HYDROFORMYLATION OF OLEFINS USING HOMOGENEOUS AND BIPHASIC CATALYSTS

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Dedicated to My Parents
Teachers
and
Friends

FORM 'A'

Certified that the work incorporated in the thesis entitled: **"HYDROFORMYLATION OF OLEFINS USING HOMOGENEOUS AND BIPHASIC CATALYSTS"**, submitted by **Shri. Vinod S. Nair** was carried under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

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Dr. R. V. Chaudhari
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Summary and Conclusions

Homogeneous catalysis of organic reactions using soluble metal complexes has become a major synthetic tool, both in laboratory and industry. The major virtue of homogeneous catalysis that has led to its wide spread use in chemical industry is its ability to selectively produce desired products in high yield with a few by-products under mild reaction conditions. Furthermore, they can be easily modified by ligand variation and their structure and reaction pathways can be characterised in detail by a range of spectroscopic techniques thereby simplifying catalyst optimisation. A wide variety of homogeneous catalysts are known such as Bronsted and Lewis acids and bases, metal complexes, metal ions, organometallic complexes, organic molecules, enzymes etc. However, those using transition metal complexes in solution have made the most significant impact on new technology development. Some of the important commercial applications of homogeneously catalysed processes are: Carbonylation of methanol to acetic acid, Hydroformylation of olefins to oxo alcohols, Commercial synthesis of L-Dopa by asymmetric catalysis, Oxidation of p-xylene to terephthalic acid, Hydrocynation of butadiene to adiponitrile, etc. [Parshall (1980)].

It was only after the landmark discovery of "Oxo Synthesis" by Otto Rolen in 1938 that homogeneous catalysis using soluble metal complexes has gained considerable importance. Oxo synthesis, which is commonly known as the hydroformylation reaction, is a reaction with carbon monoxide, hydrogen and an olefin to produce aldehydes in presence of a transition metal catalyst [Cornils and Hermann (1996)]. In recent years, numerous applications for value added intermediate products for fine chemicals and pharmaceuticals are also emerging [Siegel and Himmele (1980), Parshall and Nugent (1988)]. An important example of the latter class is the hydroformylation of styrene or its derivatives to obtain aryl propionaldehydes, which upon subsequent oxidation gives aryl propionic acid derivatives (e.g. Ibuprofen from p-isobutyl styrene substrate), which are used as largest selling anti-inflammatory class of drugs [Rieu et al. (1986)].

Inspite of producing pure products under mild reaction conditions, the use of homogeneous catalysis is often limited due to the difficulty in separating the catalyst from the products. The emergence of biphasic catalysis, wherein the reactants and products are in two different liquid phases, has extended the scope of homogeneous catalysis by simplifying the catalyst recovery from the product mixture and subsequent recycle. The separation of the catalyst can be easily achieved by simple phase separation. Some of the other important developments in this regard are coordinating the metal to a functionalized organic polymer or inorganic support and use of semipermeable membrane that can specifically exclude organometallic complex. However these methods are yet to find a commercial success.

Considering the importance of hydroformylation of branched olefins and its relevance to synthesis of a variety of value added products (e.g. pharmaceuticals and fine chemicals), it is important to study the catalysis and reaction engineering aspects for such processes. Hence, the present study was focused on both kinetic modelling of hydroformylation of styrene, which is important in understanding the reaction mechanism as well as design of reactor. The following specific problems were chosen for the present work.

1. Kinetics of hydroformylation of styrene using a homogeneous $HRh(CO)(PPh_3)_3$ catalyst: A molecular level approach.
2. Hydroformylation of styrene using water soluble Rh-TPPTS catalyst in a biphasic system: Kinetics and reaction engineering studies.
3. Hydroformylation of styrene using SAPC: studies on activity, selectivity and reaction kinetics.

Chapter 1 presents a detailed literature survey on the hydroformylation of olefins. Majority of the hydroformylation literature is related to the electronic and steric properties of organometallic complexes as catalysts with different central metal atