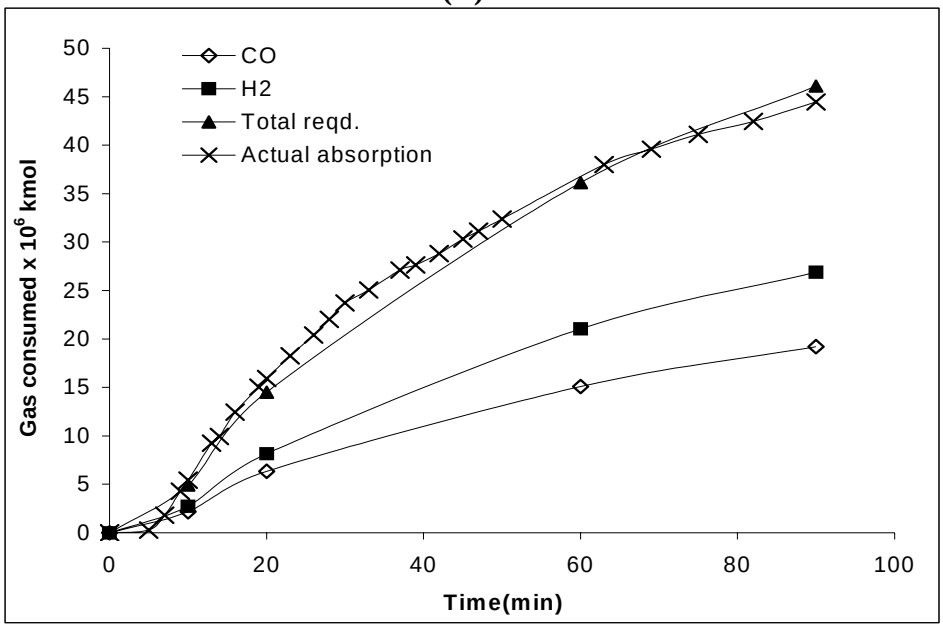


(B)

Figure 2.12. Mass balance and gas balance in 1-hexene hydroformylation

Reaction conditions: Same as Table 2.6

From the Tables 2.5 and 2.6, it is evident that the CO and H_2 % in the reactor show insignificant changes in the first 20 minutes of the reaction while in 90 minutes, the CO pressure show nearly 10-12 % decrease. The calculated and observed gas absorptions were found to match within 5-6 % experimental error.

2.3.5.5. Effect of parameters on the rate of hydroformylation

2.3.5.5.1. Initial rate data

The initial rates were calculated from the concentration-time profiles as well as the gas absorption data. It was found that for catalyst concentration and 1-hexene concentration effects, these two values match within an experimental error of 5 %. For CO and H_2 partial pressure effect studies, sampling was avoided to maintain the initial gas composition in the reactor. In these cases the rates were derived from the gas absorption. The initial rates were derived from the experimental data up to 10 % conversion of hexenes and are summarized in Table 2.7. The α_1 and α_2 values for CO and H_2 respectively were calculated using Equation 2.2 and are also listed in this Table. The gas absorption graphs and corresponding concentration-time profiles (wherever available) are presented in Figures 2.13 to 2.20.

Table 2.7. Initial rates of parametric effect reactions for kinetic study of 1-hexene hydroformylation at 453 K

Run No.	Substrate concentration	Catalyst concentration x 10^{-3}	PCO	PH_2	Initial Rate x 10^4 (Gases)	Initial Rate x 10^4 (Liquid)	α_1 x 10^2	α_2 x 10^2
	kmol/m^3	kmol/m^3	MPa	MPa	kmol/m^3/s	kmol/m^3/s		
1	0.4	3.0	1.37	2.75	0.2	-	0.028	0.020
2	0.8	3.0	1.37	2.75	1.15	1.29	0.274	0.195
3	1.2	3.0	1.37	2.75	2.43	2.43	0.580	0.413
4	1.6	3.0	1.37	2.75	2.60	2.30	0.620	0.441
5	0.8	1.8	1.37	2.75	1.92	1.95	0.457	0.325
6	0.8	3	1.37	2.75	1.15	1.32	0.274	0.195
7	0.8	6	1.37	2.75	0.91	0.58	0.083	0.059
8	0.8	12	1.37	2.75	0.69	0.78	0.111	0.079
10	0.8	3.0	0.69	2.75	0.67	-	0.174	0.062
11	0.8	3.0	1.37	2.75	1.15	1.29	0.274	0.195
12	0.8	3.0	2.75	2.75	2.52	-	0.299	0.427
13	0.8	3.0	1.37	1.37	0.52	-	0.124	0.177
14	0.8	3.0	1.37	2.75	1.15	1.29	0.274	0.195
15	0.8	3.0	1.37	4.14	2.72	-	0.649	0.368

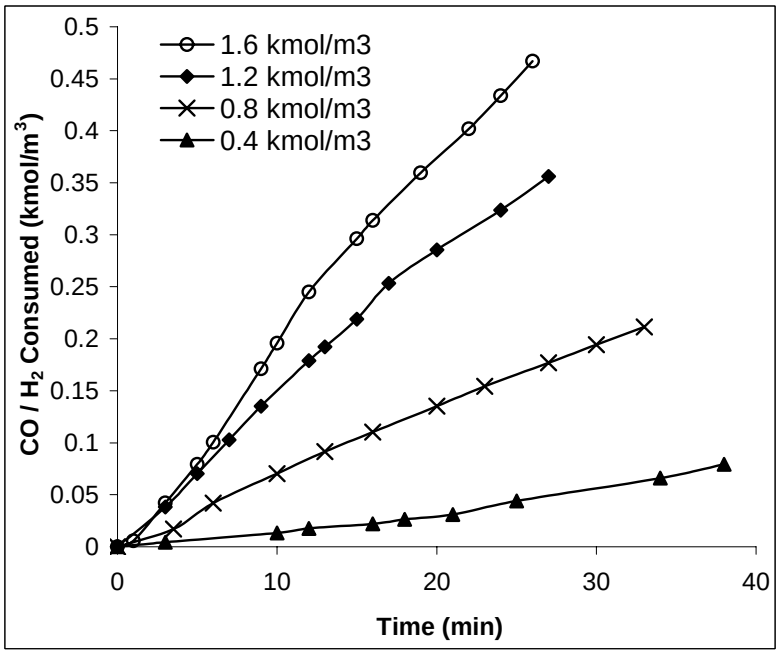


Figure 2.13. Effect of 1-hexene concentration: gas absorption profiles

Reaction conditions: *Co (II) acetate, 3 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH_2, 2.7 MPa; Agitation 20 Hz*

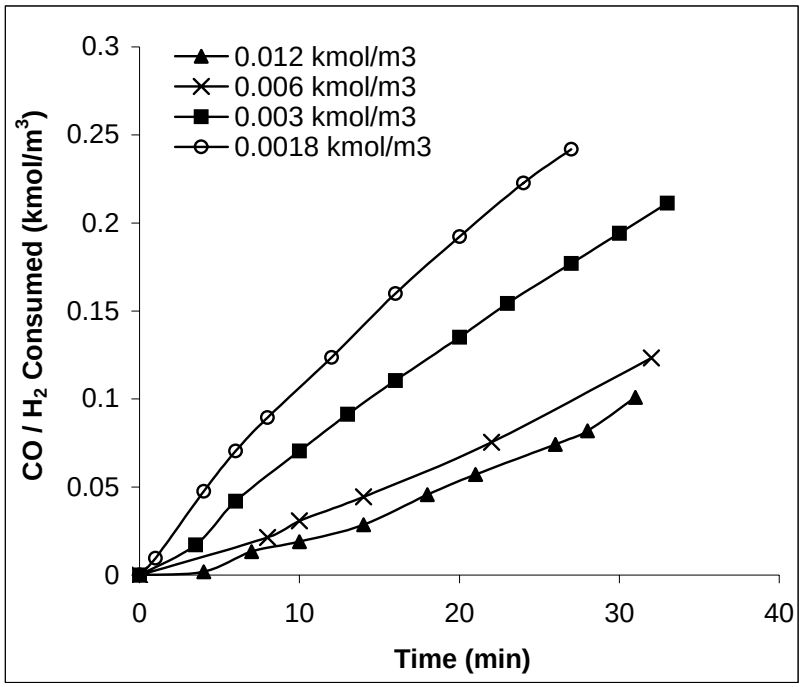


Figure 2.14. Effect of catalyst concentration: gas consumption profiles

Reaction conditions: 1-hexene, 0.8 kmol/m^3; *Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH_2, 2.7 MPa; Agitation 20 Hz*

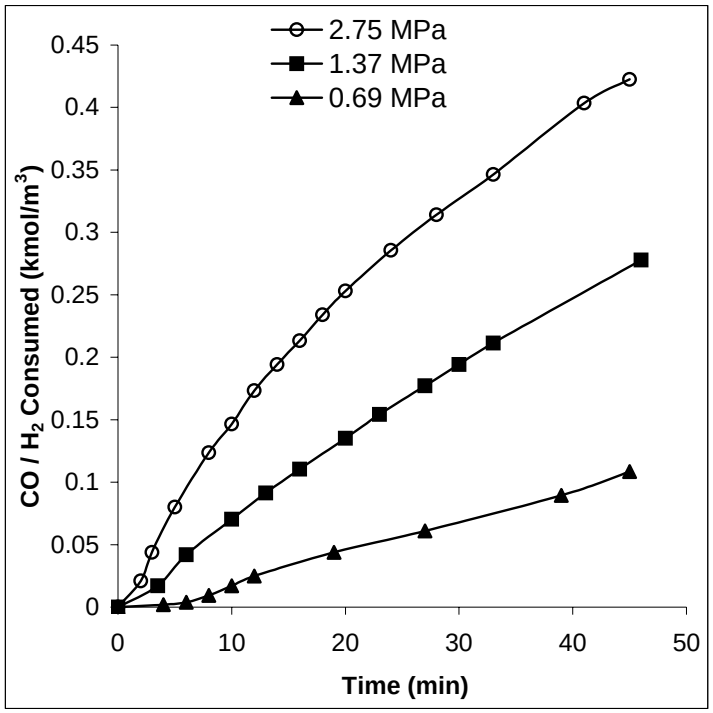


Figure 2.15. Effect of CO partial pressure: gas absorption profiles

Reaction conditions: 1-hexene, 2 kmol/m^3; Co (II) acetate, 1.8 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PH_2, 2.75 MPa; Agitation 20 Hz

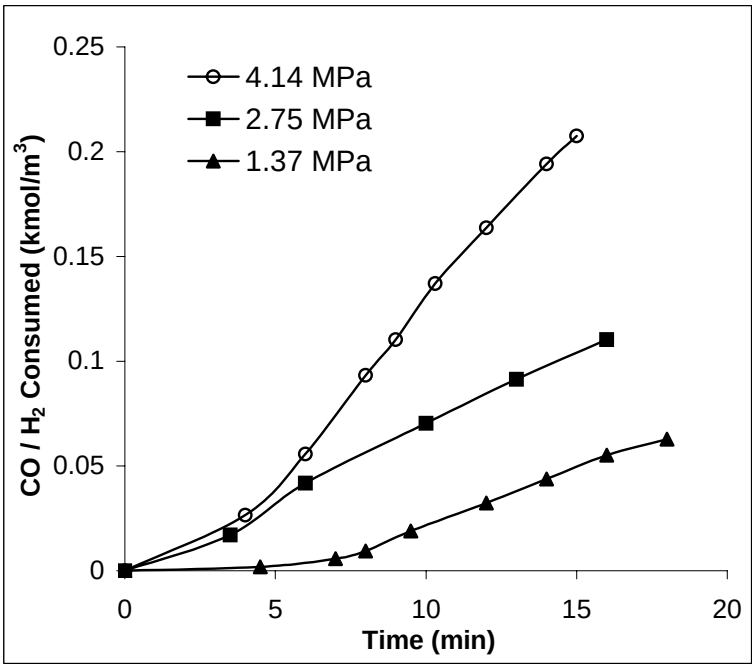
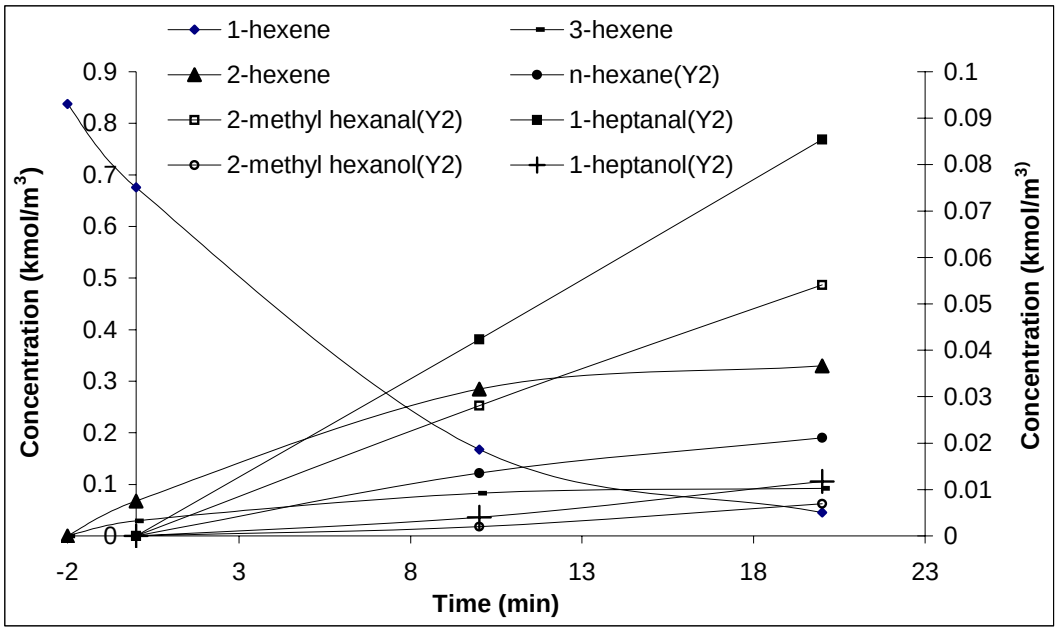
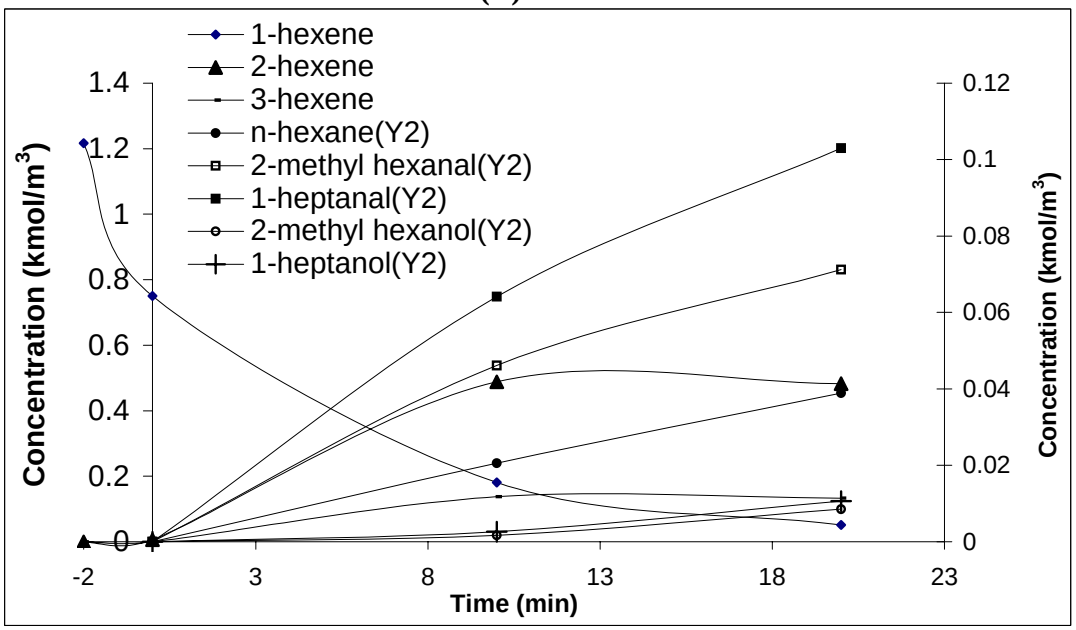


Figure 2.16. Effect of H_2 partial pressure: gas absorption profiles

Reaction conditions: 1-hexene, 2 kmol/m^3; Co (II) acetate, 1.8 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; Agitation 20 Hz



2.17 (A)



2.17 (B)

Figure 2.17. Concentration-time profile of 1-hexene hydroformylation: 1-hexene concentration effect (A) 1-hexene 0.8 kmol / m^3 (B) 1-hexene 1.2 kmol / m^3

<u>Reaction conditions:</u> Co (II) acetate, 0.3 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH_2, 2.7 MPa; Agitation 20 Hz

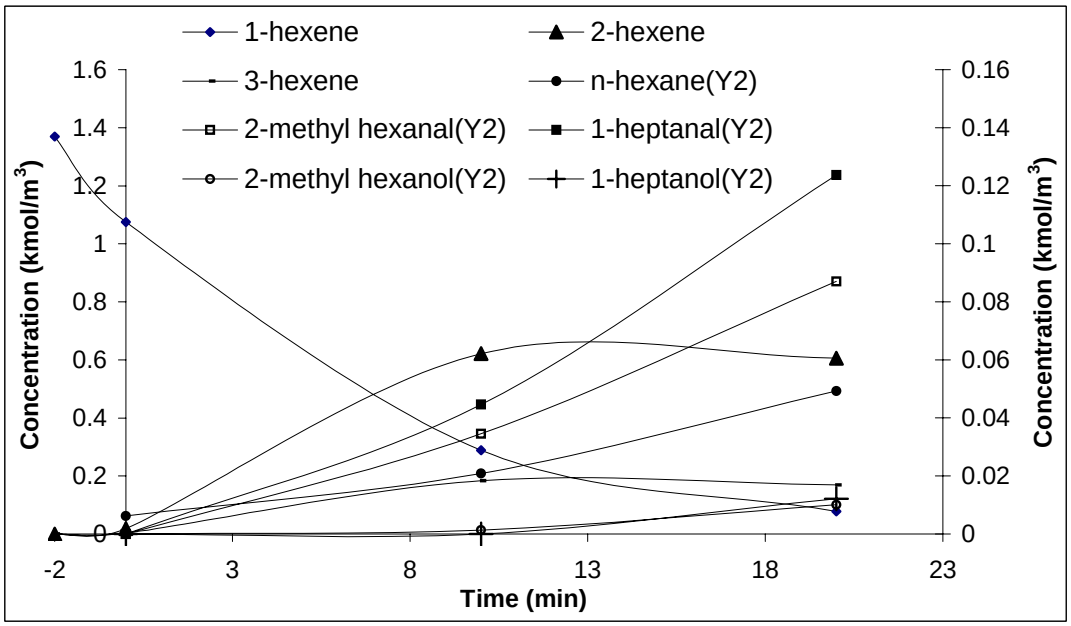


Figure 2.18. Concentration-time profile of 1-hexene hydroformylation: 1-hexene concentration effect

<u>Reaction conditions:</u> Co (II) acetate, 0.3 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH_2, 2.7 MPa; Agitation 20 Hz

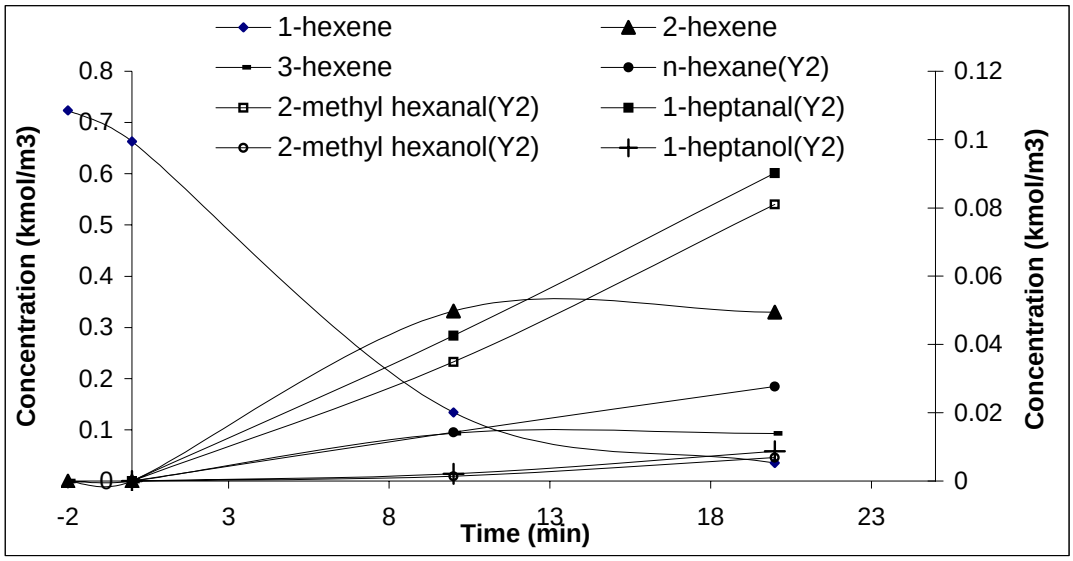
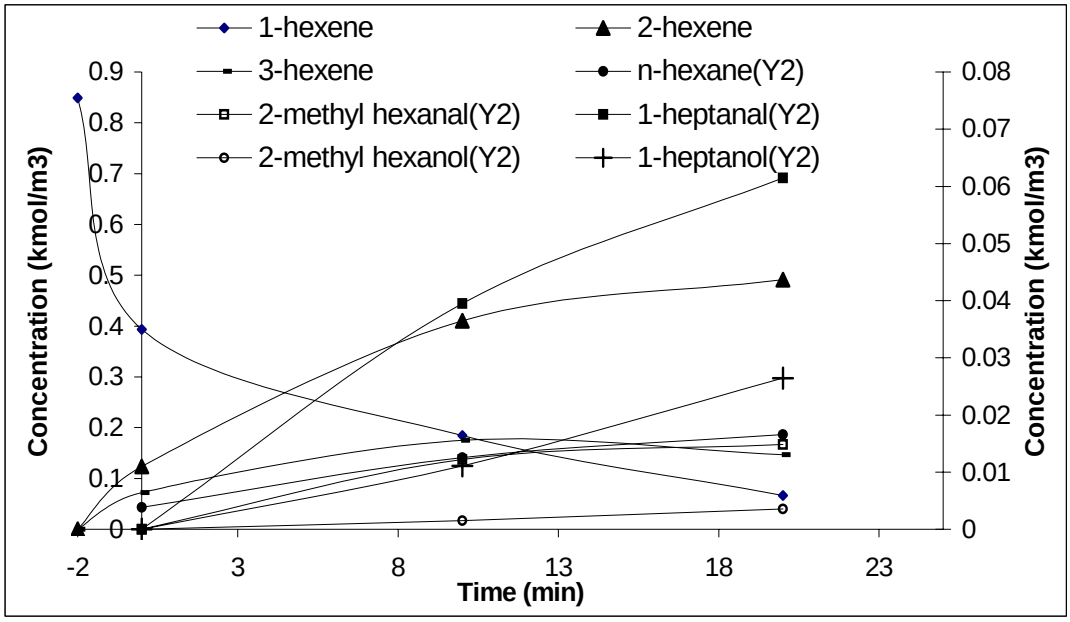
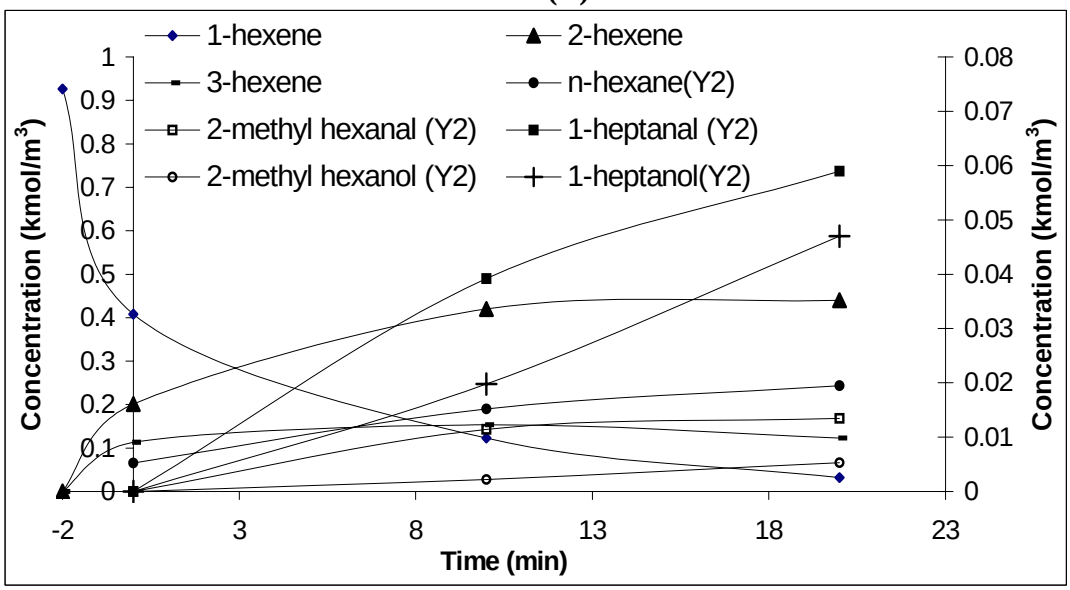


Figure 2.19. Concentration-time profile of 1-hexene hydroformylation : Co (II) acetate, 1.8 x 10^{-3} kmol/m^3

<u>Reaction conditions:</u> 1-hexene, 0.8 kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH_2, 2.7 MPa; Agitation 20 Hz



2.20 (A)



2.20 (B)

Figure 2.20. Concentration-time profile of 1-hexene hydroformylation: concentration effect (A) Co (II) acetate, 6 x 10^{-3} kmol/m^3 (B) Co (II) acetate, 12 x 10^{-3} kmol/m^3

<u>Reaction conditions:</u> 1-hexene, 0.8 kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH_2, 2.7 MPa; Agitation 20 Hz

2.3.5.5.2. Effect of catalyst concentration

The rate of hydroformylation of 1-hexene was observed to show a negative order

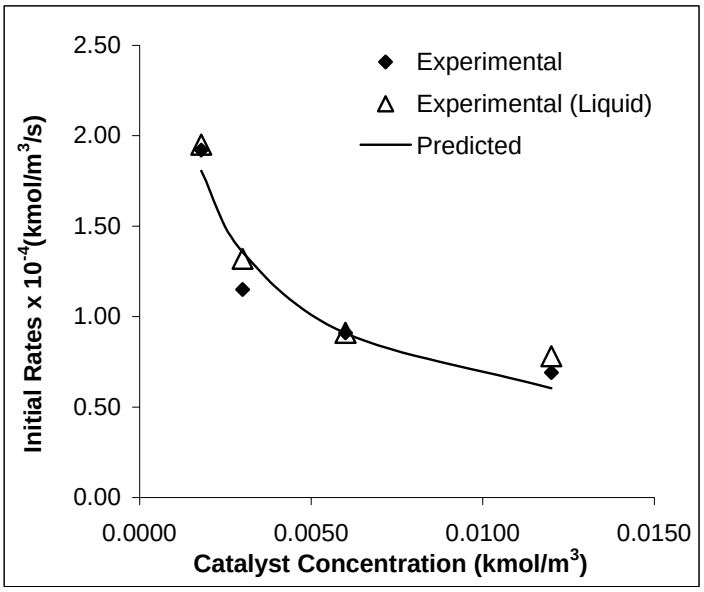


Figure 2.21. Effect of catalyst concentration
Reaction conditions: 1-hexene, 0.8 kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH_2, 4.13 MPa; Agitation 20 Hz.

dependency on the catalyst precursor, Co (II) acetate concentration. These results are shown in Figure 2.21. The negative order dependency clearly indicates the effect of isomerization between 1-hexene and 2- and 3-hexenes (Scheme 2.3.2). Figure 2.5 (A) illustrate that as the catalyst concentration was increased the 1-hexene isomerization to 2-hexene and further to 3-hexene became faster. Thus, it can be concluded that any addition of the catalyst precursor, was involved in the isomerization cycle as explained in Section 1.2.2.2 in Chapter 1. As these isomerization cycles have all the steps in equilibrium with each other, the catalyst involved in this cycle never come out of it and so is not available for the reaction. Since, thermodynamically the internal isomers are more stable compared to the terminal ones, the isomerization equilibrium always show higher concentration of 2-and 3-hexenes compared to 1-hexene. The activity of the internal olefins such as 2-hexene and 3-hexene for hydroformylation is much lower compared to the terminal olefin i.e. 1-hexene. Thus, due to high catalyst concentration, the stable internal olefins

predominate and the rate of hydroformylation decreases due to low concentration of 1-hexene.

2.3.5.5.3. Effect of 1-hexene concentration

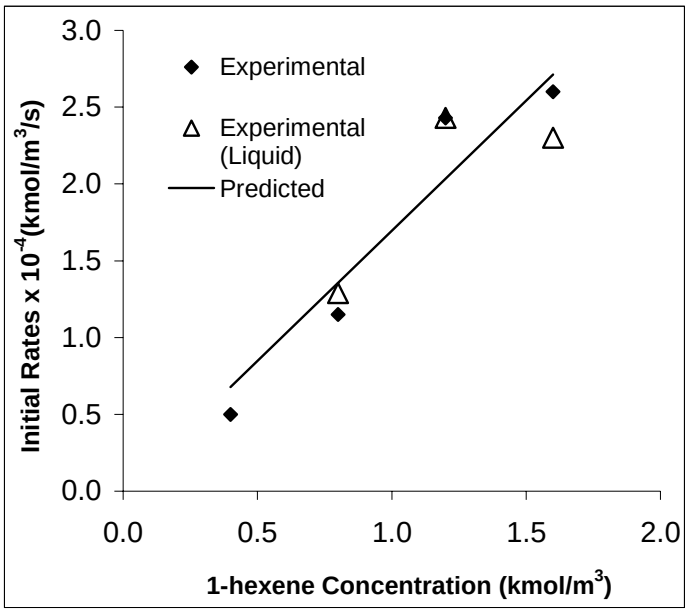


Figure 2. 22. Effect of 1-hexene concentration

Reaction conditions: Co(II)acetate, 3 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3, TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; PH_2, 4.13 MPa; Agitation 20 Hz.

The rate of hydroformylation was found to be fractional order with 1-hexene in the range of concentrations (0.81 to 1.61 kmol/m^3) studied. The results are shown in Figure 2.22. Unlike the previous reports[ix,x] wherein the kinetics was found to be first order tending to zero order with 1-dodecene, zeroth order with styrene[xi] and a negative order in case of allyl alcohol, here the rate showed a fractional order dependency on 1-hexene concentrations. The reason behind this fractional order dependency on 1-hexene concentration may again be the isomerization reaction. Higher concentrations of 1-hexene must be deactivating the catalyst by keeping it occupied in the catalytic isomerization cycle. Gholap *et al.*[va & b] with unmodified cobalt catalyst, $Co_2(CO)_8$, have shown almost first order dependency of rates on propylene concentration. With propylene, the isomerization reaction was not feasible whereas with 1-hexene, isomerization was found to be the most prominent reaction.

2.3.5.5.4. Effect of CO partial pressure

The rate of hydroformylation showed first order dependency on CO partial pressure in the range of pressures (0.69 to 2.76 MPa) studied. The results are shown in Figure 2.23. Almost all the previous hydroformylation kinetic-studies have shown a maximum in the rate dependency on the CO partial pressure. The rate of hydroformylation initially increases as the CO partial pressures and then starts decreasing after attaining a maximum. As per the mechanism of hydroformylation proposed by Evans *et al.*[xii], the inhibition of the rate with increase in partial pressure of CO in Rh-catalysed hydroformylation is due to the side reactions leading to the formation of inactive dicarbonyl [$(RCO)Rh(CO)_2(PPh_3)$] and tricarbonyl [$(RCO)Rh(CO)_3(PPh_3)$], rhodium species. With increase in CO partial pressure, the concentration of these species are excepted to increase thereby reducing the active species concentration and hence the rate of reaction. The observation of a negative order dependence with CO partial pressure is also reported for other olefinic substrates[ix,x,xiii]. The rate of $HCo(CO)_4$ catalyzed hydroformylation has also shown such maximum in the dependence on CO partial pressures[xiv]. In case of $HCO(CO)_4$ catalyst this effect was attributed to the equilibrium between the unsaturated ($HCO(CO)_3$) and saturated ($HCo(CO)_4$) hydridocarbonyl species.

Piacenti *et al.*[xv] have studied the effect of CO partial pressure on regioselectivity in the TBP-modified $Co_2(CO)_8$ catalyst system whereas Ruipilius *et al.*[xvi] have studied the effect of CO partial pressure on the chemoselectivity of hydroformylation of 1-pentene and 1-hexene . But we couldn't find any study involving the effect of CO partial pressure

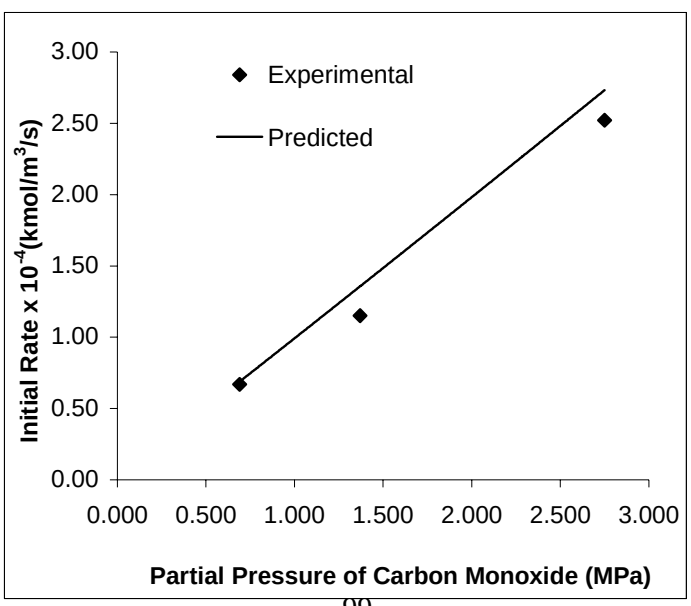


Figure 2.23. Effect of CO partial pressure

Reaction conditions: 1, hexene, 0.8 kmol/m^3; Co(II) acetate, 3 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; TBP : Co, 4; Temperature, 453 K; PH_2, 4.13 MPa; Agitation 20 Hz.

on the rate of hydroformylation reaction.

In the present study, we have got for the first time a first order dependence on CO partial pressure. Peculiar equilibriums between modified-unmodified cobalt catalysts as shown in the Scheme 2. 2 are responsible for this first order dependence. The $HCo(CO)_3(Pbu_3)$ catalyst remain in equilibrium with the unmodified tetracarbonyl species, $HCo(CO)_4$ and also phosphine dominated dicarbonyl and monocarbonyl species. The unmodified $HCo(CO)_4$ was found to be the most active species among all of them and the order of activity decreases towards the more phosphinated species. This is because phosphine ligands are poor Π-acceptor and better ∝-donor ligands compared to CO. So, in partially phosphinated species, the electron-charge on the cobalt metal is higher than the unmodified cobalt species such as $HCo(CO)_4$. Because of this higher

$$HCo(CO)(P)_3 \underset{+P}{\overset{+CO}{\rightleftharpoons}} HCo(CO)_2(P)_2 \underset{+P}{\overset{+CO}{\rightleftharpoons}} HCo(CO)_3(P) \underset{+P}{\overset{+CO}{\rightleftharpoons}} HCo(CO)_4 \underset{+P}{\overset{+CO}{\rightleftharpoons}} HCo(CO)_3$$

Scheme 2.2. Equilibrium between phosphine modified catalysts

electron charge, the remaining CO groups of such species shows stronger back bonding capacity, becomes stable and so shows difficulty to take part in the CO-insertion reaction. Thus, the phosphine modified Co-catalysts are less active than the unmodified $HCo(CO)_4$. The equilibrium between these catalytic species depends on the CO partial pressure as well as the TBP (Pbu_3) concentration. In the present study the TBP concentration was kept constant and the CO partial pressure was increased. During this increase in the CO partial pressures, the unmodified $HCo(CO)_4$ species must have formed and increased in concentration leading to higher rates of hydroformylation.

2.3.5.5.5. Effect of H_2 partial pressure

The rate of hydroformylation of 1-hexene was observed to show a first order dependency on the H_2 partial pressure. These results are shown in Figure 2.24. A first-order dependency on hydrogen is well known in the hydroformylation with both rhodium[ix,x,xi] as well as cobalt[v] catalysts. First order dependency supports the assumption that the oxidative addition of H_2 to the acyl-cobalt intermediate species is the rate-determining step.

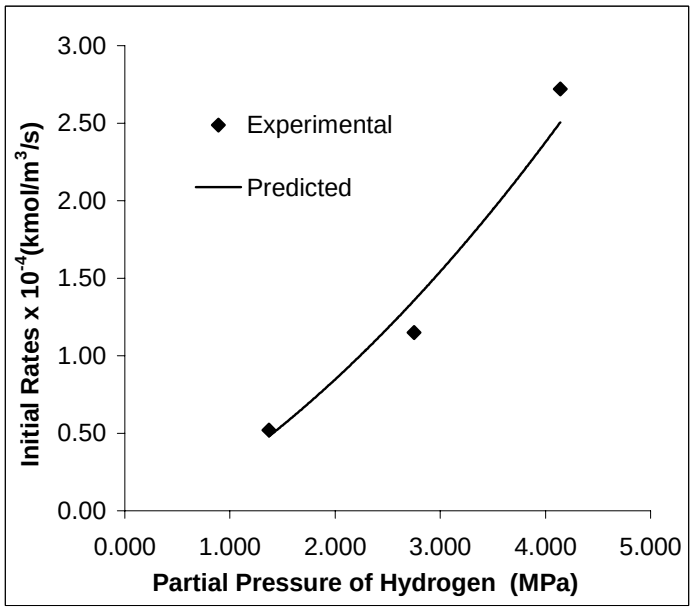


Figure 2. 24. Effect of H_2 partial pressure

Reaction conditions: 1, hexane, 0.8 kmol/m^3; Co(II) acetate, 3 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; TBP : Co, 4; Temperature, 453 K; PCO, 1.37 MPa; Agitation 20 Hz.

2.3.5.6. Kinetic model

The rate data were found to fit reasonably well with the following form of rate equation (Equation 2.4).

$$R = \frac{k\,A\,B^{1.5}\,C^{1.4}\,D}{\left(1+K_C C\right)^2} \qquad (2.4)$$

Where, A, B, C, and D , represents, concentrations of CO, H_2, catalyst, and 1-hexene respectively in unites kmol/m^3, while, k, (m^9 kmol$^{-l3.9}$ sec^{-1}) and Kc (m^3 kmol^{-1}) are the rate parameters.

The rate parameters were evaluated by fitting the observed experimental data with regression analysis, using an optimization routine based on Marquard's method. The ϕ value was calculated according to the Equation (2.5).

$$\phi = \sum_{i=1}^{n}\left(R_{\exp} - R_{predicted}\right)^2 \qquad (2.5)$$

The values of rate constant and equilibrium constant obtained are,

k, Rate constant = 2.19×10^{5} m^{9} $kmol^{-l3.9}$ sec^{-1}

Kc, Equilibrium constant for catalyst, = 2.18×10^{4} m^{3} $kmol^{-1}$

The value of ϕ obtained according to Equation (2.5) is,

$$\phi = 5.78 \times 10^{-9}$$

The experimental and predicted trends based on Equation (2.4) are shown in Figures 2.21 to 2.24, which show a reasonably good agreement.

A detailed analysis of rate equations based on mechanistic models is ideally essential. This work will be continued in our laboratory. Also, the kinetic modeling of isomerization and hydroformylation reactions is an important aspect the should be covered in the future work to enable complete understanding of the hydroformylation process using Co-tri-*n*-butyl phosphine catalyst.

2.4. CONCLUSIONS

An activity-selectivity and kinetic study of a complex reaction system of 1-hexene hydroformylation with tri-*n*-butyl phosphine modified cobalt catalyst has been discussed in this chapter. Product distribution pattern, studied from the concentration-time profiles at different reaction conditions showed very high rates of 1-hexene isomerization to 2- and 3-hexenes. Hydroformylation products showed 1-heptanal, 2-methyl hexanal and 2-ethyl pentanal with the last in very less quantity. Thus, the hydroformylation products of 1-hexene were found to dominate the products profile whereas among the hexenes, 1-hexene was found to be present in the minimum quantity while 2-hexenes (*trans* and *cis*) and 3-hexenes (*trans* and *cis*) showing major concentrations. This was accounted to the lower reactivity of internal olefins to hydroformylation compared to the terminal olefins. Hydrogenation of C7-aldehyeds leading to C7-alcohols and 1-hexene to *n*-hexane were the other side products observed in this reaction. Alcohol formation was found to start slowly after formation of a minimum amount of C7-aldehydes. The study of concentration-time profile highlighted the importance of isomerization reaction as the isomerization equilibrium controlled the hexenes concentrations, which further give hydroformylation reaction.

Effect of parameters on isomerization was studied by taking intermittent samples in the first 15 minutes of the reaction. Catalyst concentration was found to increase the isomerization whereas 1-hexene concentration was found to show a negative impact on

the isomerization reaction. Partial pressures of both CO and H_2 showed a positive influence over the isomerization reaction.

Selectivity behaviour of the hydroformylation reaction was separately studied with respect to catalyst and 1-hexene concentration. It was found that, catalyst concentration had negative influence over the overall selectivity to the hydroformylation products. However, hydrogenation was found to increase with the catalyst concentration. The regioselectivities to 1-heptanal and 1-heptanol (linear products) was found to increase with the catalyst concentration. At higher catalyst loading (>0.006 kmol/m^3) l*inear / branched* ratio of alcohols was found to be higher than that of the aldehydes indicating preferential hydrogenation of 1-heptanal. 1-hexene concentration showed negative impact on hydroformylation as well as hydrogenation reactions. The *linear / branched* ratio of aldehydes was found to decrease with the 1-hexene concentration.

Effect of parameters on the hydroformylation activity of the catalyst was studied by calculating the initial rate of reactions. 1-hexene, CO and H_2 concentration showed positive impact on the rate of hydroformylation reaction whereas catalyst concentration showed a negative impact. Based on the initial rate data, kinetics of 1-hexene hydroformylation was studied and the initial rate data were found to fit reasonably well with the following form of semi-empirical rate equation,

$$R = \frac{k\,A\,B^{1.5}\,C^{1.4}\,D}{\left(1 + K_C C\right)^2}$$

Rate parameters were evaluated by fitting the observed experimental data with regression analysis, using an optimisation routine based on Marquard's method. A detailed analysis of the rate equation based on mechanistic model is ideally essential. This work will be continued in our laboratory.

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Chapter 3

COBALT CATALYZED HYDROFORMYLATION OF VINYL ACETATE MONOMER: ACTIVITY AND SELECTIVITY STUDIES

3.1. INTRODUCTION

More than 75 years ago, in 1938, Otto Roelen discovered hydroformylation reaction (Oxo synthesis) with cobalt catalysts. However, cobalt catalyzed hydroformylation is not as thoroughly studied as rhodium catalyzed hydroformylation. In fact, after the invention of Wilkinson's catalyst *i.e.* Low Pressure (LP) oxo process in the late 1970s, almost all the attention is fetched by topics such as organic/water-soluble ligands for Rh, heterogenization techniques, and asymmetric catalysis by Pt-Sn or Rh. If the application pattern of hydroformylation technology is considered excluding the propylene share, cobalt catalyzed hydroformylation of olefins occupy a major share (~ 80 % production capacity[i]). Some of the key processes involving hydroformylation of higher olefins (Shell, BASF); acrylonitrile (Ajinomoto Corp.), ethylene oxide (Shell) *etc.* are carried out exclusively using cobalt-complexes as catalysts. Thus, the study of cobalt catalyzed hydroformylation is important both from chemistry and catalysis point of view. Process studies on hydroformylation of higher olefins are covered by many papers / patents[ii] but investigations on functionalized olefins as substrates are only a few.[iii]

The relevant literature on hydroformylation of functionalized olefins is discussed in Chapter 1. An interesting example is the hydroformylation of VAM as a route for propylene glycols. This reaction is even more important if the selectivity for linear aldehyde derivative can be increased since it is a precursor for 1,3-propanediol. In general the reaction is important for synthesis of at least a mixture of 1,2 and 1,3-propanediols. There are only two published reports on cobalt-catalyzed hydroformylation of VAM, which unfortunately have contradictory results. Adkins *et al.*[iv] in 1949, in their first report on $Co_2(CO)_8$ catalyzed hydroformylation of functionalized olefins, have tested VAM among various other substrates and reported 70 % selectivity to acetoxy propanals (ac pals) with regioselectivities of 62 % and 32 % for 2-acetoxy propanal (2-ac pal) and 3-acetoxy propanal (3-ac pal) respectively, at 398 K and 24.1 MPa of syngas pressure. Whereas, Watanabe *et al.*[v] in 1974, have reported only 2-ac pal and no 3-ac pal, with the same catalyst under similar conditions and even different conditions. Improving the selectivity of 3-acetoxy propanal using cobalt catalysts is a major challenge since, the Rh catalyzed processes give very high selectivity for 2-acetoxy propanal with less than 10% selectivity for 3-acetoxy propanal.

In this chapter, experimental results on the effects of ligands such as alkyl and aryl phosphines; diphosphines; pyridine; substituted pyridines; primary, secondary, and tertiary amines; triphenyl arsine *etc.* on the hydroformylation of VAM, are presented. Effect of various promoters and solvents on activity and selectivity was also studied. Stability of the cobalt complex catalyst during catalyst-product separation has also been discussed.

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3.2. EXPERIMENTAL

3.2.1. Materials

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Cobalt acetate, $Co(CH_3COO)_2.4H_2O$, and all the phosphine, diphosphine, pyridine, substituted pyridines, other ligands such as amines, morpholein etc., quaternary ammonium and phosphonium salts, alkali salts etc. were procured from Aldrich, USA or Fluka, Switzerland and used as such without further purification. All solvents were procured from Sd Fine Chemicals, India or Merk-India and used after proper distillation, drying and argon flushing. CO, 99.9 % purity (Matheson, USA) and H_2 99 % purity (Industrial Oxygen Company, India) were used as received without further purification. $Co_2(CO)_8$ (Dicobalt octacarbonyl) was prepared by high pressure-high temperature technique as described in Section 3.2.4.2. Water used was double distilled, demineralized, and degassed. Syngas mixture in the required CO : H_2 ratio was first prepared in a reservoir and then used for hydroformylation reactions.

3.2.2. Hydroformylation experiments

All the hydroformylation reactions were carried out in a 50 ml Parr Autoclave made of stainless steel material (Maximum pressure capacity of 20.7 MPa at 548 K), having facilities for gas inlet, outlet, intermediate sampling, temperature controlled heating (±1 K) and variable agitation speed (0 –33.3 rpm). A schematic of the reaction set-up is shown in Figure 2.1. As a safety precaution a rupture disc (gold faced), which can withstand a maximum pressure of 20.7 MPa was attached to the reactor. For experiments with ≤ 7 MPa pressure, gas is fed through constant pressure regulator attached to the syngas reservoir while for high pressure experiments, the reactor pressure is maintained by intermittent manual gas filling from the syngas reservoir, after every

drop of ~ 0.2 MPa reactor pressure. Syngas reservoir is always maintained at minimum 1.5 MPa higher pressure compared to the reactor pressure. Ice water-cooled condensers were used for intermediate sampling. For $Co_2(CO)_8$-catalyzed hydroformylation, maintaining syngas atmosphere is very critical due to instability of $Co_2(CO)_8$ at lower pressures. The safe weighing and handling procedure for $Co_2(CO)_8$ is explained in Section 3.2.4. In typical cobalt catalyzed hydroformylation experiment, known quantities of the substrate, catalyst, promoters, and the solvent were charged into the autoclave. The contents were immediately flushed thrice with syngas. The reactor was pressurized to ~2 MPa syngas pressure, the solution was saturated by keeping agitation speed of ~16.6 Hz for 2-3 minutes and then heating was started with ~ 1.66 Hz stirring. After attaining the desired temperature, the syngas was made up to the required pressure from the reservoir and the reaction started by increasing the agitation speed to 20 Hz. The pressure drop in the reservoir vessel was recorded by means of a pressure transducer (± 1 psi) as a function of time. Intermediate liquid samples were also taken at regular intervals of time. Unless-otherwise mentioned all the reactions were run till the syngas absorption nearly stopped. The autoclave was thoroughly cooled to < 293 K, syngas vented off, the reactor flushed thrice with nitrogen and the reaction mixture removed. For cobalt-catalyzed hydroformylation, N_2 flushing after the reaction is essential to avoid exposure to highly poisonous $HCo(CO)_4$. After every reaction, the reactor was cleaned thoroughly and a wash with 10 % HNO_3 was given to ensure the total removal of the metal particles. For ligand and promoter screening, unless and otherwise mentioned, the $CO_2(CO)_8$ and the ligand / promoter were charged separately and the modified catalyst was prepared *in situ*. For solvents screening, the VAM concentration and the total volume of the charge were kept constant. The analysis of the liquid samples was carried out using GC to examine the product distribution pattern quantitatively. Details of GC analysis are given in the following section. A care was taken to ensure the same addition sequence of materials in all reactions and safety precautions while handling poisonous substances like $HCo(CO)_4$, TPAs, CO *etc*.

3.2.3. Analytical methods

IR spectrums were obtained using a Bio-rad FTS *175C* machine in transmission mode using KBr pellets as well as liquid cells. NMR spectrums were obtained from a

Brucker- MSL-300 machine. GC-MS analysis was carried out on an Agilent GC machine of 6890N series equipped with 5973N Mass Selective Detector. Spectral analysis of important compounds is given in Annexure II.

Liquid samples were analyzed on a Hewlett Packard 6890 Series GC controlled by the HP-Chemstation software and equipped with an auto sampler unit, by using a HP-1 capillary column (30 m x 30 µm x 0.25 µm film thickness with a stationary phase of polymethyl siloxane). The quantitative analysis was obtained by constructing calibration curve in the range of concentrations studied. The % conversion, % selectivities and regioselectivities of aldehydes and alcohols were calculated using the following formulas % Conversion was always calculated based on the liquid substrate charged. Total aldehyde-selectivity and alcohol selectivity were calculated by addition of both linear and branched products. The standard GC conditions for analysis of products of different reactions are given in Table 3.1.

Table 3.1. Conditions for GC analysis

Injector (split) Temp	523 K		
Flame ionization detector Temp	523 K		
Inlet flow - total (He)	32.3 cm^3/min		
Split ratio	50:1		
Column Temperature	Rate (K/min)	Temp (K)	Hold time (min)
		306	5
	303	353	2
	313	498	2
Column Pressure	Rate (psi/min)	Pressure (psi)	Hold time (min)
		3	2
	10	5	3
	10	30	0

$$Conversion, (\%) = \frac{Initial\ concentration\ of\ substrate - Final\ concentration\ of\ substrate}{Initial\ concentration\ of\ substrate} \times 100$$

$$Selectivity, (\%) = \frac{No.\ of\ moles\ of\ a\ product\ formed}{No.\ of\ moles\ of\ substrate\ converted} \times 100$$

$$TOF, (h^{-1}) = \frac{No.\ of\ moles\ of\ hydroformylaion\ products\ formed}{No.\ of\ moles\ of\ catalyst \times time\ in\ hours}$$

$$TON = \frac{No.\ of\ moles\ of\ hydroformylation\ products\ formed}{No.\ of\ moles\ of\ catalyst}$$

$$\text{Regioselectivity to I} = \frac{I}{(I + II)} \times 100$$

$$\text{Regioselectivity to II} = \frac{II}{(I + II)} \times 100$$

3.2.4. Preparation and handling of $Co_2(CO)_8$

The synthesis of $Co_2(CO)_8$ was carried out in a 50 ml Parr Autoclave made-up of Hastalloy C-276 material, (Capacity -maximum pressure 20.7 MPa at temperature 548 K) having facilities for gas inlet, outlet, intermediate sampling, temperature controlled heating (±1 K) and variable agitation speed (0 – 33.3 rpm). The typical reaction set-up is shown in Figure 2.1. As a safety precaution, a rupture disc (gold faced), with a capacity to withstand a maximum pressure of 20.7 MPa (at 273 K) was attached to the reactor.

Generally, the pressures required for $Co_2(CO)_8$ synthesis are in the range of 15.2 – 16.6 MPa at temperatures in the range of 463-473 K.[x] In view of the absence of gas-cylinders of such high pressures, and non-availability of a booster or compressor of such capacity, we used a different technique to boost up the pressure. After charging the cobalt precursor and solvent to the reactor, the reactor was chilled down to 273 to 276 K. At this low temperature, the reactor was pressurized to ~ 11.2 MPa with syngas (usually with high $CO:H_2$ ratio) with constant agitation of 20 Hz. The reactor was allowed to attain the room temperature and then heated to the desired temperature at constant stirring speed of 8 Hz. The reaction was started by increasing the stirring speed to 20 Hz. Due to large temperature gradient of ~ 190 K, while attaining the temperature of 468 K, the pressure rose up to ~ 16.5 MPa (depending upon the solvent and initial pressure). Even at this temperature and pressure, an induction period of ~ 20-40 minutes was observed. The induction period was found to vary with the $CO : H_2$ ratio of the syngas. All the reactions

were run till the gas absorption stopped. After cooling the reactor to ~ 280-285 K, it was depressurized slowly, flushed thrice with argon and the liquid contents were poured in a 100 cm^3 beaker. The black particles obtained (if any) were weighed and discarded. The solvent was removed by argon bubbling, dark-shining red crystals of $Co_2(CO)_8$ obtained were immediately transferred into the high-pressure container (described in section 3.2.4.3). The Infra-red analysis of the $Co_2(CO)_8$ prepared was found to be consistent with the reported spectra[vi,vii,viii] with a characteristic absorption band at 1857 cm^{-1} (Annexure II, IR-3). Different variations in solvent, syngas ratio, amount of precursor *etc.*, in the catalyst preparation were studied and the results are presented in Table 3.2.

Table 3.2. High pressure-high temperature preparation of $Co_2(CO)_8$

Run no.	Solvent	Co (II) acetate	Temp	Pressure #		Ind. Period	Time	Yield $
				*P*CO	*P*H_2			
		G	K	MPa	MPa	Min.	Min.	%
1	Toluene	1	473	1050	670	5	31	31
2	Cyclohexane	1	463	1380	360	11	31	69
3*	Hexane	1	473	1050	625	-	-	-
4	95 % Hexane	2	473	860	860	38	45	26
5	95 % Hexane	1	473	1050	600	19	44	64
6	95 % Hexane	1	473	1225	500	16	50	81
7	95 % Hexane	1.6	463	1350	410	27	52.5	59
8	95 % Hexane	1.5	453	1540	280	19	68.2	65
9	95 % Hexane	2	453	1550	250	30	63.5	61

*Reaction conditions: Solvent, 22.5 x 10^{-6} m^3; Agitation, 20 Hz; # =Partial pressures filled at ~ 280 - 285K. $ = Isolated yields after solvent evaporation. * = petrolium ether fraction of hexane containing moisture.*

$Co_2(CO)_8$ synthesis was tried in three solvents *viz.* toluene, cyclohexane (Run 1 & 2 respectively) and hexane. In toluene, the induction period was less (5 min.) so also the yields. Cyclohexane was a better solvent compared to toluene in terms of both yield and induction period, but hexane proved to be the best solvent considering the yields and run time. One added advantage of hexane solvent was its low boiling point, which helped in

its evaporation under argon flow. It was found that hexane from the petrolium-ether fraction was not a suitable solvent as no gas absorption occurred in that solvent (Run 3). At the end of the reaction a separate pink layer was obtained, which was a Co-aqua complex formed due to moisture in the Pet-ether fraction. In 95 % hexane as a solvent, the catalyst preparation took place, but with an induction period. The induction period was found to depend upon *P*CO, $Co(CH_3COO)_2.4H_2O$ concentration, and temperature. Since, the induction period was less for toluene and cyclohexane, it can be concluded that the major reason behind the induction period must be less solubility of $Co(CH_3COO)_2.4H_2O$ in organic solvents. As can be seen from the table, keeping the total initial pressure constant, when only the *P*CO & PH_2 were varied, the induction period reduced as the *P*CO was increased. The yield and reaction rate were also increased with *P*CO (Run 4, 5 & 6). When $Co(CH_3COO)_2.4H_2O$ concentration was increased from 1 to 1.5 and 2 g, the % yield was found to decrease, and some unreacted, solid $Co(CH_3COO)_2.4H_2O$ was observed at the end of the reaction. At high *P*CO, the catalyst could be prepared even at low temperatures, such as 463 K and 453 K. The effect of temperature on gas absorption is shown in Figure 3.1. In Run 7, 8 & 9, the % yields were less due to high charging of $Co(CH_3COO)_2.4H_2O$ and not due to low temperature.

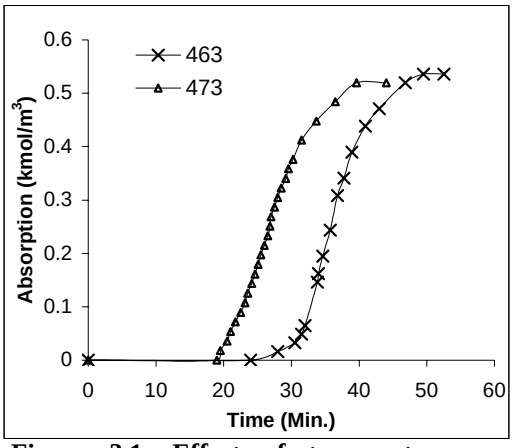


Figure 3.1. Effect of temperature on $Co_2(CO)_8$ preparation
Reaction conditions: Same as those of Table 3.2

Thus, the catalyst preparation was found to be highly dependant on *P*CO whereas PH_2 was found to have almost no effect. But the mechanism of $Co_2(CO)_8$ formation demands presence of H_2 as $Co_2(CO)_8$ is formed via formation of a reduced Co(0) species from

$$Co_2(CO)_8 + H_2 \underset{\text{Cooling, Degassing}}{\overset{\text{Temperature, Syngas}}{\rightleftharpoons}} 2HCo(CO)_4$$

Scheme 3.1. Cobalt carbonyl equilibrium

Co(II) salt (in the present case $Co(CH_3COO)_2$). The reduced Co(0) species on reaction with CO leads to $Co_2(CO)_8$ in which the Co retains formal oxidation state of zero. In the presence of H_2 at high-temperatures, the $Co_2(CO)_8$ is converted to $HCo(CO)_4$ which after cooling and degassing again converts back to $Co_2(CO)_8$ (Scheme 3.1). For the present study $Co_2(CO)_8$ was prepared in batches by using conditions of Run 6 in Table 3.2.

Since $HCo(CO)_4$ and $Co_2(CO)_8$ are highly unstable as well as hazardous, a brief survey of their properties was done. $HCo(CO)_4$ is a very light yellow, almost colorless solid (mp, 243 K). An estimated boiling point of $HCo(CO)_4$ is 320 K,[ix] but there are references which quote it to be below 298 K.[x] Although $HCo(CO)_4$ has limited solubility in water (5.6×10^{-2} mol/L), it is much more soluble in organic solvents, *e.g.* distribution of $HCo(CO)_4$ between equal volumes of water and toluene favors toluene by a factor of 7. It is a protic acid in water with a P*Ka* between that of HNO_3 and HCl. The NMR spectrum of $HCo(CO)_4$ shows a single proton at very high field (τ = 20), which is a characteristic of metal hydrides.[x] Thus, it is apparent that $HCo(CO)_4$ is very versatile and can act either as a protonating agent or a reducing agent. Structure of $HCo(CO)_4$ is a distorted tetrahedron with a linear OC-Co-H bond-axis and three carbon monoxide atoms equally spaced around this axis, to give a molecule with C_{3v} symmetry. $HCo(CO)_4$ is highly toxic and since it has very low boiling point, a great caution must be taken while handling it.

$Co_2(CO)_8$ is a red-violet colored, highly unstable compound soluble in organic solvents. Under ambient conditions, it decomposes to $Co_4(CO)_{12}$ and higher nuclearity clusters of Co. At slightly higher temperatures (~ 305 K), it releases poisonous CO almost instantaneously. Ungvary and Marko[xi] have reported that decomposition of $Co_2(CO)_8$ is an inverse second order with respect to CO concentration. Thus, to avoid decomposition of $Co_2(CO)_8$ to $Co_4(CO)_{12}$ (which is a irreversible reaction[xii]) it must be stored under positive CO pressures and at low temperatures (~ 273 K).

Because of the unstable nature of $Co_2(CO)_8$, a general practice is to synthesize it fresh and use immediately. This procedure is inconvenient due to the high temperatures and pressures involved in the synthesis,. To avoid this, we have synthesized it in batches as described in Section 3.2.4.1 and stored it under high pressures of CO at 275 K. A

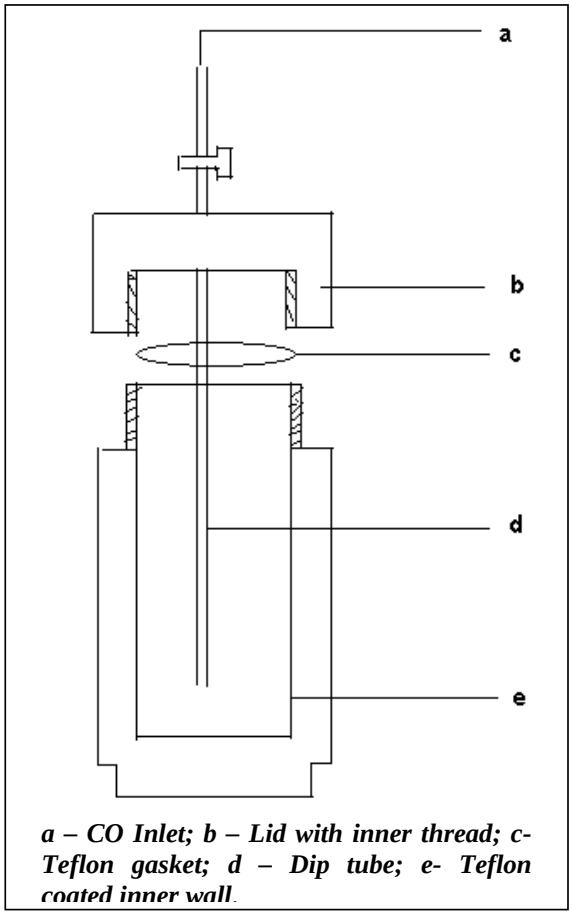


Figure 3.2. High pressure container for $Co_2(CO)_8$ storage

special Teflon coated high-pressure container was designed, as shown in Figure 3.2, for this purpose. $Co_2(CO)_8$ moistened with 95 % n-hexane, was stored in this container under positive CO pressure of 4.13 MPa. A screw cap with a Teflon gasket ensured pressure safety and leak-proof nature of the container. The container was always kept at 275-277 K temperature. Solid $Co_2(CO)_8$ stored in the container was weighed before the reaction and charged to the reactor (reaction solvent) immediately. Every time after taking out the catalyst, the container was tightened, flushed twice with CO and pressurized with 4.13 MPa CO before keeping in the refrigerator. The container was also provided with a dip-tube, to enable the transfer of a $Co_2(CO)_8$ stock solution directly to the reactor under pressures.

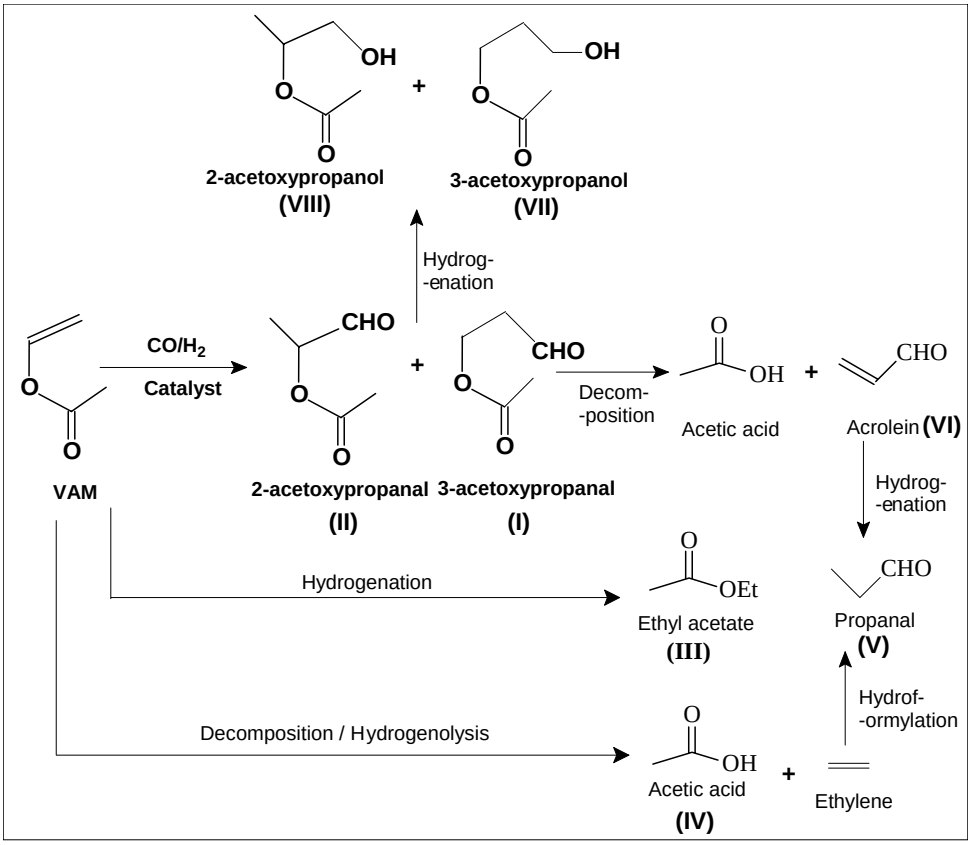
3.2.5. Preparation of 3-acetoxy propanal standard

Authentic 3-acetoxy propanal sample required for analysis was prepared according to a procedure described by Ballard *et al.*[xiii]. Glacial acetic acid and Acrolein in a mole ratio of 4.5:1 of were mixed and heated in a glass-lined reactor for four hours at 402 K. The mixture was then subjected to fractional distillation. Acetic acid and acrolein

were removed as lighter fractions below 323 K. 3-acetoxy propanal were distilled at 334 K at 8 mm vacuum.

3-acetoxy propanal is highly unstable and decomposes rapidly to acrolein and acetic acid. Acrolein, being an α, β-unsaturated aldehyde where a double bond and a carbonyl group are in conjugation, is more stable and so 3-acetoxy propanal shows a tendency to decompose. So purification of 3-acetoxy propanal through distillation was futile, as the purity of the distillate didn't go beyond 80 %. Attempts to purify 3-acetoxy propanal with column chromatography were also unsuccessful as it was decomposed on TLC plate as well as on the column silica. Therefore, the same 80 % pure 3-acetoxy propanal was used as a standard by subtracting the quantities of acrolein and acetic acid with the help of pre-calibration of acrolein and acetic acid.

3.3. RESULTS AND DISCUSSION



Scheme 3.2. Hydroformylation of VAM along with side reactions

A detailed experimental study of the cobalt-catalyzed hydroformylation of VAM is presented in this section. Preliminary study of the effect of parameters on activity and aldehyde-regioselectivity was carried out. Ligands, promoters, solvents *etc.* were tested to check their effect on the activity, chemoselectivity and regioselectivity of hydroformylation of VAM. The Scheme 3.2 shows all the reactions occurring in a standard cobalt catalyzed hydroformylation of VAM. Throughout this chapter, unless mentioned, wherever hydroformylation of VAM is used, it must be taken as cobalt catalyzed hydroformylation of VAM. Spectral analysis of the important compounds is presented in Annexure II.

3.3.1. Effect of cobalt-precursors

Few reactions with different cobalt precursors were carried to find out the best precursor. The important results are presented in Table 3.3. All the cobalt precursors used for hydroformylation catalyze the reaction by forming (*in-situ*), hydridocobalt carbonyls $HCo(CO)_n(L)_m$ ((n + m) = 3 or 4) as the active species. Unlike hydridorhodium carbonyls, hydridocobalt carbonyls are difficult to prepare and are highly sensitive. In the present study, we have tried for *in-situ* preparation of $HCo(CO)_4$ or $HCo(CO)_3$ from different cobalt precursors. $Co(acetate)_2$ and $Co(acac)_3$ i.e. $Co(C_5H_7O_2)_3$ are known as active precursors for $Co_2(CO)_8$ synthesis, and so were used directly for VAM hydroformylation. No reaction occurred even at maximum temperature of 453 K and syngas pressures of 9.65 MPa (Run 1 &2, Table 3.3).

Since, the said precursors were insoluble in toluene at ambient conditions, they were also tested in solvents like MIBK, MEK, MeOH and MTBE but no conversion of VAM was observed. Similar inactivity, in different solvents and under varying conditions, was observed with other cobalt metal salts and stable complexes such as, Co(SMDPT), $Co_4(CO)_{12}$ and $CoCl_2.6H_2O$ (Run 3, 4 & 5). Since, all these complexes were known precursors for $Co_2(CO)_8$ synthesis under very high pressures and temperatures (> 20.6 MPa and > 473 K)[xiv], it is evident that formation of active species for hydroformylation- from all the above precursors is difficult unless very high pressures and temperatures are applied. Less activity of VAM as a hydroformylation substrate may also be responsible for failure of the above precursors as active catalysts,

e.g. Co(II)acac is known to work well for hydroformylation of cyclohexene at 423K and 10.3 MPa syngas pressure[xv] but didn't work for VAM under the similar conditions.

Table 3.3. Screening of different catalyst precursors

Run No.	Catalyst	Catalyst Conc.	TEMP	Press.	Conv.	Ald. Sel.	REGIOSELECTIVITY		Side products	
							II	I	III	IV
		Kmol/m^3	K	MPa	%	%	%	%	%	%
1	$Co(acac)_3$	0.013	453	6.55	0	0	-		0	0
2	$Co(OAc)_2$	0.025	453	9.65	0	0	-		0	0
3	Co (SMDPT)	0.015	433	9.65	0	0	-		0	0
4	$Co_4(CO)_{12}$	0.028	393	10.3	0	0	-		0	0
5	$CoCl_2.6H_2O$	0.024	453	12	0	0	-		0	0
6*	Reduced Co-metal	60 mg	473	10.3	40	30.5	100	0	13.6	56.1
7$	Reduced Co-metal	54 mg	453	10.3	45	51.1	70.4	29.6	13.6	24.9
8	$Co_2(CO)_8$	0.006	393	4.1	90	95.7	55	45	4	0

*<u>Reaction conditions:</u> Solvent, Toluene; VAM, 1.3 kmol/m^3; Total charge, 25 x 10^{-6} m^3; CO:H$_2$ = 1:1; Agitation, 20 Hz; Minimum contact time, 60 minutes; * = The reaction didn't go at 453K; $ = Acetonitrile as solvent.*

Surprisingly reduced-cobalt-metal showed activity under high temperature (473K) and syngas pressure of 10.3 MPa (Run 6 Table 3.3). The reaction was very slow and required 180 minutes to absorb 1.38 MPa syngas. Conversions and chemoselectivity of the reaction in toluene were poor at 46.5 % and 30.5 % respectively. AA (56 %)and EA (13.6%) were formed in large quantities while acrolein, in the equivalent amount of AA was observed. Among the aldehydes, regioselective formation of 2-acetoxy propanal (II) was found to take place. The reason behind high regioselectivity to II and AA formation was the same - decomposition of 3-acetoxy propanal to acrolein and AA (Reaction (VI) in Scheme 3.2), may be due to very high temperature. The final solution appeared to be transparent and faint-yellow colored.

The same reaction in acetonitrile solvent showed different results. At 453 K, after an induction period of 5-6 minutes, very rapid gas absorption started and stopped in 1.5-2

minutes after absorbing ~ 1.7 MPa syngas. Compared to the reaction in toluene, improved conversion and selectivities were obtained in acetonitrile reaction (Run 7 in Table 3.3). Thus, reduced-Co-metal can form the active hydroformylation catalysts under severe conditions (473 K), but the conversion and selectivities were poor. Solvent type played an important role in the formation of active hydroformylation catalyst from reduced-cobalt-metal.

The most commonly used precursor for cobalt catalyzed hydroformylation reactions is $Co_2(CO)_8$. For VAM hydroformylation, $Co_2(CO)_8$ showed markedly improved results compared to the one obtained with reduced Co-metal. Nearly equal formation of 3-ac pal and 2-ac pal giving linear/branched ratio of 0.876, was the most striking feature of $Co_2(CO)_8$ catalyzed hydroformylation of VAM. It differed markedly from the regioselective formation of branched aldehyde (2-ac pal) obtained with Rh-catalysts (Run 5 & 6 in Table 3.4). Thus, with cobalt catalyst, the chances of obtaining high regioselectivity for 3-acetoxy propanal, (a potential precursor for 1,3-Pdo) were higher. So, preliminary experiments such as effect of temperature, syngas pressure etc., were carried out with an aim to study the activity-selectivity pattern of the $Co(CO)_8$ catalyzed VAM hydroformylation reaction.

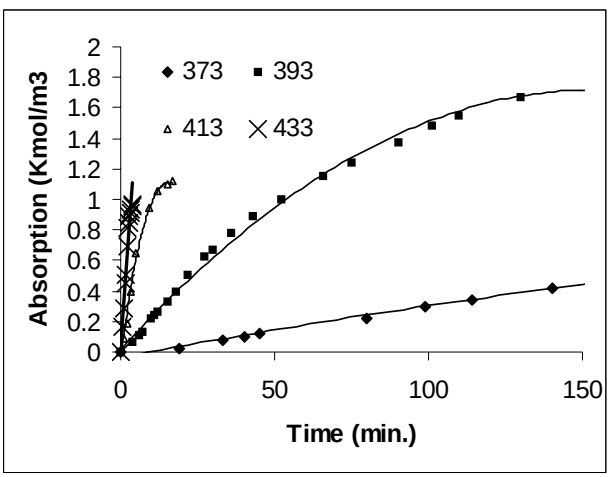


Figure 3.3. Effect of temperature on hydroformylation of VAM
Reaction conditions: VAM,1.1 kmol/m^3; $Co_2(CO)_8$, 0.006 kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; Syngas, 4.1 MPa; CO:H_2, 1:1, Agitation, 20 Hz.

3.3.2. Effect of temperature

Effect of temperature, at different catalyst concentrations and syngas pressures was studied in the range of 353 K to 433 K. A graphical representation of syngas absorption pattern, at different temperatures is presented in Figure 3.3.

Important results on the temperature effect are presented in Table 3.4. Figure 3.3 very clearly highlights a strong effect of temperature on Cobalt catalyzed hydroformylation of VAM. The reaction was too slow at 373 K whereas too fast at 413 K and 433 K. In fact, at 373 K the reaction continued for 300 minutes at slow rates whereas at 413 and 433 K, the reaction abruptly stopped after 17 minutes and 4 minutes respectively (See Table 3.4, entries 2-5). The reason behind such abrupt reaction termination was catalyst decomposition. At 413 K and 433 K, the reaction occurred was so fast that it must have occurred under mass-transfer limitation zone and so the concentration of dissolved syngas must have reduced to negligible amounts leading to catalyst decomposition. At these temperatures even 4.1 MPa pressure and agitation of 60 Hz were not sufficient to keep the catalyst active and violet $Co_4(CO)_{12}$ catalyst precipitated before complete conversion of VAM. The reaction didn't go to completion at 373 K also; here the reason was too slow reaction – leading to side products formation. In this reaction, due to long contact times, some 3-acetoxy propanal (I) was decomposed to acetic acid and acrolein (Reaction (VI) in Scheme 3.2), leading to lower *l/b*. Acetic acid formed in the reaction at 373 K, deactivated the catalyst by precipitating pink colored $Co(CH_3COO)_2$. At 393 K, 95 % conversion with 95.7 % selectivity to aldehydes and *l/b* ratio of 0.8. Alcohols (Total selectivity of ~ 1 – 2 %) of *i.e.* 2-acetoxy propanol and 3-actoxy propanol were observed in the reactions with temperatures 393 K and above.

To avoid the catalyst decomposition at higher temperatures, one reaction at double catalyst concentration *i.e.* 0.012 kmol/m^3 and 13.8 MPa syngas pressure ($CO:H_2$ = 3.5:1) was taken at 433 K (Run 6 in Table 3.4). On comparison of the results with low pressure-low catalyst reaction (Run 5 in Table 3.4) it was found that the product profile improved with a jump in chemoselectivity from 78 % to 92.4 % and a quantum jump in regioselectivity with *l/b* ratio increasing from 0.66 to 0.95.

From the above results on temperature effect, it can be concluded that, with temperature, ethyl acetate formation augment whereas regioselectivity decrease. High syngas pressures are necessary to avoid catalyst decomposition at temperatures higher than 393K.

Table 3.4. Effect of temperature

Run No.	Run time	$Co_2(CO)_8$ x 10^3	VAM concn.	Temperature	Conv.	Ald	EA	AA	L/b $ Ald.	Initial rate x 10^3
	Min	kmol/m^3	kmol/m^3	K	%	%	%	%		kmol/m^3/s
1[a]	41	6.9	0.88	353	8	92	0.9	-	0.8	0.0233
2#	309	6	1	373	55	80	9.8	9.2	0.64	0.053
3	154	6	1	393	95	95.7	4	0	0.8	0.44
4	17	6	1.18	413	59.1	92.6	9	0	0.68	2.6
5	4	6	1.1	433	68	77.8	15.4	0	0.66	6.2
6*	10	12	1.3	433	81.3	92.4	5.9	1.2	0.95	7.97

*Reaction conditions: Solvent, Toluene; Total charge, 25 x 10^{-6} m^3; Syngas, 4.1 MPa; CO:H_2, 1:1; Agitation, 20 Hz; a, Syngas 11 MPa; # = Acrolein equivalent to AA amount is formed; * = CO:H_2 = 3.5:1, Syngas, 13. 8 MPa. $ = Linear/branched.*

3.3.3. Effects of catalyst, substrate and gas concentration

To understand the activity-selectivity dependence on parameters, some preliminary experiments by varying one of the parameters among, catalyst concentration, substrate concentration, and syngas pressure, were carried out. The important results are summarized in Table 3.5. It was observed that, on doubling the catalyst concentration from 0.006 kmol/m^3 to 0.012 kmol/m^3, the rate of reaction was increased by more than 1.5 times, at the same time augmenting the side reaction - hydrogenation (Run 1 & 3 in Table 3.5). Thus, nearly double selectivity to EA (8.7 %) and 4 % alcohols were obtained when the catalyst concentration was doubled. By doubling catalyst concentration, nominal increase in the aldehyde linearity was observed. Increase in substrate concentration decreased reaction rates, chemoselectivity and also product linearity (Run 2 & 3). Syngas pressure had substantial effect on Co-VAM system (Run 3, 4 & 5). With doubling and tripling the syngas pressures, the product linearity and alcohol formation were increased but the reaction rates were nearly unaffected by pressure effect.

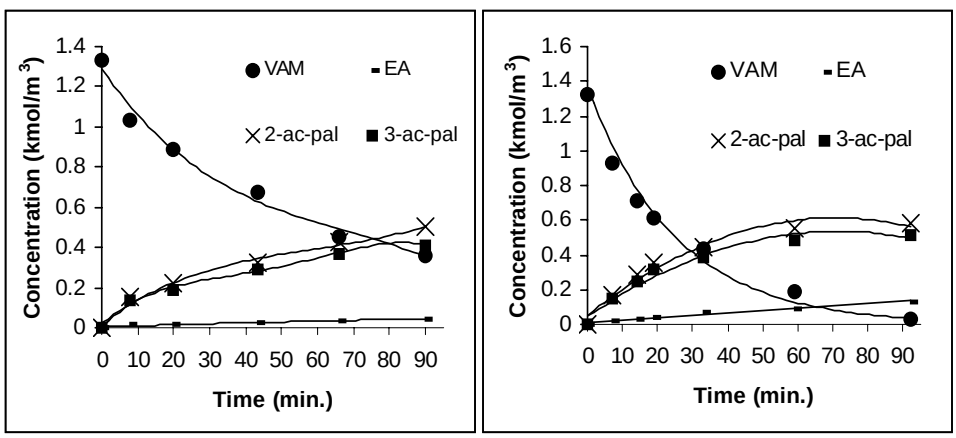
Table 3.5. Effect of parameters

Run No.	Run time	Cata concn x 10^3	Sub. Concn	Press.	Conv.	Ald. Sel.	L/b Ald.	Alc. Sel.	L/b Alc.	AA	EA	Initial rate x 10^3
	Min	**kmol/ m^3**	**kmol/ m^3**	**MPa**	**%**	**%**		**%**		**%**	**%**	**kmol/ m^3/s**
1	90	6	1.3	4.1	72.8	94.4	0.83	0	-	0	4.8	0.68
2	270	12	2.4	7.6	95.6	94	0.82	0	-	3.7	2.4	0.71
3	90	12	1.3	4.1	98	87.3	0.88	4	0.8	0	8.7	1.1
4	64	12	1.3	9.65	91.2	88.2	0.91	4.3	1.1	1	6.5	1.1
5	120	12	1.3	12.7	98.9	88.5	0.94	8.5	1.1	0	3	0.98

Reaction conditions: Toluene, 22.5 x 10^{-6} m^3; Total charge, 25 x 10^{-6} m^3; Temperature, 393K; CO:H_2, 1:1; Agitation, 20 Hz.

From the above preliminary experiments, it can be concluded that the syngas pressure play a very important role in maintaining the hydridocarbonyl-cobalt stability and activity, improving product linearity and carrying out tandem hydrogenation in the cobalt catalyzed hydroformylation of VAM.

3.3.4. Concentration – time profiles

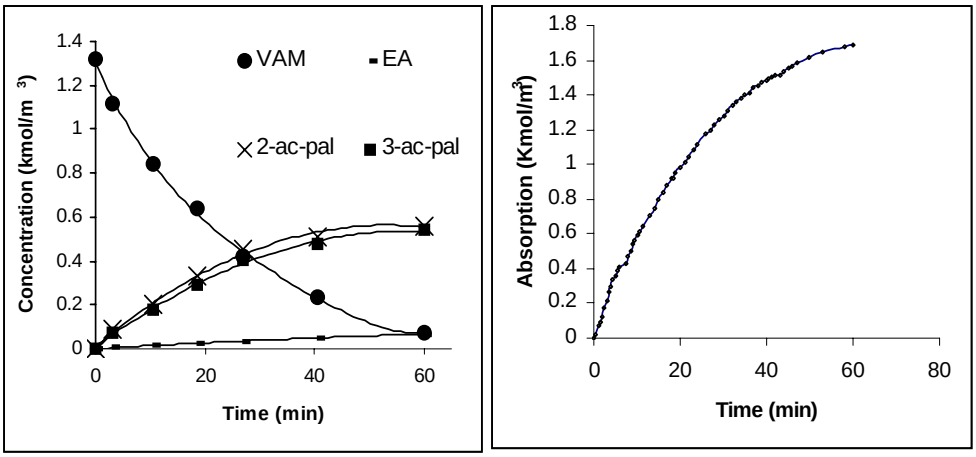


(A) (B)

Figure 3.4. Concentration-time profiles for hydroformylation of VAM at low syngas pressures (A) Low catalyst concentration (B) High catalyst concentration.

Reaction conditions: Toluene, 22.5 x 10^{-6} m^3; VAM, 1.3 kmol/m^3; Total charge, 25 x 10^{-6} m^3; Temperature, 393 K; CO:H_2 = 1:1 ; Syngas, 4.1 MPa; Agitation, 20 Hz; (A) $Co_2(CO)_8$, 6 x 10^{-3} kmol/m^3 (B) $Co_2(CO)_8$, 12 x 10^{-3}kmol/m^3

Since, the possibility of getting many products in the hydroformylation of VAM is high, a concentration-time profile was thought to be the best way to get an overall picture of the reactions happening. As was seen in the last section, (Section 3.3.3) the catalyst concentration and syngas partial pressures have a considerable impact on the activity and selectivity of the hydroformylation of VAM. Considering this, two C-T profiles of reactions with low syngas pressures at low catalyst concentration and high catalyst concentration respectively (Figure 3.4 A & B); and one C-T profile with high catalyst concentration at high pressures (Figure 3.5), were drawn by taking intermittent samples.



(A) **(B)**

Figure 3.5. Concentration-time profiles for hydroformylation of VAM at high pressure (A) Liquid sample Concentration profile (B) Syngas absorption profile

Reaction conditions: *$Co_2(CO)_8$, 12 x 10^{-3}kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; VAM, 1.3 kmol/m^3; Total charge, 25 x 10^{-6} m^3; Temperature, 393 K; Syngas, 9.65 MPa; CO:H_2 = 1:1; Agitation, 20 Hz*

Even though the possibility of getting many side products in the hydroformylation of VAM is high, we found that in the absence of promoters and under appropriate conditions EA was the only side product present in the reaction. The absorption data was found to match perfectly with the liquid sample analysis (Figure 3.5 A and B). The same data of Figures 3.4 and 3.5 is presented in the digital form in the Table 3.6. The conversion, initial-rate, and chemoselectivity for the aldehydes were found to be strongly

dependent on the catalyst concentration (Run no. 1, 2 Table 3.6). For low-pressure reaction at low catalyst concentration (Substrate / Catalyst = 110), the rate of the reaction was found to be less and after ~ 70 % conversion, the reaction became too slow to complete. At high catalyst concentration, the conversion was increased to 98 % but the aldehyde selectivity was reduced and EA formation was increased. At high pressure-high catalyst concentration the initial rate, conversion, and aldehyde selectivity increased, thus showing the strong inter-dependency of catalyst and syngas pressure (Section 3.3.3). Regioselectivity to linear aldehyde (I) was found to increase with both catalyst concentration and syngas pressure. Due to better performance at 9.65 MPa syngas pressure and 12 x 10^{-3} Kmol/m^3 catalyst concentration, these conditions were used for most of the screening studies in the following sections.

Table 3.6. Activity-selectivity of $Co_2(CO)_8$ for hydroformylation of VAM

Run No.	Run time	$Co_2(CO)_8$ x 10^3	Pressure	Conv.	Selectivity		Regioselectivity		Initial rate x 10^3
					Ald.	EA	I	II	
	Min	kmol/m^3	MPa	%	%	%	%	%	kmol/m^3/s
1	90	6	4.13	72.8	95.2	4.72	45.2	54.8	0.687
2	90	12	4.13	98	90.2	9.8	47	53	0.967
3	60	12	9.65	96	94.5	5.5	49.1	50.9	1.2

Reaction conditions: Toluene, 22.5 x 10^{-6} m^3; VAM, 1.3 kmol/m^3; Total charge, 25 x 10^{-6} m^3; Temperature, 393 K; CO : H_2 = 1:1; Agitation, 20 Hz

Since, VAM and its oxo-products are dual functionalized compounds and tend to form AA under suitable conditions (Scheme 3.2), the selectivity of the reaction shows high sensitivity to the catalyst environment. Also, the activity of the cobalt catalyzed hydroformylation varies considerably on altering the lignads surrounding it. In such scenario, effects of ligands, promoters, solvents *etc* on the activity-selectivity of the cobalt-catalyzed hydroformylation of VAM would be interesting. So, we have studied the effects of different phosphine, nitrogen and arsine containing ligands; promoters; and solvents on hydroformylation of VAM and the results are presented in the following sections.

3.3.5. Effect of phosphine ligands

Most of the commercial applications of modified cobalt carbonyl catalyst utilize trialkyl phosphine ligands. Especially, TBP is considered to be one of the best ligand for modified cobalt-catalyzed hydroformylation.[xx] In the present section, results on the effect of alkyl and arene phosphines, diphosphines, phosphine oxides, phosphites *etc.*, on activity and selectivity of hydroformylation of VAM, are discussed.

3.3.5.1. Monophosphines as ligands

Selected results of tertiary alkyl and aryl, phosphines; phosphites; and phosphine oxides, are presented in Table 3.7. In the preliminary experiments at *ligand: Co* ratio of 9 at 453 K, total conversion of VAM and corresponding syngas absorption was observed (Run 1,2). Surprisingly, aldehyde selectivity was very low at ~ 5-6 % so also the EA and AA formation. Many small peaks of high boilers were observed in the gas chromatogram. From GC-MS, some of them were found to be oligomers of ac-pals. A separate study of ac-pals decomposition by phosphines, was studied and is presented in section 3.3.5.3. To avoid the aldehyde decomposition, all the other reactions were carried out at the minimum phosphine concentration and low temperature.

It was observed that, even at 373 K, all the phosphine ligands readily formed catalyst with $Co_2(CO)_8$, which was evident by the typical crimson red color of the phosphine modified cobalt catalyst and inactivity of the catalyst (unmodified $Co_2(CO)_8$ is active at 373 K in absence of phosphines). Also, in the literature, it is known that from $Co_2(CO)_8$ and PBu_3, complex $[Co(CO)_3(PBu_3)]_2$ forms even at temperatures below 373 K.[xxi] The inactivity of this complex for hydroformylation at low temperature, was due to high stability of the $[Co(CO)_3(PBu_3)]_2$ and lack of formation of the active species $HCo(CO)_3(PBu_3)$ at low temperature. But, at a minimum temperature of 433 K, $HCo(CO)_3(PBu_3)$ formation occurred and the catalyst showed activity. Whatever little activity that was obtained below 433 K was due to unmodified $Co_2(CO)_8$ as is evident from the regioselectivity pattern (Run 6,7).

Table 3.7. Effect of mono-phosphine as ligands

Run No.	Ligand	$Co_2(CO)_8$ x 10^3	Temp	Syn gas	Conv.	Chemoselectivity			Regioselectivity	
						Ald.	EA	AA	I	II
		kmol /m^3	K	Mpa	%	%	%	%	%	%
1#	TPP	6	453	4.1	100	6.2	3	9	0	100
2#	TBP	6	453	4.1	100	4.1	7	15	0	100
3	TPP	6	453	4.1	11.6	40.5	25	31.1	9.91	90.09
4*	TPP	24	453	4.1	0	0	0	0	-	-
5$	TPP	12	433	9.6	85.1	70.3	23	7.3	17.09	82.91
6$	*m*-TP	6	433	9.6	74.4	33.8	6.4	57	28.57	71.43
7	TBP	12	373	4.1	12	11	26	62.6	44.44	55.56
8	TBP	12	410	4.1	40	10.5	15	70	41.18	58.82
9$	TBP	12	433	4.1	95	9	6	81	33.33	66.67
10$	TBP	12	433	9.6	77.6	15.2	4.6	71	20	80
11$	TMP	12	433	9.6	82	10.2	5.6	49	37.50	62.50
12	TPPO	12	453	9.6	8.17	29.5	28.8	18.1	0	100
13	TPPi	12	433	9.6	8	90	8.1	1.9	0	100
14	TBPi	12	433	9.6	4	73	11.7	16.3	0	100

*<u>Reaction conditions:</u> VAM, 1.3 kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; Ligand/Co = 3, Co:H_2 = 1:1; Total charge, 25 x 10^{-6} m^3; Agitation, 20 Hz; * = $Co(OAc)_2$ is used as a precursor, catalyst preformed at 453 K, 4.1, MPa, 1:1 Syngas for 45 minutes. $ = Aldehyde hydrogenation occurred with ~ 5-6 % overall selectivity for alcohols. # = Ligand/Co = 9. TPP = Triphenyl phosphine; m-TP = m-tolyl phosphine; TBP = Tributyl phosphine; TMP = Trimethyl phosphine; TPPO = Triphenyl phosphine oxide; TPPi = Triphenyl phosphite; TBPi = Tributyl phosphite.*

With TPP ligand at low $Co_2(CO)_8$ concentration, very less conversion of VAM and less aldehyde selectivity was observed (Run 3). Preformed modified catalyst (with Co-acetate and TPP) didn't give any reaction. Thus, it can be concluded that the little conversion in Run 1 may be due to unmodified $Co_2(CO)_8$. At 433 K and 12 x 10^{-3} kmol/m^3 catalyst concentration, the TPP-modified cobalt catalyst worked better with 85 % conversion and 70 % chemoselectivity (Run 5), though the regioselectivity favored branched aldehyde. Among the other aryl phosphines tested, only tri-*m*-tolyl phosphine showed little activity with 9.5 % conversion, but with poor selectivities (Run 6).

Preliminary investigation of TBP modified cobalt (Co) catalyst for hydroformylation of VAM showed high decomposition of VAM to ethylene and AA (Scheme 3.2). Reactions were carried out in the temperature range of 373 K to 433 K at 4.1 and 9.65 MPa pressure, but in all the reactions AA was the major product (Run 7-10). Major source of AA must be decomposition of VAM, as acrolein formed by 3-ac pal decomposition (Scheme 3.2) was in much less quantity compared to the AA formed. VAM conversion was found to increase with the temperature. The regular sampling showed progressive formation of AA and drop in concentration of VAM. Selectivity to aldehydes was very poor and decreased with the increase in temperature. Regioselectivity was also found to drop from 0.8 at 373 K to 0.5 at 433K. This was due to decomposition of 3-ac pal in the presence of Co-phosphine catalyst at higher temperatures. Interestingly, in spite of formation of acetic acid in high concentrations, $HCo(CO)_3(PBu_3)$ catalyst didn't decompose to cobalt acetate, thus highlighting the increase in stability of Co-carbonyls due to phosphine ligands. Trimethyl phosphine showed nearly similar activity as that of tributyl phosphine (Run 11). Triphenyl phosphite, tributyl phosphite, and triphenyl phosphine oxide were poor ligands for hydroformylation of VAM (Run 12,13,14).

In some reactions, aldehyde hydrogenation to alcohols was also observed, but the selectivity to alcohols was only ~ 5-6 %. Since, aldehyde formation itself was less for all these reactions, the chances of phosphine modified Co, acting as hydrogenation catalyst were further reduced. But, hydrogenation of VAM to some extent took place in almost all the reactions.

Overall, it can be concluded from the above results that tertiary alkyl or aryl phosphines are not suitable ligands for hydroformylation of VAM. They are active only at high temperatures and in fact act as a poison for both VAM (by decomposition) and the aldehydes formed (Section 3.3.5.3).

3.3.5.2. Diphosphine as ligands

The diphosphine ligands showed improved activity pattern for Rh-catalyzed hydroformylation of VAM under atmospheric pressure of syngas, (Sections 4.3.1.4 and 4.3.1.5). Such catalytic hydroformylation under atmospheric syngas pressure is not possible in case of $Co_2(CO)_8$ catalyst as, $Co_2(CO)_8$ require high partial pressures of CO

for stability. So testing the activity of diphosphines at atmospheric syngas pressure was not possible. In view of this the diphosphine ligands were tested for high-pressure cobalt catalyzed VAM hydroformylation and the selected results are presented in Table 3.8. Because of the anticipated chelating ability of the lower diphosphines, they were used in 1:1 ratio, whereas larger carbon chain diphosphines (such as DPPH) were used in 1:3 ratios.

Table 3.8. Effect of diphosphine ligands

Run No.	Ligand	Lig/ Co	Conv.	Chemoselectivity				Regioselectivity (Aldehydes)		Regioselectivity (Alcohols)	
				Ald.	Alc.	AA	EA	Linear	Branc.	Linear	Branc.
			%	%	%	%	%	%	%	%	%
1	DPPE-e	1	83.1	42.3	9.6	36.2	10.4	24.8	75.2	56.5	43.5
2	DPPE-a	1	80.6	39.0	7.9	42.2	11	23.1	76.9	50.0	50.0
3	DPPP	1	88.9	35.4	5.4	50.6	8.8	22.5	77.5	35.1	64.9
4*	DPPP	3	51.9	23	10.9	28.8	27.8	17.4	82.6	52	48
5*	DPPH	3	38.4	27.2	11.8	51	8.2	20.6	79.4	58.3	41.7

Reaction conditions: *$Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; VAM, 1.3 kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; Temperature, 433 K; CO:H_2 = 1:1; Syn gas pressure, 9.65 MPa; Agitation, 20 Hz; * = Ligand:Co, 3; T, 443 K .DPPE-e = 1,2-bis(diphenyl phosphino)ethene. DPPE-a = 1,2-bis(diphenyl phosphino)ethane. DPPP = 1,3-bis(diphenyl phosphino)propane. DPPH = 1,6-bis(diphenyl phosphino)hexane. Ald. = Aldehyde, Alc. = Alcohol, AA = Acetic acid, EA = Ethyl acetate, Branc. = Branched.*

1,2-*bis*(diphenyl phosphino) ethene and 1,2-*bis*(diphenyl phosphino) ethane (Run 1, 2) showed nearly similar behavior. 1,2-*bis*(diphenyl phosphino) propane (DPPP) had shown more activity at Co:DPPP ratio of 1 compared to the ratio of 3 (Run 3 ,4). In fact at DPPP:Co ratio of 3, the temperature required for reaction to occur was 443 K whereas at ratio 1 the reaction occurred at 433 K. Thus, it can be concluded that, as shown in the Scheme 3.3, the equilibrium between modified and un-modified catalytic species favors unmodified species at diphos: Co ratio of 1, whereas at higher ratios such as 3, the equilibrium favors modified species, which is less active (and so required higher temperature). With 1,2-*bis*(diphenyl phosphino)

$$HCo(CO)_3(P) \underset{+\,L}{\overset{+\,CO}{\rightleftharpoons}} HCo(CO)_4$$

Scheme 3.3. Modified-unmodified catalyst equilibrium

hexane (DPPH), AA formation was highest (Run 5). DPPH also showed higher tendency for aldehyde hydrogenation. All the diphosphine ligands showed poor aldehyde selectivity (below 40 %). High amount of AA formation (due to decomposition of VAM) was responsible for low chemoselectivity to aldehydes. Formation of aldehyde dimmers and acrolein was also observed in minor quantities in almost all the reactions. Interestingly, the diphosphine ligands showed better hydrogenating tendency than the monophosphine ligands. Both VAM as well as acetoxy aldehydes were hydrogenated. The linear: branched ratio of the alcohols was higher than that of the corresponding aldehydes. This result is consistent with the one observed for 1-hexene hydroformylation in Section 2.3.3.

It can be concluded from the above study of diphosphine-ligands that, Co-phosphine system was not suitable for hydroformylation of VAM. Side reactions such as hydrogenolysis of VAM, and decomposition of 3-ac pal, occurred predominantly, whereas, selectivity to hydroformylation was very poor.

3.3.5.3. Instability of acetoxy propanals in presence of Co-phosphine catalyst

The phosphine modified cobalt carbonyl catalysts are known to catalyze various reactions, of aldehydes *viz.* hydrogenation, oligomerization, and acetal-formation. Margheri *et al.* [xvi] have studied the use of phosphine-modified cobalt catalyst, for oligomerization of aldehyde and it's the only report of such study in the literature. Our results in the previous section have shown that, at higher phosphine concentration, the aldehyde selectivity was reduced (Table 3.7, Run 3 & 4). This can either be due to decomposition or oligomerization of aldehydes. In order to understand the instability of acetoxy propanals and to check whether the drop in aldehyde selectivity is uniform for both 2-ac pal and 3-ac pal, two pot reactions with a mixture of aldehydes and Co-TPP catalyst in toluene were carried out and the results are presented in Table 3.9.

The aldehyde mixture taken for this study composed of 58 % 2-ac pal and 42 % 3-ac pal. In the first reaction at the room temperature, 98 % of 3-ac pal vanished in 8 hrs, whereas, only 7 % of 2-ac pal was converted. Similar reaction at 373 K was very fast and within 3 hrs, ~ 99 % and 88 % of 3-ac pal and 2-ac pal respectively were consumed. Thus, 3-ac pal was found to be more vulnerable to the catalyst action. A cluster of small

peaks appeared in the GC chromatogram which when analyzed by GC-MS were found to be dimmers and trimers *etc*. of the ac-pals. Exact composition and quantification of products was not done, as the aim was only to establish the fact that extra phosphines act as a poison for ac-pals, especially 3-ac pal.

Table 3.9. Effect of temperature on the conversion of ac-pals by Co-TPP

Run no.	Temperature	Aldehyde	Time (hr.)			
			0.5	2	3	8
1	303	2-ac pal	97.9	95	-	93
		3-ac pal	89.8	62	-	2
2	373	2-ac pal	95	90	88	-
		3-ac pal	82.8	13.9	0.97	-

Reaction conditions: Toluene, 22.5 x 10^{-6} m^3; ac-pals, 0.8 kmol/m^3; 2-ac pal:3-ac-pal, 58:42; Co-TPP, 0.1 kmol/m^3(preformed before the reaction); Agitation, 20 Hz.

3.3.6. Effect of *N*-containing ligands

In the present section, experimental results on the preliminary evaluation of effects of various *N*-containing ligands on the activity and selectivity of the hydroformylation of VAM are presented. *N*-containing ligands such as pyridines, amines, amides, *etc.* are important modifiers for cobalt catalysts. Both phosphines and pyridines have nearly opposite effects on the activity of the hydroformylation reaction. Generally, phosphines impart extra stability to the cobalt carbonyl catalyst making it less active but more selective (higher linear/branched ratio)[xvii], whereas, pyridine increase the rate of hydroformylation, thus increasing the activity but scantily affecting the regioselectivity.[xviii]

Many ligands such as 1,10-phenanthroline, Shiff-base ligands such as salen; SMDPT, anthranilic acid, picolinic acid, nicotinic acid *etc* were found to be inactive for hydroformylation of VAM. They were tested under various reaction conditions and in different solvents but there was no syngas absorption when any of these ligands were used as Co-modifier. These ligands, in fact, acted as poison for Co-carbonyl catalyst by making it inactive. With ligands such as nicotinic acid, piconilic acid and anthranilic acid, precipitation of fluffy orange-pink complex was observed whereas with Shiff-base ligands like Salen and SMDPT brick red colored precipitation was observed. No

characterization of the precipitated complexes was done but we postulate that with their strong binding and chelating ability, most of these ligands must have replaced the carbonyl groups of $Co_2(CO)_8$. Experimental results on the use of other N-ligands such as amines and pyridines are presented in the following sections.

3.3.6.1. Effect of amines as ligands

Different primary, secondary and tertiary amines were used as ligands with $Co_2(CO)_8$ catalyst. In all the runs, ligands were added separately to the standard reaction charge. The results are presented in Table 3.10.

Run 1 in Table 3.10 was a reaction performed under standard conditions with unmodified $Co_2(CO)_8$ catalyst and was considered as a benchmark for comparison. Aryl amines such as triphenyl amine (TPA) and diphenyl amine (DPA) didn't pose much impact on the activity and selectivity pattern of cobalt-catalyzed hydroformylation of VAM (Run 2-5). The activity of TPA-modified cobalt carbonyl catalyst under different conditions (Run 2-4) was similar to the corresponding reactions with unmodified $Co_2(CO)_8$ catalyst. Even the TPA: Co ratio of 6 didn't make any impact on the conversion and selectivity of the hydroformylation of VAM (Run 4). With tribenzyl amine (TBzA) as a ligand, nearly complete conversion was achieved in 60 minutes with aldehyde regioselectivity of 0.96 (Run 6). But with TBzA ligand, alcohol formation was found to be higher compared to unmodified cobalt carbonyl catalyst. Tertiary alkyl amine ligands such as triethyl amine (TEA) and tributyl amine (TBA) didn't carry out hydroformylation at 393 K (Run 7,8). With TEA ligand, syngas absorption started only at 433 K temperature (Run7), whereas for TBA ligand the minimum temperature required for syngas absorption was 413 K (Run 8). Thus trialkyl amines were found to form a more stable cobalt complex compared to the triaryl amine ligands, which are active even at 393 K. TBA at 433 K showed poor performance and the reaction stopped in 15 minutes at 36 % conversion (Run 13).

Table 3.10. Amines as ligands

Run No.	Ligand	Run time	Lig. / Co	TEMP.	Press.	Conv.	Chemoselectivity				Regioselective. $	
							Ald	Alc.	AA	EA	Ald.	Alc.
		Min		K	MPa	%	%	%	%	%		
1	-	64	-	393	9.65	91.2	87.8	4.7	1	6.5	0.94	1.1
2	TPA	161	2	373	4.1	46.5	85.5	0	0	7.4	0.64	-
3#	TPA	90	3	393	9.65	98.1	86.2	4.3	0	9.1	1.0	1.2
4	TPA	60	6	393	9.65	92.6	89.1	4.9	0.9	3.9	0.94	1
5	DPA	147	2	393	4.14	71	93.5	0	3.9	2.5	0.74	-
6	TBzA	60	3	393	9.65	99.2	85.7	8.9	1	4	0.96	0.7
7	TEA	123	3	433	9.65	97.3	7.41	0	59.5	6.1	0.2	-
8	TBA	211	3	413	9.65	81.2	23.9	1.2	62.8	6.1	0.04	0.24
9	DBA	122	3	413	9.65	94.3	37.8	3.5	52.4	5.2	0.46	0.8
10	BA	169	3	393	9.65	95.5	50.4	1.8	43.0	3.0	0.05	0.2
11	MA	226	3	393	9.65	97.4	61	1.1	32.3	5.5	0.54	2.9
12*	CHA	162	3	393	9.65	83.9	47.7	3.1	32.1	5.8	0.03	0.3
13	TBA	15	3	433	11.3	36.6	65.7	0	20	12	0.03	-

*Reaction conditions: Toluene, 22.5 x 10^{-6} m^3; $Co_2(CO)_8$ = 0.012 kmol/m^3; VAM = 1.21 kmol/m^3; Co:H_2 = 1:1; Total charge, 25 x 10^{-6} m^3; Agitation, 20 Hz; # = Solvent, DCM; * =Methyl amine is a 33% solution in ethanol; $ = Linear/Branched ratio; TPA = Triphenylamine; DPA = Diphenylamine; TBzA = Tribenzylamine; TEA = Triethylamine; MA = Methyl amine; CHA = Cyclohexyl amine; BA = Butyl amine; DBA = Dibutyl amine; TBA = Tributylamine; All the reactions were run till complete absorption*

Like tertiary phosphine ligands such as TBP, TPP (Table 3.7 Run 3,7-9), tertiary amine ligands also lead to the formation of large amount of acetic acid (AA) and propanal. In these reactions, the chemoselectivity to the desired acetoxy propanals was very low, 7.4 % with TEA and 23.9 % with TBA. With TBA, nearly 100 % regioselectivity for 2-ac pal was observed with Linear: Branched ac pal ratio of 0.04.

Runs 8, 9 and 10 in Table 3.10 revealed an interesting effect of basicity of tertiary amine – tributyl amine (TBA), secondary amine – dibutyl amine (DBA) and primary amine – butyl amine (BA), on the hydroformylation of VAM. Because of the inductive effect of the butyl groups, the basicity of the alkyl amine ligands increase in the order of primary amine < secondary amine < tertiary amine *e. g.* BA < DBA < TBA. With BA, the Cobalt catalyst was active at 393 K (Run 10), albeit slower than the unmodified

$Co_2(CO)_8$ catalyst (Run 1). With DBA the cobalt catalyst was inactive at 393 K and 403 K but showed adequate activity at 413 K (Run 9) whereas with TBA, the catalyst was not only inactive at 393 K and 403 K but was very slow even at 413 K with nearly 1/3 rd reaction rate compared to DBA (Run 8). Thus, the increasing basicity of primary – secondary and tertiary butyl amines showed an inverse effect on the activity of the modified cobalt catalyst formed. The chemoselectivity to acetoxy propanals was 50.4 %, 37.8 %, and 23.9 % for reactions with BA, DBA and TBA ligands respectively, thus showing an inverse effect of basicity. AA formation increased from 43 % to 52.4 % and 62.8 % on using BA, DBA and TBA respectively. Less basic methyl amine (MA) ligand showed better activity compared to BA by giving products with 61 % chemoselectivity to acetoxy propanals (Run 11). Cyclohexyl amine (CHA) modified cobalt catalyst showed nearly comparable results with BA in terms of aldehyde chemoselectivity and regioselectivity but was less active (Run 12). Thus, the results clearly show a retarding effect of ligand-basicity on the activity and chemoselectivity of the cobalt catalyzed hydroformylation of VAM.

None of the amine ligands tested could improve the linearity of the acetoxy propanals beyond *l/B* ratio of 0.94, which was obtained with unmodified $Co_2(CO)_8$. With unmodified cobalt catalyzed hydroformylation of VAM, small amount of hydrogenation products were observed (Table 3.5 Runs 3-5). Modification with amine ligands didn't alter this tendency of hydrogenation but the total hydrogenation products (EA and acetoxy propanols) were always limited to the maximum of 13-15 %. In almost all the reactions the formation of EA was in the range of 4 % -6 %. Linearity in the acetoxy propanols was found to be higher than the corresponding aldehydes, indicating more preference to the hydrogenation of linear aldehyde 3-ac pal.

The alkyl amine modified cobalt catalysts were found to be stable as in spite of formation of large amount of AA in the VAM hydroformylation reaction, no formation of $Co(acetate)_2$ (Pink precipitate) was observed. The color of the final solutions of all the reactions was brown (without any precipitation) except for a reaction with TEA where a purple precipitate was obtained along with colorless solution (Run 7).

From the results, it can be concluded that amine modification didn't improve the activity and chemoselectivity hydroformylation of VAM over the unmodified catalyst. Aryl amine ligands showed comparable results with $Co_2(CO)_8$, but alkyl amines showed very poor activity and catalyzed side reactions in preference to hydroformylation.

3.3.6.2. Pyridines as ligands

A typical concentration-time profile of a pyridine-modified cobalt catalyzed VAM hydroformylation is shown in Figure 3.6. Under identical conditions, reaction with unmodified Cobalt catalyst (Figure 3.4A, Table 3.6 Run 1) didn't show total conversion. Thus, with modification of pyridine, found to enhance the activity for hydroformylation with more than 90 % conversion in 35 minutes compared to the 72.8 % conversion in 90 minutes with the unmodified catalyst. No side product, except EA (4%), was observed. Both 2-ac pal and 3-ac pal were formed in almost equal quantities.

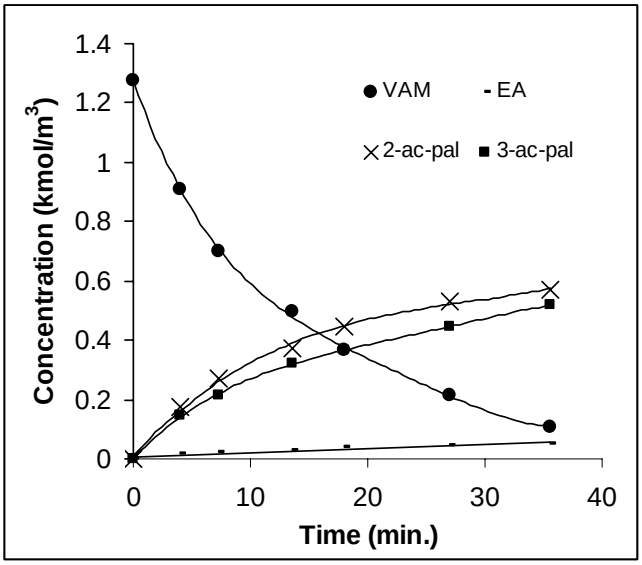


Figure 3.6. Concentration-time profile of a pyridine-modified cobalt catalyzed hydroformylation of VAM

Reaction conditions: VAM, 1.3 kmol/m^3; $Co_2(CO)_8$, 6 x 10^{-3} kmol/m^3; Pyridine, 36 x 10^{-3} kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; Temperature, 393 K; Pressure, 4.1 MPa; Agitation, 20 Hz.

Pyridines (mono-, bi- and tri-) and substituted pyridines were tested for cobalt catalyzed hydroformylation of VAM under different conditions and the results are presented in following three sections.

3.3.6.2.1. Effect of parameters

Experimental results on the preliminary study of the effects of various parameters on the activity and selectivity of the pyridine modified cobalt-catalyzed hydroformylation of VAM are presented in Table 3.11.

Table 3.11. Cobalt catalyzed hydroformylation of VAM with pyridine as a ligand

Run No.	Run time	$Co_2(CO)_8$ x 10^{-3}	TEMP	Py/Co	Conv.	Selectivity [b]			Regioselectivity		Initial rate x 10^3
						Ald	AA	EA	I	II	
	Min	Kmol/m^3	K		%	%	%	%			Kmol /m^3/s
1	328	12	373	-	58.2	96.1	0	2.1	40	60	0.1
2	249	12	373	3	88.8	88.4	6.5	4.1	31.5	68.5	0.14
3	172	12	373	9	60.5	42.2	40.1	4	18.7	81.3	0.43
4	90	6	393	-	72.8	94.4	0	4.8	47.1	52.9	0.7
5	35	6	393	3	91.4	93	0	4.4	47.4	52.6	2.1
6 #	66	6	393	3	80.2	76.2	20	3.4	35.9	64.1	2
7 @	15	-	453	3	40.6	40.7	29.3	30	20.0	80.0	10
8 *	40	12	393	3	67.1	70.1	23.3	4	27.0	73.0	1.0

*<u>Reaction conditions:</u> Toluene, 22.5 x 10^{-6} m^3; VAM = 1.3 kmol/m^3; Temperature, 393K; Pressure = 4.1 MPa; CO:H_2, 1:1; Agitation, 20 Hz. b = No alcohol formation observed, propanal is observed whenever AA is formed. # = VAM, 2.66 kmol/m^3. Py = Pyridine. @ = Co(acetate)$_2$, 24 x 10^{-3} kmol/m^3; Induction period of 12 minutes. * = DCM solvent; Pressure, 12.41 MPa.*

At 373 K, the pyridine modified cobalt complex was found to catalyze the hydroformylation of VAM to ~ 90 % conversion in 250 minutes as compared to only 58 % in 328 minutes, with unmodified cobalt catalyst (Run 1,2). With modification of pyridine, the initial rate was found to increase from 0.1 x 10^{-3} kmol/m^3 to 0.14 x 10^{-3} kmol/m^3, but the product linearity was found to decrease. Also, chemoselectivity to aldehydes was found to decrease from 96.1 % to 88.4 % with increase in the formation of AA and EA after modification with pyridine. On increasing the pyridine/Co ratio from 3

to 9, the initial rate was found to increase more than four times compared to the unmodified cobalt catalyst, but at the cost of conversion and aldehyde-selectivity (Run 3). With increase in pyridine concentration, product linearity decreased with substantial increase in AA formation. Along with AA, acrolein and propanal formation also increased indicating decomposition of 3-ac pal due to increased pyridine. Thus, at 373 K, pyridine modification helped the activity of the cobalt carbonyl catalyst, but at the cost of aldehyde selectivity. As shown in the Figure 3.7, longer run times required at 373 K must have augmented the side reaction of AA formation.

At 393 K, the effect of pyridine modification was very evident, showing three

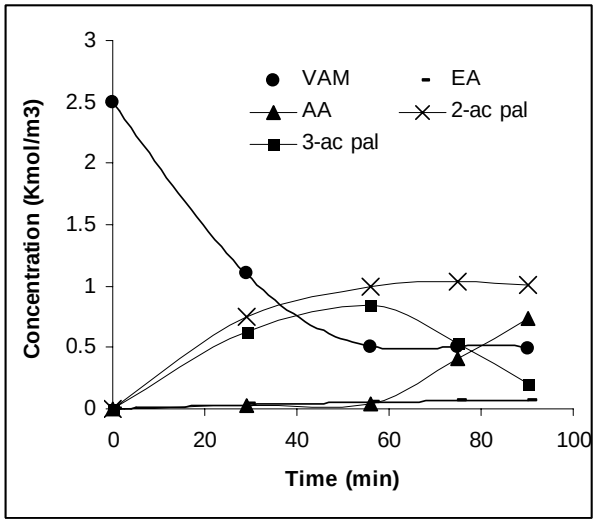


Figure 3.7. Enhanced formation of acetic acid in pyridine-modified cobalt catalyzed hydroformylation of VAM
Reaction conditions: Same as those of Run 6 in Table 3.11.

fold increase in the initial rates with Pyridine/Co ratio of 3 (Run 4,5). Even at this temperature, pyridine modification helped to achieve 91.4 % conversion as compared to the 72.8 % conversion with unmodified catalyst. Chemoselectivity and regioselectivity of ac-pals in both the cases was nearly same. Thus, at 393 K, pyridine modification greatly helped to increase the activity of cobalt carbonyl catalyst, without affecting the selectivity of the reaction. The syngas absorption profiles shown in Figure 3.8 clearly demonstrate the positive effect of pyridine modification on hydroformylation activity of cobalt carbonyl catalyst. Increase in VAM concentration from 1.3 Kmol/m^3 to 2.66 Kmol/m^3,

inversely affected the conversion, and augmented the AA formation reducing the chemoselectivity of ac-pals and regioselectivity of 3-ac pal (Run 6).

In Run 7, Co(acetate)$_2$ was used as a catalyst precursor. With pyridine as ligand, we thought that the formation of active hydroformylation catalyst (hydrido carbonyl) from Co(acetate)$_2$ would take place at lower temperature than the otherwise required 453 K. But, the reaction didn't take place at temperatures lower than 453 K (Runs not reported). At 453 K, an induction period of 12 minutes was observed. After the induction period, the reaction was very fast with initial rate of ~ 0.01 Kmol/m^3 as compared to 0.0021 kmol/m^3 at 393 K. But the reaction stopped abruptly after 3 minutes after the induction period and showed only 40 % conversion. The selectivity to aldehydes was only 40 % with selectivities for AA and EA of 40 % and 30 %. Syngas mass transfer limitations must be responsible for the abrupt end of the reaction and catalyst

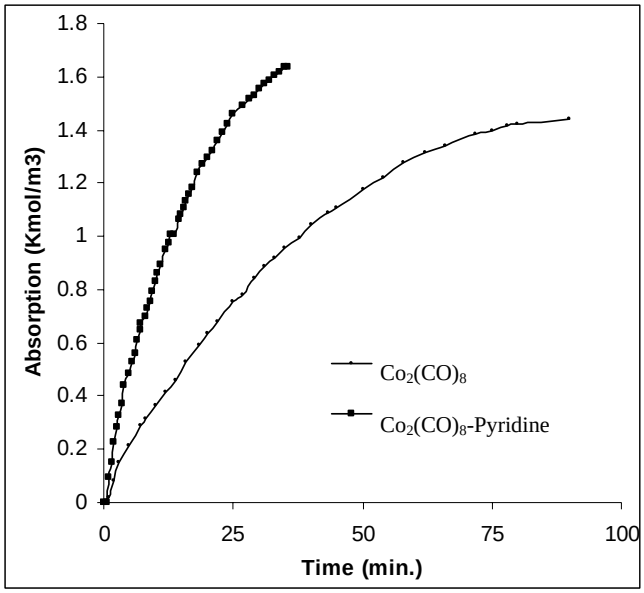


Figure 3.8. Comparison of syngas absorption profiles of pyridine-modified and unmodified $Co_2(CO)_8$ catalyzed hydroformylation of VAM

Reaction conditions: Same as those of Run 4 &5 in Table 4.11

deactivation. One reaction of pyridine modified $Co_2(CO)_8$ catalyst system in DCM solvent was taken with an aim to improve the aldehyde linearity as shown in Section 3.3.9.2. The results were rather unexpected, with decrease in the activity of Co-pyridine

catalyst system (Run 8, Initial rate came down to 0.001 Kmol/m^3 compared to 0.0021 Kmol/m^3 in toluene solvent). The reaction stopped at 67 % conversion with only 70 % selectivity to ac-pals and *linear /branched* ratio of 27 / 73. Thus, halogenated solvents were not found to be suitable for Co-pyridine catalyst system.

In all the reactions of hydroformylation of VAM with Co-pyridine catalyst system, the side reaction of aldehyde hydrogenation to alcohols was either absent or very minor (> 1 %), but AA formation was found to be higher compared to that with unmodified cobalt catalyst. Along with AA, propanal was also formed in proportion. A study of a concentration-time profile of Run 6 in Table 3.11 revealed an interesting observation of substantial increase in AA formation when VAM conversion was stopped. AA was formed by decomposition of 3-ac pal (Scheme 3.2). Acrolein formed by this decomposition of 3-ac pal, must have been hydrogenated to propanal. It is known in the literature that acrolein under hydroformylation conditions give propanal and not the hydroformylation product[xix]. More discussion on AA formation is given in Section 3.3.11.

From the study of the Co-pyridine catalyst system for hydroformylation of VAM, it can be concluded that pyridine modification substantially improves the cobalt carbonyl activity (nearly three times increase in the initial rate). Compared to the plain cobalt carbonyl catalyst, pyridine modified catalyst didn't show any effect on the regioselectivity of the aldehyde products, but longer run times and higher pyridine concentration (especially at temperatures higher than 393 K) led to the decomposition of 3-ac pal leading to substantial loss in chemoselectivity and regioselectivity of the hydroformylation reaction.

3.3.6.3. Bipyridine and terpyridine as ligands

Since, the modification of pyridine increased the activity of the cobalt carbonyl catalyst without increase in the product linearity, some reactions with bipyridine (bipy) and terpyridine (terpy) as ligands were taken hoping that the chelating-ability and bulkiness of these ligands would show a positive effect on the product linearity. The results with bipy and terpy as ligands are presented in Table 3.12.

Table 3.12. Cobalt catalyzed hydroformylation of VAM with chelating pyridines as ligands

Run No.	Ligand (L)	Run time	L / Co	Temp	Conv.	Selectivity [b]			Regioselectivity		Initial rate x 10^3
						Ald.	AA	EA	I	II	
		Min		K	%	%	%	%	%	%	kmol/m^3/s
1	Terpy	60	1	413	0	-	-	-	-	-	-
2*	Terpy	60	1	393	0	-	-		-	-	-
3	Terpy	89	0.33	413	24.5	75.2	11.8	9.9	5	95	0.24
4[a]	Terpy	10	0.33	413	24.8	81.5	10.4	7.2	38	62	1.02
5*	Terpy	212	0.33	393	95.2	91.4	0	2.6	45	55	0.27
6	Bipy	60	1	393	0	0	0		-	-	0
7[$]	Bipy	60	1	413	2.2	0.64	0		-	-	0
8*[$]	Bipy	120	0.5	393	97.8	84.1	13.2	2.7	32	68	0.27

*<u>Reaction conditions:</u> VAM, 1.3 kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; $Co_2(CO)_8$, 6 x 10^{-3} kmol/m^3 ; Temperature = 393 K; Pressure = 4.1 MPa; CO:H_2, 1:1; Agitation, 20 Hz. L/Co = Ligand/Co. Terpy. = Terpyridine. Bipy. = Bipyridine; b = No alcohol formation observed, propanal is observed whenever AA is formed; * = 2 x 10^{-6} m^3 acetone is used as a co-solvent. a = Preformed catalyst, addition device used; $ = Pressure, 12.3 MPa; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3*

When terpy was used as a ligand with ligand:Co ratio of 1:1, the reaction didn't take place at temperatures 393 K, 403 K (Runs not reported) and 413 K (Run 1). Orange colored precipitate was observed in all these reactions, indicating the formation of a toluene-insoluble complex from $Co_2(CO)_8$ and terpy. This complex was found to dissolve in acetone and so Run 2 was performed with 2 x 10^{-6} m^3 acetone as a co-solvent. In this run, no precipitation was observed and the final reaction solution was orange-red but without any syngas absorption. Considering the highly chelating nature of terpy as a ligand, we hypothesized that it must be forming a stable non-carbonyl complex with cobalt. To avoid the formation of a non-carbonyl complex, in the subsequent runs, terpy concentration was reduced to 0.3 molar equivalent to cobalt. Even at terpy : Co ratio of 0.3, no reaction was observed at 393 K and 403 K (Runs not reported). At 413 K, after an induction period of 52 minutes, the reaction started but stopped immediately after ~ 24 % conversion (Run 3). To avoid the induction period, in Run 4, the active catalyst of Co-terpy was preformed at 413 K for 30 minutes and the reaction was started by addition of

VAM with the help of addition device. Even in this reaction the conversion was limited to 24 % only. AA formation was observed in both the reactions but it was nearly halved (6.4 %) in the reaction with preformed catalyst. In Run 4, chemoselectivity to aldehyde was increased from 75 % to 85 % and so also the linearity of ac-pals. Nevertheless, red precipitate formed in both the reactions, indicated a need for co-solvent. In Run 5, 2 cm^3 acetone was used as a co-solvent with terpy:Co ratio of 0.3 and nearly complete conversion (95 %) of VAM was observed with 91 % chemoselectivity to ac pals and linear : branched ratio of 45:55. The activity of this Co-terpy catalyst system was less than plain $Co_2(CO)_8$ catalyst but it must be more stable than unmodified $Co_2(CO)_8$ catalyst, as it could give 95 % conversion as compared to 72 % with $Co_2(CO)_8$ (Run 4 in Table 3.11). Thus, it can be concluded that terpy, at 1:1 ratio with Co, forms a chelating complex, which shows no activity for hydroformylation (Run 2 Table 3.12) however the complex formed at 0.3:1 ratio is less active but more stable than plain $Co_2(CO)_8$ catalyst and leads the reaction to nearly complete conversion (Run 5 Table 3.12).

Bipy ligand showed similar results as that of terpy. At bipy:Co ratio of 1, no conversion of VAM was observed at 393 K and 4.1 MPa syngas pressure (Run 6 in Table 3.12). Even at 413 K, three time higher syngas pressure (12.4 MPa) and double catalyst concentration (0.012 $Kmol/m^3$), there was no reaction observed (Run 7). In both these reaction brown precipitate was observed after opening the reactor. Thus, similar to the observations with terpy, we concluded that bipy must have also been forming a chelating complex with cobalt, making it inactive. Hence, in Run 8, bipy:Co ratio of 0.5 was taken and 2 cm^3 acetone was added as a co-solvent. Nearly 98 % conversion of VAM was found to take place but chemoselectivity to aldehydes was less at 84 % and the linear : branched ratio was also reduced to 32:68, mainly due to formation of AA (13 %).

From the study of bipy and terpy as ligands for cobalt-catalyzed hydroformylation of VAM, it can be concluded that the strong chelating abilities of nitrogen atoms of bipy and terpy made the cobalt carbonyl catalyst less active for hydroformylation. The steric and electronic effects of these chelating ligands didn’t impart any positive effect on the linearity of ac pals.

3.3.6.4. Substituted pyridines as ligands

Pyridines substituted at position/s 2,3,4, and 6 were used as ligands for cobalt catalyzed hydroformylation of VAM and the results are presented in Table 3.13. The main aim of this work was to study the effects of steric, electronic as well as coordinating abilities of these ligands on activity and regioselectivity.

Table 3.13. Cobalt catalyzed hydroformylation of VAM with substituted-pyridines as ligands

Run No.	Ligand	Run time	Conv.	Selectivity [b]			Regioselectivity		Initial rate x 10^3
				Ald.	AA	EA	I	II	
		Min	%	%	%	%	%	%	Kmol/m^3/s
1	3-phenylpyridine	40	95.2	93.3	0	6.7	44.1	55.9	2.47
2	4- acetylpyridine	99	89	59.3	30.4	4.5	10.7	89.3	0.94
3#	2-Chloropyridine	58	50	85	1.1	4.4	28.1	71.9	0.92
4$#	2-Chloropyridine	8.5	32.4	58.9	8.3	20.3	28.1	71.9	3.80
5	2-acetylpyridine	27	21.9	69.2	12.9	5.3	11.5	88.5	0.35
6	2.3-dihydroxy pyridine	7	11.2	73.2	-	-	37.9	62.1	0.44
7	2-hydroxy,5-nitropyridine	45	14.8	66.9	-	-	35.9	64.1	0.07
8	2,6- Bis(chloro methyl) pyridine	15	15.9	73.9	-	4.0	20.0	80.0	0.25
9*	2,6-dimethyl pyridine	53	89.3	75.7	22.1	2.0	32	68	1.1

*Reaction conditions: VAM, 1.3 kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; $Co_2(CO)_8$, 6 x 10^{-3} kmol/m^3; Lig / Co = 3; Temperature = 393K; Pressure = 4.1 MPa; CO:H_2, 1:1; Agitation, 20 Hz. b = propanal is observed whenever AA is formed. $ = Temperature 413 K. # = ~ 10-12 % 3-ac pal converted to 3-ac pol. * = $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Pressure, 9.65MPa*

In the previous section it was observed that the chelating ligands with two or three nitrogen donor atoms, such as bipy and terpy respectively, made cobalt carbonyl catalyst less active for hydroformylation and such chelation didn't improve the product linearity. In this section pyridine ligands, with potential secondary coordinating groups such as chloro, acetyl, hydroxy *etc* at the adjacent position/s (2, 6 *etc*) of nitrogen, were used as ligand. Cobalt carbonyl with 3-phenyl pyridine gave 95.2 % conversion of VAM with 93.3 % selectivity to ac-pals and linear: branched ratio of 44:56 (Run 1). The initial rate of this reaction was 2.5 Kmol/m^3, which is substantially higher than that of unmodified

$Co_2(CO)_8$ and marginally higher than Co-pyridine system (Run 4, 5 in Table 3.11). Thus, 3-phenyl pyridine behaved nearly similar to pyridine as a ligand and there was a nearly negligible steric or electronic effect of substitution of phenyl ring at position 3. With 4-acetyl pyridine as a ligand, the reaction was slower and less selective to aldehydes (Run 2), compared to the reaction with pyridine. Substantial formation of AA was responsible for less aldehyde selectivity and product linearity in this reaction.

With 2-chloro pyridine as ligand, the reaction was very slow and stopped at 50 % conversion (Run 3). The same reaction at higher temperature of 413 K, stopped at 32 % conversion in 8.5 minutes. Substantial hydrogenation was observed in both the reactions. At 393 K (Run 3), 13 % 3-ac pol was formed. Surprisingly, no 2-ac pol was observed. At 413 K, hydrogenation of VAM to EA was a prominent reaction with 20 % selectivity to EA, 3-ac pol was also observed with 6 % selectivity. Thus, due to the presence of electron donating chloro group at *ortho*-position, the basicity of pyridine increases and hydrogenation is augmented. With 2-acetyl pyridine, the syngas absorption stopped at 22 % conversion (Run 5). Similar inactivity was observed for reactions with 2,3-dihydroxy pyridine, 2-hydroxy-5-nitro pyridine and 2,6-bis(chloromethyl) pyridine as ligands (Run 6, 7, 8). All these ligands contain coordinating groups at *ortho* positions. Thus, overall, it can be concluded that *ortho*-substitution to pyridine, of potentially coordinating groups such as acetyl, chloro, and hydroxy, makes it a bidented ligand, which forms a chelating complex with cobalt replacing the carbonyl groups. Thus, these ligands act more or less in the same way as that of bipyridine. Run 9 was taken with 2,6-dimethyl pyridine, at double catalyst (0.012 $Kmol/m^3$) and double syngas pressure (9.6 MPa) as compared to the other reactions in the Table 3.13. In this reaction, 89 % conversion and 75 % aldehyde selectivity was obtained with AA formation increased to 22 % and linear : branched ratio decreased to 32:68 compared to 0 % and 47:53 respectively for pyridine. 2,6-dimethyl pyridine has Methyl groups at both the *ortho*-positions of pyridine; still it could modify the cobalt carbonyl catalyst to give 89 % conversion whereas with coordinating groups such as hydroxy, chloro, and acetyl the conversion never exceeded 20 %. This clearly illustrates that steric hindrance due to methyl groups from both the sides of pyridine-nitrogen didn’t play as important role as the chelating ability of the

coordinating groups at the *ortho*-position, which make cobalt carbonyl inactive for hydroformylation.

Overall, it can be concluded from the study of nitrogen containing ligands for cobalt-catalyzed hydroformylation of VAM, that activity enhancement over the unmodified cobalt carbonyl catalyst is possible with these ligands but none of the ligands tested could improve upon the linearity of the ac pals product. Also, in many cases, such modification enhanced the decomposition of unstable 3-ac pal thus reducing the chemo- and regioselectivity of hydroformylation.

3.3.7. Triphenyl arsine as ligand for cobalt catalyzed hydroformylation of VAM

Table 3.14. Cobalt catalyzed hydroformylation of VAM with triphenyl arsine as ligand

Run No.	AS / CO	Temp	Press.	Conv.	Selectivity				Regioselectivity @		TOF
					Ald.	Alc.	AA	EA	Ald.	Alc.	
		K	MPa	%	%	%	%	%			h^{-1}
1	**-**	393	12.4	98.9	88.5	8.5	0	2.8	0.94	1.1	93.8
2	**0.25**	393	12.4	97	87.4	9.2	0	2.4	0.95	1.23	180
3	**0.5**	393	12.4	97.7	83.6	10.4	1.4	2.4	0.92	1.4	237.6
4	**1**	393	12.4	96.2	84.6	11.4	1.2	2.3	0.90	1.7	204.7
5	**3**	393	12.4	89.2	83.9	11.4	1.4	2.3	0.87	2.6	128.9
6	**3**	393	4.1	59.7	86.5	8.1	3	2.3	0.86	4.2	93.7
7	**3**	413	4.1	88	75.4	11.2	7.1	4.8	0.97	4.3	267.8
8	**1.5**	413	4.1	91.9	73.8	9.6	8.3	7.7	0.76	3.7	750
9 $	**3**	393	12.4	80.1	84	10.3	0.4	2.5	0.96	5.1	65
10 $	**3**	413	9.3	35.7	77.2	10.3	4	8.5	0.69	13	41.3
11 *	**3**	413	4.1	92.1	75.3	11.1	10.9	1.4	0.88	3.5	412.5
12 *	**9**	413	4.1	69.4	72.6	17.0	10.4	1.2	0.98	4.9	206.2

*Reaction conditions: VAM, 1.3 kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3 ; $CO:H_2$, 1:1; Agitation, 20 Hz. TOF is calculated at the time of ~ 20 % of the total absorption. As/Co = Triphenyl arsine/Co. @ = Linear/Branched ratio. $ = Solvent, DCM. # = $Co_2(CO)_8$ = 6 x 10^{-3} kmol/m^3 . * = $CO:H_2$, 1:2.*

In the periodic table, element arsenic (As) appears in the Group VA, below elements 'N' and 'P' with same outer shell electronic configuration and their analogous compounds show comparable electronic properties. Like *N*- and *P*- compounds, many organic arsine compounds act as electron donating lignads in many organometallic

complexes of transition metals. In the present section we have used triphenyl arsine as a ligand to check its effect on the activity and selectivity of the cobalt catalyzed hydroformylation of VAM. Since the study of *P*-containing and *N*-containing ligands showed a strong dependence on the reaction parameters, triphenyl arsine (TPAs) was tested under different conditions and the results are presented in Table 3.14.

Run 1 of Table 3.14 was taken as a standard run with unmodified $Co_2(CO)_8$ and its results are considered as a benchmark for comparison with TPAs modified catalyst. Run 2-5, show the effect of As/Co ratio in the range of 0.25 to 3, on the activity and selectivity. All these reactions showed 90 % or higher conversion, with ~ 95 % selectivity to the hydroformylation products (ac pals and as pols), with selectivity to AA between 1.2-1.4 % and to EA between 2.3-2.8. Modification of cobalt carbonyl with TPAs enhanced the side reaction of aldehyde hydrogenation. Thus, even at As/Co ratio of 0.25, 9.2 % ac pols were obtained as compared to the 8.5 % with unmodified catalyst. Regioselectivity (linear/branched ratio) for alcohols (ac pols) was higher than that of aldehydes (ac pals), indicating more selective hydrogenation of 3-ac pal compared to 2-ac pal. This observation is consistent with the results obtained for 1-hexene

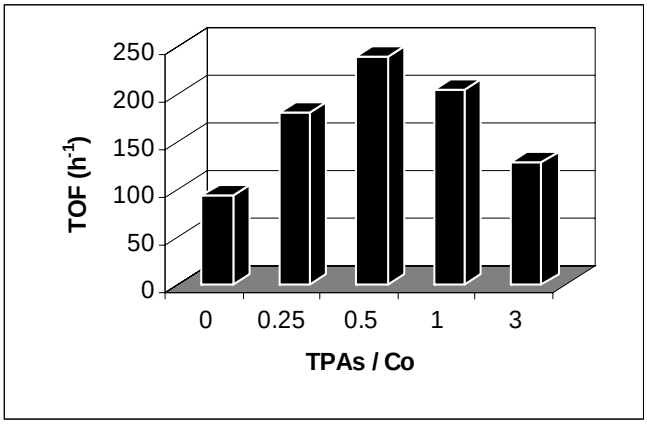


Figure 3. 9. Effect of TPAs/Co ratio on hydroformylation of VAM

Reaction conditions: Same as those for reaction 1-5 in Table 3.14

hydroformylation with TBP modified cobalt carbonyl catalyst system (Section 2.3.3). With the increase in As/Co ratio, the linearity of alcohols was found to increase, whereas aldehyde linearity was found to decrease marginally, mainly because of selective

hydrogenation of linear aldehyde. Even though, increase in As/Co ratio enhanced aldehyde hydrogenation, VAM hydrogenation to EA was not affected. The most prominent effect of As/Co variation was observed on the TOF. The TOF calculated at ~ 20 % conversion of each reaction, was found initially to increase with the As/Co ratio and then decreased with a maximum TOF at ratio 0.5. The results can be more clearly visualized in Figure 3.9.

When reaction was carried out at reduced pressure of 4.1 MPa (Run 6, Table 3.14) compared to 12.4 MPa of Runs 1-5, it stopped at 59.7 % conversion and the TOF was reduced to 98 h^{-1} as compared to 128 h^{-1} at 12.4 MPa syngas pressure (Run 5). The reason behind this substantial decrease in activity may be, the difficulty in the formation of active hydroformylation catalyst species at lower pressures as shown in Scheme 3.4.

$$Co_2(CO)_8 + 2AsPh_3 \rightleftharpoons CO_2(CO)_6(AsPh_3)_2 + 2CO \quad \text{..... (1)}$$

$$CO_2(CO)_6(AsPh_3)_2 + H_2 \rightleftharpoons 2\,HCo(CO)_3(AsPh_3) \quad \text{..... (2)}$$

Scheme 3.4. Formation of arsine modified cobalt carbonyl catalyst

Step 2, in this two-step synthesis, must be hindered due to lower hydrogen partial pressure.[xx] From the literature it is clear that higher temperatures can accelerate the formation of the active hydroformylation complex.[xxi] Thus, in the reaction at 4.1 MPa pressure and 413 K temperature (Run 7), 88 % conversion of VAM with TOF of 269 h^{-1} was obtained. Due to higher temperature, side products, such as ac pols, AA and EA were also formed in slightly higher quantities *viz* 11.1 %, 7.2 % and 4.8 % respectively. Under the same conditions of Run 7, when the As/Co ratio was reduced from 3 to 1.5 (Run 8), TOF shot up to 750 h^{-1} from 269 h^{-1}, but at the cost of aldehyde-linearity (l/b ratio decreased from 0.97 to 0.76). Two reactions were carried out in DCM solvent, at 393 K and 413 K, but the conversions were low at 80 % and 39 % respectively, with poor TOFs for both the reactions (Run 9, 10). EA formation was increased for the reaction at 413 K (Run 10) and no improvement in product linearity was observed in both the reactions. Thus, DCM was not found to be a suitable solvent for triphenyl arsine ligand. Since the aldehyde hydrogenation was higher with triphenyl arsine ligand, two reactions were taken at CO: H_2 ratio of 1:2 instead of usual 1:1 (Runs 11,12). With As/Co ratio of 3, the CO: H_2 ratio of 1:2 was found to enhance the activity of the catalyst by improving the TOF to

412 h^{-1} from 267 h^{-1}at $CO:H_2$ ratio of 1:1 (Run 7). Product linearity was reduced slightly, but surprisingly increased H_2 partial pressure showed no effect on alcohol formation. Under $CO:H_2$ ratio of 1:2, when the As/Co ratio was increased from 3 to 9, the alcohol formation was enhanced from 11 % (Run 11) to 17 % (Run 12) but the TOF was reduced to 206 h^{-1}. The product linearity for this reaction (Run 12) was highest among all the reactions with TPAs ligand, thus showing the positive effect of excess ligand addition.

It can be concluded from the above study of preliminary effect of parameters that TPAs is the best ligand among all the tested phosphines, diphosphines, amines and pyridines as far as both activity and selectivity are concerned. Either high syngas pressure (12.4 MPa at 393 K) or high temperature (413 K for 4.1 MPa pressure) are required for TPAs reaction to obtain proper activity and selectivity. Nevertheless, TPAs modified $Co_2(CO)_8$ didn't show substantial improvement over unmodified $Co_2(CO)_8$ in terms of the product linearity.

3.3.8. Promoters for cobalt catalyzed hydroformylation of VAM

As stated in the introduction (Section 3.1), researchers from Shell Oil Company have obtained many patents on the use of quaternary salts; halide salts of alkali and alkaline earth elements; transition metal acetates *etc*, as promoters for cobalt-catalyzed hydroformylation of ethylene oxide (EO). These patents claim that the use of these promoters with cobalt enhanced the rate of hydroformylation of EO. Other than these patents, hydroformylation literature doesn't show any report on the use of such promoters and their effect on activity and selectivity of the products. We have taken up this study for hydroformylation of VAM with an aim of improving the activity and selectivities of the reaction. In the present section, we have used the same promoters used by Shell for cobalt-catalyzed hydroformylation of VAM. Promoters at various concentrations were tested under standard conditions of hydroformylation of VAM and the results are presented in Table 3.15.

Run 1 in the Table 3.15 was taken as a standard reaction with only $Co_2(CO)_8$ (without any promoter), for comparison of the results of other reactions. Among the alkali metal salts, LiCl was tested at Co: Li ratio of 1, in which poor results with conversion 78.3 %, aldehyde selectivity 60.4 % and *l/b* ratio of 0.33, were obtained (Run

2). With LiCl, the initial rate of syngas absorption was increased to 1.6 kmol/m^3/s compared to the standard 0.98 kmol/m^3/s (Run 1), but AA was formed considerably with 27 % selectivity. Thus, LiCl had promoted the cobalt-catalyzed hydroformylation of VAM, but with poor selectivities.

Table 3.15. Effect of promoters on cobalt-catalyzed hydroformylation of VAM

Run No.	Promoter[1]	Pro / Co	Conv.	Selectivity				Regioselectivity (l/b) @		Initial rate x 10^3
				Ald.	Alc.	AA	EA	Ald.	Alc.	
			%	%		%	%			kmol/m^3/s
1	-	-	98.9	88.5	8.5	0	2.8	0.95	1.1	0.98
2	LiCl	1	78.3	60.4	0	27	2.7	0.33	-	1.6
3	Cs-acetate	0.5	39.7	88.2	3.1	2.8	8	0.40	1	0.37
4 #	PTSA	2	24.7	72	0	20.8	4.1	0.50	-	-
5 #	PTSA	1	95	75.7	3.5	12.6	8.6	0.76	0.8	0.13
6	TEAB	1	85.6	90.7	6	0	3.3	0.91	0.9	1.3
7 $	TEAB	1	96.3	93.8	0	0	2.7	0.93	-	1.1
8	TBAB	1	0	0	0	0	3.1	-	-	-
9	TBAC	1	83.7	77	4.9	14.3	3.7	0.57	0.8	0.37
10	TBAC	0.065	99.3	88.5	8.8	0	2.6	0.93	0.9	1.1
11	TBAB	0.065	99	87	9.9	0	2.7	0.98	0.84	0.74
12	TBAI	0.065	98.9	88	9.1	0	2.5	0.95	0.8	0.91
13	TBPB	2	5	0	0	0	2.6	-	-	-
14	TBPB	0.5	5	0	0	0	2.6	-	-	-
15	TBPB	0.065	94	90.1	6.3	0	3.5	0.92	0.95	0.74

Reaction conditions: VAM, 1.3 kmol/m^3; Toluene, 22.5 x 10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature = 393 K; Syngas, 12.7 MPa; CO:H_2, 1:1; Agitation, 20 Hz. @ - l/b = linear/branched. 1 = Promoter names in full form are given in Appendix I. $ = Bromobenzene solvent, no aldehyde hydrogenation. # = Temperature 413K.

Another alkali metal salt, cesium acetate was tested at promoter/Co ratio of 0.5 (Run 3) and it showed bad performance with only 39.7 % conversion at 1/3rd rate of standard reaction. Thus, alkaline earth promoters, which promoted hydroformylation of EO,[xiv] were not suitable for hydroformylation of VAM. *P*-toluene sulfonic acid (PTSA) was used as a promoter at 393 K and 413 K (Run 4,5), but the reactions didn't take place. In a reaction with PTSA/Co ratio of 2, large amount of AA was formed (21 % selectivity)

and the conversion was only 24 % (Run 4). At PTSA/Co ratio of 1, the reaction was very slow but could attain 95 % conversion and 75.7 % selectivity to aldehydes (Run 5). In both these reactions, the product linearity was not found to improve even marginally over that of standard reaction.

Quaternary ammonium halide salts with chloride, bromide and iodide counter-ions were studied as promoters in Runs 6-12. Tetraethyl ammonium bromide (TEAB) was used in toluene as well as in bromobenzene as solvent. In both the reactions (Run 6, 7), compared to the standard run, the initial rates were slightly higher and conversions as well as selectivities were nearly similar. On moving to tetrabutyl ammonium bromide (TBAB) from TEAB, no reaction occurred at TBAB/Co ratio of 1 (Run 8). When instead of TBAB, tetrabutyl ammonium chloride (TBAC) was used at TBAC/Co ratio of 1(Run 9), the reaction occurred but the initial rate was reduced nearly to the 1/3 rd of the standard run. In this reaction, more AA was formed (selectivity 14.3 %) and the linear/branched ratio was also reduced to 0.57 compared to 0.95 in the standard reaction. TBAC, TBAB and TBAI (Tetrabutyl ammonium iodide) were tested at 0.065 equivalent of cobalt (Shell researchers have used the same ratio in their work) in Runs 10, 11 and 12 but not much different results, compared to the standard reaction were observed. Runs 8, 9, 10, and 11 prove that chloride promoters are better than bromide and iodide promoters.

With tetrabutyl phosphonium bromide (TBPB) promoter (Runs 13, 14, and 15) at TBPB/Co ratio of 2 and 0.5, no reaction could take place. Compared to the standard reaction, at 0.065 equivalent of cobalt, TBPB gave slower reaction, whereas conversion and selectivities were nearly similar.

Thus, from this study of the promoters for cobalt-catalyzed hydroformylation of VAM, it can be concluded that at high concentrations these promoters either give side products such as AA or poisons the catalyst, thus terminating the reaction. At low concentrations (0.065 equivalent to Co, same as that of Shell-patents), most of them gave nearly similar selectivities at, in fact, slightly reduced rates. Thus, excepting for LiCl (Run 2), the claim of Shell researchers that these compounds act as promoters, was not validated for hydroformylation of VAM.

3.3.9. Effect of solvents on cobalt catalyzed hydroformylation of VAM

Solvents affect the catalysis of hydroformylation reaction in many ways *viz* affecting the catalyst-metal environment through coordination with the metal, acting as diluents for ligands as well as poisons, affecting solubility of CO and H_2, affecting the pH of the system *etc*. As seen in the previous sections, cobalt catalyzed hydroformylation of VAM is a sensitive reaction, which shows considerable change in the activity-selectivity of the reaction on slight variation in the catalyst environment. So, we thought that it would be interesting to see the effect of solvents on hydroformylation of VAM. Various, hydrocarbons, ethers, halogenated solvents, alcohols *etc* were tested and the results are presented in the following sections.

3.3.9.1. General screening of solvents

This random screening of solvents for cobalt-catalyzed hydroformylation of VAM was carried out with double distilled dry solvents. In all the reactions only solvent was varied keeping the total volume of the charge constant. It was observed in the study that, in coordinating solvents such as dimethyl formamide, dimethyl acetamide, and acetonitrile no reaction could take place. The final solution after these reactions was purple or green instead of usual saffron-red. This color change indicates coordination of the solvents with cobalt, forbidding the possibility of formation of the active hydridocarbonyl species. Other important results obtained in this study are presented in the Table 3.16.

In neat VAM, without any solvent (Run 1 in Table 3.16), no reaction occurred and the VAM remained unconverted. Initially $Co_2(CO)_8$ was found to dissolve completely in VAM but in the final sample, blue colored catalyst particles were observed indicating formation of cobalt-VAM complex (not characterized). This reaction illustrated the importance of solvent in VAM hydroformylation, especially due to dual functionality and coordinating ability of VAM. Runs 2 and 3 were carried out in hexane and cyclohexane solvents. Surprisingly, these solvents proved to be inapt to carry out efficient hydroformylation of VAM. Syngas absorption in both these solvents was very slow and the reactions couldn’t proceed after 30 % - 35 % conversion of VAM. Chemoselectivity to aldehydes was above 90 % but the product linearity was poor with

23 % - 27 % regioselectivity to 3-ac pal. These results are peculiar for hydroformylation of VAM, as hexane is considered to be an effective solvent for hydroformylation of a linear olefins by both modified and non-modified $Co_2(CO)_8$.[xxii] Also, cyclohexane was proved to be a useful solvent for Rh-catalyzed hydroformylation of VAM (Section 4.3.1.2).

Toluene and benzene were found to be effective solvents for hydroformylation of VAM. In toluene, ~ 99 % conversion with > 95 % chemoselectivity to the hydroformylation-products and 48.5 % product linearity was obtained at 12.7 MPa syngas pressure (Run 5). Approximately 5 - 10 % hydrogenation of ac-pals to ac-pols was observed in reactions with toluene as solvent, the only other side product observed was EA with 3%-4% selectivity. Similar results were observed with benzene as solvent (Run 6). Thus, among the hydrocarbon solvents, toluene was found to be the best solvent for hydroformylation of VAM.

Table 3.16. Effect of solvents on cobalt catalyzed hydroformylation of VAM

Run No.	Solvent	Run time	Press.	Conv.	Selectivity			Regioselectivity		Initial rate x 10^3
					Ald.	AA	EA	I	II	
		Min	Mpa	%	%	%	%	%	%	kmol/m^3/s
1	VAM	60	12.4	0	-	-	-	-	-	0
2	Hexane	81	4.1	30	27.4	0	0	27.0	73.0	0.002
3	Cyclohexane	150	4.8	35	91	5	3.1	23.1	76.9	0.002
4 *	Toluene	154	4.1	90	95.7	0	4	46.7	53.3	1.1
5 *	Toluene	120	12.7	98.9	88.5	0	3	48.5	51.5	0.74
6	Benzene	60	11	93.8	93	0	2	47.7	52.3	0.8
7	MTBE	60	9.7	96	97	0	3.4	44	56	1.3
8	1,4-dioxane	65	4.1	96	98.3	0	2.5	50.5	49.5	1.3
9	THF	55	9.7	97	90.8	0	4	42.5	57.5	1.9

*Reaction conditions: VAM, 1.3 kmol/m^3; Solvent, 22.5 x 10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature = 393 K; CO:H_2, 1:1; Agitation, 20 Hz. * = 4 % and 8.5 % ac pols were observed for runs 4 & 5 respectively.*

Cyclic and linear ethers, such as tetrahydrofuran (THF); 1,4-dioxane and methyl *t*-butyl ether (MTBE) were found to be better solvents compared to the hydrocarbons. With all these solvents, conversions and chemoselectivity to the aldehyde products was more than 95 % and 97 % respectively (Runs 7-9). In these reactions, the initial rates and

regioselectivity to 3-ac pal were better than those obtained in toluene. In fact in 1,4-dioxane the aldehyde linearity crossed the 50 % barrier for the first time. None of the ligands and promoters tested could achieve 50 % or higher regioselectivity to 3-ac pal.

This general screening of the solvents revealed an important effect of enhancement in product-linearity in some solvents such as ethers. The results obtained with halogenated solvents and alcohols are presented in the following separate sections.

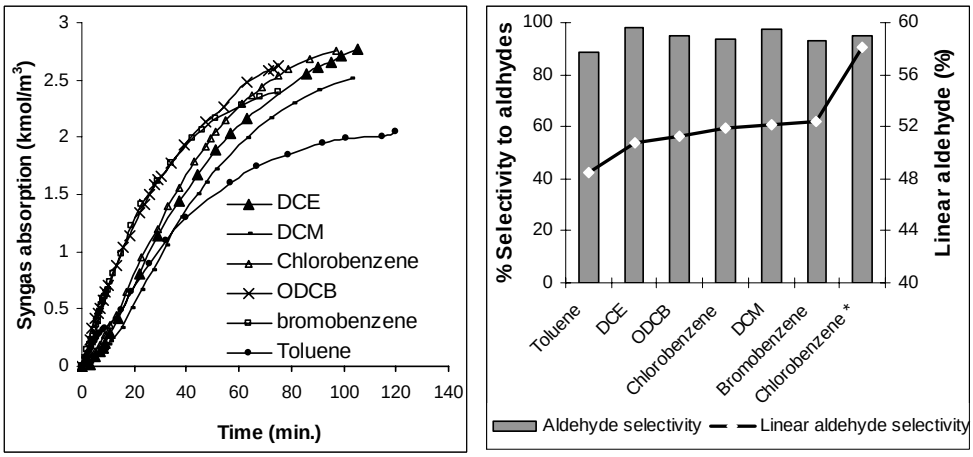
3.3.9.2. Halogenated solvents

Generally, halogenated solvents are not preferred, especially for synthesis of bulk commodities, due to corrosion problems and environmental reasons. For hydroformylation reactions also, halogenated solvents are least preferred and to the best of our knowledge, there is no report on the study of halogenated solvents for hydroformylation. In fact in our study on Rh-catalyzed hydroformylation of VAM, halogenated solvents such as dichloro ethane (DCE) was found to deactivate the $HRhCo(PPh_3)_3$ catalyst (Run 7 in Table 3.4). However, for cobalt catalyzed hydroformylation of VAM, halogenated solvents were found to be effective in terms of better activity, chemoselectivity as well as regioselectivity to linear aldehyde, the results are presented in Table 3.17 and Figure 3.10.

Table 3.17. Effect of halogenated solvents on cobalt catalyzed hydroformylation of VAM

Run No.	Solvent	Run time	Conv.	Selectivity			Regioselectivity		Initial rate x 10^3
				Ald.	AA	EA	I	II	
		Min	%	%	%	%	%	%	kmol/m^3/s
1	DCM	120	98.4	97.2	0	2.5	52.2	47.8	0.67
2	DCE	100	100	97.9	0	3.1	50.7	49.3	0.7
3	Chloro - benzene	100	97.9	93.4	0.3	3.4	51.9	48.1	0.64
4	Bromo - benzene	75	97.2	93	0	2.4	52.4	47.6	1.4
5	ODCB	75	99.8	95	3	1.2	51.2	48.8	2.3
6	$CHCl_3$	25	0	-	-	-	-	-	-
7	CCl_4	150	100	0	0	0	-	-	-

*Reaction conditions: VAM, 1.3 kmol/m^3; Solvent, 22.5 x 10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature = 393 K; Syngas, 12.4 MPa; CO:H_2, 1:1; Agitation, 20 Hz. No alcohol formation observed. * = Syngas, 4.1 MPa.*



(A) **(B)**

Figure 3.10. Effect of halogenated solvents on the cobalt catalyzed hydroformylation of VAM on (A) Activity (B) Chemoselectivity and regioselectivity

Reaction conditions: Same as those of Table 3.17

In alkyl-halogenated solvents such as dichloromethane (DCM) and dichloroethane (DCE), 100 % conversion was achieved with > 97 % chemoselectivity to the aldehydes (Run 1,2 Table 3.17). The only side product obtained was EA (~ 2.5 %) and no alcohol or AA formation was observed. The most important observation was regioselectivity to 3-ac pal, which crossed the 50 % barrier usually associated with hydrocarbon solvents like toluene (Figure 3.10 (B)). These solvents also show a better overall activity compared to toluene (Figure 3.10 (A)). Among the aryl halogenated solvents chlorobenzene, bromobenzene, and *o*-dichloro benzene (ODCB) were tested and found to give higher product linearity of ~ 52 % (Run 3, 4, 5 Table 3.17). More than 97 % conversion and 93 % selectivity to aldehydes, obtained with these solvents made them the best among the tested halogenated solvents. From Figure 3.10 (A), it can be clearly seen that these solvents are better than toluene as well as DCM and DCE in terms of overall activity. Figure 3.10 (B) clearly depicts the increased chemoselectivities and regioselectivities with the halogenated solvents. Thus, halogenated solvents proved to be very effective for cobalt catalyzed hydroformylation of VAM with nearly no formation of AA (indicating absence of decomposition of 3-ac pal) and higher product linearity at better rates compared to toluene.

In $CHCl_3$ however, no hydroformylation could occur (Run 6 Table 3.17). In CCl_4, fast absorption of syngas was observed and the actual absorption didn't stop even after surpassing the expected absorption. GC analysis showed no hydroformylated products and the final charge showed high acidity with pH 2. Thus, a polymerization reaction initiated by CCl_3 radical might have taken place.[xxiii]

In view of the higher product linearity obtained in halogenated solvents, it was

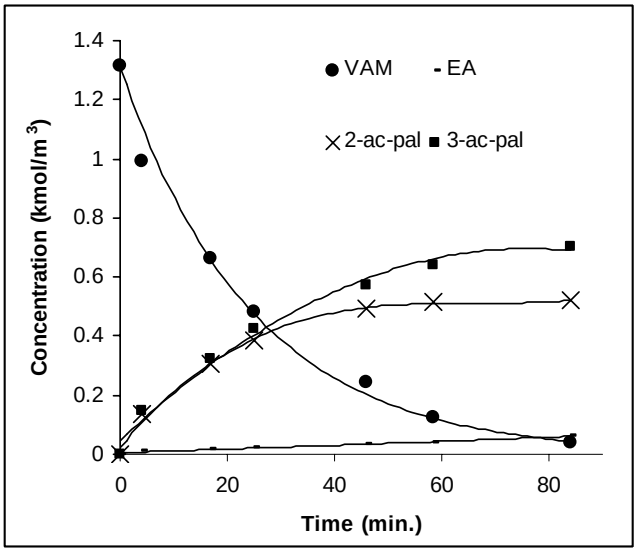


Figure 3.11. Concentration-time profile of a cobalt catalyzed hydroformylation of VAM in chlorobenzene solvent
Reaction conditions: VAM, 1.3 kmol/m^3; Chlorobenzene, 22.5 x 10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature, 393 K; Pressure, 4.1 MPa; Agitation, 20 Hz.

thought appropriate to obtain a concentration-time profile. So, in chlorobenzene solvent, a concentration time profile for cobalt-catalyzed hydroformylation of VAM was obtained at 4.1 MPa syngas pressure and is presented in Figure 3.11.

Two distinct features of this concentration time profile are, absence of side products and increase in the product linearity after nearly 50 % conversion of VAM. From the CT-profile, it can be concluded that in halogenated solvents, VAM concentration effect may be critical for product linearity. So, a preliminary investigation of parametric effects was pursued and the results are presented in Table 3.18.

Table 3.18. Preliminary study on the effect of parameters on the hydroformylation of VAM in halogenated solvents

Run No.	Solvent	Run time	VAM concn.	Press.	Conv.	Selectivity			Regioselectivity		Initial rate x 10^3
						Ald	AA	EA	I	II	
		Min	kmol/m^3	MPa	%	%	%	%	%	%	kmol/m^3/s
1	DCM#	180	5.44	9.6	74.9	89.2	11.6	1.3	46.2	53.8	1.5
2	DCM#	193	2.7	11.5	98.4	88.6	4.5	2.5	51.7	48.3	1.6
3	DCM	150	1.3	12.4	98.4	97.2	0	2.5	52.2	47.8	0.67
4	DCM	66	1.3	9.65	96.3	95.3	0	3.8	52.4	47.6	1.13
5	DCM	67	0.53	9.6	100	99	0	1	54.5	45.5	0.41
6	DCM@	640	0.18	10	100	63.5	0	3.1	53.9	46.1	0.004
7	DCE	179	0.52	12.4	100	96.7	0	2.2	54.1	45.9	0.23
8	DCE	111	1.31	12.4	100	97.9	0	3.1	50.7	49.3	0.7
9	DCE*	48	1.3	12.4	95.6	99	0	0.8	53.9	46.1	1.6
10	ODCB#	93	5.34	12.4	79.3	84.8	12.7	1.7	46.5	53.5	3.1
11	ODCB	75	1.3	12.4	99.8	95	3	1.2	51.2	48.8	2.3
12	DCM[b]	15	1.3	13.8	75.9	94.6	0	4.6	49.5	50.5	4.03
13	Chloro benzene	100	1.3	12.4	97.9	93.4	0.3	3.4	51.9	48.1	0.64
14	Chloro Benzene	80	1.3	4.1	97.1	94.7	0	4.7	58.1	41.9	1.1

*Reaction conditions: Solvent, 22.5 x 10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature = 393K; $CO:H_2$, 1:1; Agitation, 20 Hz. # = Total charge, 20 x 10^{-6} m^3. @ = 29 % ac pols were observed, some side products were also seen. * = $CO:H_2$, 1:2. b = Temperature, 433 K; $CO:H_2$ = 7:2*

3.3.10. Catalyst-products separation techniques

The high solubility of product acetoxy propanals in water was helpful for effective separation of cobalt catalyst from the organic reaction mixture. The general method employed for catalyst separation was addition of aqueous phase (saturated with the syngas) to the organic mixture and extracting out the acetoxy aldehydes and unreacted VAM into the aqueous phase by stirring under syngas pressure of 1.37 MPa. Syngas pressure was found to be essential to save the catalyst from formation of cobalt-aqua complex.[xxiv] Reverse biphasic system, (Section 4.3.1.7.1 Chapter 4) didn't work for the separation of cobalt catalyst from the hydroformylation mixture. In the study it was found that the reactions in which acetic acid was formed with more than 10 % selectivity,

the catalyst was precipitated as Co (II) acetate.

3.4. CONCLUSIONS

Testing of various ligands and promoters for cobalt catalyzed hydroformylation of VAM showed that, none of the ligands or promoters tested could improve the product linearity above the nearly 50-50 obtained by unmodified cobalt carbonyl catalyst. Modification of the cobalt catalyst by phosphine ligands proved futile as it led to the decomposition of VAM. Among the nitrogen containing ligands, aryl amines showed results comparable with unmodified cobalt catalyst whereas alkyl amines showed poor activity and catalyzed side reactions in preference to hydroformylation. Pyridine has found to enhance the reaction rates by nearly 4 times. Pyridine didn't impart any change in the chemoselectivity of the reaction and it reduced the regioselectivity to 3-acetoxy propanal marginally. Bipyridine and terpyridine as ligands showed poor activity for hydroformylation of VAM. This effect may be attributed to the strong chelating ability of the above said ligands. Substituted pyridine ligands didn't show any improvement over pyridine. Cobalt modification with triphenyl arsine ligands didn't show substantial improvement over the unmodified cobalt catalyst.

Quaternary ammonium and phosphonium salts were used as promoters but didn't show any improvement in the activity or selectivity of the hydroformylation reaction. The most prominent effect was observed when halogenated solvents were used for hydroformylation of VAM. The regioselectivity to 3-acetoxy propanal was improved from ~ 50 % to 58 % in chlorobenzene solvent. Thus, halogenated solvents were found to improve the efficiency of hydroformylation of VAM for synthesis of 1,3-propandiol (Chapter 4). Further study on the solvent effect in cobalt-catalyzed hydroformylation of VAM would be carried out in our laboratory.

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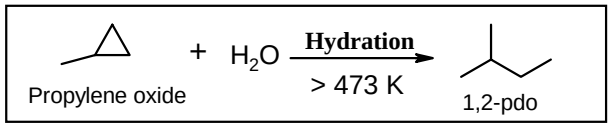
Chapter 4

HYDROFORMYLATION OF VINYL ACETATE MONOMER AS A POTENTIAL ROUTE FOR PROPYLENE GLYCOLS: ACTIVITY-SELECTIVITY STUDIES WITH Rh-CATALYSTS

4.1. INTRODUCTION

Both C_3-glycols, *i.e.* 1,2-propanediol (1,2-pdo) and 1,3-propanediol (1,3-pdo), are very important bulk commodity chemicals. 1,2-pdo is a bulk product for many years (world production capacity ~ 1.03 X 10^6 TPA in 1990)[i] whereas till the beginning of this century, 1,3-pdo was considered as a scarce and expensive specialty chemical due to unavailability of viable technology.[ii] 1,2-pdo is used as heat transfer fluid, anti-freeze agent in food and pharmaceuticals, synthetic lubricants, anti-foam agent, non-ionic surfactants *etc*. 1,2-pdo has numerous applications in polymer industry as well, and is used in latex paints, inks and dyes. 1,3-pdo finds uses in polyurethane, adhesive, and resin industry. Polytrimethylene terephthalate (PTT) synthesized from 1,3-pdo, is an excellent fabric fiber combining best properties of polyethylene terephthalate (PET) and NYLON®. In fact, it is also observed that, 1,3-pdo can replace 1,4-butanediol in many polymers.

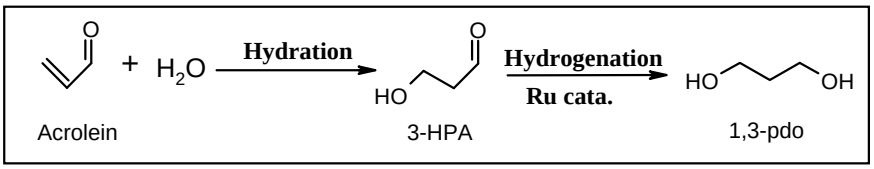
1,2-pdo [57-55-6] is a colorless, odorless, hygroscopic, and water soluble liquid with a boiling point of 461.2 K. Propylene oxide (PO) hydration is the major route for 1,2-pdo production (Scheme 4.1). To avoid the formation of polypropylene glycol, the commercial process is typically run using an excess of water (12 – 20 mol water / mol propylene oxide).[iii] Acid or base catalysts can be used to enhance the reaction rates or product selectivity, however generally the commercial processes are non-catalytic.



Scheme 4.1. Synthesis of 1, 2-pdo

1,3-pdo [504-63-2] (also known as trimethylene glycol) is also a colorless and completely water soluble liquid with a boiling point of 487.4 K. Because of its importance in the PTT fiber, efforts for economical and safe synthesis of 1,3-pdo were initiated way back in 1953. Presently, there are three commercially significant 1,3-pdo processes. The oldest process is Degussa-Huels process via acrolein hydration. Two steps (Scheme 4.2) involved in this route are: (1) acrolein hydration to 3-hydroxy propanal (3-HPA) and (2) hydrogenation of 3-HPA to 1,3-pdo. Acrolein hydration is carried out on acidic resin catalyst with acrolein : water ratio of 1:3 to 1:6.[iv] The main drawback of this route is, less overall selectivity to 3-

HPA (~ 86-88 %). As the acrolein conversion increases, the selectivity to 3-HPA decreases due to which acrolein conversion of only 40 to 60 % is preferred. Thus after the hydration step, removal of unreacted acrolein is a must. Hydrogenation of HPA solutions in water is carried out at ~7 % concentration either with Ni or Ru catalyst.



Scheme 4.2 Acrolein route for 1,3-pdo

The second process is, Du pont's enzyme catalyzed transformation of glucose to 1,3-pdo.[v] It is claimed to be the first green route based on renewable resource like carbohydrates. Main drawbacks of this route are high dilution and lower reaction rates. According to the Du Pont schedule, a commercial plant was expected to commence in the forth quarter of 2001, however no reports on plant commencement are published as yet.

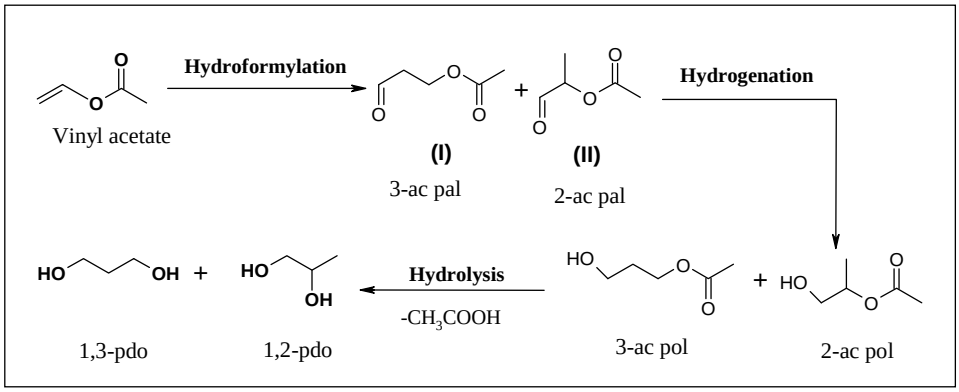
Shell process for 1,3-pdo is the most recent one and involves two steps, hydroformylation of ethylene oxide (EO) to 3-HPA, followed by hydrogenation of 3-HPA to 1,3-pdo.[vi] Because of high commercial value of 1,3-pdo, the success of Shell inventors was highly acclaimed and they have won an American Chemical Society award for this process. Shell is using this process for commercial production of 1,3-pdo. The main drawback of this route is acetaldehyde formation accounting for nearly 12- 15 % loss of the substrate.

All commercial processes for propylene glycol synthesis uses hazardous starting materials like EO, PO and acrolein. Both EO and PO are flammable and are toxic to humans; they are termed as carcinogens, and poses problems to the central nervous system and respiratory systems. Acrolein is also carcinogenic and highly irritant. Thus, a safe and environmentally benign route for propylene glycols is desirable.

In this work we have proposed for the first time, VAM hydroformylation route for simultaneous synthesis of both propylene glycols. It involves three steps: hydroformylation, hydrogenation, and hydrolysis (Scheme 4.3). As described in the first chapter, most of the work on VAM hydroformylation in the literature is carried out with Rh-catalysts, mainly for asymmetric hydroformylation.[vii] Rh-catalysts give 90 % or higher selectivities for 2-acetoxy

propanal (2-ac pal) which is a branched aldehyde and a precursor for 1,2-pdo. The maximum selectivity for linear aldehyde 3-acetoxy propanal (3-ac pal), which is a precursor for 1,3-pdo, with Rh-catalyst, is 13 %.[viii] Abatjoglou *et al.*[viii] have studied Rh-catalyzed VAM hydroformylation in greater details including effects of solvents, phosphines, poisons such as acetic acid on activity and selectivity of the catalyst. They have also proposed a mechanism for the formation of side products like acetic acid, ethylene *etc*. Thus, it can be concluded from the VAM hydroformylation literature that getting higher regioselectivity to linear product (3-ac pal) is a challenge. Only one report (Watanabe *et al.* [ix]) on hydrogenation and hydrolysis of 2-ac pal to 1,2-pdo is present in the literature. The authors have studied asymmetric hydroformylation of VAM, and have also carried out hydrogenation of 2-ac pals with $LiAlH_4$ and hydrolysis of 2-acetoxy propanol with 1 M HCl. Kitamura *et al.*[x] in their patent (Kuraray Co., Ltd., Japan) have carried out Raney Ni catalyzed hydrogenation of 2-ac pal to 2-acetoxy propanol but no detailed study on such type of hydrogenation has been reported. It is clearly evident from the literature that nobody has studied hydroformylation of VAM as a potential route for propylene glycols. In view of this, the objective of the present work was to develop the total synthesis of propylene glycols via hydroformylation of VAM as shown in Scheme 4.3.

Since ethylene to vinyl acetate is a fairly matured process,[xi] this route is particularly attractive when ethylene is visualized as a starting material. In effect, it involves ethylene, syngas, and water as the raw materials with complete recycle of acetic acid and high atom efficiency due to high selectivity for the two propylene glycols. A comparison of this route



Scheme 4.3. Total synthesis of propylene glycols from VAM

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with the conventional processes for propylene glycols from EO and PO respectively, clearly indicates the following advantages,

- Elimination of toxic and hazardous EO and PO
- Elimination of the concentration limitations associated with EO
- More efficient utilization of ethylene
- High selectivity and atom utilization

In this chapter, experimental results of hydroformylation of VAM with different catalyst precursors of Rh, Ru, and Ir are presented. Rh catalyzed VAM hydroformylation has been studied in details including the effect of various precursors, solvents, and ligands on the activity and selectivity to acetoxy propanals (ac pals). Methods for effective recycling of Rh catalysts are presented. Different heterogeneous catalysts for hydrogenation of acetoxy propanals are screened. Ion exchange resin catalyzed hydrolysis of acetoxy propanols is also studied with an aim to obtain propylene glycols. Thus VAM hydroformylation as a novel route for propylene glycols has been demonstrated with recyclable catalysts for all the three steps involved.

4.2. EXPERIMENTAL

In the present study, different transition metal complexes and heterogeneous catalysts are used for hydroformylation and hydrogenation respectively. Since they differ in their stability, safety-storage properties, operating conditions etc. proper experimental techniques for their evaluation were followed and explained in this section.

4.2.1. Materials

$RhCl_3$-$3H_2O$, $RuCl_3 \cdot aq$, $(CH_3COO)_2Co \cdot 4H_2O$, $IrCl_3 \cdot aq$, PBu_3, TPP, DPPB, DPPP, DPPH, trioctyl phosphine oxide, TPA, TBA, bypyridine, terpyridine, TPAs, COD, acac, (all from Aldrich, USA or Fluka, Switzerland), sodium borohydride, lithium aluminium hydride, conc. HCl, pyridine and all solvents (Sd Fine Chemicals, India), Raney Ni (Kallin Industries, India), CO, 99.9 % purity (Matheson, USA) and H_2 99 % purity (Industrial Oxygen Company, India) were used as received without further purification. $RuCl_2(CO)_2Py_2$ and $RuCl_2(CO)_2(PPh_3)_2$ were gift samples from the division. Water used was double distilled, demineralized and degassed. Syngas mixture in the required $CO:H_2$ ratio was first premixed in a

reservoir and then used for hydroformylation reactions. All the solvents were distilled and degassed with argon before use.

4.2.2. General reaction procedures

All the hydroformylation and hydrogenation reactions were carried out in a 50 x 10^{-6} m^3 Parr Autoclave (total void space, 77 x 10^{-6} m^3) made of stainless steel (Maximum pressure capacity of 20.7 MPa at 548 K), having facilities for gas inlet, outlet, intermediate sampling, temperature controlled heating (± 1 K) and variable agitation speed (0 – 33 Hz). The typical reaction set-up is shown in Figure 2.1. As a safety precaution, a rupture disc (gold faced), which can withstand a maximum pressure of 20.7 MPa was attached to the reactor for Co-catalyzed hydroformylation while one with 14 MPa capacities was used for Rh-catalyzed hydroformylation and hydrogenation experiments. For experiments with ≤ 7 MPa pressure, gas was fed through constant pressure regulator attached to the syngas reservoir while for high pressure experiments, the reactor pressure was maintained by intermittent gas filling from the reservoir after every drop of ~ 0.2 MPa. Syngas reservoir was always maintained at minimum 1.5 MPa higher pressure compared to the reactor pressure. Ice water-cooled condensers were used for intermediate sampling.

4.2.2.1. General procedure for hydroformylation experiments

In a typical Rh-catalyzed hydroformylation experiment, known quantities of the substrate, catalyst, promoters, and the solvent were charged into the autoclave. The contents were flushed twice each with nitrogen and syngas and heated to the desired temperature with ~ 3.3 rpm stirring speed. After attaining the temperature, the autoclave was pressurized with syngas to the required pressure and the agitation speed was increased to 16.6 Hz to initiate the reaction. The pressure drop in the reservoir vessel was recorded by means of a pressure transducer (± 1 psi) as a function of time. Intermediate liquid samples were also taken at regular time-intervals. Unless-otherwise mentioned, all the reactions were run till the syngas absorption nearly stopped. The autoclave was cooled to room temperature and syngas was vented. Autoclave was flushed with nitrogen and the reaction mixture was removed. The analysis of the liquid samples was carried out using GC to examine the product distribution

pattern, quantitatively. Details of GC analysis are given in the following section. The same reaction procedure is followed for Ir and Ru catalyzed hydroformylation experiments.

The products were confirmed by GC-MS, NMR and IR analysis. Spectral data of all compounds prepared are given in Appendix II.

4.2.2.2. General procedure for hydrogenation experiments

Hydrogenation reactions were carried out either in water or in organic solvent used for hydroformylation. For water as a solvent, the acetoxy propanals were extracted in the aqueous phase as discussed in section 4.8 and 3.3.7, thus, separating them from the hydroformylation catalyst system. For hydrogenation in the hydroformylation solvents (organic), the catalyst was either removed by activated charcoal and silica treatment (mostly used for Rh-catalysts) or it was precipitated out as discussed in section 4.3.7 (mostly used for Co-catalysts). The reaction procedure is similar to the Rh-catalyzed hydroformylation experiment procedure excepting the use of H_2 instead of syngas. The analysis of the liquid samples was carried out using GC to examine the product distribution pattern.

Special care was taken while handling pyrrophoric catalysts like Raney-Ni. Raney-Ni was weighed using its density value, which is 1 when it is stored under water. Suspended Raney Ni in water was taken in a measuring cylinder. After letting the catalyst settle down completely, the number of cm^3 occupied by the catalyst directly correspond to the Raney Ni amount in gram. Thus, the amount can be made up to the desired quantity of the Raney Ni needed. The upper water layer was removed and the desired amount of aldehyde-water mixture added to the measuring cylinder. For hydrogenation reactions using solvents other than water, solvent washings were given to remove water from the catalyst, as follows. After removing the water layer over the catalyst, 5 washings, each of 5×10^{-6} m^3 ethanol followed by 5 washings (5×10^{-6} m^3 each) by the reaction solvent were given to the catalyst. While handling Raney Ni, precautions were always taken not to expose the catalyst to the atmosphere due to its pyrophoric nature.

4.2.2.3. General procedure for hydrolysis experiments

Hydrolysis of acetoxy propanols was carried out in a 100 ml two-necked round bottom flask in water or organic-aqueous biphasic mode. Desired amounts of aldehydes, water, and hydrolyzing agents were stirred at 353 K for 3 hours using magnetic stirrer. When resins were used as hydrolyzing agent, temperature was controlled properly, as at temperatures higher than 353 K, the resins used are not thermally stable. Since, this was just a preliminary study, the reaction conditions were not optimized. The analysis of the liquid samples was carried out using a GC.

4.2.2.4. Reagent catalyzed reduction and hydrolysis

Watanabe's procedure[ix] was followed for these reactions. Lithium aluminum hydride (LAH) was taken in dry THF in a round bottom flask. A drop-by-drop addition of the required amount of acetoxy propanols (in THF) was carried out at room temperature under constant stirring with the help of a magnetic stirrer. After complete addition, the solution was refluxed for 4 hrs. The resultant solution was hydrolyzed with 1 M HCl. Precipitate formed was filtered off and the filtrate was concentrated.

4.2.3. Analytical methods

Liquid samples were analyzed using a Hewlett Packard 6890 Series GC controlled by the HP Chemstation software and equipped with an auto sampler unit, by using an HP-1 capillary column (30 m x 30 µm x 0.25 µm film thickness with a stationary phase of polymethyl siloxane). The quantitative analysis was carried out by constructing calibration-table in the range of concentrations studied. The % conversion, % selectivities TON and TOF (hr^{-1}) were calculated using the following formulae. The % Conversion was always calculated based on the liquid substrate charged. The standard GC conditions for the analysis of products of different reactions are given in Tables 4.1 and 4.2.

$$Conversion, (\%) = \frac{Initial\ concentration\ of\ substrate - Final\ concentration\ of\ substrate}{Initial\ concentration\ of\ substrate} \times 100$$

$$Selectivity, (\%) = \frac{No.\ of\ moles\ of\ a\ product\ formed}{No.\ of\ moles\ of\ substrate\ converted} \times 100$$

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$$TOF, (h^{-1}) = \frac{No.\ of\ \ moles\ of\ \ hydroformylaion\ \ products\ \ formed}{No.\ of\ \ moles\ of\ \ catalyst \times time\ in\ hours}$$

$$TON = \frac{No.\ of\ \ moles\ of\ \ hydroformylation\ \ products\ \ formed}{No.\ of\ \ moles\ of\ \ catalyst}$$

$$\text{Regioselectivity to I} = \frac{I}{(I + II)} \times 100$$

$$\text{Regioselectivity to II} = \frac{II}{(I + II)} \times 100$$

Table 4.1. Conditions for GC analysis of VAM hydroformylation reaction

Injector (split) Temperature	523 K		
Flame ionization detector Temp	523 K		
Inlet flow – total (He)	32.3 ml/min		
Split ratio for Injector	50:1		
Column Temperature	Rate (K/min)	Temp (K)	Hold time (min)
		306	5
	303	373	1
	313	473	2
Column Pressure	Rate (psi/min)	Pressure (Psi)	Hold time (min)
		3	2
	10	5	3
	10	30	0

Table 4.2. Conditions for GC analysis of hydrogenation and hydrolysis reactions

Injector (split) Temperature	523 K		
Flame ionization detector Temperature	523 K		
Inlet flow - total (He)	28.5 ml/min		
Split ratio	50:1		
Column Temperature – Ramp	Rate (K/min)	Temp (K)	Hold time (min)
		333	2
	303	373	1
	313	383	2
Column Pressure – Ramp	Rate (psi/min)	Pressure (Psi)	Hold time (min)
		3	2
	10	5	3
	10	30	0

IR spectra was recorded using a Bio-rad FTS *175C* machine in transmission mode using KBr pellets as well as liquid cells. NMR was obtained using a Brucker- MSL-300 machine. GC-MS analysis was carried out on a Agilent GC machine of 6890N series equipped with 5973N Mass Selective Detector. Elemental analysis of the complexes was carried out on a CHNS-O EA1108, Elemental analyzer of Carlo Erba Instruments, Italy.

4.2.4. Preparation of Rh complexes

4.2.4.1. Preparation of $Rh(CO)_2$ (acac)

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$Rh(CO)_2$(acac) was prepared by a method used by Varshavskii *et al.*[xii]. To a solution of 3 gms of rhodium trichloride trihydrate (40 %) in 60 x 10^{-6} m^3 dimethyl formamide, 12 x 10^{-6} m^3 acetyl acetonate was added with stirring. The solution was refluxed for thirty minutes and then cooled to the room temperature. It was diluted to twice the volume with distilled water. Addition of water resulted in a voluminous crimson precipitate. The precipitate was filtered and washed with alcohol. The complex was recrystallised from hexane solution. The needle-shaped red-green crystals were obtained by slow cooling of the hexane solution. The yield was about 70%. The complex was confirmed from its elemental analysis, which is given below. The IR spectrum of this complex is shown in Appendix II (IR-2).

	Calculated %	Observed %
C	23.25	23.31
H	2.71	2.68

4.2.4.2. Preparation of $[Rh(COD)Cl]_2$

1.0 g of rhodium trichloride trihydrate (40 %) in ethanol was boiled under reflux with 1,5-cyclooctadiene (COD) (2 x 10^{-6} m^3) for 3 hours. After cooling the solution, $[Rh(COD)Cl]_2$ was obtained as a orange solid. It was filtered, washed with ethanol, dried, and recrystalised from acetic acid. The yield of the complex obtained was 60 %.

	Calculated %	Observed %
C	39.05	38.6
H	5	4.9
Cl	14.4	14.4

4.2.4.3. Preparation of $[Rh(CO)_2Cl]_2$ catalyst

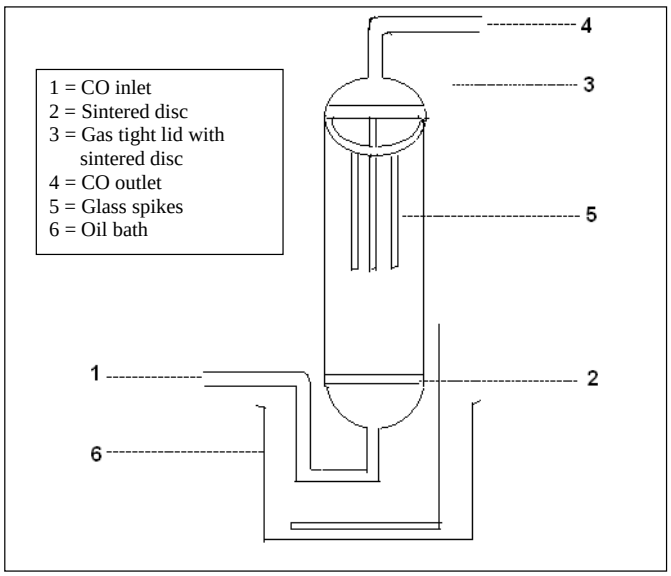


Figure 4.1. Apparatus for preparation of $[Rh(CO)_2Cl]_2$

The Preparation of $[Rh(CO)_2Cl]_2$ was carried out in a special reactor (Figure 4.1). 1.0 g rhodium trichloride trihydrate (40 %) was charged in the reactor and the system was purged with CO. The reactor was immersed in a heated oil bath (373 K), and a stead stream of CO was passed through the reactor. The water vapors formed in the course of reaction were

removed. The $[Rh(CO)_2Cl]_2$ complex was formed, and got sublimed. Bright orange red, needle shaped crystals were formed on condensation of the sublimate over the inner upper part of the reactor, which was kept cool. The glass spikes probing into the interior of the reactor helped the condensation of the sublimed complex. The complex was carefully removed from the reactor, and purified further, by resublimation. This complex is extremely sensitive to moisture and was stored under very dry conditions. The elemental analysis (C=12.31% Cl=18.20%) was consistent with $[Rh(CO)_2Cl]_2$.

4.2.4.4. Preparation of $HRh(CO)(PPh_3)_3$

The procedure for the synthesis of $HRh(CO)(PPh_3)_3$ was followed from the work of Evans *et.al.*[xiii] . $Rh(CO)(Cl)(PPh_3)_2$ (1.0 g) and PPh_3 (1.5 g) were added to ethanol (100 x 10^{-6} m^3) and the mixture was refluxed under constant stirring. To this solution, $NaBH_4$ (0.5g in 60 x 10^{-6} m^3 ethanol) was added very slowly. After complete addition, the mixture was refluxed till a small sample of suspended catalyst (washed and dried) showed no absorption at 1960 cm^{-1} corresponding to $Rh(CO)(Cl)(PPh_3)_2$. A small absorption band at 2024 cm^{-1} (new Rh-H) and a carbonyl stretch at 1920cm^{-1}, are typical of this complex. The complex was filtered from a hot solution, washed several times with hot ethanol followed by cold ethanol and dried. The IR spectrum of this complex is shown in Appendix II (IR-1). The elemental analysis was:

	Theoretical %	Experimental %
C	71.9	71.94
H	5.01	5.3
P	10.13	10.1

4.2.5. Preparation of hydrogenation and hydrolysis catalysts

4.2.5.1. Preparation of Ru/Al_2O_3 catalyst

Activated Al_2O_3 (9 g) was added to distilled water (150 x 10^{-6} m^3) and the slurry was stirred for two hours in a round-bottomed flask provided with stirrer, condenser and an addition funnel in a water bath maintained at 368 K. To this mixture, 0.752 g (for 3 % Ru, and 1.25 g for 5 % Ru loading) of (40 %) $RuCl_3 \cdot aq$, dissolved in distilled water, was added drop wise. After stirring for three hours, aqueous ammonia solution (30 x 10^{-6} m^3) was added (pH ~ 10) to precipitate ruthenium as ruthenium hydroxide. The suspension was allowed to stir for 3-4 hr. The contents were then filtered, washed using hot distilled water, dried in oven

at 393 K for 8 hrs and then activated at 573 K for 7 hr. under hydrogen flow. After activation, the catalyst was brought to room temperature, flushed with nitrogen and used for reaction.

4.2.5.2. Preparation of Ni/ SiO_2 and Ni/ Al_2O_3 catalysts

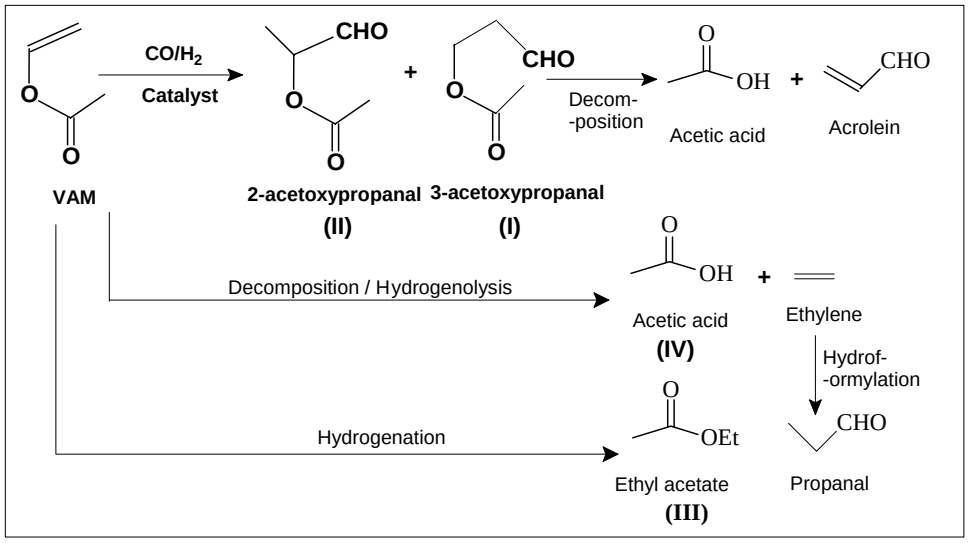
Activated Al_2O_3 or SiO_2 support (8 g) was charged along with distilled water (100 x 10^{-6} m^3) and the slurry was stirred for two hours at 363 K. Nickel nitrate hexahydrate (3.8 g) dissolved in distilled water (20 x 10^{-6} m^3) was added to this mixture drop wise. After stirring for six hours at room temperature, the contents were filtered, washed using hot distilled water and dried under vacuum and in an oven at 383 K for 10 hrs and then activated at 673 K for 10 hr. under hydrogen flow. After activation, the catalyst was brought to room temperature, flushed with nitrogen and used for reactions.

4.2.5.3. Acid treatment to resins

A resin bed was prepared in a glass column and soaked with water. Three preliminary washings were given by distilled water. One washing each with 0.1 M HCl and 0.1M NaOH was given to make the resin free of all the acid and base soluble impurities. Cation exchange resin was then prepared by treating the resin bed with 0.1 M HCl solution. A thorough washing with distilled water was given for removal of free acid as ensured with the help of pH measurement of the effluent water. The wet resin was then dried in oven at 343 K for 5 hours.

4.3. RESULTS AND DISCUSSION

Experimental work to establish VAM hydroformylation as a potential route for propylene glycols is presented in this section. VAM hydroformylation was studied in detail with Rh-catalysts and preliminary investigations were carried out with Ru and Ir catalysts. Hydrogenation of ac-pals and hydrolysis of ac-pols was studied to establish the total synthesis of propylene glycols with recyclable catalysts. The results are presented in the following sections.



Scheme 4.4. Hydroformylation of VAM along with side products

Scheme 4.4 presents VAM hydroformylation reaction including the side products. Numbers in the parenthesis are used throughout this chapter for referring compounds indicated by them. Also, the short forms used for respective compounds are elaborated in Appendix I.

4.3.1. Concentration-time profiles

In order to understand the catalytic aspects and optimize catalyst-product separation, several experiments were carried out in which effect of catalyst precursors, ligands, solvents, and reaction conditions on the activity, selectivity as well as product distribution was studied for hydroformylation of VAM. Some aspects of catalyst-product separation were also investigated. The results are presented in the following sub-sections.

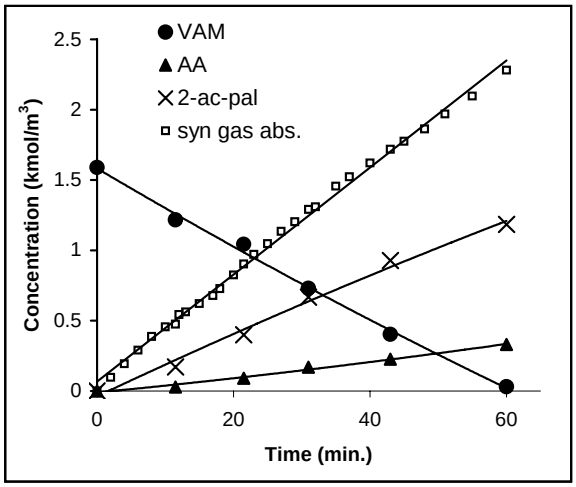
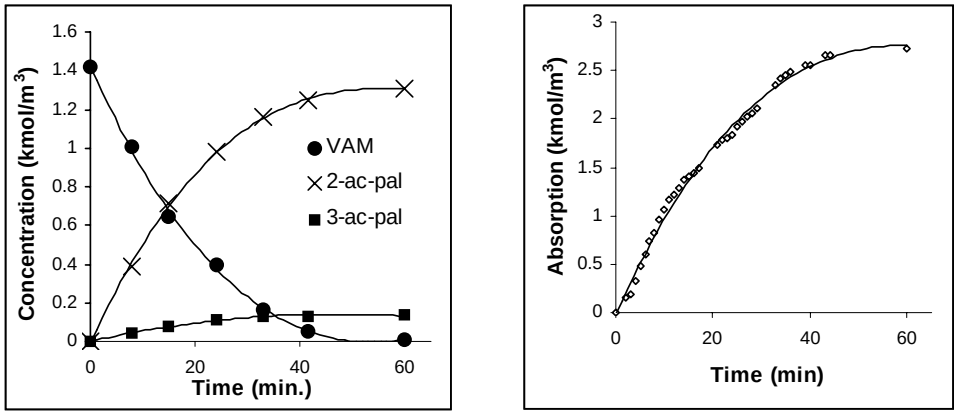


Figure 4.2. Concentration-time profile of a typical $Rh(CO)_2(acac)$ catalyzed VAM-hydroformylation
Reaction conditions: VAM, 1.46 kmol/m^3; $Rh(CO)_2acac$, 5.51 x 10^{-4} kmol/m^3; Cyclohexane, 22.5 x 10^{-6} m^3; Syngas, 6.2 MPa; CO : H_2, 1:1; T, 373 K; Agitation, 16.6 Hz.

Typical concentration-time profiles of a VAM hydroformylation products with $Rh(CO)_2(acac)$ and with $HRh(CO)(PPh_3)_3$ catalysts, are presented in Figure 4.2 and Figure 3 .3 respectively. Under certain conditions, hydroformylation of VAM with Rh-catalyst was highly selective for aldehydes with only negligible formation of ethyl acetate and acetic acid (1-1.5 % of the total VAM charged). Because of the absence of any side products, the syngas ($CO+H_2$) consumption profile matched well with the concentration time profile of the liquid samples as per stoichiometry. Regioselectivities, as reported in the literature, favored formation of branched aldehyde (2-ac pal) with a maximum linear: branched ratio of 0.11.



(a) **(b)**

Figure 4.3. Concentration-time profile of a typical $HRh(CO)(PPh_3)_3$ catalyzed hydroformylation of VAM – (a) Liquid concentrations (b) Syn gas absorption
Reaction conditions: VAM, 1.463 kmol/m^3; $HRh(CO)(PPh_3)_3$, 5.51 x 10^{-4} kmol/m^3; Solvent, Cyclohexane; Total charge, 25 x 10^{-6} m^3; Syn gas, 6.2 MPa; PCO : PH_2, 1:1; T, 373 K; Agitation, 16.6 Hz.

4.3.1.1. Effect of different Rh-precursors

Even though the active catalytic species in hydroformylation is a metal hydridocarbonyl, different precursors and ligands affect the electronic environment around the metal and thus affect activity and selectivity of the catalyst. Results of VAM hydroformylation with different Rh-precursors are presented in Table 4.3. $HRh(CO)(PPh_3)_3$ was found to be the best catalyst with 99 % selectivity to aldehydes. Under similar conditions, the TOF (hr^{-1}) for $HRh(CO)(PPh_3)_3$ catalyzed VAM hydroformylation was nearly 5 times higher than that with $Rh(CO)_2(acac)$ precursor (Run 1, 2). Catalyst precursors with -Cl as one of the ligands were least active. Both $[Rh(COD)Cl]_2$ and $[Rh(CO)_2Cl]_2$ showed poor activity and selectivities (Run 3,4 & 5). In fact, in the catalyst concentration range studied, $[Rh(CO)_2Cl]_2$ was active in alcoholic solvents only (see section 4.3.1.6) and under the same conditions, gave no reaction in toluene as a solvent (Run 4 in Table 4.3). $[Rh(CO)_2Cl]_2$ in ethanol showed 100% regioselectivity to branched aldehyde i.e. 2-ac pal which further transformed into acetals such as 1,1-diethoxy-2-acetoxy propane. Except for $HRh(CO)(PPh_3)_3$, all the active Rh-precursors produced acetic acid as a side product. The lack of activity with $RhCl_3$ and $RhPy_3Cl_3$ catalyst precursors (Run 6 & 7 in Table 4.3) is

consistent with the observation of Deshpande *et al.*[xiv] The metal salts and non-carbonyl precursors with strong binding ligands such as pyridine were thus found to be unable to form the active hydridocarbonyl species.

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It can be concluded from the results obtained on catalyst precursor studies that phosphine modification enhances rates and chemoselectivity of VAM hydroformylation but with slightly reduced regioselectivity to the branched aldehyde. For ~ 100 regioselectivity, unmodified Rh-catalyst such as $Rh(CO)_2(acac)$ were more suitable (Figure 4.2). Beside lower rates, the main drawback of $Rh(CO)_2(acac)$ catalyst was formation of acetic acid. Since, 3-ac pal or acrolein was not observed, the acetic acid must have been a decomposition product of VAM (more discussion in section 4.3.1.8)

Table 4.3. Effect of catalyst precursors

Run No	Cata-Prec.	Solvent	Catalyst x 10^3	VAM	Conv.	Chemoselectivity, %			Regioselectivity, %		TOF
			kmol / m^3	kmol / m^3	%	Ald	EA	AA	**I**	**II**	hr^{-1}
1	A	Cyclohexane	0.55	1.46	100	99	1	0	9	91	6565
2	B	Cyclohexane	1.09	2.36	99	94	0.4	5.6	0.7	99.3	1229
3*	C	Hexane	2.02	1.55	100	93	1.6	5.4	0	100	111
4	D	Toluene	0.5	1.94	0	0	0	0	-	-	0
5	D	Ethanol	0.5	1.94	100	11$	0.6	7.3	0	100	-
6	E	Methanol	1.85	1.46	0	0	-	-	-	-	-
7	F	Hexane	2.02	2.43	0	0	-	-	-	-	-

Reaction conditions: No extra ligand added. Temperature 373 K; Syn Gas Pressure, 4.1 MPa; CO:H_2, 1:1; Total charge, 25 x 10^{-6} m^3*; * = T, 383 . $ = Aldehydes are converted to acetals (more discussion in section 4.3.1.6). TOF is calculated at 90 % conversion level. Cyclohe. = Cyclohexane;* A = $HRh(CO)(PPh_3)_3$; B = $Rh(CO)_2(acac)$; C = $[Rh(COD)Cl]_2$; D = $[Rh(CO)_2Cl]_2$; E = $RhCl_3$; F = $RhPy_3Cl_3$.

4.3.1.2. Effect of solvents

In many homogeneous reactions, solvents not only act as diluents and homogenizing media but also play an important role in activity-selectivity behaviour. In view of this, several solvents were screened for different Rh-precursors and the results are presented in Table 4.4.

With $[Rh(COD)Cl]_2$ as a precursor, the reactions went well at 373 K in ethanol as a solvent albeit with a major side reaction of acetalization (See section 4.3.1.6). In hexane, the reaction was very slow with nearly half the rate compared to that in ethanol, whereas in solvents like benzene no reaction occurred at 373 K and reaction was slow at 383 K (Run 1, 2 & 3). In all the solvents, regioselectivity to the branched aldehyde (2-ac pal) was highly favored. In hexane, the side products such as acetic acid and ethyl acetate were less but increased in benzene due to prolonged contact time and higher temperature. The reasons behind formation of higher amount of ethyl acetate and acetic acid in ethanol were tandem acetalization and transesterification.

Table 4.4. Effect of solvents

Run No	Solvent	VAM	Catalyst x 10^3	Conv.	Chemoselectivity, %			Regioselectivity, %		Initial Rate x 10^3
		kmol/ m^3	kmol /m^3	%	Ald	EA	AA	I	II	kmol /m^3/s
$[Rh(COD)Cl]_2$										
1	Ethanol	1.92	2.03	100	7.8	38.8	10	0	100	0.226
2	Hexane	1.98	2.02	88.8	96	1.8	0	0.9	99.1	0.118
3*	Benzene	1.96	2.08	100	87	2.1	9	2.91	97.1	0.0907
$Rh(CO)_2(acac)$										
4	Hexane	5.01	1.86	99	94	0.3	5.2	1.4	98.6	0.28
5	Cyclohe.	2.36	1.09	95	95	0.5	4.5	1	99	0.29
6	Toluene	1.08	0.4	96	95	0.2	4.6	0.9	99	0.19
$HRh(CO)(PPh_3)_3$										
7	DCE $	1.46	2.84	12	99	0	0	11.5	88.5	-
8	Cyclohe.	1.46	0.55	100	99	1	0	9	91	1.88
9#	Toluene	1.08	0.54	100	98	0.5	0.7	5	95	0.21

<u>Reaction conditions:</u> Total charge, 25 x 10^{-6} m^3; T, 373 K; Syn gas, 4.1 MPa; CO:H_2, 1:1; Agitation, 16.6 Hz. ∗ = T, 383K and Syn gas = 5.5 MPa; $= Pressure, 10 MPa; # = T, 353K; AA = Acetic Acid; Cyclohe. = Cyclohexane.

For $Rh(CO)_2(acac)$, solvents showed no significant effect on the activity and selectivity. Compared to toluene and hexane, cyclohexane was found to be more suitable as far as rates and selectivity are concerned (Run 4, 5 & 6).

For $HRh(CO)(PPh_3)_3$, cyclohexane was found to be the best solvent with higher rates and good regioselectivity. Enhanced activity compared to toluene, was observed in cyclohexane (Run 8, 9). Whereas in toluene, regioselectivity to the branched aldehyde (2-ac pal) was higher than that obtained in cyclohexane, side products like acetic acid and ethyl acetate were observed in minor quantities (~ 1 %) in both the reactions. In halogenated solvents like dichloroethane, the catalyst was nearly inactive with only 12 % conversion in 180 minutes compared to 100 % conversion in 60 minutes in cyclohexane (Run 7, 8). This clearly proved the interaction (may be in the form of weak ligation at vacant sites) of solvents with the active organometallic catalyst. Thus, the presence of halogens as ligands or in solvent was not tolerated by Rh-VAM system. It is interesting to note that the same halogenated solvents showed better regioselectivity to linear aldehydes in cobalt catalyzed VAM hydroformylation (section 4.3.6).

Solvents like cyclohexane and hexane revealed an interesting property of phase separation with the VAM hydroformylation products. After completion of the reaction it was observed the solution was observed to separate into two layers on standing, bottom layer with ~ 75 % of 2-ac pal along with acetic acid and some solvent and an upper layer containing predominantly the solvent and some amount of 2-ac pal. Both the layers retained the color of the final solution thus confirming presence of catalyst in both the phases. On keeping the solution at sub-ambient temperatures, the phase separation was faster and a more concentrated (81 %) bottom layer of 2-ac pal was obtained. Since the solidification range of cyclohexane is 278.5 to 279.5 K, keeping the solution in the deep freezer solidified cyclohexane. The remaining solution contained > 90 % of 2-ac pal along with cyclohexane. This type of easy separation of products and solvent can be highly useful in isolating optically pure and sensitive products of VAM hydroformylation. Solvents like toluene, benzene didn't show this property even at higher concentrations of VAM hydroformylation products. More results on alcohol solvents are discussed in a separate section 4.3.1.6.

4.3.1.3. Substrate / catalyst ratio variation

Two Rh-precursors were tested at various catalyst/substrate ratios in order to examine their effect on the TON and TOF of the catalyst. The results are presented in Tables 4.5-A and 4.5-B. $HRh(CO)(PPh_3)_3$ was studied because of its higher activity and chemoselectivity

and $Rh(CO)_2(acac)$ was studied because of its ability to deliver aldehyde with nearly 100 % regioselectivity for 2-ac pal (section 4.3.1.1).

$HRh(CO)(PPh_3)_3$, with only 0.24 x 10^{-3} kmol/m^3 catalyst and 11000 times substrate concentration (Run A1), showed highest TON of 19823 however the TOF was not very high (7191) as the reaction required longer contact time of 180 minutes due to very small catalyst concentration and lower temperature. As the catalyst concentration was increased the TON and TOF reduced so also the AA **(IV)** formation and regioselectivity to 2-ac pal (Run A1-A3). Increasing the syngas pressure to 11.4 from 4.1 MPa, increases the TOF by ~1.5 times thus increasing the rate of reaction (Run A2 & A4).

Table 4.5. Effect of substrate/catalyst ratio
(A) $HRh(CO)(PPh_3)_3$ catalyst

Run No.	VAM	Catalyst x 10^3	Sub./ Cata	Conv.	Chemoselectivity, %		Regioselectivity, %		TON	TOF
	kmol/m^3	kmol/m^3		%	Ald.	**AA**	**I**	**II**		(h^{-1})
A1	2.66	0.24	11000	94.5	94	4.2	5	95	19823	7191
A2	1.22	0.52	2334	100	96	3.5	7.9	92.1	2251	3644
A3	2.1	1.1	2000	99	98	1.5	8.8	91.2	1954	2549
A4	1.3	0.48	2700#	100	96	3.5	7.8	92.2	2625	5637

Reaction conditions: Catalyst, $HRh(CO)(PPh_3)_3$; T, 373 K; Syn gas, 4.1 MPa, $CO:H_2$, 1:1; Solvent, Cyclohexane; Total charge, 25 x 10^{-6} m^3; Agitation, 16.6 Hz. No extra ligand added. # = 11.4 MPa. TOF is calculated at 90 % conversion level.

(B) $Rh(CO)_2(acac)$ catalyst

Run No.	VAM	Sub./ Cata	Conv.	Chemoselectivity, %		Regioselectivity %		TON	TOF
	kmol/m^3		%	Ald.	AA	I	II		(h^{-1})
B1	2.36*	2150	95	98	1	0.9	99.1	2072	791
B2	4.2	4538	97	90	8.2	0.8	99.2	3618	6270
B3	6.4	6785	93	89	9.5	08	99.2	5380	7031
B4	8.4	9275	93	78.7	18.66	0.6	99.4	6795	9430

*Reaction conditions: $Rh(CO)_2(acac)$, 0.96 x 10^{-3} kmol/m^3; T, 393 K; Syngas, 9 MPa; $CO:H_2$, 1:1; Solvent, Cyclohexane; Total charge, 25 x 10^{-6} m^3; Agitation, 16.6 Hz. No extra ligand added; * = 4.1 Mpa, 373K. TOF is calculated at 90 % conversion level.*

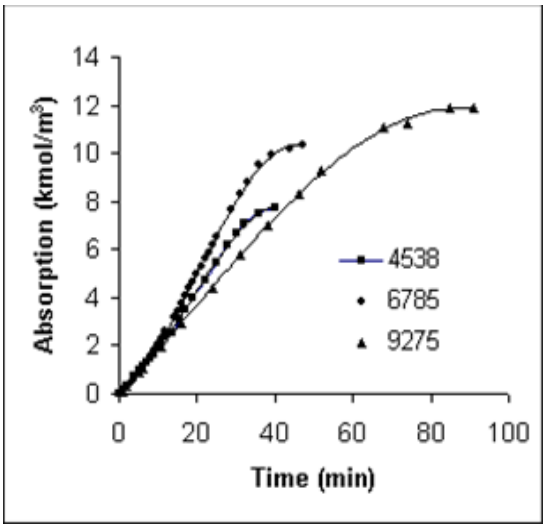


Figure 4.4. Effect of VAM: Rh ratio
Reaction conditions: As described in Table 4.5 (B).

With $Rh(CO)_2(acac)$, the catalyst concentration was kept constant at 0.96 kmol/m^3 and substrate concentration was increased to test its effect on the activity and selectivity. It was observed that at 373 K and 4.1 MPa syngas pressure, slower reaction rates with an overall TOF of only 791 were observed, but the side products (AA) reduced to only 1 % (Run B1). As the substrate concentration was increased, both the TON and TOF increased with a maximum TOF of 9430 h^{-1} at 8.4 kmol/m^3 VAM concentration. On increasing the substrate concentration, the regioselectivity to 2-ac pal and AA formation also increased. Increase in AA formation on increasing substrate concentration confirms that AA is formed as a VAM decomposition product (section 4.3.1.8). As shown in Figure 4.4, the initial rate of reaction was found to be the same for VAM: Rh ratio of 4538 to 9275. Increasing the ratio from 4538 to 6785, increased the overall activity of the catalyst whereas at a ratio of 9275 the overall activity reduced instead of further increase. The reason must be higher amount of AA formation at 9275 ratio (Run B4 in Table 4.5).

4.3.1.4. Effect of ligands at high syngas pressure (4.1 MPa)

Preliminary evaluation of the general P, N, and As containing ligands was done for Rh-catalyzed VAM hydroformylation with the aim of obtaining a class of ligands which have maximum positive effect on the activity and selectivity in the reaction towards desired products. The results are presented in Table 4.6. With almost all the ligands tested, the initial rate of hydroformylation was found to be higher compared to that with unligated $Rh(CO)_2(acac)$ catalyst. This may be due to difficulty in the formation of active hydrido-carbonyl species with $Rh(CO)_2(acac)$ as a precursor. Ligands must be facilitating the

formation of active species *e. g.* with TPP, immediate formation of active 16 electron species, $HRh(CO)(PPh_3)_2$ must be taking place. Another possible reason for hindrance posed by ligands to the substrate chelation with Rh (More discussion in section 4.3.1.8). Since, TPP showed increased product linearity compared to the other ligands, a separate study on the effect of TPP/Rh ratio was carried out, the results of which are shown in Figure 4.5. With an increasing TPP/Rh ratio from 3 to 6, the rate of reaction was found to decrease considerably whereas further increase in TPP: Rh ratio to 12 and 18 showed no further decrease in the initial rate. Product linearity enhanced considerably with *I/II* ratio increasing from ~ 0.08 to 0.14 at TPP:Rh ratio of 3 and 12 respectively. At TPP : Rh ratio of 18, the *I/II* ratio remained constant at 0.14.

Table 4.6. Effect of ligands

Run no.	Catalyst	Ligand	Run time	Conv.	Ald.	Regioselectivity %		Initial Rate x 10^3
			Min.	%	%	I	II	kmol/m^3/s
1@	$Rh(CO)_2acac$	-	170	96	98	1.01	98.99	0.1
2	$Rh(CO)_2acac$	TPP	80	100	93	6.5	93.4	0.69
3	$Rh(CO)_2acac$	TPAs	95	94	99	4.5	95.5	0.38
4*	$Rh(CO)_2acac$	TPAs	65	99	98.4	10.5	89.5	0.69
5	$Rh(CO)_2acac$	TOPO	114	59	100	0	100	0.2
6	$Rh(CO)_2acac$	TPPO	110	70	100	0	100	0.19
6	$Rh(CO)_2acac$	Pyridine	125	99.6	89.4	1.5	98.5	0.3
7	$Rh(CO)_2acac$	Bipyridine	100	34	84	0.96	99.14	0.14
8	$Rh(CO)_2acac$	An. Acid	197	95	98	0.8	99.2	0.21
9$	$HRh(CO)(PPh_3)_3$	-	60	99.4	99.5	5.7	94.3	1.8
10$	$HRh(CO)(PPh_3)_3$	TPA	60	99	98	1.2	98.8	0.96
11$	$HRh(CO)(PPh_3)_3$	TBA	50	93	98	1.2	98.8	0.90

<u>Reaction conditions:</u> Toluene, 22.5 x 10^{-6} m^3; Total charge, 25 x 10^{-6} m^3; VAM, 1.3 kmol/m^3; Catalyst, 1.01×10^{-3} kmol/m^3; Ligand / Rh, 3; T, 353K; Syngas, 4.1 MPa; CO:H_2,1:1; Agitation, 16.6 Hz; @= T, 373 K; ∗ = Ligand/Rh ratio, 16; $ = Solvent, Cyclohexane at T = 373K.

Decreasing rates and increasing linearity with increasing ligand concentration are known phenomenon in hydroformylation reactions,[xv] in fact, commercial Rh-based processes

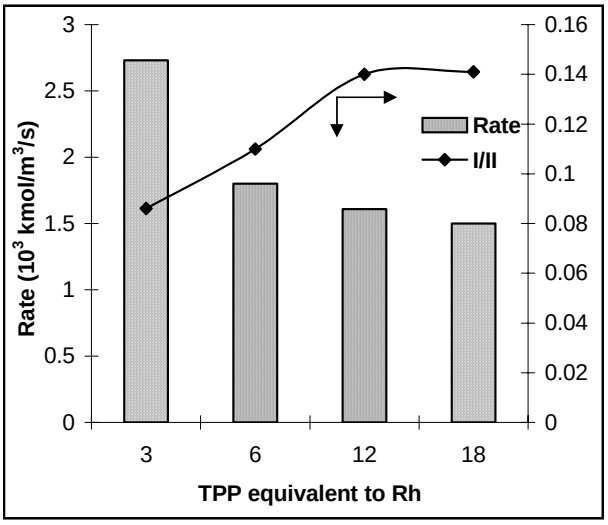
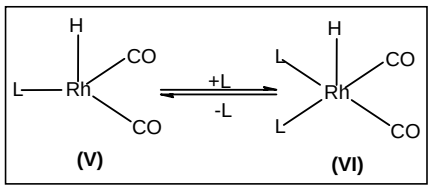


Figure 4.5. Effect of TPP concentration on Rh-catalyzed VAM hydroformylation
Reaction conditions: VAM, 1.22 kmol/m^3; Cyclohexane, 22.5 x 10^{-6} m^3; $HRh(CO)(PPh_3)_3$, 0.52 x 10^{-3} kmol/m^3; T, 373 K; Syngas, 4.1 MPa; $CO:H_2$, 1:1; Agitation, 16.6 Hz.

are operated at large excess of ligands to obtain higher linearity. However, for VAM, the effect of ligand concentration was not as prominent as is in the case of linear olefins. The reason behind the observed ligand concentration effect of lower activity and higher regioselectivity to the linear products, is thought to be, an abundance of more ligated species (VI) compared to less ligated species (V) at higher phosphine concentrations, as shown in the adjoining figure.



Species (VI) is a 18 e$^-$ species *i.e.* a saturated species and hence is more stable compared to species (V) which is a 16 e$^-$, unsaturated species. The associative mechanism of hydroformylation with species (VI) increases the linearity slightly. A decrease in the rates with (VI) is due to its lower reactivity (saturated species) compared to (V).

TPAs, concentration effect was studied for TPAs: Rh ratio of 3 and 16 (Run 3,4 in Table 4.6). The rate of hydroformylation as well as regioselectivity to linear aldehyde (3-ac pal, **I**) increased with increase in TPAs concentration. However, even at TPAs: Rh ratio of 16, the regioselectivity to 3-ac pal (**I**) was ~ 10 % and that to 2-ac pal **(II)** was ~ 90 %. TOPO, TPPO and anthranilic acids were found to be nearly inert as ligands (Run 5,6 & 8 in Table 4.6).

Among the N-containing ligands, bipyridine deactivates the catalyst (Run 7), perhaps by forming a chelated complex and thus prohibiting the formation of active species. Amines

like triphenyl amine and tributyl amine were found to reduce the activity of $HRh(CO)(PPh_3)_3$ catalyst (Run 10,11). The idea behind testing these ligands with $HRh(CO)(PPh_3)_3$ instead of $Rh(CO)_2(acac)$, was to see the effect of mixed N- and P-containing ligands.

These results clearly indicate that, in the case of VAM hydroformylation, Rh-catalysts always favor regioselective formation of branched aldehyde product (2-ac pal) irrespective of the ligand used. This general screening of ligands marks phosphines to be the most suitable ligands for further investigations. Since, Aboutgloue *et al.*[viii] have already studied substituted triphenyl phosphines and trialkyl phosphines as ligands for Rh-catalyzed hydroformylation of VAM, in the present work bis(diphosphino) alkanes were studied in more detail. The effect of these ligands was tested at atmospheric syngas pressure and also at higher syngas pressures and the results are discussed in the following sections.

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4.3.1.5. Effect of ligands at atmospheric syngas pressure (Tamura's reaction)

The promoting effect of bis(diphenylphosphino) alkanes (hereafter abbreviated as diphos alkanes) on $HRh(CO)(PPh_3)_3$ catalyzed hydroformylation has been reported in the literature, [xvi,xvii,xviii] *e.g.* Tamura *et al.*[xviii] have observed that for ethene, propene, butenes and allyl alcohol, in the presence of DPPP, the rate and selectivity of hydroformylation increased even at atmospheric pressures. Even Fell *et al.*[xix] also have shown that Co carbonyls modified with dialkyl phosphines when used for higher olefins, the double bond isomerization is suppressed substantially. In view of these studies three reactions at atmospheric pressures of syngas were carried out with or without additional ligands and the results are presented in Table 4.7.

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Table 4.7. Rh-catalyzed hydroformylation of VAM at atmospheric syngas pressure

Run No.	Catalyst	Ligand	Run time	Conv.	Ald. Sel.	Regioselectivity, %		Ini. Rate x 10^3
			Min.	%	%	II	I	kmol/m^3/s
1*	$HRh(CO)(PPh_3)_3$	DPPP	60	70.2	58.5	100.00	0	0.42
2	$HRh(CO)(PPh_3)_3$	-	60	0	0	0	0	0
3	$Rh(CO)_2acac$	DPPP	180	16	100	100.00	0	0.09

*Reaction conditions: VAM, 1.3 kmol/m^3; Catalyst, 1.4 x10^{-3} kmol/m^3; Ligand/Rh, 1; Toluene, 22.5 x 10^{-6} m^3; Total Charge, 25 x 10^{-6} m^3; Temperature, 353 K; CO:H$_2$ = 1:3; atmospheric pressure, * = Ethyl acetate (III) is formed with 42 % selectivity.*

Under atmospheric pressure conditions, $HRh(CO)(PPh_3)_3$ showed no catalytic activity for hydroformylation of VAM in 60 minutes (Run 2). Under exactly similar conditions of Run 2, if 1 equivalent of DPPP ligand is added, 70 % VAM conversion was observed (Run 1) but with unexpected hydrogenation of VAM to EA (42 %) and only 58 % chemoselectivity to aldehydes. Thus, it was clear that DPPP facilitates Rh-catalyzed hydroformylation of VAM as well as hydrogenation. When only DPPP was used as a ligand with $Rh(CO)_2(acac)$ precursor, under similar conditions, only 16 % conversion was achieved with 100 % chemoslelectivity to aldehydes in 180 minutes of run time (Run 3). In both the runs with DPPP ligands, 100 % regioselectivity to the branched aldehyde 2-ac pal was obtained. Thus, it can be concluded from the above experiments that for atmospheric pressure VAM hydroformylation, TPP alone is inactive, DPPP alone is less active whereas a combination of TPP and DPPP is active for both hydroformylation and hydrogenation. Possible mechanistic explanation to the above observations is discussed in section 4.3.1.8. The anticipated effect of DPPP on regioselectivity was not obtained at atmospheric conditions, but an interesting activity pattern prompted curiosity and so the effect of diphos ligands at higher syngas pressure was studied and the results are presented in Table 4.8.

Table 4.8. Rh-catalyzed hydroformylation of VAM at high syngas pressures

Run no.	Ligand	Run time	Conversion	Aldehyde selectivity	Regioselectivity %	
		Min.	%	%	II	I
1	-	170	96	98	98.99	1.01
2	DPPE	80	97	99	99	1
3	DPPP	85	94	98	98.99	1.01
4	DPPB	84	99	98	98.52	1.48
5	DPPH	105	96	98	98.99	1.01
6*	TPP	80	100	98	94.3	5.7

*Reaction conditions: VAM, 1.085 kmol/m^3; Rh(CO)$_2$(acac), 0.54x10^{-3} kmol/m^3; Ligand/Rh, 1; Toluene, 22.5 x 10^{-6} m^3; Total Charge, 25 x 10^{-6} m^3; Temperature, 373K; CO:H$_2$ = 1; Pressure, 4.1 MPa. Agitation, 20 Hz; * = Ligand/Rh, 3.*

The diphosphine ligands were tested under high-pressure conditions, at 1 molar equiv. ratio to Rh. The idea was to generate a chelating species $HRh(CO)(P)_2$ with an increasing carbon chain between two phosphine ligands. Even though the diphos ligands showed an impact on reaction rates, no change in the regioselectivity of the products was observed. With ligands such as DPPP and DPPB, the rates were nearly similar to that of TPP whereas with higher diphos ligands such as DPPH, the reaction rates were reduced to half of those with lower diphos like DPPP. Thus, instead of acting as a chelating diphosphine ligand, DPPH may be behaving more as a diaryl-alkyl phosphine. All the diphos ligands exhibited excellent chemoselectivity of > 98 % and all the ligands favored regioselective formation of 2-ac pal**.**

Comparison of different ligands on the basis of Syngas Absorption Vs. Time is presented in Figure 4.6. All the reactions with ligand-modified Rh catalyst showed higher hydroformylation rates compared to the unligated Rh.

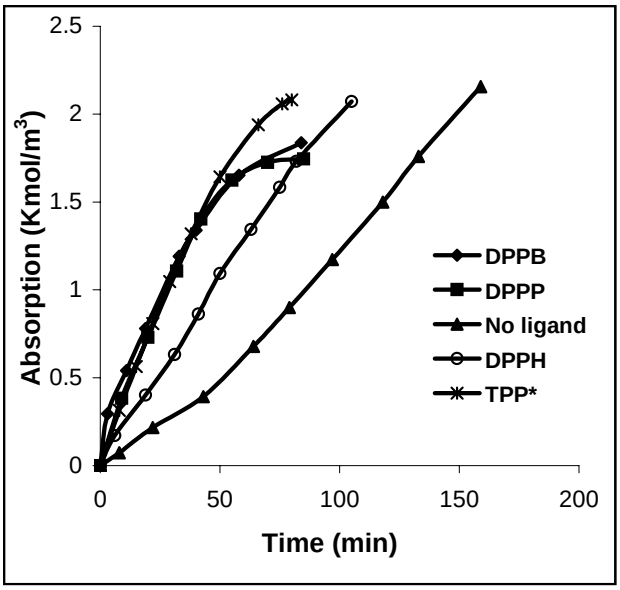
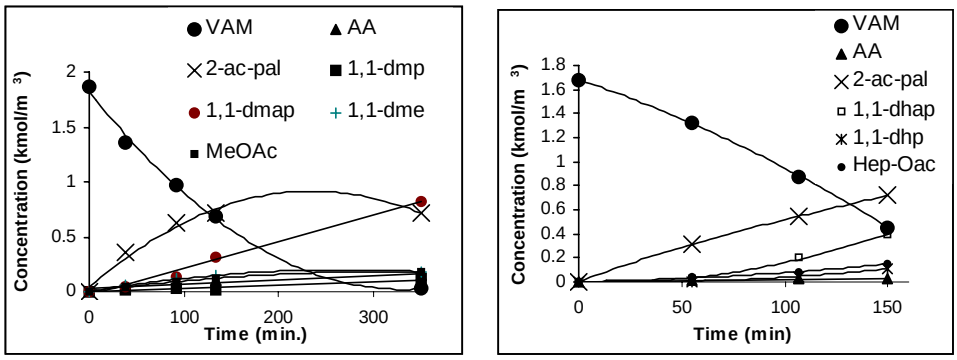


Figure 4.6. Effect of ligands on Rh-catalyzed hydroformylation of VAM
Reaction conditions: Same as those for Table 4.8

4.3.1.6. Tandem hydroformylation - acetalization in presence of alcohol solvents

Aldehydes with extra functional group/s are generally unstable and reactive.[xx] An excellent example of such unstable aldehyde is 3-aetoxypropanal (Section 4.2.6). Such aldehydes when produced by hydroformylation, lead to many side products. I*nsitu* protection of the aldehyde functionality could be a solution to avoid such decomposition and oligomerisation of aldehydes, and the best way to protect aldehydes was to convert them to acetals. This tandem hydroformylation - acetalization reaction can be an important tool for preparing multifunctional compounds, especially from functionalized olefins. For substrates like VAM, where a prochiral center is present, a tandem sequence of hydroformylation - acetalization can be very important to generate large libraries of chiral acetal compounds. This type of *insitu* protection of the aldehyde functionality can prove to be useful for chiral aldehydes such as + /- 2-ac pal as well as unstable aldehydes such as 3-ac pal.

In the present study, tandem hydroformylation - acetalization study has been carried out using unmodified Rh precursors such as $[Rh(COD)Cl_2]_2$ and $Rh(CO)_2Cl_2$. Typical concentration time profiles for $[Rh(CO_2Cl]_2$ catalyzed VAM hydroformylation-acetalization reactions with two solvents namely methanol and heptanol, are presented in Figure 4.7. All the products were characterized by GC-MS and the selected spectra are presented in

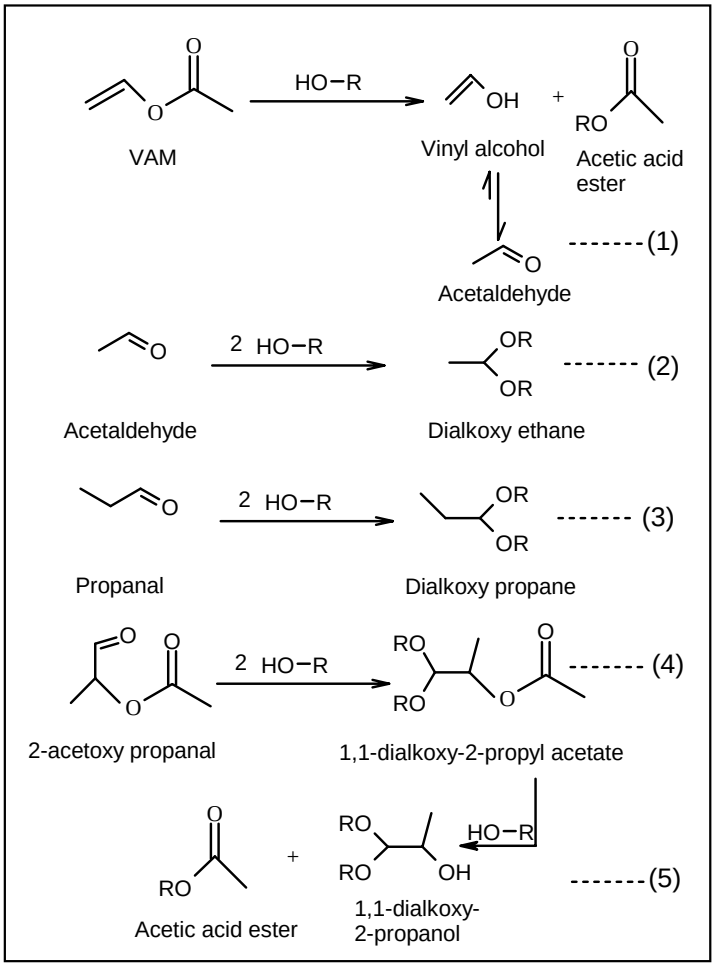


(a) **(b)**

Figure 4.7. Concentration-time profiles of hydroformylation – acetalization in (a) Methanol and (b) Heptanol solvents

<u>Reaction conditions:</u> VAM, 1.7 kmol/m^3; $Rh(CO)_2Cl_2$, 4.17 x 10^{-4} kmol/m^3; Solvent, 22.5 x 10^{-6} m^3; Syngas, 6.2 MPa; PCO : PH_2, 1:1; T, 373 K; Agitation, 16.6 Hz.

Appendix II. Possible side reactions that lead to different side products under hydroformylation conditions are shown in Scheme 4.5 and with the help of this scheme, explanation of the products from the concentration-time profiles is given below.



Scheme 4.5. Hydroformylation of VAM in alcoholic solvents

Acetalization was faster with lower alcohols like methanol and it started slowly with higher alcohols such as heptanol. In case of heptanol, 1,1-diheptoxy-2-propanol (dhpol) was observed along with conventional acetal i. e. 1,1-diheptoxy-2-propyl acetate (dhpac), whereas with methanol only 1,1-dimethoxy-2-propyl acetate (dmpac) was observed and 1,1-dimethoxy-2-propanol was absent. dhpol must be a transesterification product of dhpac and heptanol (Reactions (5) in Scheme 4.5). Formation of alcoholic esters like methyl acetate (MA) and heptyl acetate (HA) was observed with methanol and heptanol respectively. In case of heptanol, HA was produced by two transesterification reactions, that of VAM as well as of dhpac (Reactions (1) & (5) in Scheme 4.5) whereas in case of methanol, MA was produced exclusively by transesterification of VAM. With methanol as a solvent, 1,1-dimethoxy ethane (dme) and

1,1-dimethoxy propane (dmp) were observed, but they were absent in heptanol. dme and dmp were formed by acetalization of acetaldehyde and propanal respectively (Reactions (2) & (3) in Scheme 4.5). Propanal in turn was formed by ethylene hydroformylation, which in tern was formed by VAM hydrogenolysis (Reaction no. (2,3) in Scheme 4.9).

As shown in Scheme 4.5, VAM transesterification to vinyl alcohol and acetic acid was an important side reaction observed only in alcoholic solvents especially with lower alcohols such as methanol, ethanol etc. Since, vinyl alcohol is a highly unstable compound, it was immediately transformed to acetaldehyde (Reactions (1) in Scheme 4.5). Transesterification of VAM was not observed when only VAM and alcohol were refluxed. Thus, this must be a catalytic reaction, might be catalyzed under acidic conditions. In non-alcoholic hydrocarbon solvents such as toluene, cyclohexane etc., transesterification with solvent is not possible but hydrogenolysis of VAM to ethylene and acetic acid was a common reaction in both alcoholic and non-alcoholic solvent (Reaction no. (2) in Scheme no 4.9). The activity-selectivity results on tandem hydroformylation - acetalization with $[Rh(CO)_2Cl]_2$ catalyst in methanol, ethanol and heptanol are presented in Table no. 4.9.

Table 4.9. Tandem hydroformylation-acetalization reaction in alcohol solvents

Run no.	**Solvent**	Run Time	VAM conv.	AA	EA	AAc	2-ac pal	dae	dap	Dapol	Dapac
		Min.	%	%	%	%	%	%	%	%	%
1	Methanol	350	98.7	7.9	0.6	9.9	38.6	9	6.4	-	44.8
2	Ethanol	100	100	7.4	62	-	7.7	34.9	10.5	18.1	40.7
3*	Heptanol	120	73	2.6	-	12.5	58.6	-	-	9.1	32.2
4#	Ethanol	160	100	10	39	-	8.6	15.8	8.8	14.8	48.4

*Reaction conditions: VAM, 1.92 kmol/m^3; $Rh(CO)_2Cl_2$, 0.4 x 10^{-3} kmol/m^3; Solvent, 21 x 10^{-6} m^3; T, 373k; Syngas, 6.2 MPa; $CO:H_2$, 1:1; Agitation, 16.6 Hz; # = Catalyst used is $[Rh(COD)Cl]_2$, 2.035 x 10^{-3} kmol/m^3 ; * = 2.4 % 3-acetoxy propanal is formed.*

Quantification of all the acetals in the Table 4.9 was done by applying the response factor of 2-ac pal and so there may be an error of ~ 5 % in the quantification. Because of many consecutive side reactions involving both the functionalities of VAM (double bond and acetate) the product balance in alcoholic solvents was always much more than 100 % compared to VAM charged.

In methanol, hydroformylation of VAM was very slow under the reaction conditions studied (Run 1 in Table 4.9). In methanol, the syngas absorption prolonged for more than five hours whereas under similar conditions, in ethanol significantly higher rate were observed. Negligible formation of MA indicated less activity towards transesterification reaction in methanol. The small amount of MA (9.9 %) formed must be only from VAM – transesterification as dme (acetal of acetaldehyde) was observed but dmpol was absent. Even, acetalization reaction was slow as only 44.8% of dmpac was formed and 38.6 % of 2-ac pal remained intact at the end of 5 hr.

With ethanol as a solvent the gas absorption was faster and stopped in 100 minutes (Run 2 in Table 4.9). GC analysis showed 100 % conversion of VAM but selectivity to aldehyde was lower compared to other products. More than hydroformylation, the other reactions such as transesterification, hydrogenolysis, and acetalization dominated in the selectivity profile. Formation of 62 % ethyl acetate and 7.4 % acetic acid along with 34.9 % dee and 18.1 % depol, clearly proved that the source of EA was transesterification of VAM and depac and not hydrogenation of VAM. Only 7.7 % 2-ac pal remained unreacted, the remaining was converted into depac (58.8 %), a part of which (18.1 %) was further converted to depol by transesterification. 10.5 % dep confirmed presence of propanal obtained via VAM hydrogenolysis.

Higher alcohol like heptanol as a solvent was found to protect VAM from side reactions such as transesterification, hydrogenolysis and hydrogenation as only 2.6 % of AA and 12.5 % of HA were formed. However, on comparison with the results in ethanol as a solvent, hydroformylation rate was also slower in heptanol as only 73 % VAM conversion was obtained in 120 minutes. Thus, apart from acetalization of 2-ac pal to dhpac (32.2 %), the only side reaction that took place in heptanol was transesterification of dhpac to dhpol (12 %). Presence of 58.6 % of 2-ac pal intact without acetalization confirms lower catalyst activity for acetalization in heptanol as compared to ethanol.

Tandem hydroformylation –acetalization was also carried out with $[Rh(COD)Cl]_2$ catalyst in ethanol (Run no. 4 in Table no 4.9). In spite of using 4 times higher catalyst concentration, the reaction was slower and required 160 minutes for completion. The slower reaction can be due to slower formation of active Rh-carbonyl catalyst from $[Rh(COD)Cl]_2$.

Comparison with Run 2, shows that, with $[Rh(COD)Cl]_2$ transesterification of VAM as well as depac were slow, so also the formation of dee and dep.

Thus, from the present study, it can be concluded that in alcoholic solvents many simultaneous reactions take place along with VAM hydroformylation. Dual functionality of VAM increases complications over the expected hydroformylation – acetalization sequence. By proper manipulation of solvents, reaction conditions and time, a tandem sequence of hydroformylation-acetalization and transesterification can be achieved with formation of 1,1-dialkoxy-2-propanol as the major product. It would be interesting to study the reaction in different mono-alcohols, diols, aryl alcohols, cyclic alcohols etc. If chiral ligands are used, a library of chiral compounds can be generated by using such alcohols and by proper manipulation of reaction conditions.

4.3.1.7. Catalyst-product separation

Major problem in any homogeneous catalytic process is the recycle of catalyst system (including ligands / promoters, if used). Our study revealed an interesting property of partial aqueous solubility of acetoxy propanals, which can be advantageous for catalyst-product separation. The main advantage of this is the easy separation from the reaction mixture and thus avoiding the conventional way of distillative separation. We have studied two ways of effective catalyst-product separation, using this solubility property, *in situ* extraction (reverse biphasic) and conventional extraction after complete reaction.

4.3.1.7.1. Reverse biphasic system

Generally, phase separation of a catalyst is considered to be the most economical and environmentally friendly approach for recycle of catalyst. Aqueous biphasic hydroformylation has already found commercial applications for propylene hydroformylation, but because of partial solubility of acetoxy propanals in the aqueous phase, the conventional biphasic catalysis was not useful for VAM hydroformylation system. Reverse biphasic system, in which conventional homogeneous reaction is carried out with just an addition of a separate aqueous phase to the reaction charge, is a useful technique for such systems. Thus, the products are *insitu* extracted in the aqueous phase during the reaction[xxi]. With this technique, the catalyst/product separation can be achieved more

economically and both catalyst and products can be protected from decomposition as they remain in separate phases. A preliminary study of reverse biphasic system for hydroformylation of VAM was carried out and the results are presented in Tables 4.10 and 4.11.

Wilkinson catalyst without any addition of a ligand or a promoter was used for this reverse biphasic study. The organic phase (containing catalyst) was recycled after applying one aqueous extraction to the system. Figure 4.8 clearly shows nearly perfect recyclability of the catalyst.

Mass balance of the first reaction with an additional aqueous phase is presented in Table 4.10. 2-ac pal (II) was found to have higher solubility in water compared to 3-ac pal (I). 73 % of 2-ac pal was extracted out in the aqueous phase whereas only 49 % of 3-ac pal went into the aqueous phase. Enhancement in the acetic acid formation was a major drawback of this system. Since, acrolein was not observed in either of the phases and trace amount of propanal was observed in the organic phase, the acetic acid must be formed by VAM decomposition (more discussion in section 4.3.1.8). 1.1 mmol of ethyl acetate was also formed and 80 % of it was found to remain in the organic phase.

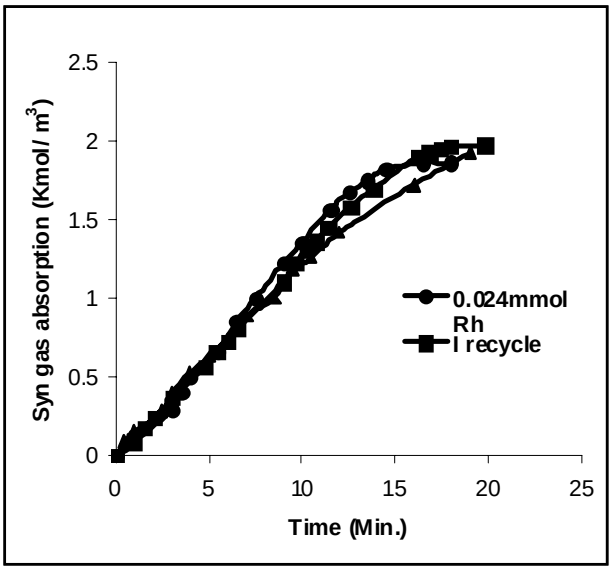


Figure 4.8. Catalyst recycle in Rh-catalyzed reverse biphasic hydroformylation
Reaction conditions: Similar to table no. 4.10.

Table 4.10. Mass balance for a reverse biphasic reaction (figures in the brackets indicate % of each compound in the respective phase)

	VAM	Aldehydes		Side products		Mass balance
		I	II	III	IV	
	mmol (%)	mmol (%)	mmol (%)	mmol (%)	mmol (%)	mmol (%)
INITIAL	48	-	-	-	-	48 (100)
Aq. Final	0.18 (7.1)	1.67 (49.1)	26.4 (73.1)	0.27 (20.4)	3.85 (80.5)	
Org. Final	2.31 (92.3)	1.73 (50.9)	9.77 (26.9)	1.06 (79.6)	0.93 (19.5)	
Total Final	2.49	3.40	34.89	1.33	4.78	47.89 (99.8)

Reaction conditions: VAM, 1.915 kmol/m^3; HRh(CO)(PPh$_3$)$_3$, 0.97x10^{-3} kmol/m^3; Solvent, Toluene + water (50% each); Total Charge, 25 x 10^{-6} m^3; Temperature, 373 K; CO:H$_2$ = 1; Pressure, 4.1 Mpa

Table 4.11. Catalyst recycle in Rh-catalyzed reverse biphasic hydroformylation

	Conversion	Ald. Selectivity	Regioselectivity %		Side Products %		Rates
	%	%	II	I	III	IV	10^3 kmol/m^3/s
Initial reaction	94.8	86.63	91.1	8.9	2.92	10.45	2.5
I recycle	95.9	85.16	91	9	2.41	12.43	1.96
II recycle	99	84.96	95.6	4.4	1.05	13.99	2.01

Reaction conditions: Initial reaction - Similar to Table no. 4.10. For recycle I and II, the organic phases of initial reaction and I recycle are used as such for recycle I and II respectively, VAM, 1.915 kmol/m^3 and water, 11 x 10^{-6} m^3.

Thus, the present reaction suffered from incomplete extraction of products from the organic phase. Since in case of Rh, 2-ac pal is obtained with more than 90 % selectivity, the problem of 3-ac pal remaining in the aqueous phase was not much severe but 27 % of 2-ac pal remaining in the organic phase was not tolerable for the organic phase recycle. There were two ways to solve the problem, applying second extraction after the reverse biphasic reaction or increasing the aqueous phase hold-up. Because of the limitation of the reactor size for increasing aqueous phase hold-up, for the present work, first technique was used for complete extraction of products from the organic phase.

The conversion and selectivity of the recycle runs is presented in Table 4.11. The values are based on combined concentration of products in both the phases. For all the recycles, the aqueous phase remained totally colorless and the organic phase retained its dark brown color intact. This gives preliminary indication of a leaching free recycle system. Selectivity to 3-ac pal was found to decrease in each recycle, whereas there was an increase in the AA formation. Due to the increased formation of AA, aldehyde selectivity reduced after every recycle. EA formation was minor and it was found to reduce after every recycle. Since, acetic acid has higher solubility in the aqueous phase, more than 80 % of it was extracted out in the aqueous phase. Thus, acetic acid, which acts as a poison[viii] for active hydroformylation catalyst could be kept away from the organic phase, saving it from decomposition due to acetic acid. This proves one of the advantages of *insitu* extraction of products in the reverse biphasic system.

From the above study many drawbacks of a reverse biphasic reaction for VAM hydroformylation were noticed. Problems such as, higher amount of side products formation; solubility of side products in both the phases; and most importantly the presence of acetoxy propanals in both the phases, made it mandatory to run further water extractions for complete removal of products from the organic phase. Improvement in the selectivity and recyclability of the catalyst can be achieved by addition of excess of ligand (PPh_3 in case of $HRh(CO)(PPh_3)_3$). The increased ligand is expected to increase the aldehyde selectivity by reducing acetic acid formation and stabilize the active Rh catalyst in the organic phase. More improvement in the *insitu* extraction of the products can be achieved by proper manipulation of organic and aqueous phase hold up ratios and proper choice of organic phase. Also, the problem of incomplete extraction is more applied to a batch mode operation, whereas, for a continuous mode of operation, in which the aqueous phase is continuously removed and organic phase remains stationary in the reactor, there will not be any question of products remaining in the organic phase.

4.3.1.7.2. Conventional extraction after hydroformylation reaction

Since, the solubility of acetoxy propanal in water is limited, a problem of poor separation is encountered in the reverse biphasic reaction. Repetitive extractions with water are required for complete separation of the products from the catalyst phase. For all the

reactions after hydrogenation of 2-ac pal in the aqueous phase (section 4.3.4.2), the products were separated with this conventional extraction method. Important observations made while using this technique are listed below.

1) For a 25 x 10^{-6} m^3 reaction product mixture containing 1.3 kmol/m^3 concentration of 2-ac pal, at least 5 extractions with 5 x 10^{-6} m^3 water are needed for complete extraction of the aldehydes in the aqueous phase.
2) For solutions with ≥ 15 % acetic acid (formed in hydroformylation reaction), leaching of Rh-catalyst (faint color) in the aqueous phase was observed.
3) Hydroformylation reactions in which ligands such as PPh_3, TPAs etc. were used with Rh-catalyst, effective separation of the catalyst phase was observed, even in presence of >10 % acetic acid. Use of excess ligands helped Rh-catalyst to remain in the organic phase.
4) Acetoxy propanals, especially 2-ac pal, formed oligomers (dimmers, trimers) in the aqueous phase. The oligomerisation was found to increase on keeping the aldehydes for longer time in the aqueous phase.

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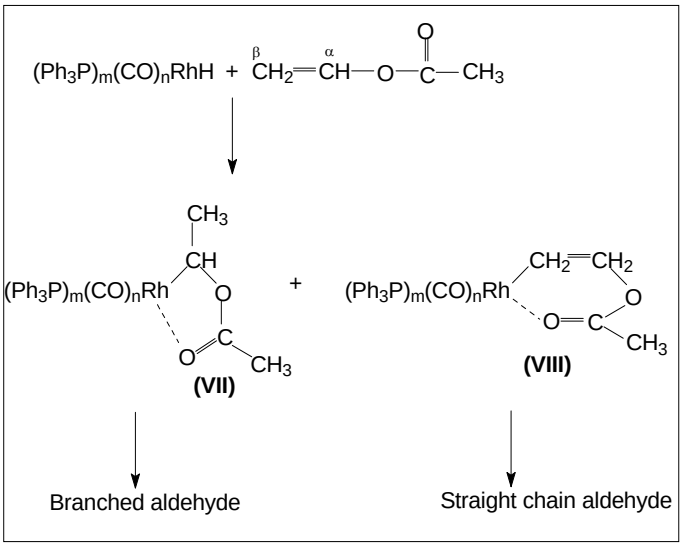
4.3.1.8. Mechanistic interpretation of the results

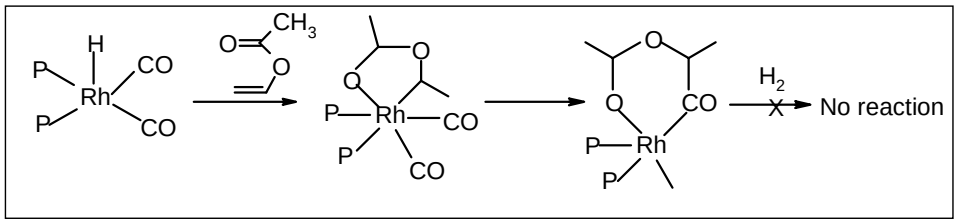
VAM is an interesting substrate with a dual functionality of a double bond and an ester (acetate) group. Even though it is the olefinic double bond, which is transformed in the hydroformylation reaction, the presence of an acetate group plays an important role in deciding the reactivity of this double bond and the chemoselectivity and regioselectivity of the products. It is already known in the literature that (Section 1.2.3.2), be it a hydroformylation or a carbonylation of VAM, invariably formation of branched products are favored. It is the 'α' carbon atom where formyl, ester or acid group is formed. In this section, a mechanistic interpretation of the activity-selectivity patterns in VAM hydroformylation is presented and attempts have been made to explain the results based on these interpretations.

4.3.1.8.1. Catalyst activity in hydroformylation of VAM

It is well known from the previous literature on hydroformylation and amidocarbonylation reactions, that multifunctional compounds form chelating ring complexes with the transition metal catalysts consisting of Rh, Co etc.[xxii] It is proposed in the literature[viii] that VAM with its acetate functionality forms a chelating ring with the catalyst metal. As shown in the Scheme 4.6, two such rings are possible based on whether the metal (Rh in the present case) forms an alkyl species with 'α' or with 'β' carbon atom of VAM. The activity of VAM for hydroformylation reduces due to such chelation. It is reported that the activity of VAM is one fifth of that of 1-pentene under similar conditions.[xxiii] The substrate chelation can be reduced by use of bulky lignads. This is a reason behind the observed effect of rate enhancement by lignads such as TPP, TPAs *etc.* in comparison to the unligated species formed from $Rh(CO)_2acac$ (Table 4.6).



Scheme 4.6. VAM chelation with Rh

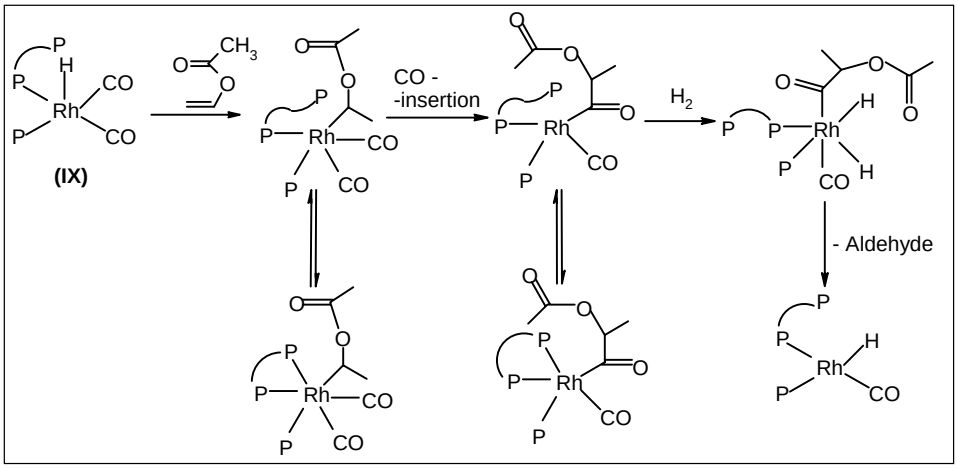


Scheme 4.7. Less activity of VAM due to substrate chelation

As shown in Scheme 4.7, the substrate chelation leads to the formation of chelated (Ring form) acyl species. Reductive elimination of such acyl species to give aldehyde becomes difficult because of higher stability of the species and lack of vacant sites for

hydrogen. This must be the reason for no activity of $HRh(CO)(PPh_3)_3$ for VAM hydroformylation at atmospheric pressures (Run no. 2 Table 4.7) whereas for linear hydrocarbon olefins, since there is no such chelation, $HRh(CO)(PPh_3)_3$ is known to work at room temperature and atmospheric pressures.

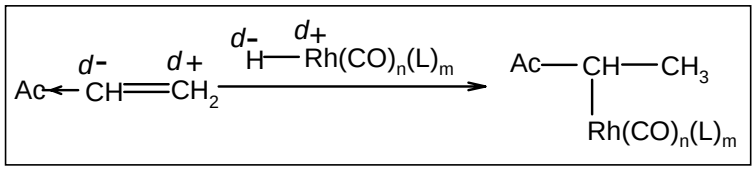
To explain the activity of diphos ligands at room temperature, we propose a hypothesis that when diphos alkane ligands were used along with $HRh(CO)(PPh_3)_3$ catalyst, the substrate chelation is reduced. DPPE and DPPP are known to possess strong bidantate character (act as monodentate ligands in certain cases) and so are ligated with both the phosphines most of the times.[xxiv] When DPPP was used along with monodentate phosphine such as TPP, the catalytic species formed can be depicted as (IX) shown in the Scheme 4.8. Thus, this bidantate ligand will either be ligated with both the phosphines or will have one phosphine ready for ligation as soon as a vacant site is created. Because of such combination of ligands, substrate chelation is hindered and reductive elimination of the acyl species becomes feasible even at atmospheric pressures (Run no.1 Table 4.7). When only DPPP is used with a Rh precursor, the steric hindrance to chelation is reduced and so the reaction rate drops further compared to the one with TPP.



Scheme 4.8 Combined effect of bidanted and monodentated phosphine ligands

4.3.1.8.2. Regioselectivity in hydroformylation of VAM

Two probable reasons for very high regioselectivity to the branched aldehyde in hydroformylation of VAM are, substrate polarity and substrate chelation. Due to inductive



effect of the carbonyl group of acetate functionality, a partial negative charge is developed on the 'α' carbon atom and a partial positive charge is developed on 'β' carbon atom, as shown in the adjoining figure. Hydridorhodium carbonyl complexes are known to possess, hydride character of the hydrogen and so a partial positive charge on the metal. Due to these partially charged species, anti-Markownikoff addition of $HRh(CO)_n(L)_m$ takes place and Rh-alkyl species of 'α' carbon atom is preferentially formed which leads to a branched aldehyde. Such an effect of substrate polarity is also elucidated for substrates like styrene.[xxv]

The second probable reason for high regioselectivity to the branched aldehyde, as proposed by Abatjoglou *et al.*[viii] is, high stability of the metal containing five-membered ring (VII) compared to six-member ring (VIII) as shown in scheme 4.6. Generally for metal containing rings with 4 or more atoms, smaller rings are more stable compared to larger rings. Thus, intermediate (VII) is formed preferentially and give further reactions of acyl species formation and reductive elimination. Our study with sterically bulkier ligands such as diphosphines, triaryl arsine etc. reveal that more than the effect of ring stability, the partial polarity of the substrate is more responsible explanation for higher regioselectivity to 2-ac pal. It is clear from the activity pattern that the above said bulkier ligands hinder VAM chelation, which should have lead to high product linearity. But, this does not happen and the sterically bulky ligands also produce aldehydes with higher regioselectivity to 2-ac pal.

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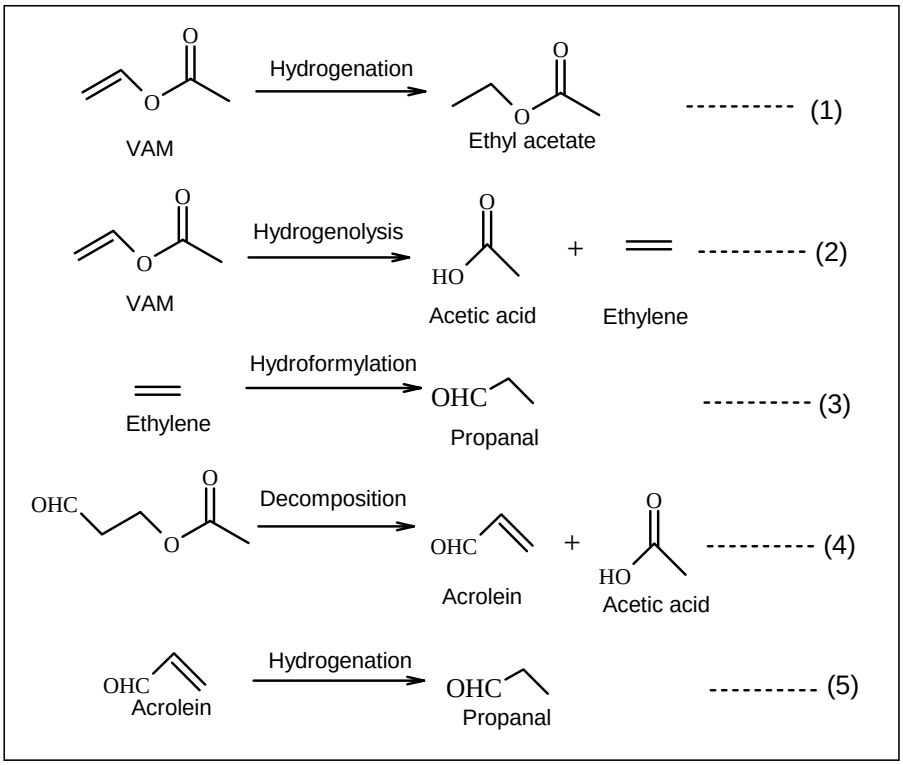
4.3.1.8.3. Side reactions in hydroformylation of VAM

Ethylene, acetic acid, ethyl acetate, propanal and acrolein were the major side products observed in Rh-catalyzed hydroformylation of VAM. The possible reactions producing these products are listed in Scheme 4.9. Ethyl acetate formation is a straightforward hydrogenation of VAM. Such hydrogenations are not very common with Rh-complexes under hydroformylation conditions. In most experiments, ethyl acetate is formed ~ 1-2 % concentration, based on VAM charged. Hydrogen rich syngas increases the hydrogenation reaction rate. Generally, Rh-catalysts with chloro ligands are active for hydrogenation reaction under hydroformylation conditions. (Run 3 Table 4.3).



Scheme 4.9. Side reactions in hydroformylation of VAM

VAM hydrogenolysis to ethylene and acetic acid is a major side reaction with Rh catalysts. Scheme 4.10 shows a mechanism proposed by Abatjoglou *et al.* for VAM hydrogenolysis. The authors have isolated Rh species $Rh(CO)(OCOCH_3)(PPh_3)_2$ by simple reflux of VAM with $HRh(CO)(PPh_3)_3$, thus confirming the Rh-catalyzed mechanism of acetic acid formation. Since, the acetic acid formed is in large excess of Rh-catalyst used, acetic acid formation must be a catalytic reaction. Authors have proposed catalytic cycle involving steps (7) and (8) in Scheme 4.10, for continuous formation of acetic acid. The ethylene formed in this reaction hydroformylates further to give propanal (Reaction (3) in Scheme 4.9). Thus, in most of the hydroformylation experiments, propanal is formed along with acetic acid, it is sure that VAM hydrogenolysis is the source of acetic acid.

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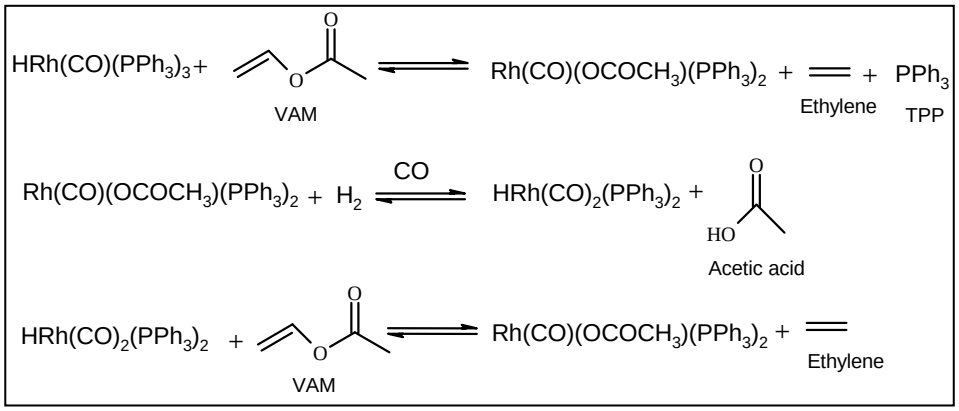

Scheme 4.10. Proposed mechanism for hydrogenolysis of VAM

3-ac pal decomposition (Reaction (4) in Scheme 4.9) is another source of acetic acid in the VAM hydroformylation reaction. Acrolein formed, is stable because of presence of double bond in conjugation with carbonyl group so 3-ac pal tends to decompose under suitable conditions. Abatjoglou *et al.* have proposed that in Rh-VAM hydroformylation system, acetic acid is formed by both these routes. Our results contradict with Abatjoglou's results. We haven't observed any acrolein in our Rh-VAM reactions, thus confirming the absence of 3-ac pal decomposition. Since nearly equivalent amount of propanal was observed along with AA, VAM hydrogenolysis must be the confirmed source of AA in Rh-VAM system. The contradiction in the results must be due to different amount of catalyst loading. Abatjoglou has used very high concentrations of $Rh(CO)_2$acac and PPh_3, with VAM/Rh ratio of ~80 and PPh_3/Rh ratio of 15 compared to our ratios of ~ > 2500 and 3 respectively. In Abatjoglou's reactions, the excess phosphine must be catalyzing decomposition of 3-ac pal, which is not the case in our study.

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4.3.2. Hydroformylation of VAM with ruthenium and iridium catalysts

Transition metal catalysts other than Rh and Co metal complexes are not very active for hydroformylation[xv] and so are more of the academic interest only. Because Rh-complexes have limitation in hydroformylating VAM to 3-ac pal, which is a precursor of 1,3-pdo, complexes based on transition metals such as Ru, Ir and Co were screened with an aim of

obtaining ac pals with higher l/b ratio. Selected experimental results with Ru and Ir catalysts are listed in Table 4.12.

The Ru-catalysts were tested in the range of 393 K to 423 K but they were found to be active only at 423 K. Among the Ru-catalysts, $RuCl_2(CO)_2Py_2$ (G) (in toluene) was the only precursor found to be active for hydroformylation. With complex G (in toluene) 19.4 % selectivity to aldehyde was obtained with 100 % regioselectivity to 2-acetoxy propanal (II) (Run 2 in Table 4.12). Complex G in MeOH catalyzed side reactions such as VAM hydrogenation and transesterification (reaction (1) in Scheme 4.9 and reaction (1) in Scheme 4.5) leading to products such as methyl acetate, 1,1-diethoxy ethane and 1,1-diethoxy propane (Run 1). Complex G in methyl-ethyl ketone (MEK) catalyzed only hydrogenation and hydrogenolysis (Scheme 4.9) to ethyl acetate and acetic acid respectively (Run 3). With $RuCl_3.H_2O$ H in MEK, 100 % conversion of VAM was obtained but hydroformylation didn't occur (Run 4). Even syngas absorption (~ 80 % of the stoichiometric requirement of VAM) was observed in this reaction. GC-MS analysis showed formation of many side products viz. propanal, ethyl acetate, ethanol, propanal, propanol, acetic acid, 2-ethoxy butane, 3-pentanone, 2-butyl isopropyl ether, 2-butyl acetate, di-(2-butyl) ether and 2-butyl propionate. From the products it can be concluded that MEK hydrogenation to 2-butanol had taken place. The other possible reactions that can give the above products are VAM hydrogenolysis, transesterification of VAM with 2-butanol along with many other condensation reactions. Complex I (in MEK) was found to be inactive, giving no conversion of VAM at the end of 2 hr. (Run 5).

With $IrCl_3$ *i. e.* J (in acetonitrile) 75 % conversion of VAM was obtained with only 6.6 % aldehyde selectivity (100 % regioselectivity to 2-ac pal), ethyl acetate and acetic acid were the side products. $IrCl_3$ with 2 equiv. TPP (catalyst system K) was inactive under the same conditions and even at higher temperature *i.e.* 393 K.

Thus, the results made it clear that the tested catalyst precursors are not suitable for chemoselective hydroformylation of VAM. It was observed that due to dual functionality in VAM, side reactions and many tandem reactions predominate with most of the Ru and Ir catalysts.

Table 4.12. Hydroformylation of VAM with Ru and Ir catalysts

No	Cata	Solvent	Temp	Press.	Time	Absorption	Conv.	Chemoselectivity, %			Regioselectivity %	
			K	MPa	min.	*kmol/* m^3	%	Ald.	EA	AA*	I	II
1#	G	MeOH	423	10.3	140	1.9	100	0	8.2	6.5	-	-
2	G	Tol.	423	10.3	215	0.89	36.6	19.4	33.6	35	-	100
3	G	MEK	423	10.3	80	0.21	11.9	0	33.5	66	-	-
4	H	MEK	423	10.3	112	1.92	100	0	11.1	10	-	-
5	I	MEK	423	10.3	120	0	0	-	-	-	-	-
6	J	AN	373	10.3	260	1.3	75	6.6	31	60	-	100
7	K	AN	393	10.3	180	0	0	-	-	-	-	-

*Reaction conditions: VAM,1.127 kmol/m^3; Catalyst, 0.0091 kmol/m^3; Solvent, 22.5 x 10^{-6} m^3; Agitation, 16.6 Hz; # = Many side products as discussed in Section 4.3.1.8; * = Wherever acetic acid is present propanal is observed in the GC*

G = $RuCl_2(CO)_2Py_2$; H = $RuCl_3.H_2O$; I = $RuCl_2(CO)_2(PPh_3)_2$; J = $IrCl_3$; K = $IrCl_3$ – PPh_3.

4.3.3. Propanediols from VAM-hydroformylation-products (ac pals)

As discussed in section 4.1, for total synthesis of propanediols from VAM, hydrogenation, and hydrolysis are the two reactions to be followed after hydroformylation. In this section, results on hydrogenation of acetoxy propanals (3-ac pal & 2-ac pal) and further hydrolysis of the products to propanediols are discussed. Reagent catalyzed hydrogenation and hydrolysis is discussed first, followed by transition metal catalyzed hydrogenation and resin catalyzed hydrolysis. For these reactions, 2-ac pal was obtained by distillation of Rh-catalyzed hydroformylation products and mixture of 2- and 3-ac pal was obtained by distillation of Co-catalyzed hydroformylation products (Chapter 3). For aqueous phase reactions, the acetoxy propanals were obtained by extracting them in the aqueous phase from organic phase (Section 4.3.1.7 and 3.3.10)

4.3.3.1. Reagent catalyzed hydrogenation and hydrolysis of acetoxy propanals

To judge the feasibility of simultaneous synthesis of propylene glycols via ac-pals reagent catalyzed hydrogenation and hydrolysis were carried out, Three experiments, with

the Watanabe's procedure[ix] (section 4.2.2.4) were performed, one experiment with only 2-ac pal and two experiments with mixtures of 2- and 3-ac pals, the results are presented in Table 4.13.

When only 2-ac pal was converted to 1,2-pdo, comparatively good yield of 89 % was obtained with some high boilers as the remaining products (Run 1). However under similar conditions a mixture of 2-ac pal and 3-ac pal gave only 78 % yield. Some unreacted 2-ac pal, acrolein, and propanal were observed in the gas chromatogram of the final sample of Run 2. This indicates, decomposition of 3-ac pal, and incomplete hydrogenation of 2-ac pal. The expected ratio of 1,2-pdo : 1,3-pdo was 57:43, but the yields showed it to be 71:29, indicating higher decomposition of 3-ac pal. The results improved to some extent with 85 % yield when higher amount of LAH was used (Run 3), but decomposition of 3-ac pal was observed in this experiment also. In run 3, the ratio of 1,3-pdo : 1,2-pdo was 70:30.

Table 4.13. Reagent catalyzed hydrogenation and hydrolysis of acetoxy propanals

Run no.	LAH	Aldehyde	Aldehyde concn.	1M HCl	Conversion	Yield*	1,2-pdo: 1,3-pdo
	G		**Mol**	**x 10^{-6} m^3**	**%**	**%**	
1	1	2-ac pal	0.017	10	100	89	-
2$	1	As pals	0.017	10	92	78	71:29
3$	1.5	Ac pals	0.085	10	95	85	70:30

*<u>Reaction condition:</u> THF, 10 x 10^{-6} m^3 each for LAH, and aldehydes; Reflux for 4 hrs; $ = Mixture contained 43% 3-acetoxy propanal and 57 % 2-aetoxy propanal) * = Total Yield of propylene glycol/s.*

It is clear from the above results that the reagent catalyzed reduction and hydrolysis of acetoxy propanals lead to poor yields especially with respect to the unstable 3-ac pal. As associated with most of the reagent-assisted transformations, formation of unwanted byproducts are associated with this reduction also. Use of mineral acid (corrosive and hazardous) was another drawback of this conventional way of hydrolysis. Thus, an alternative, environmentally benign route for synthesis of propylene glycols from acetoxy propanals was always desired. Our attempts to find alternatives for these reagent-assisted transformations are presented in the following sections.

4.3.3.2. Transition metal catalyzed hydrogenation of acetoxy propanals in aqueous phase

Hydrogenation of acetoxy propanals is more desirable in the aqueous phase as water is the most convenient, environmentally benign solvent and in this case, the hydrogenation product mixture as such can be further transferred for hydrolysis reaction. As discussed in Section 4.3.1.7, and 3.3.8, the acetoxy propanals were conveniently extracted in the aqueous phase, leaving the homogeneous hydroformylation-catalyst in the organic phase. The aldehyde solutions thus obtained were further hydrogenated with different catalysts. Important observation noted here was, 2-ac pal, if added to water in pure form, immediately formed a white emulsion. GC-MS confirmed them to be oligomers (fragmentation pattern was same as that of 2-ac pal). Thus, it was concluded that only dilute aqueous solutions; formed by extractions, keeps 2-ac pal stable and so aqueous phase hydrogenation was carried out only with these solutions.

Supported transition metal catalysts were screened for hydrogenation of 2-ac pal or mixtures of 2- and 3- ac pals to the corresponding ac pols and the results are presented in Table 4.14. The ^{1}H NMR and GC-MS analysis of 2-aectoxy propanal and 2-acetoxy propanol are presented in Annexure II (NMR-1 and –2; MS-1 and –2). Among the tested catalysts, only Ru/Al_2O_3 and Raney Ni showed activity for aqueous phase hydrogenation. 5 % Pd /C and Ni/ Al_2O_3 didn't show any activity for hydrogenation (Run no. 3, 4) whereas Ni /SiO_2, hydrolyzed 2-ac pal to 2-hydroxy propanal and acetic acid (Run no. 5). Not much difference in the activity and selectivity of 3 % and 5 % Ru / Al_2O_3 was observed (Run 1 & 2). Raney Ni was found to be very active, may be because of very high metal loading compared to (Run no.6, 7 &9). Both $Ru/Al_2O_3$and Raney Ni catalysts showed reasonable activity at low temperatures of 323 K and 353 K respectively, the activity was very poor below these temperatures.

Ru /Al_2O_3 showed very high activity initially up to ~ 20 % conversion and then the activity diminished indicating poisoning of the catalyst. This might be happening due to irreversible adsorption of acetoxy propanols (hydrogenation products) on the catalyst. Due to this poisoning, the activity of the catalyst reduced and so proper recycling was not possible without repeated washings with polar organic solvent such as methanol (Run 9). Raney Ni was found to be very active and the gas absorption finished in 10-15 minutes (Run 7, 9 and

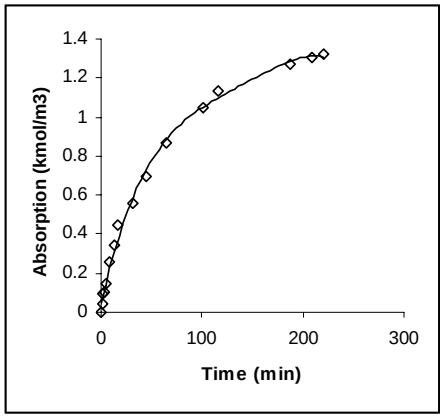
10). Slightly less selectivity in case of Raney Ni, was due to high boilers formation. The activity profiles of both these catalysts are shown in Figure 4.9. Reduction in the activity of Ru/Al_2O_3 after initial 20 - 25 % conversion can be clearly seen in this figure.

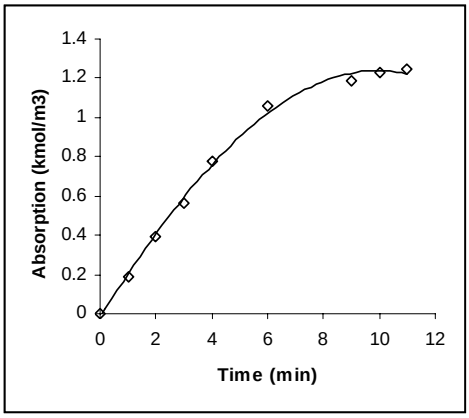
Table 4.14. Hydrogenation of acetoxy propanals in water

Run no.	Catalyst	Substrate	Run time	Cata weight	Tempera ture	Convers ion	Select ivity$	Initial rates x 10^3
			Min	g	K	%	%	*kmol*/m^3/s
1*	Ru/Al_2O_3	2-ac pal	200	0.2	323	95	98	0.5
2	Ru/Al_2O_3	2-ac pal	200	0.2	323	96	99	0.6
3	Pd /C	2-ac pal	120	0.2	373	0	-	-
4	Ni/Al_2O_3	2-ac pal	120	0.2	373	0	-	-
5[a]	Ni /SiO_2	2-ac pal	120	0.2	373	80	0	-
6	Raney Ni	2-ac pal	11	0.2	353	97	98	1.8
7	Raney Ni	2-ac pal	16	0.1	353	96	98	1.2
8*	Ru/Al_2O_3	Ac pals[b]	200	0.2	323	95	95	0.5
9*	Ru/Al_2O_3 Recycled	Ac pals[b]	200	0.2	323	93	95	0.5
10[b]	Raney Ni	Ac pals[b]	17	0.1	353	96	94	1.2

*Reaction conditions: Aldehyde concentration, 1.3 kmol/m^3; water, 22.5 x 10^{-6} m^3; PH_2, 6.9 MPa; Agitation, 16.6 Hz; * = Except for runs 1, 8 & 9 (3 %), all the supported catalyst have 5 % metal loading; a = Hydrolysis of 2-acetoxy propanal occurred; b, substrate is a mixture of 2- and 3-acetoxy propanals with 57% and 43% ratio respectively. $ = Total selectivity to acetoxy propanals*

Since the temperature conditions for hydrogenation and hydrolysis (Section 4.3.3.4) experiments were similar, few experiments for tandem hydrogenation and hydrolysis of 2-ac pal were also attempted. Both Ru /Al_2O_3 and Amberlite IR 120 resin (0.2 g) were used at a time under hydrogenation conditions. The results were poor with very slow rates of both the reactions. In fact, hydrogenation was stopped after ~ 20 % conversion of acetoxy propanal. The reason may be acetic acid formed by hydrolysis.





(A) **(B)**

Figure 4.9. Absorption-time graphs of acetoxy propanals hydrogenation (A) with 5 % Ru/Al_2O_3 (B) Raney Ni

Reaction conditions: ***(A)*** *Same as those of run 8 from Table 4.14* ***(B)*** *Same as those of run 9 from Table 4.14*

Deleted: ¶

4.3.3.3. Transition metal catalyzed hydrogenation of acetoxy propanals in organic phase

Since the solubility of acetoxy propanals in water is less (it forms emulsion at higher concentrations), it was difficult to run aqueous phase hydrogenation at high concentrations. So, for higher concentrations, hydrogenation in the organic phase (same solvent as that of hydroformylation) was found to be more convenient. In the present study, the aldehyde/s obtained after hydroformylation were first freed from the hydroformylation-catalyst and then subjected to the hydrogenation reaction without further purification. In case of Rh-catalyzed hydroformylation, the catalyst removal was achieved by repeated treatments of activated charcoal and silica. Even though the concentration of Rh-catalyst was generally very less, faint color was always associated (indicating presence of minor amounts of Rh) with the aldehyde solutions obtained by this method of purification. For Co-catalyzed hydroformylation reaction, catalyst separation was relatively easier, in spite of high concentrations of the catalyst. Addition of acetic acid in two equivalent concentrations with respect to cobalt, and warming the solution to 323 K lead to precipitation of cobalt as $Co(CH_3COO)_2$.

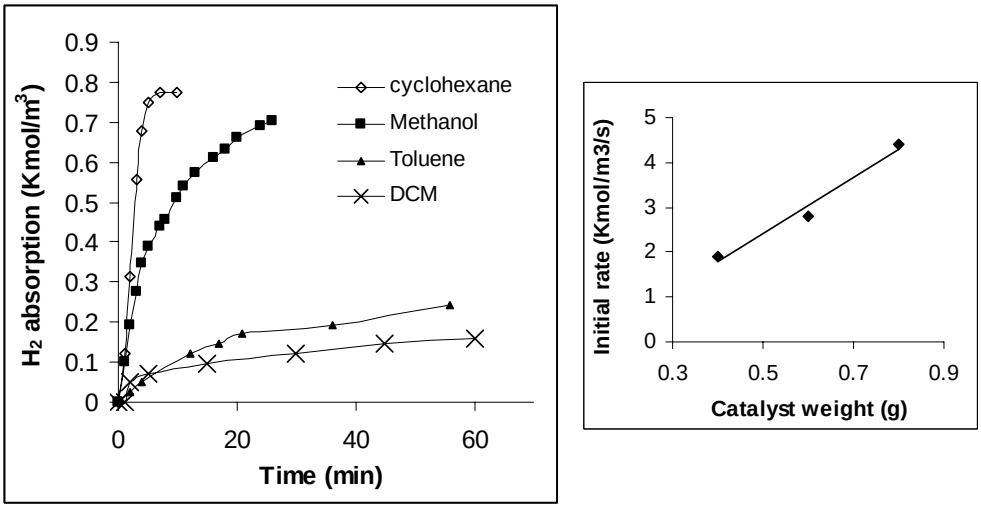
Ru/Al_2O_3, Pd/C, Ni/Al_2O_3 and Ni/SiO_2 were found to be inactive for 2-ac pal hydrogenation in toluene. In fact, at higher temperature, 423 K, Pd/C and Ru/Al_2O_3 catalyzed hydrogenation of toluene whereas 2-ac pal was not hydrogenated. Only Raney Ni was found to be active in organic solvents and hence was tested in different solvents, the results are presented in Table 4.15.

Two reactions with a mixture of 2- and 3- acetoxy propanals (57 : 43 mixture) in benzene and toluene solvents were carried out (Run 2 and 4) and the activities were found to be similar to the reactions with only 2-ac pal as substrate (Run 1 and 3). Less selectivity to acetoxy alcohols was due to a small decomposition reaction of 3-ac pal to acrolein and acetic acid. Because of this decomposition, the l / b ratio (regioselectivity) of the products was also reduced slightly. Acetoxy propanal mixture with more than 50 % linearity couldn't be hydrogenated with Raney Ni as they were obtained in halogenated solvents (Section 3.) and Raney Ni showed poor activity in halogenated solvents (Figure 4.10).

Table 4.15. Raney Ni catalyzed hydrogenation of acetoxy propanals in organic solvents

Run no.	Substrate	Solvent	L/ b of substrate	Conversion	Selectivity*	L/ b of products
				%	%	
1	2-ac pal	Benzene	-	95	98	-
2	Ac pals	Benzene	0.94	96	94	0.9
3	2-ac pal	Toluene	-	93	97	-
4	Ac pals	Toluene	0.94	93	94	0.91

*Reaction conditions: Aldehyde concentration, 1 kmol/m^3; Solvent, 23 x 10^{-6} m^3; Raney Ni, 0.3 g; T, 353 K; pH_2, 6.9 MPa; Agitation, 16.6 Hz; Ac pals is a 57:43 mixture of 2- and 3-acetoxy propanals respectively; * = Total selectivity to acetoxy propanols. L/ b = Linear / branched ratio*



(A) **(B)**

Figure 4.10. Raney Ni for hydrogenation of 2-acetoxy propanal (a) Effect of solvents (b) Effect of catalyst concentration

Reaction conditions: Same as that of Table 4.15.

Different organic solvents were screened for organic phase hydrogenation of ac-pals and the results are presented in Figure 4.10 (A). Raney Ni was found to be highly active for hydrogenation of 2-ac pal in cyclohexane and methanol as solvents. The reaction was relatively slow in toluene (In the Figure, the Raney Ni concentration for toluene was 0.2 g compared to 0.6 g for other solvents) and was very slow in dichloro methane. Surprisingly acetal formation was not observed in a reaction with methanol as solvent and the selectivity to ac-pols was ~ 97 %. One reason for this high activity in methanol may be polarity of the solvent. In cyclohexane, the product 2-acetoxy propanol was not soluble and so formed a separate phase. Due to this immiscibility of products in cyclohexane, the poisoning of the catalyst due to irreversible adsorption of the products (Section 4.3.4.3) was avoided and so Raney Ni was highly active in cyclohexane solvent. In Figure 4.10 (B), the effect of Raney Ni concentration on 2-ac pal hydrogenation in cyclohexane is shown. The initial rate was found to increase with the Raney Ni concentration. For all the reactions shown in Figure 4.10, the selectivity for 2-acetoxy propanol was always higher than 95 % and > 90 % conversions could be achieved.

4.3.3.4. Hydrolysis of acetoxy propanols to propylene glycols

Reagent catalyzed hydrolysis requires corrosive mineral acids or bases. In view of the environmental hazards and waste generation from these reagents, they are considered as a last choice from process point of view. Many solid acids like zeolites, ion-exchanged resins etc. are environmentally benign and effective substitutes for such reagents. In the present study, to complete the synthesis of propylene glycols via VAM hydroformylation, resin catalyzed hydrolysis of acetoxy propanols as well as acetoxy propanals was successfully achieved.

For hydrolysis reactions, the same solutions of hydrogenation reactions were used after filtration of solid catalyst. In the preliminary screening, the solid acid catalysts such as K^+/silica, Dowax resin, Amberlite IR 120 resin, and zeolite H-β were tested. The Amberlite IR 120 resin was found to be the most active resin for carrying out this type of hydrolysis. Selected experimental results on acetoxy propanol hydrolysis with Amberlite IR 120 resin are presented in Table 4.16.

Both 2- acetoxy propanol and 3-acetoxy propanol were hydrolyzed as a single component and mixture respectively. The solvent media for hydrolysis was either the aqueous phase (for aqueous phase hydrogenation solutions) or an organic-aqueous two-phase (for organic phase hydrogenation solution). The reactions were carried out at 353 K for 180 minutes with 0.2 g activated resin (The reaction conditions are not optimized).

Conversions for resin-catalyzed hydrolysis were in the range of 92-93 % only. Reversible nature of the hydrolysis reaction may be responsible for less conversion. For reactions in aqueous mode, slightly reduced selectivity, compared to aqueous-organic biphasic mode, was obtained because of minor amount of high boilers formation (< 2 %). Both, 2-acetoxy propanol and mixture of acetoxy propanols, in aqueous as well as biphasic mode, leads to propylene glycols with high selectivity of 99 %. Mixture of 2-acetoxy and 3-acetoxy propanols (57:43) on hydrolysis gave 1,2-pdo and 1,3-pdo with nearly same Linear: Branched ratio as that of the substrate. Acetic acid in the stoichiometric amount of the substrate could be obtained in all the experiments. In biphasic reactions, the products were

obtained in aqueous phases only and the organic phase didn't show even traces of propylene glycols.

2-ac pal, hydrolyzed under the similar conditions showed reduced selectivity compared to acetoxy propanols, due to formation of oligomers (Run 5). As shown in run 6, the Resin catalyst was recycled (without purification or activation) without any loss of activity.

Table 4.16. Resin catalyzed hydrolysis of acetoxy propanols to propylene glycols

Run no.	Substrate	Solvent	Conversion	Selectivity
			%	%
1	2-ac pol	Water	92	97
2	2-ac pol	Cyclohexane-water	93	99
3	Ac pols	Water	92	97
4	Ac pols	Benzene – Water	93	99
5	2-ac pal	Toluene-water	93	91
6*	Ac pols	Benzene – Water	91	99

*Reaction conditions: Substrate, 1.3 kmol/m^3; Solvent, 22 x 10^{-6} m^3; Amberlist IR 120 resin, 0.2 g; Run time, 180 min; T, 353 K; For solvent mixture, the ratio is 1:1; Ac pals is a 57:43 mixture of 2- and 3-acetoxy propanals respectively; * = recycled resin of experiment 4 was used as a catalyst*

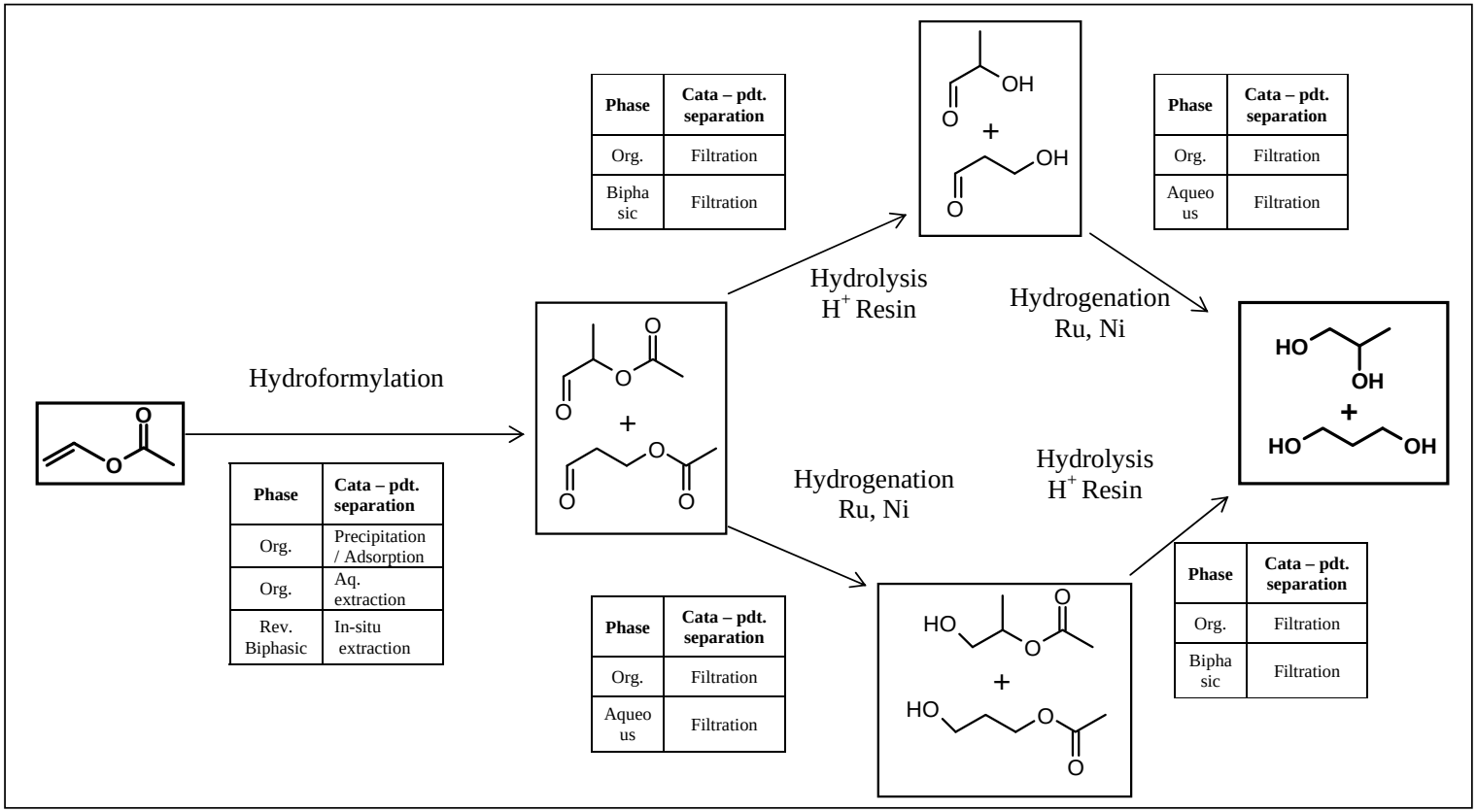
4.4. CONCLUSIONS

Novel route for simultaneous synthesis of 1,2- and 1,3- propanediols, via VAM hydroformylation was established. VAM hydroformylation was carried out with complexes of Rh, Co, Ru and Ir metals. Rh-catalyzed VAM hydroformylation was explored in more detail with a study of effect of precursors, solvents and ligands. Rh complexes have shown nearly regioselective synthesis of 2-ac pal with negligible effect of ligands on regioselectivity. Effect of diphosphine ligands at atmospheric pressures of syngas revealed interesting property of activity enhancement. Attempts to stabilize the acetoxy aldehydes with *insitu* acetals formation in alcohol solvents lead to interesting tandem hydroformylation-acetalization-transesterification reactions. Preliminary study of reverse biphasic system for Rh-catalyzed VAM hydroformylation was carried out and catalyst-product separation was

achieved with three recycles of the catalyst phase. Another technique of aqueous extraction of products was demonstrated for very effective catalyst-product separation. Mechanistic discussion leading to logical explanation of the observed effects is carried out. Ru and Ir catalysts didn't find to carry out chemoselective hydroformylation of VAM. Among the different cobalt precursors tested, $Co_2(CO)_8$ was found to yield aldehydes with better Linear : Branched ratio as compared to Rh-catalysts. Preliminary parametric effects on $Co_2(CO)_8$ catalyst were studied and nearly stoichiometric formation of 2-ac and 3-ac pals (53 : 47) was achieved.

Hydrogenation of 2-ac pal alone and mixtures of 2-ac and 3-ac pals in both aqueous as well as organic phase was successfully carried out. Ru / Al_2O_3 and Raney Ni were found to be very effective catalysts showing ~ 96 % conversion and > 96 % selectivity. Only Raney Ni was found to be active for the organic phase hydrogenation of acetoxy propanals. With Raney Ni the hydrogenation reaction was found to be very fast with maximum initial rate of 1.8×10^{-3} kmol/m^3/s. 2-acetoxy propanol and mixtures of 2-acetoxy and 3-acetoxy propanols were hydrolyzed with Amberlite IR 120 resin and maximum conversion of 92 % with 99 % selectivity to the respective propylene glycol was achieved.

Thus, complete synthesis of propylene glycols from VAM was achieved with recyclable catalysts for all the three steps involved. As shown in Scheme 4.11, Catalysts used in all the three steps could be used in any of the phases from organic, aqueous, and aqueous biphasic mode. Since, the acetic acid formed in the hydrolysis step can be easily recycled, in principle, a process for commercially important propylene glycols from cheap row materials such as ethylene, CO, H_2, and water was developed using recyclable catalysts.



Scheme 4.11. Propylene glycol via hydroformylation of VAM–full scheme

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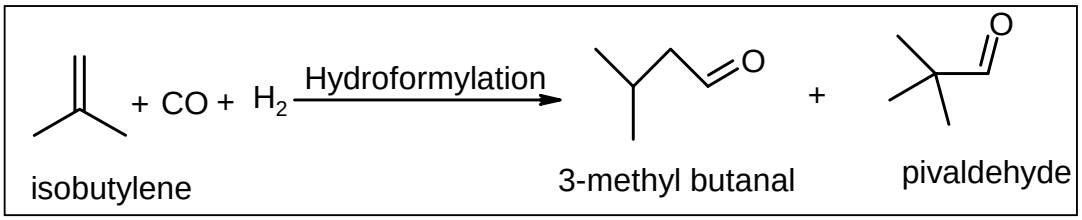
Chapter 5

HYDROFORMYLATION OF ISOPROPENYL ACETATE: ACTIVITY AND SELECTIVITY OF RHODIUM AND COBALT CATALYSTS

5.1. INTRODUCTION

Hydroformylation of olefins has been extensively studied to understand the regioselectivity behavior with respect to linear / branched ratio of the aldehyde products. Results presented in Chapters 2, 3 and 4 have clearly indicated the complex dependence of the Linear / Branched ratio on the catalyst types, ligands and reaction conditions. An important issue concerning the role of olefin structures and position of substituent groups needs to be investigated. In this context, the Keulemans Law[i] and is proven for many hydroformylation reactions involving hydrocarbon olefins. Nienburg and Keulemans[ia]



Scheme 5.1. Hydroformylation of Isobutylene

have recognized that under the standard hydroformylation conditions hardly any quaternary carbon atoms are formed or the formyl group is not found at the carbon atom where the branching takes place. For example, as shown in Scheme 5.1, isobutylene forms 3-methyl butanal almost exclusively with only 5 % of the isolated product being pivaldehyde. Even under extreme conditions of 493 K temperature and 420 MPa pressure (which normally favor the formation of branched structures) the pivaldehyde yield amounts to only 8 %. Another interesting example proving the Keulemans law is comparison of hydroformylation of styrene and 1-methyl styrene reported by Botteghi *et al.*[ii] These authors found that in cobalt catalyzed hydroformylation of styrene, more than 87 % of the product shows formyl group at α-carbon atom whereas under similar conditions, in case of α-methyl styrene, all the product shows formyl group at β-carbon atom (100 % selectivity). The effect was found to be valid even at higher temperatures. Tanaka *et al.*[iii] have found similar results in case of Rh-catalyzed hydroformylation of acrylates such as methyl methacrylate, ethyl acrylate, methyl crotonate and methyl tiglate. Thus, it is clear that the Keulemans Law is applicable to cobalt as well as rhodium catalyzed hydroformylation reactions with hydrocarbon olefins or functionalized olefins. However we have observed that, in the literature, a comparative study of Rh and cobalt-

catalyzed hydroformylation of such α-substituted olefins is not investigated. Also, the effect of α- substitution on the chelating substrate such as VAM is not found to be studied in the literature. To bridge this knowledge-gap, we have used α-methyl vinyl acetate *i.e.* isopropylene acetate (IPAc) as a model substrate for our study. The literature doesn't show any work on the hydroformylation of IPAc.

In the present work, we have tried to explore the implications of Keulemans Law in hydroformylation of chelating olefinic ester such as IPAc. The effect of Rh-precursors under different conditions was studied. cobalt-catalyzed hydroformylation in different solvents, with ligands such as pyridine, tri-*n*-butyl phosphine (TBP) and diphenyl phosphino propane (DPPP) was performed. Tandem hydroformylation-acetalization in alcoholic solvents was also studied. A comparison of hydroformylation of VAM and IPAc concludes this chapter.

5.2. EXPERIMENTAL

5.2.1. Materials

$Co(CH_3COO)_2.4H_2O$ (cobalt acetate), $RhCl_3.3H_2O$, pyridine, TBP, DPPP were procured from Aldrich, USA or Fluka, Switzerland and used as such without further purification. Rh-precursors were prepared as described in Section 4.2.4. All solvents were procured from Sd Fine Chemicals, India or Merk-India and used after proper distillation, drying and argon flushing. CO of 99.9 % purity (Matheson, USA) and H_2 of 99 % purity (Industrial Oxygen Company, India) were used as received without further purification. $Co_2(CO)_8$ (Dicobalt octacarbonyl) was prepared by high pressure-high temperature technique as described in section 3.2.4. Syngas mixture in the required $CO:H_2$ ratio was first premixed in a reservoir and then used for hydroformylation reactions.

5.2.2. Hydroformylation experiments

For the present work, the experimental set up and procedure described in chapters 3 and 4 was followed.

5.2.3. Analytical methods

IR spectrums were obtained using a Bio-rad FTS *175C* machine in transmission mode using KBr pellets as well as liquid cells. GC-MS analysis was carried out on an Agilent GC machine of 6890N series equipped with 5973N Mass Selective Detector.

Liquid samples were analyzed on a Hewlett Packard 6890 Series GC controlled by the HP-Chemstation software and equipped with an auto sampler unit, by using a HP-1 capillary column (30 m x 30 µm x 0.25 µm film thickness with a stationary phase of polymethyl siloxane). The quantitative analysis was obtained by constructing calibration curve in the range of concentrations studied. The % conversion, % selectivities and regioselectivities of aldehydes and alcohols were calculated using the following formulae. Conversion of substrates was always calculated based on the liquid substrate charged. Total aldehyde-selectivity was calculated by addition of both linear and branched products. The standard GC conditions for analysis of products of different reactions are given in Table 5.1.

Table 5.1. Conditions for GC analysis

Injector (split) Temp	523 K		
Flame ionization detector Temp	523 K		
Inlet flow - total (He)	32.3 ml/min		
Split ratio	100:1		
Column Temperature	Rate (K/min)	Temp (K)	Hold time (min)
		323	5
	303	363	2
	313	498	2
Column Pressure	Rate (psi/min)	Pressure (psi)	Hold time (min)
		5	2
	10	10	3
	10	30	0

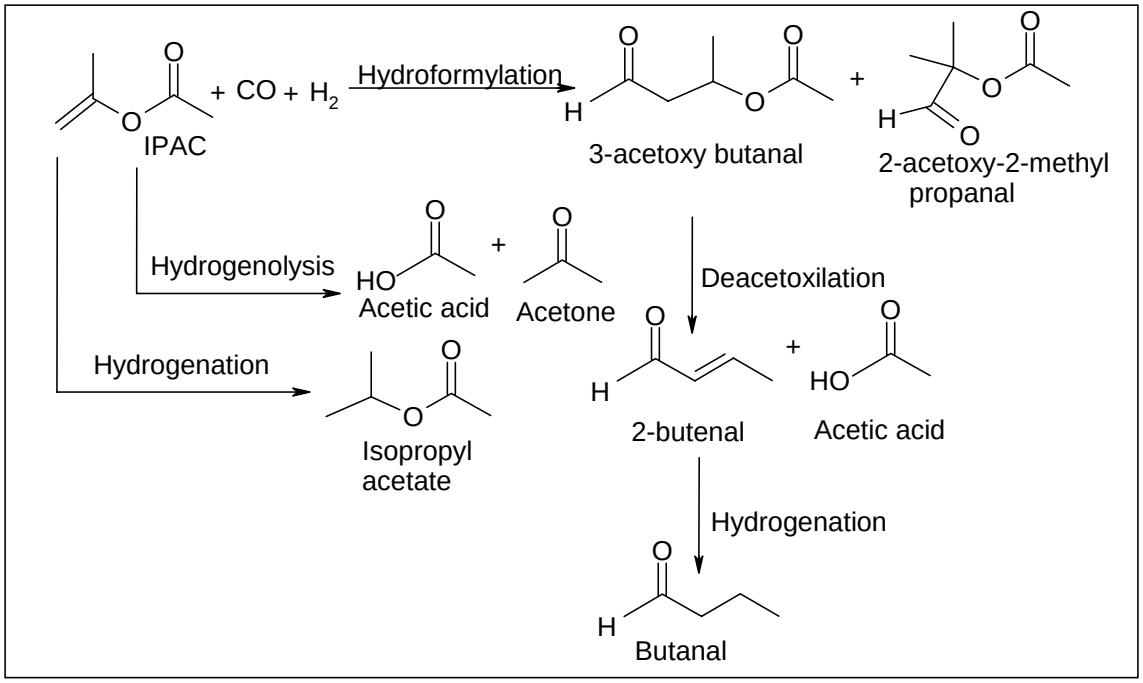
$$Conversion, (\%) = \frac{Initial\ concentration\ of\ substrate - Final\ concentration\ of\ substrate}{Initial\ concentration\ of\ substrate} \times 100$$

$$Selectivity, (\%) = \frac{No.\ of\ moles\ of\ a\ product\ formed}{No.\ of\ moles\ of\ substrate\ converted} \times 100$$

$$\text{Regioselectivity to I} = \frac{I}{(I+II)} \times 100$$

$$\text{Regioselectivity to II} = \frac{II}{(I+II)} \times 100$$

5.3. RESULTS AND DISCUSSION



Scheme 5.2. Reactions occuring under hydroformylation conditions with IPAc

An experimental study of the Rhodium as well as cobalt-catalyzed hydroformylation of IPAc is presented in this section. The focus of the study was to compare the results of hydroformylation of VAM (Carried out in Chapter 3 and 4) and that of IPAc under similar conditions and explore the implications of the α-methyl group in IPAc on activity and selectivity behaviour. In case of Rh, few Rh-precursors were tested whereas in cobalt-catalyzed hydroformylation, different solvents, ligands such as pyridine, TBP *etc* were studied. Tandem hydroformylation-acetalization reactions were carried out for a specific time of 15 minutes so as to know the different intermediate products formed. Scheme 5.2 shows all the reactions occurring in a cobalt-catalyzed hydroformylation of IPAc. All these reactions *viz* olefin hydrogenolysis, olefin

hydrogenation and linear-aldehyde deacetoxylation were also found to occur during VAM hydroformylation reaction.

5.3.1. Rh-catalyzed hydroformylation of IPAc

Different Rh-precursors were tested for hydroformylation of IPAc and the results are presented in Table 5.2.

Table 5.2. Rh-catalyzed hydroformylation of isopropylene acetate

Run No	Cata-Prec.	Temp	Syngas	Catalyst x 10^3	Conv.	Ald. selectivity	Regioselectivity, %	
		K	MPa	Kmol / m^3	%	%	**linear**	**branched**
1	A	353	4.1	0.84	0	-	-	-
2	B	373	4.1	0.84	3	85	73.6	26.4
3	C	373	4.1	0.84	0	-	-	-
4	D	373	4.1	0.84	0	-	-	-
5*	A	373	8.2	1.68	0	0	-	-
6	A	373	8.2	1.68	0	-	-	-
7$	A	393	8.2	1.68	5	78	78.3	21.7
8#	A	353	0.2	0.84	0	0	-	-

*Reaction conditions: IPAc, 1.09 kmol/m^3; Toluene, 22 x 10^{-6} m^3; CO:H_2, 1:1; Total charge, 25 x 10^{-6} m^3; Agitation, 20 Hz. Linear, 3-acetoxy butanal; Branched, 2- acetoxy -2- methyl propanal; * = Extra triphenyl phosphine (3 eqv. to Rh) added.$, Cyclohexane was used as a solvent; #, 3 eqv. DPPP (Compared to Rh) added as a ligand A = $HRh(CO)(PPh_3)_3$; B = $Rh(CO)_2(acac)$; C = $[Rh(COD)Cl]_2$; D = $[Rh(CO)_2Cl]_2$.*

In Reaction 1 (Table 5.2) standard hydroformylation conditions were used with IPAc as a substrate and $HRhCO(PPH_3)_3$ catalyst (Wilkinson catalyst), but there was no conversion obtained. VAM gives excellent results under similar reaction conditions (Table 4.4, Run 9, in Chapter 4). In Run 2, $Rh(CO)_2$acac was used as a catalyst precursor to avoid the phosphine ligand, in which only 3 % conversion with 85 % selectivity to the expected oxo products was obtained. The regioselectivity favored heavily to the 3-acetoxy butanal (73.6 %), which, is the linear-aldehyde with only 26.4 % formation of 2-acetoxy-2-methyl propanal, which is a branched-aldehyde. Under similar conditions, in hydroformylation of VAM (Table 4.4 Run 6) 96 % conversion was obtained. Another

striking difference was found in regioselectivity which in case of VAM favors heavily to the formation of branched-aldehyde (99 %) *i.e.* 2-acetoxy propanal. Other Rh-precursors such as $[Rh(COD)Cl]_2$ (Run 3 Table 5.2) and $[Rh(CO)_2Cl]_2$ (Run 4 Table 5.2) didn't give any reaction under similar conditions. Runs 5, 6, 7 were performed at higher syngas pressures (8.2 MPa) wherein no conversion of IPAc was observed and addition of extra triphenyl phosphine for catalyst stability also proved futile (Run 5 and 6 Table 5.2) At 393 K, only 5 % IPAc conversion with 78 % selectivity to oxo aldehydes is obtained. Even for such low conversion 210 minutes of run time was required. As shown in Scheme 5.2, the side products such as acetone and acetic acid (AA) by hydrogenolysis of IPAc, were formed and so the chemoselectivity to oxo aldehydes was lowered. In this reaction also, formation of 3-acetoxy butanal was favored with 78.3 % regioselectivity. One reaction (Run 8) with DPPP as an extra ligand along with Wilkinson catalyst was carried out at low syngas pressure of 0.2 MPa and 353 K temperature (Tamura's reaction), but there was no conversion of IPAc. Similar conditions of Tamura's reactions showed better results in case of hydroformylation of VAM (Section 4.3.1.5)

Thus, it was found that Rh-catalyzed hydroformylation of IPAc just doesn't take off. The conditions under which hydroformylation of VAM could be easily performed, showed nearly no activity for IPAc. In contrast to hydroformylation of VAM, in case of IPAc, whatever little conversion obtained showed favored formation of linear-aldehyde. Thus, the presence of α-methyl group in IPAc drastically lowers its activity for hydroformylation and also heavily influences the regioselectivity of the aldehyde products. This supports the general observation in the literature that Rh-catalysts are less active for hydroformylation of internal as well as hindered double bonds[iv]. These results also support the hypothesis of substrate chelation in olefinic acetates such as VAM and IPAc (Section 4.3.1.8.1).

5.3.2. Cobalt-catalyzed hydroformylation of IPAc

Unlike rhodium catalysts, cobalt-catalysts were found to perform hydroformylation of IPAc with far better conversions and selectivities. A typical concentration-time profile of a cobalt-catalyzed hydroformylation of IPAc in dichloro ethane (DCE) solvent is presented in Figure 5.1.

The Concentration-Time profile clearly depicts the favored formation of 3-acetoxy butanal (linear-aldehyde). Minor amounts (total side products were < 10 %) of acetone, isopropyl acetate, 2-butenal and butanal were also observed.

Considering the better results obtained with cobalt-catalysts, effects of various solvents and some variation in parameters on activity and selectivity of the catalyst was studied and the results are presented in Table 5.3.

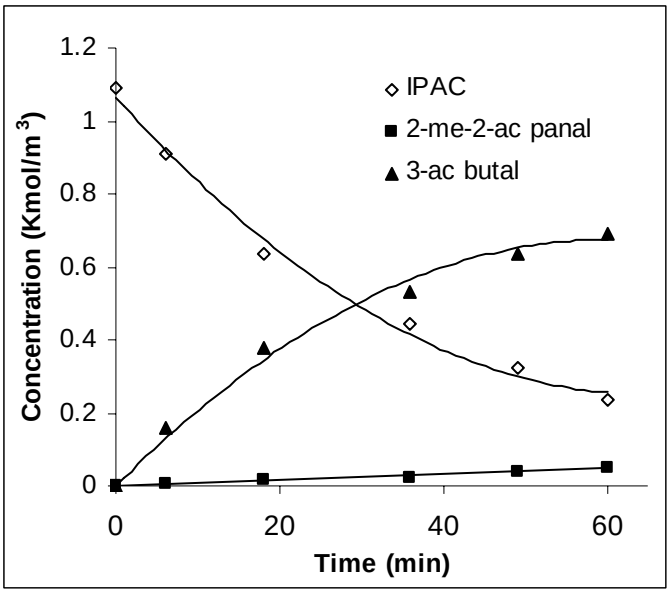


Figure 5.1. Concentration-time profile of Co-catalyzed hydroformylation of IPAc
Reaction conditions: IPAc, 1.09 kmol/m^3; DCE, 22 x 10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature, 393 K; Pressure, 4.1 MPa; CO:H_2, 1:1; Agitation, 20 Hz; Run Time, 60 min.

In toluene, 95 % conversion of IPAc was obtained with ~ 83 % selectivity to oxo aldehydes. Side products such as acetone (5.3 %) and isopropyl acetate (ISP-Ac) 4.17 % were observed along with minor amounts of 2-buteneal and 2-butanal. The regioselectivity favored heavily to linear-aldehyde with 95.5 % formation of 3-acetoxy butanal and only 4.5 % 2-acetoxy-2-methyl propanal. The initial rate was found to be 0.0006 Kmol/m^3/s, which is far superior to that of Rh-catalyzed hydroformylation of IPAc. Since in hydroformylation of VAM, halogenated solvents showed marked effect on regioselectivity (Section 3.3.9.2), dichloro methane (DCM) and dichloro ethane (DCE) were used as solvents in Runs 2, 3 & 4. In these solvents, the chemoselectivity to oxo aldehydes was improved to > 90 % as compared to 83 % in toluene. The *linear*-regioselectivity was however lower (~ 88 –90 %) especially for Runs 2 and 4 with higher syngas pressures of 8.2 MPa and 9.6 MPa. At 4.1 MPa, the *linear*-regioselectivity was

93.9 %, which nearly equals that of toluene. The initial rate of reaction in DCM was half of that observed in toluene. Thus, in contrast to hydroformylation of VAM, with IPAc, the halogenated solvents didn't affect regioselectivity but increased chemoselectivity to oxo-aldehydes and lowered the activity by lowering the initial rates.

Table 5.3. Effect of solvents

Run No	Solvent	IPAc	Syngas	Conv.	Chemoselectivity %			Regioselectivity %		Initial rates x 10^3
		Kmol/ m^3	Mpa	%	C_4-Ald.	Acet.@	ISP-Ac	*Linear*	*Bran--ched*	Kmol/m^3/s
1	Toluene	1.1	4.1	95.1	82.9	5.3	4.17	95.5	4.5	0.603
2	DCM	0.8	8.2	96.7	91.5	2	1.07	88.8	11.2	0.3
3	DCE	1.1	4.1	78.4	90.9	3.1	0	93.9	6.1	0.5
4	DCE	1.1	9.6	100	90.6	8.7	0.8	87.4	12.6	0.41
5	EA	1.0	4.1	73.6	79.2	9.8	2.7	96.4	3.6	0.7
6	MTBE	1.2	11.7	94.7	86.3	2.6	2.9	88.8	11.2	0.3
7	THF	1.1	4.1	89.9	66.7	12.9	0.9	94.9	5.1	0.9
8	THF	2.2	4.1	84.8	64.6	14.3	2.7	96.5	3.5	1.6
9#	THF	1.1	4.1	95.1	62	21.6	3.8	89.2	10.8	1.4
10	THF	1.2	9.6	84.6	63.4	12.7	3.2	95.9	4.1	0.7
11*	Toluene	0.85	4.1	100	0	66.7	3.7	-	-	-
12$	Toluene	0.8	7.6	94.1	52.6	29.4	0	71	29	0.7

*<u>Reaction conditions:</u> IPAc, 1.09 kmol/m^3; Solvent, 22 x 10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature, 393 K; Pressure, 4.1 MPa; CO:H_2, 1:1; Agitation, 20 Hz. @, Nearly corresponding amount of AA was also formed; *, 6 eqv. tri-n-butyl phosphine (Compared to Co) is used as a ligand. $, 6 eqv. pyridine (Compared to Co) is used as a ligand; #, $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; C_4-Ald, linear & branched added; Linear, 3-acetoxy butanal; Branched, 2- acetoxy -2- methyl propanal; Acet, acetone; ISP-Ac, isopropyl acetate, DCM, dichloro methane; DCE, dichloroethane; EA, ethyl acetate; MTBE, methyl-t-butyl ether; THF, tetrahydrofuran.*

Another group of solvents tested was oxygenated solvents such as ethers and esters. In ethyl acetate (EA) the conversion was reduced to 73.6 % as compared to 95.1 % in toluene (Run 5) whereas the initial reaction rate was marginally higher at 0.0007 kmol/m^3/s as compared to toluene. In methyl-*t*-butyl ether (MTBE), the reaction rate was half of that with toluene and the *linear*-regioselectivity was also less. Tetrahydrofuran

(THF) was found to give faster reaction rate with one and half times higher initial rate (0.0009 Kmol/m^3/s) compared to toluene (Run 7). In THF, the chemoselectivity to aldehydes was found to be only 66.7 % with more formation of acetone and butanal. When the IPAc concentration was doubled in THF (Run 8), the initial rate increased to 0.0016 Kmol/m^3/s but at the cost of lower conversion and chemoselectivity. On doubling the catalyst concentration than that of Run 7, higher conversion of 95.1 % was obtained but the chemoselectivity to oxo aldehydes was reduced further to 62 % (Run9). In Run 10, at double syngas pressure as compared to Run 7, the initial rate fell down to 0.7 Kmol/m^3/s from 0.9 Kmol/m^3/s. All the reactions in THF solvent showed higher n-regioselectivity (> 90 %).

In Run 11, TBP was added as a ligand. 100 % conversion of IPAc was obtained but no chemoselectivity to oxo aldehydes was found whereas acetone, AA and ISP-Ac were observed. Thus, similar to VAM, cobalt-phosphine system was found to be not suitable for hydroformylation of IPAc.

In the study of hydroformylation of VAM with cobalt-pyridine system, the enhancement in initial rates compared to unmodified catalyst system was observed (Section 3.3.6.2). Similar use of pyridine ligand for hydroformylation of IPAc (Run 12) was found to be much less effective, as the initial rate was increased from 0.0006 kmol/m^3/s to 0.0007 kmol/m^3/s *i.e.* a marginal increase of 0.1 kmol/m^3/s. The use of pyridine also reduced the oxo aldehyde chemoselectivity to 52.6 % and *linear*-regioselectivity to 71 %. Thus, pyridine was not found to be a suitable ligand for cobalt-modification for hydroformylation of IPAc.

The graphical presentation of the effect of solvents on the activity and selectivities of hydroformylation of IPAc is shown in Figures 5.2 and 5.3. Figure 5.2 clearly shows the property of THF to give reaction with highest initial rates among the tested solvents whereas for higher % conversion toluene was found to be the best. DCM was found to be a poor solvent as far as initial rate and % conversion are concerned.

The effect of these solvents on the selectivities shows nearly a reverse picture (Figure 5.3). DCM showed highest chemoselectivity to the oxo aldehydes whereas THF showed the lowest. The *linear*-regioselectivity was found to be nearly similar for all the solvents.

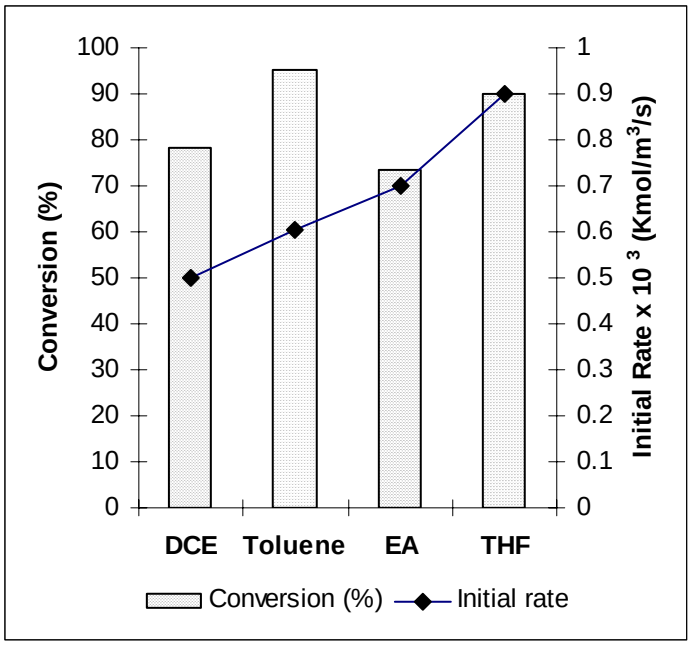


Figure 5.2. Effect of solvents on the activity of Co-catalyzed hydroformylation of IPAc
Reaction conditions: IPAc, 1.09 kmol/m^3; Solvent, 22x10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature, 393 K; Pressure, 4.1 MPa; CO:H_2, 1:1; Agitation, 20 Hz.

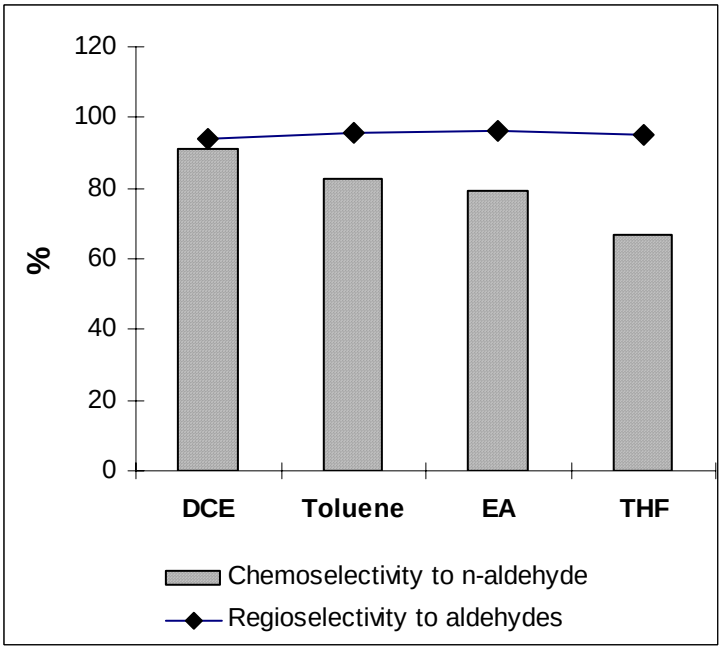


Figure 5.3. Effect of solvents on the selectivity of Co-catalyzed hydroformylation of IPAc
Reaction conditions: IPAc, 1.09 kmol/m^3; Solvent, 22x10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature, 393 K; Pressure, 4.1 MPa; CO:H_2, 1:1; Agitation, 20 Hz.

5.3.3. Tandem hydroformylation-acetalization with IPAc as a substrate

Substituted aldehydes are generally unstable and reactive.[v] As seen in Chapters 3 and 4, an excellent example of such unstable aldehyde is 3-aetoxy propanal (Section 3.2.5). 3-acetoxy butanal is such aldehyde, which under hydroformylation conditions leads to side products such as butanal and AA. *Insitu* protection of the aldehyde functionality could be a solution to avoid such decomposition and oligomerisation of aldehydes, and the best way to protect aldehydes was to convert them to acetals. In view of this, alcohols were taken as solvents for hydroformylation of IPAc for tandem hydroformylation-acetalization. In the present study, we have taken methanol as a lower alcohol, butanol as a middle range alcohol, octanol as a higher one and cyclohexanol as a cyclic alcohol for hydroformylation of IPAc. All the reactions were run for a fixed time of 15 minutes. The results obtained in these alcohols are presented in Table 5.4. As seen in the previous chapters, (Sections 4.3.1.6) many side products form in alcohols as solvents. Side reactions in alcoholic solvents are presented in Scheme 5.3. Such side reactions were also found to take place during VAM hydroformylation in alcoholic solvents (Scheme 4.5). All these side products were confirmed by GC-MS analysis and

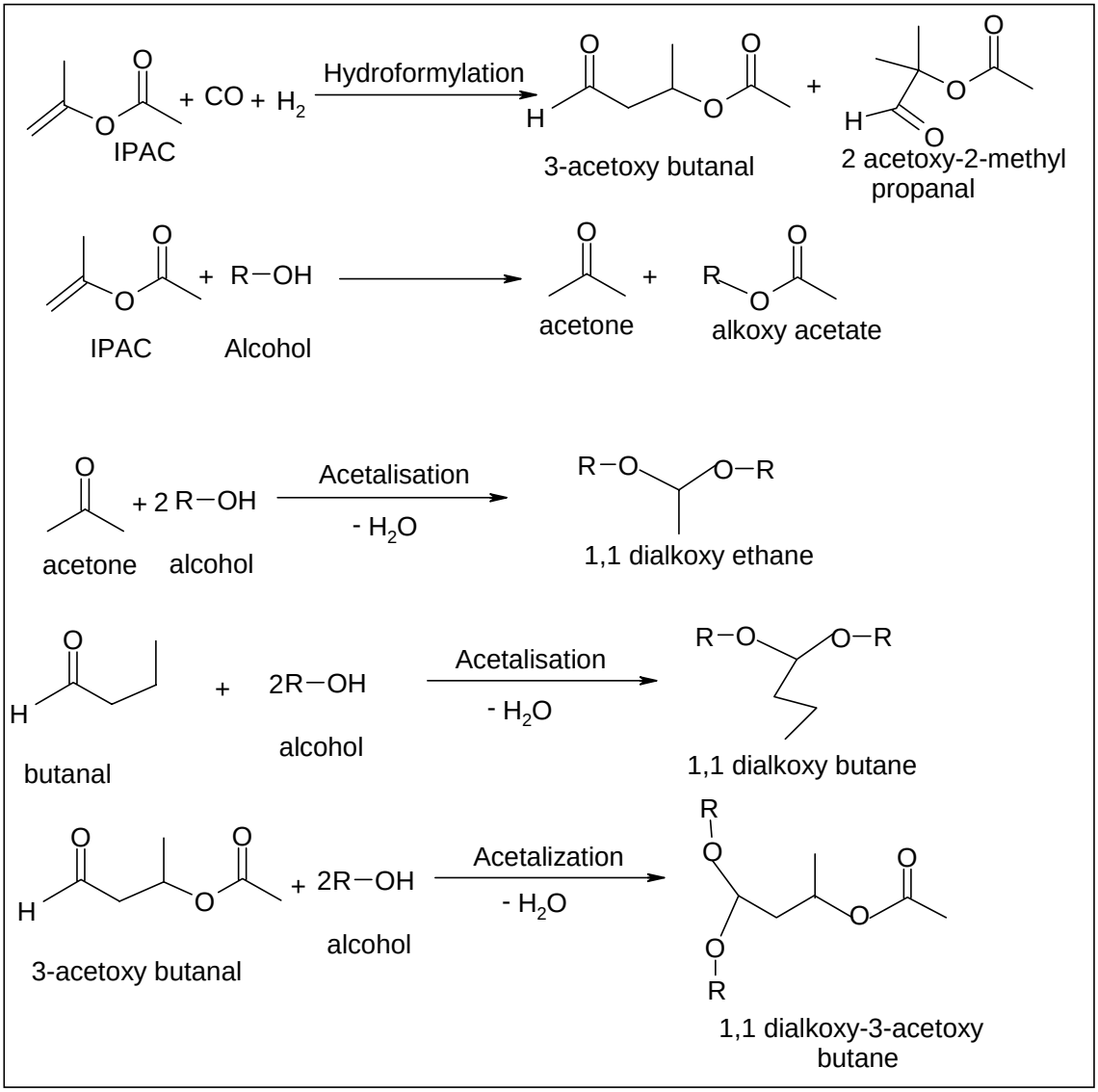
Table 5.4. Tandem hydroformylation-acetalization with IPAc as a substrate

Run No	Solvent	Conv.	Chemoselectivity %					
		%	linear-Ald	Acetone	AlAc	DAE	DAB	Ac-DAB
1	Methanol	11.6	0	0	37.4	34	0	18
2	Butanol	65.5	0.71	15.2	19.6	4.5	9.73	41.1
3	Octanol	35.4	3.06	4.4	8.0	3.7	0	69.8
4	Cycloxol[@]	90.5	3.22	2.18	14.4	11.8	27.7	35.7

<u>Reaction conditions:</u> IPAc, 1.09 kmol/m^3; Solvent, 22 x 10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature, 393 K; Pressure, 4.1 MPa; CO:H_2, 1:1; Agitation, 20 Hz; Run time, 15 min. linear-Ald, 3-acetyl butanal; AlAc, alkoxy acetate; DAE, 1,1-dialkoxy ethane; DAB, 1,1-dialkoxy butane; Ac-DAB, 1,1-dialkoxy-3-acetoxy butane; @, Cycloxol, Cyclohexanol.

the selected spectra are presented in Annexure II (MS-7 to 17). The quantitative analysis was done by area % in the GC-charts.

In methanol as a solvent (Run 1 Table 5.4), the syngas absorption was very negligible and it stopped immediately after ~ 10 % conversion. Methyl acetate (37 %), 1,1-dimethoxy ethane (34 %) and 1,1-dimethoxy-3-acetoxy butane (18 %) were the products observed. Thus, methanol was not found to be a suitable alcoholic solvent for tandem hydroformylation-acetalization. Similar inactivity of cobalt-catalyst in methanol was also observed in case of VAM.



Scheme 5.3. Tandem hydroformylation-acetalization with IPAc as a substrate

When butanol was used as a solvent (Run 2) 65.5 % conversion of IPAc was obtained with 41 % selectivity to the desired 1,1-dibutoxy-3-acetoxy butane. Thus, compared to methanol, butanol was found to be a much superior solvent. In the same

series, when octanol was used as a solvent, the reaction rates again fell down and only 35.4 % conversion of IPAc could be obtained. The reaction was found to be very fast in cyclohexanol and completed 90 % conversion of IPAc in just 15 minutes (Figure 5.4). However, in cyclohexanol, the selectivity to the desired 1,1-dicyclohexoxy-3-acetoxy butane was much lower to ~ 35.7 %. Formation of 1,1-dicyclohexoxy butane was fount to be enhanced (27.7 %) in cyclohexanol, indicating higher trans-esterification activity in cyclohexanol.

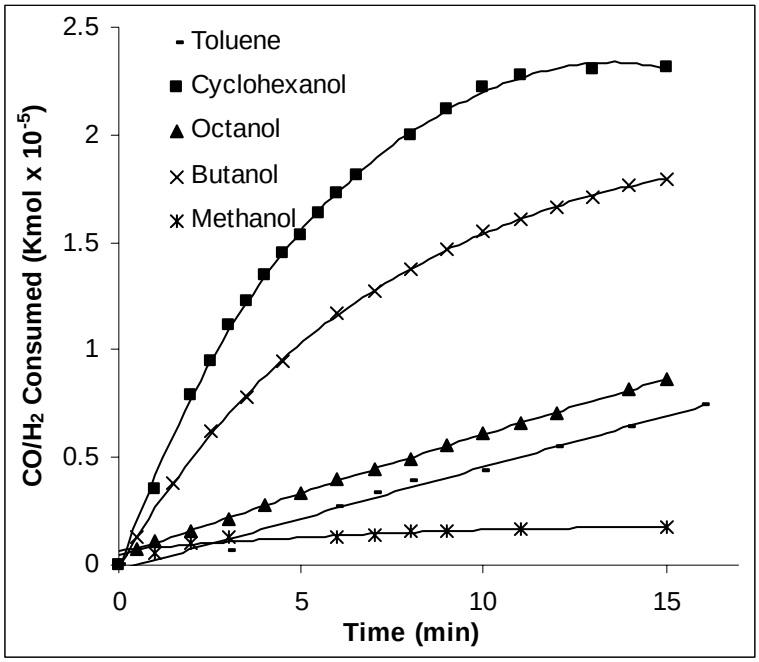


Figure 5.4. Alcohols as solvents for cobalt-catalyzed hydroformylation of IPAc
Reaction conditions: IPAc, 1.09 kmol/m^3; Solvent, 22 x 10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature, 393 K; Pressure, 4.1 MPa; CO:H_2, 1:1; Agitation, 20 Hz.

It was found that different alcohols affect the rate of hydroformylation in different ways. Figure 5.4 clearly depicts the variation in the initial rates with different solvents. The hydroformylation rate was found to be higher in alcohols as compared to toluene (with methanol as an exception). The reaction was found to be slowest in methanol solvent and the rate was found to be higher for middle range alcohol such as butanol. For higher alcohol such as octanol, the initial rate was found to be less than butanol and nearly as much as that in toluene. Fastest reaction occurred in cyclohexanol.

Exact reasons for these variations in rates are not known. It can be postulated that in methanol, the expected hydroformylation reaction occurs scarcely because of direct

reaction between methanol and IPAc to form thermodynamically more favorable and stable methyl acetate and acetone. In middle range alcohols such as butanol and higher alcohols such as octanol this substrate decomposition reaction must be slower because of steric reasons.

5.3.4. Comparison between VAM and IPAc as substrates for hydroformylation

The main distinguishing features of hydroformylation of VAM and IPAc are listed below.

1) **Activity with Rh-catalysts:** Rh-catalysts carry out hydroformylation of VAM to nearly 100 % conversion with regioselective formation of branched-aldehyde whereas for hydroformylation of IPAc, Rh-catalysts are almost inactive and show nearly regioselective formation of linear-aldehyde.

2) **Activity with cobalt-catalysts:** The results of hydroformylation of VAM and IPAc under exactly similar conditions are presented in Table 5.5. cobalt-catalysts carry out hydroformylation of VAM as well as IPAc to almost complete conversion (> 95 %) but the reaction rates are lower for hydroformylation of IPAc. Chemoselectivity to aldehydes is lower in case of IPAc mainly because of more hydrogenolysis. Olefin hydrogenation was found to be higher with VAM. The major distinction appears in the regioselectivities as with VAM nearly equal formation of linear- and branched-aldehydes was observed whereas with IPAc more than 95.5 % linear-aldehyde is formed with only 4.5 % branched-aldehyde. Moreover, the positive effect of rate enhancement with pyridine as ligand observed in VAM hydroformylation was not observed in IPAc so also is true for the effect of halogenated solvents on the regioselectivity.

Table 5.5. Cobalt-catalyzed hydroformylation of VAM & IPAc: comparison

Properties / Substrate	Run time	Conv.	Ald. Selectivity	Hydrogen olysis	Olefin hd	linear-ald.	*branched*-ald.	Initial rate x 10^3
	Min.	%	%	%	%	%	%	kmol/m^3
VAM	90	98	87.3	0	8.7	46.8	53.2	1.1
IPAc	105	95.1	82.9	5.3	4.2	95.5	4.5	0.6

Reaction conditions: Substrate, 1.1 kmol/m^3; Toluene, 22 x 10^{-6} m^3; $Co_2(CO)_8$, 12 x 10^{-3} kmol/m^3; Temperature, 393 K; Pressure, 4.1 MPa; CO:H_2, 1:1; Agitation, 20 Hz.

The graphical presentation of the difference in regioselectivities in hydroformylation of VAM and IPAc, with Rh as well as cobalt-catalysts, is presented in Figure 5.5.

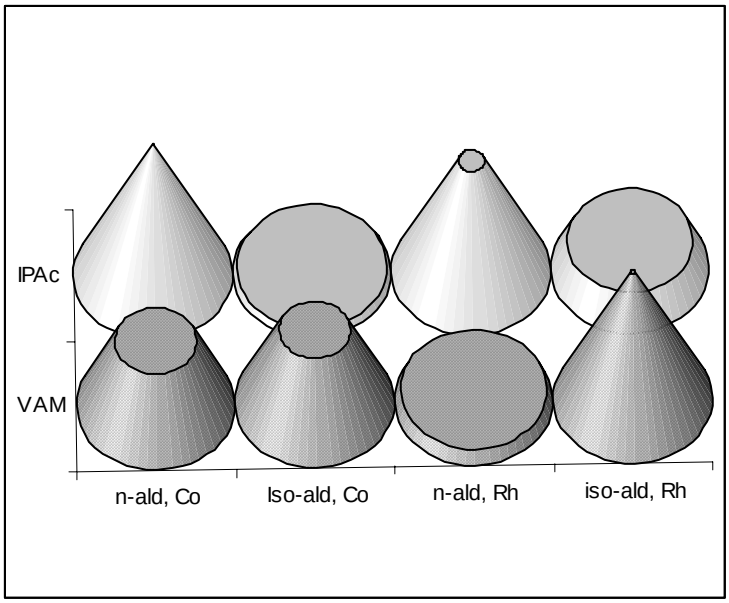


Figure 5.5. Comparison of selectivities in hydroformylation of VAM and IPAc
Reaction conditions: Same as those in Table 5.5.

5.4. CONCLUSIONS

Abiding by the Keulemans Law, the α-methyl vinyl acetate i.e. isopropenyl acetate showed preferential formation of 3-acetoxy butanal, drastically reducing the formation of 2- acetoxy -2- methyl propanal, which require formation of a quaternary carbon atom. As, seen in the literature α-methyl-substitution in hydrocarbon olefins or functionalized olefins such as acrylates, abides the Keulemans Law, but doesn't make it inactive for hydroformylation.[iii] However, the presence of α-methyl substitution along with the acetate group in IPAc reduces its activity drastically for Rh-catalyzed hydroformylation. Different rhodium carbonyl catalysts tested showed that only $Rh(CO)_2acac$ and $HRh(CO)(PPh_3)_3$ were marginally active for hydroformylation of IPAc. The activity of VAM is less than ethene (corresponding non-functional hydrocarbon olefin) due to the chelating effects of the acetate group whereas in IPAc the hindered

double bond as well as the presence of chelating acetate group makes the olefin nearly inactive for Rh-catalyzed hydroformylation. However, $Co_2(CO)_8$ (*i.e.* $HCo(CO)_4$ under hydroformylation conditions) was found to be active for IPAc hydroformylation. The reason behind the activity of $HCo(CO)_4$ for IPAc hydroformylation may be the ability of Co-catalysts to hydroformylate the internal as well as hindered double bonds. Concentration-time profile of the Co-catalyzed hydroformylation of IPAc was studied. Contrary to hydroformylation of VAM, the study of the effect of solvents on hydroformylation of IPAc indicated less influence of halogenated solvents.

Attempts were made for tandem hydroformylation-acetalization reaction in presence of alcohol solvents but major formation of side products was observed. Higher alcohols such as ocatanol were found to be better than the lower alcohols for such tandem hydroformylation-acetalization. Comparison of the hydroformylation results of VAM and IPAc was done.

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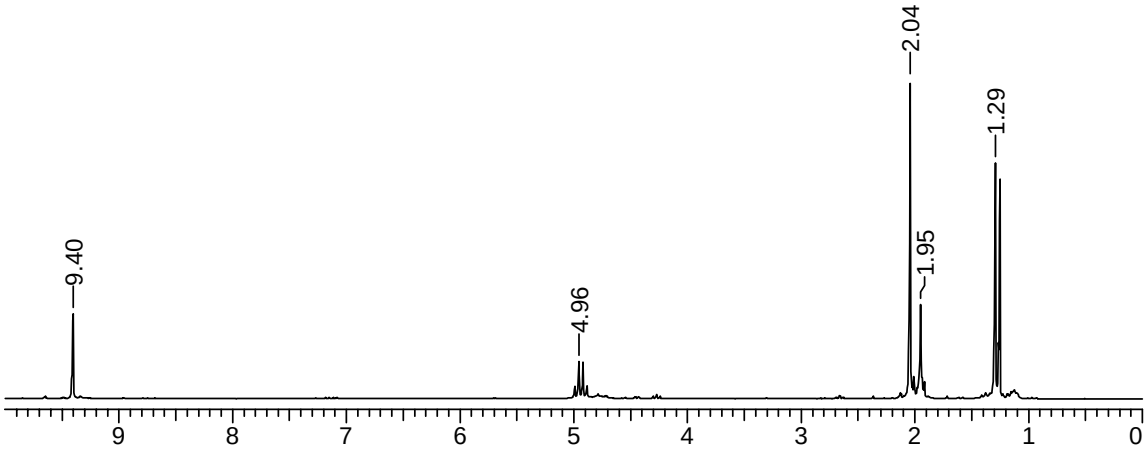
ANNEXURE I: List of abbreviations

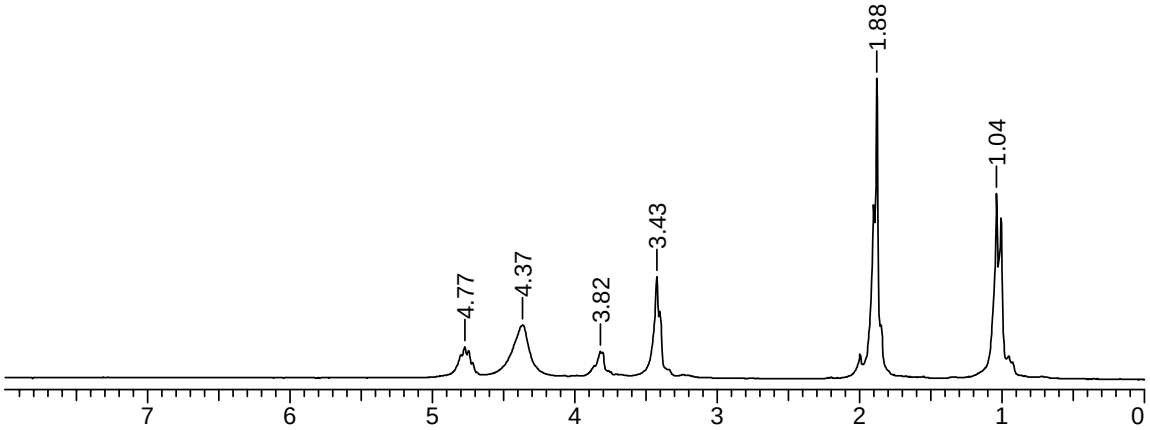
Abbreviations used	Instead of
2-ac pal	2-acetoxy propanal
2-ac pol	2-acetoxy propanol
AA	Acetic acid
Ac pals	Acetoxy propanals
Ac pols	Acetoxy propanols
acac	2,4-pentanedione
b-	Branched
b.p.	Boiling point
Bipy	1,1'-bipyridine
COD	1,5-cyclooctadiene
C-T	Concentration-time
DCE	Dichloro ethane
DCM	Dichloro methane
Diphos	*Bis*-(Diphenyl phosphino) alkanes
DPPE-e	1,2-*bis* (diphenyl phosphino) ethene
DPPE	1,2-*bis* (diphenyl phosphino) ethane
DPPB,	1,4-*bis* (diphenyl phosphino) butane
DPPH	1,6-*bis* (diphenyl phosphino) hexane
DPPP	1,3-*bis* (diphenyl phosphino) propane
EA	Ethyl acetate
e.g.	For example
i. e.	That is
viz.	Namely
EO	Ehtylene oxide
GC	Gas Chromatography
HPA	3-hydroxy propanal
IPAc	Isopropenyl acetate
IsP-Ac	Isopropyl acetate

l/b	Linear/branch
l-	Linear
LAH	$LiAlH_4$
MEK	Methyl ethyl ketone
MIBK	Methyl isobutyl ketone
MTBE	Methyl *tert*-butyl ether
n-	normal
pdo	Propane diol
PET	Polyethylene terphthalate
PO	Propylene oxide
PTT	Polytrimethylene terphthalate
SMDPT	N',N''-*bis*(salicyledene)-N-methyl-, dipropyl triamine
TBA	Tribenzyl amine
TBP	Tri-n-butyl phosphine
TbzA	Tribenzyl amine
Terpy	1,1',1''-terpyridine
THF	Tetra hydro furan
TLC	Thin layer chromatography
TOF	Turnover frequency
TON	Turnover number
TOPO	Tri-octyl phosphine oxide
TPA	Triphenyl amine
TPAs	Triphenyl arsine
TPP	Triphenyl phosphine
VAM	Vinyl acetate monomer

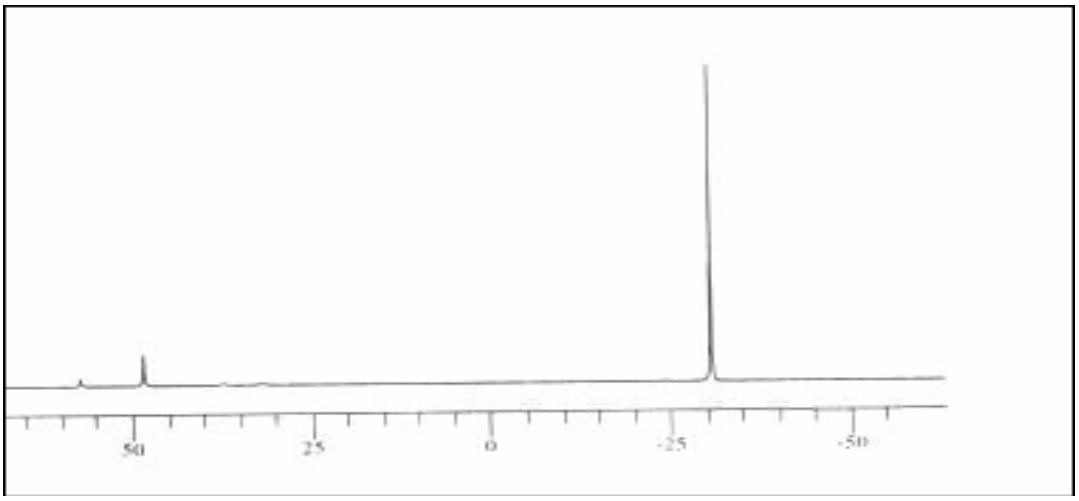
Annexure II: Spectral data



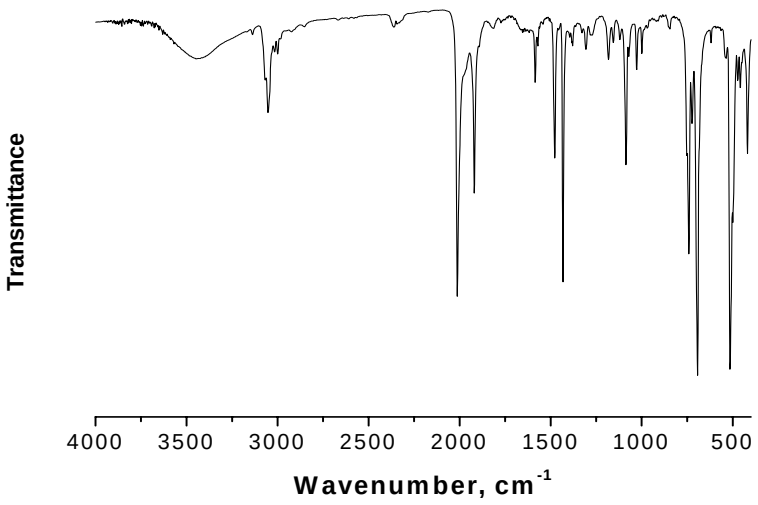
NMR-1. ^{1}H NMR Spectra of **2-acetoxy propanal**



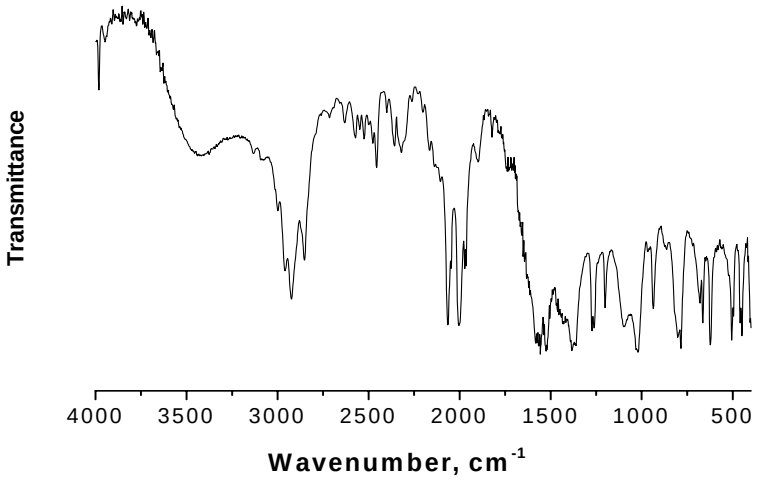
NMR-2. ^{1}H NMR Spectra of **2-acetoxy propanol**



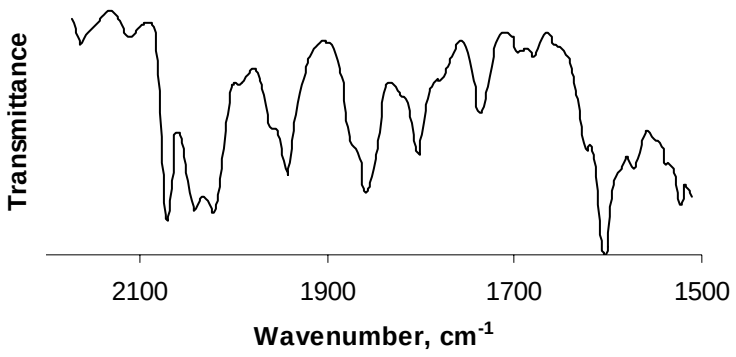
NMR-3. ^{31}P NMR Spectra of **Tri-*n*-butyl phosphine**



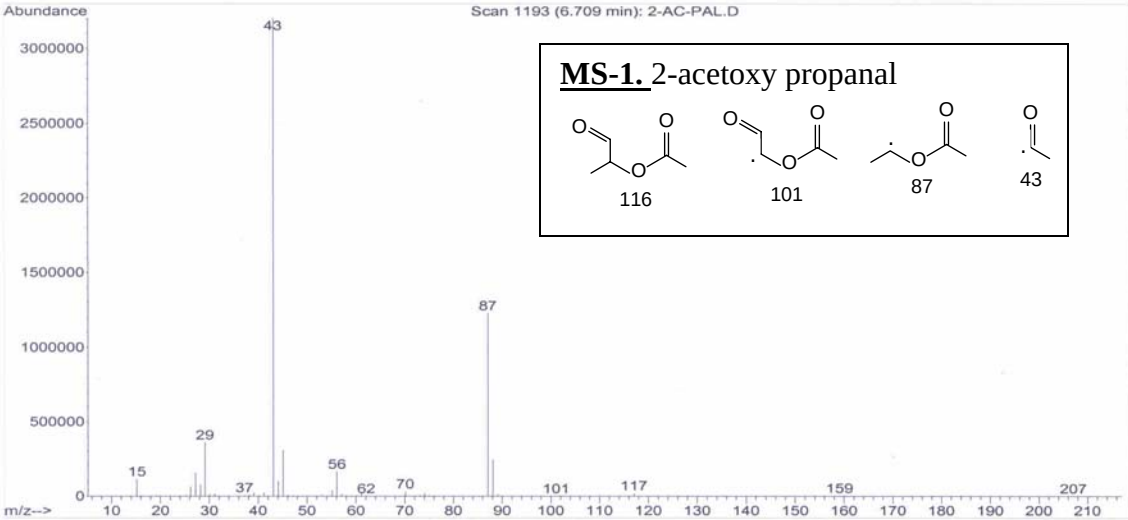
<u>IR-1.</u> FTIR spectra of **$HR(CO)(PPh_3)_3$**

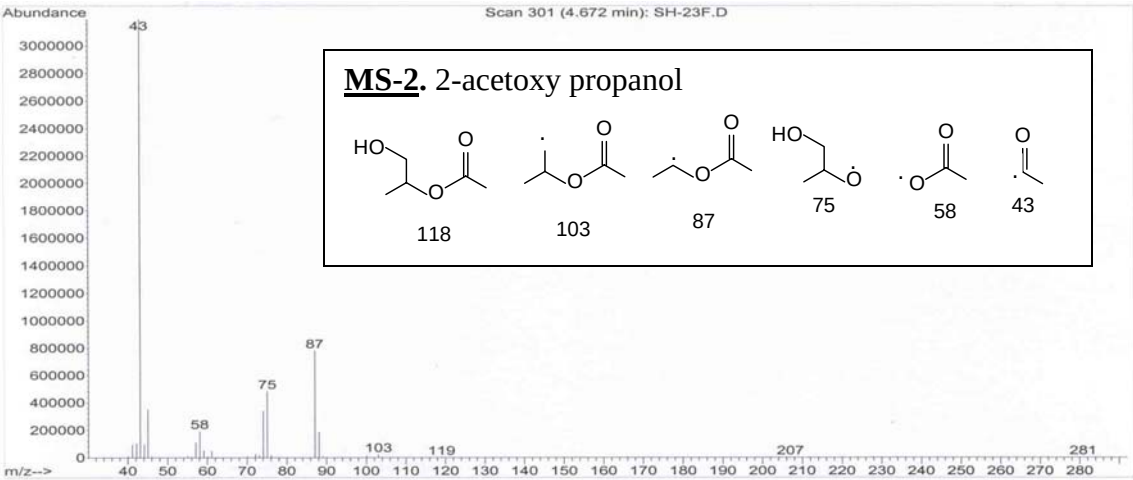


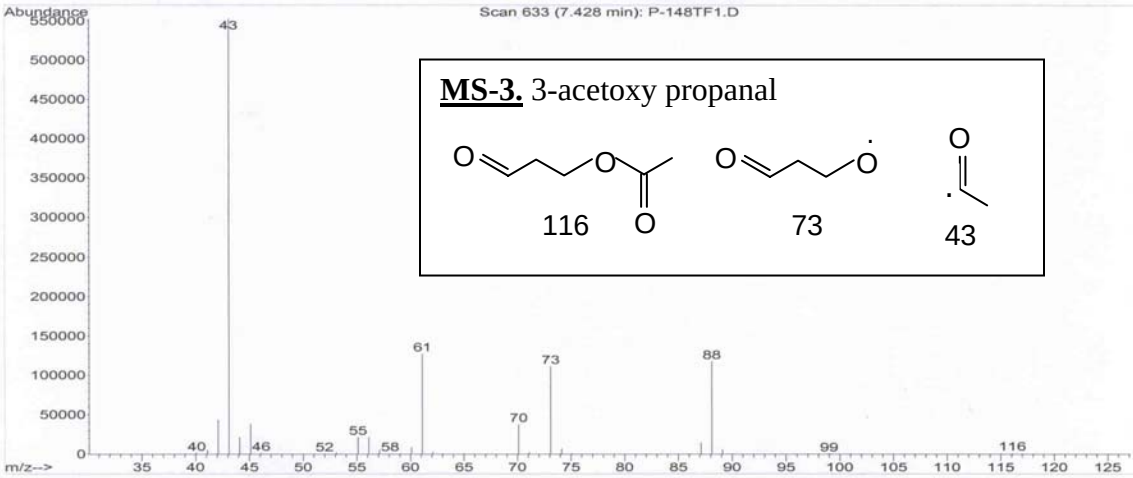
<u>IR-2.</u> FTIR spectra of **$Rh(CO)_2acac$**

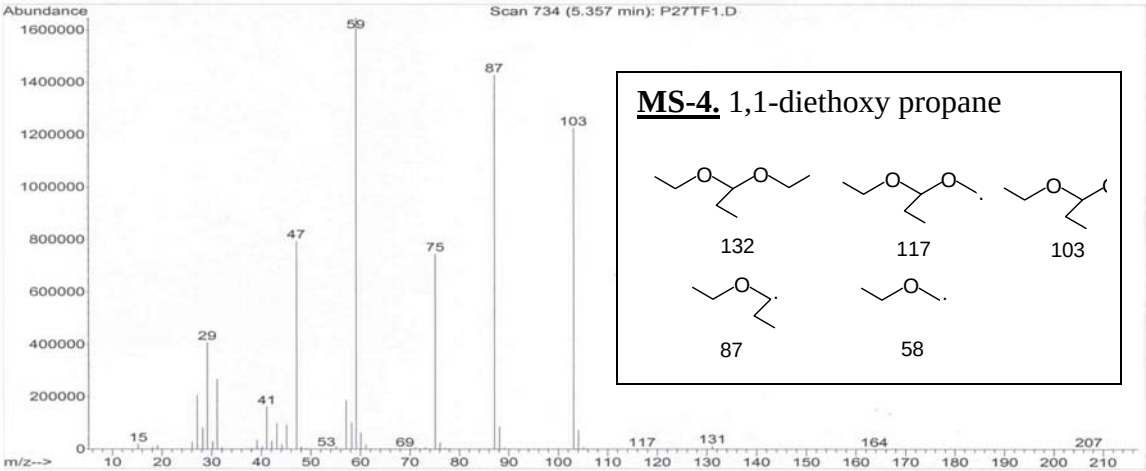


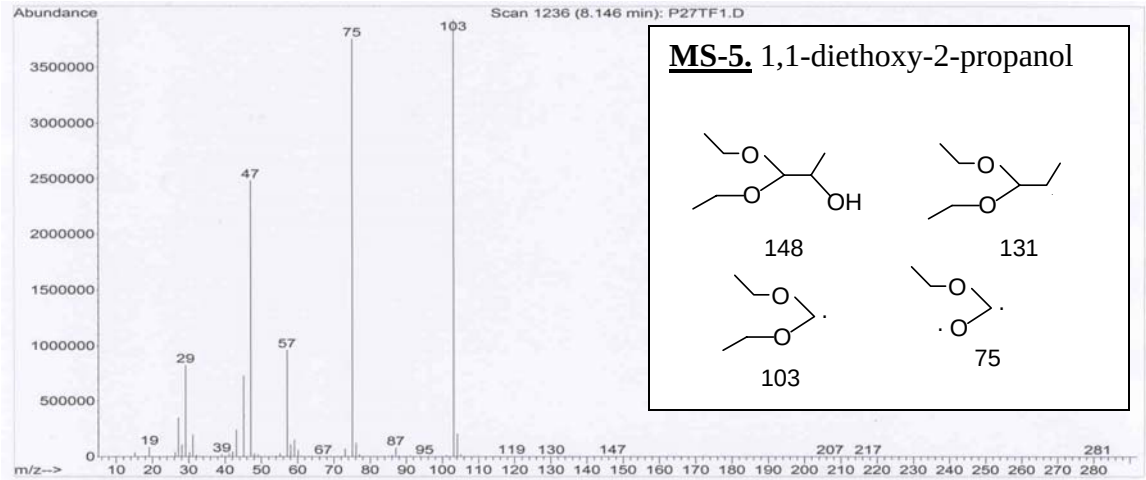
<u>IR-3.</u> FTIR spectra of **$Co_2(CO)_8$**

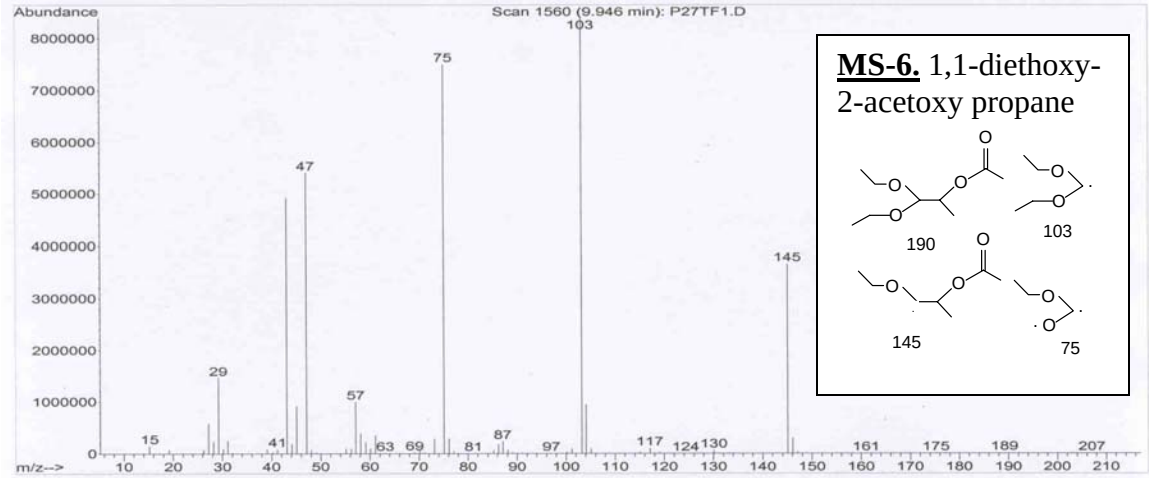

Abundance
Scan 1193 (6.709 min): 2-AC-PAL.D
MS-1. 2-acetoxy propanal
116
101
87
43
m/z-->

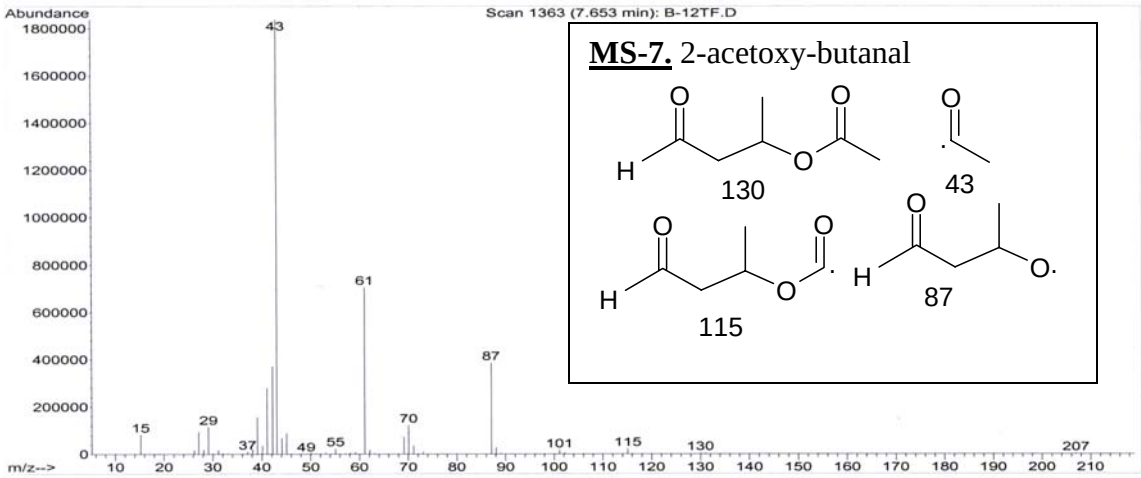

Abundance
Scan 301 (4.672 min): SH-23F.D
MS-2. 2-acetoxy propanol
118
103
87
75
58
43
m/z-->

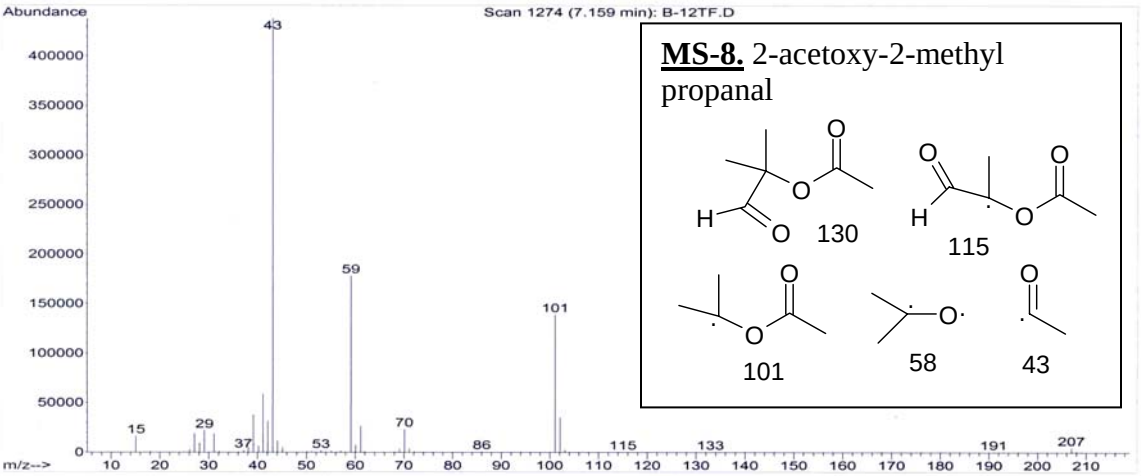

Abundance
Scan 633 (7.428 min): P-148TF1.D
MS-3. 3-acetoxy propanal
116
73
43
m/z-->

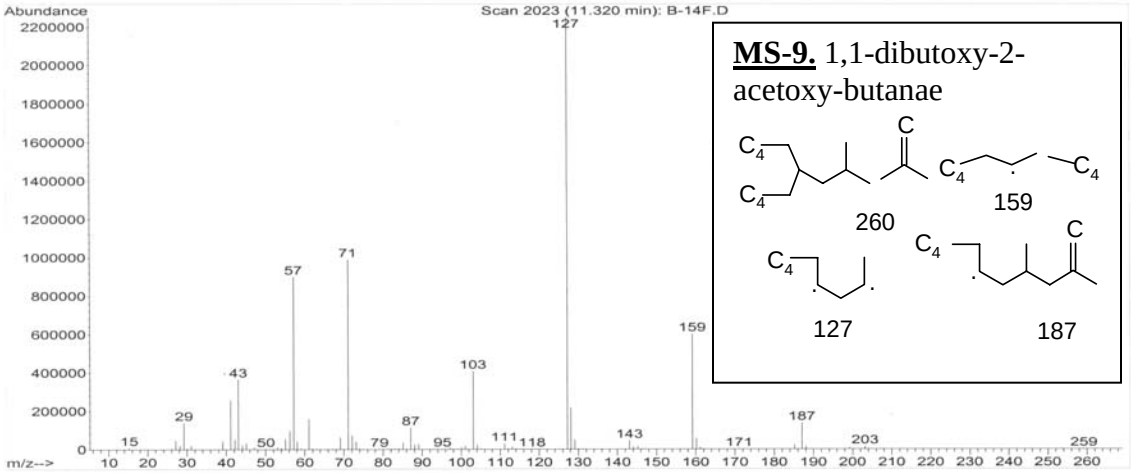

Abundance
Scan 734 (5.357 min): P27TF1.D
MS-4. 1,1-diethoxy propane
132
117
103
87
58
m/z-->

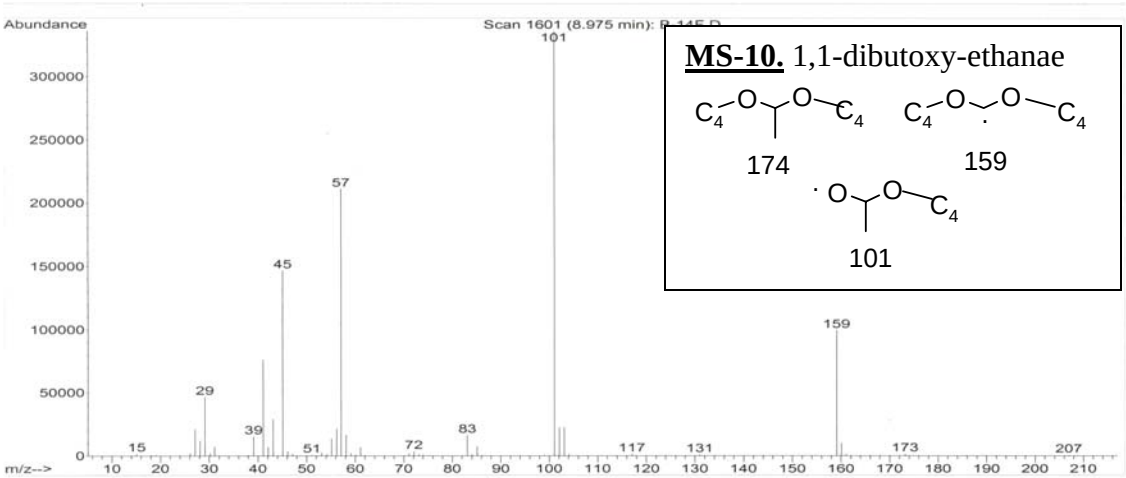

Abundance
Scan 1236 (8.146 min): P27TF1.D
MS-5. 1,1-diethoxy-2-propanol
148
131
103
75
m/z-->

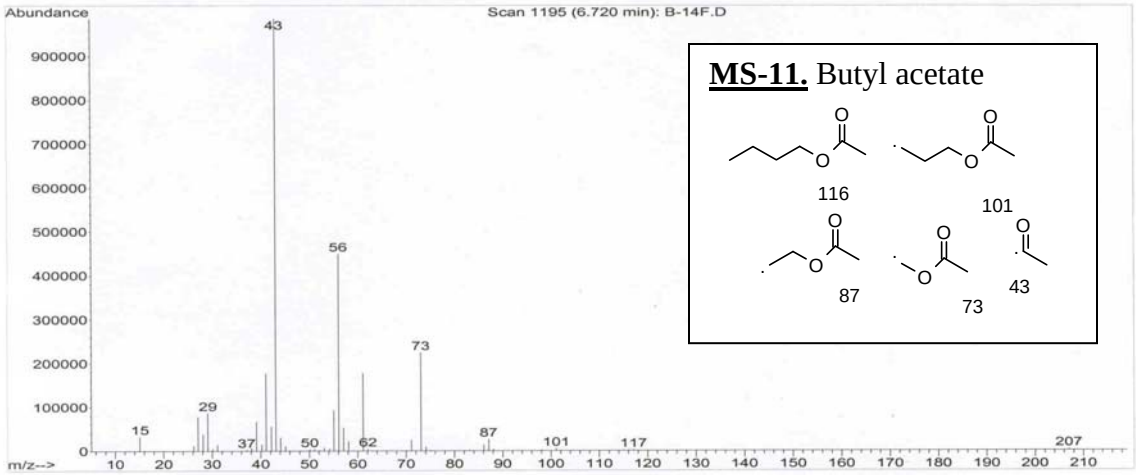

Abundance
Scan 1560 (9.946 min): P27TF1.D
MS-6. 1,1-diethoxy-2-acetoxy propane
190
103
145
75
m/z-->

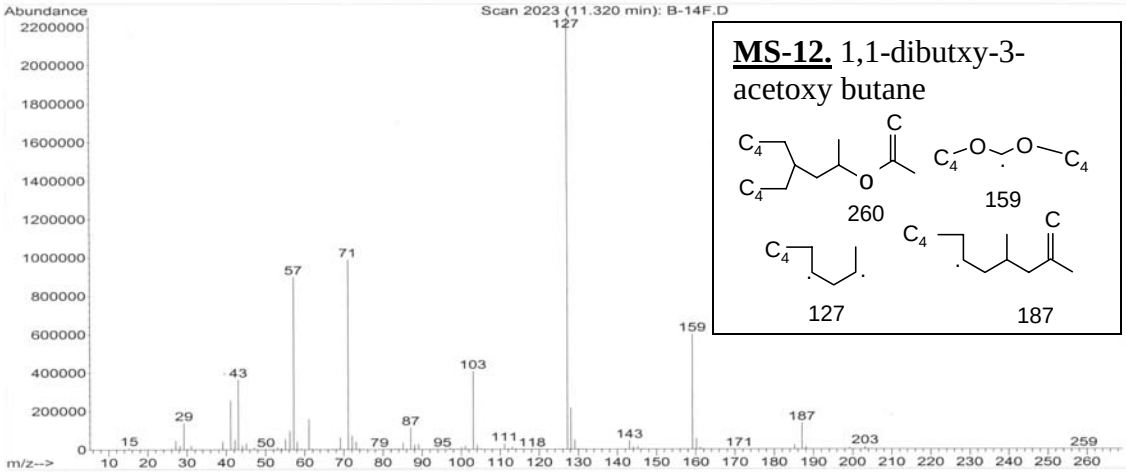

Abundance
Scan 1363 (7.653 min): B-12TF.D
MS-7. 2-acetoxy-butanal
130
43
115
87
m/z-->

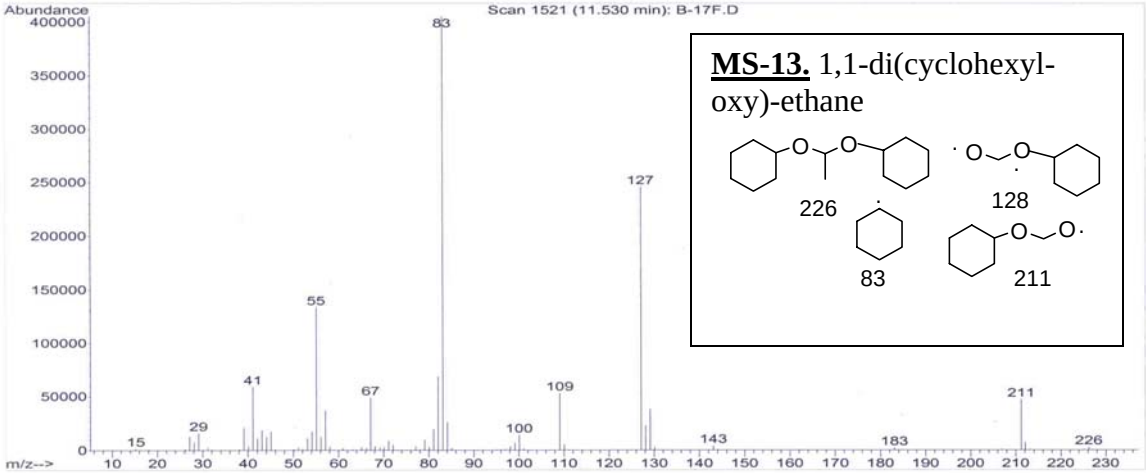

Abundance
Scan 1274 (7.159 min): B-12TF.D
MS-8. 2-acetoxy-2-methyl propanal
130
115
101
58
43
m/z-->

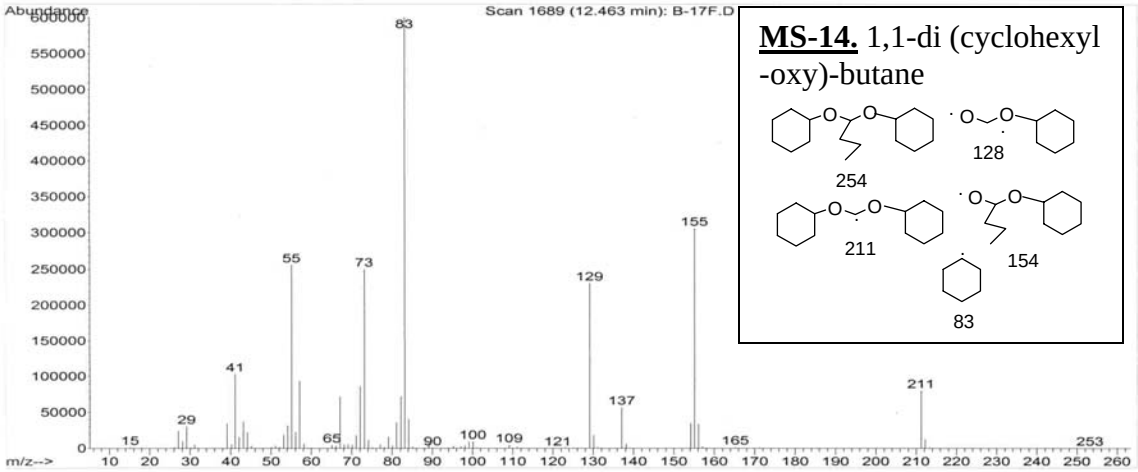

Abundance
Scan 2023 (11.320 min): B-14F.D
MS-9. 1,1-dibutoxy-2-acetoxy-butanae
260
159
127
187
m/z-->

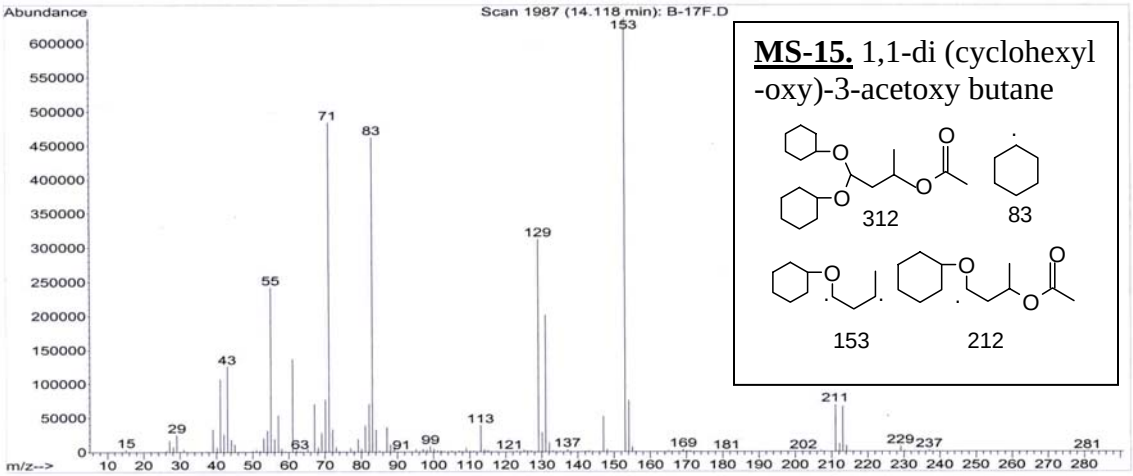

Abundance
Scan 1601 (8.975 min): B-14F.D
MS-10. 1,1-dibutoxy-ethanae
174
159
101
m/z-->

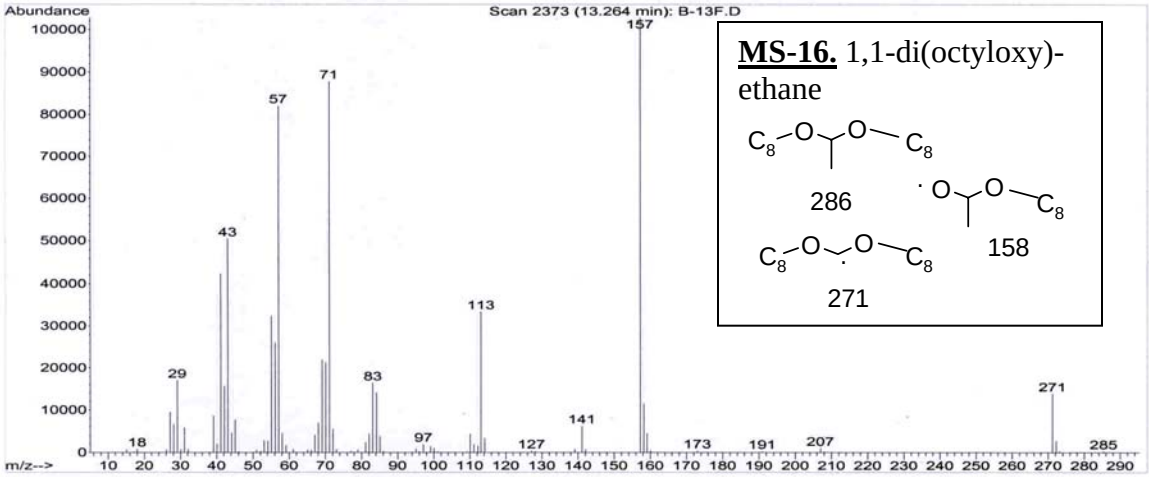

Abundance
Scan 1195 (6.720 min): B-14F.D
MS-11. Butyl acetate
116
101
87
73
43
m/z-->

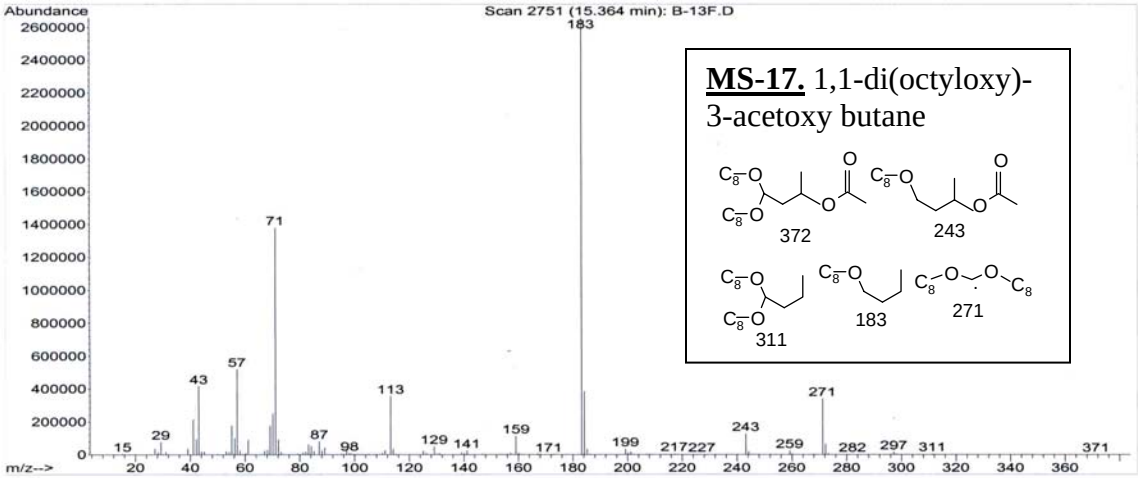

Abundance
Scan 2023 (11.320 min): B-14F.D
MS-12. 1,1-dibutxy-3-acetoxy butane
260
159
127
187
m/z-->

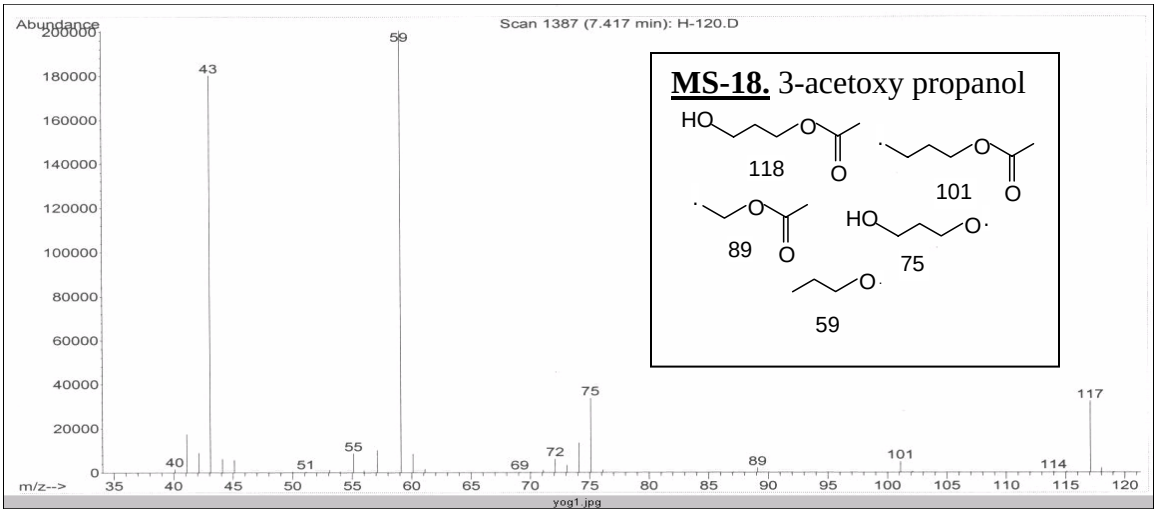

Abundance
Scan 1521 (11.530 min): B-17F.D
m/z-->
MS-13. 1,1-di(cyclohexyl-oxy)-ethane
226
128
83
211


Abundance
Scan 1689 (12.463 min): B-17F.D
m/z-->
MS-14. 1,1-di (cyclohexyl -oxy)-butane
254
128
211
154
83


Abundance
Scan 1987 (14.118 min): B-17F.D
m/z-->
MS-15. 1,1-di (cyclohexyl -oxy)-3-acetoxy butane
312
83
153
212


Abundance
Scan 2373 (13.264 min): B-13F.D
MS-16. 1,1-di(octyloxy)-ethane
286
158
271
m/z-->


Abundance
Scan 2751 (15.364 min): B-13F.D
MS-17. 1,1-di(octyloxy)-3-acetoxy butane
372
243
311
183
271
m/z-->


Abundance
Scan 1387 (7.417 min): H-120.D
MS-18. 3-acetoxy propanol
118
101
89
75
59
m/z-->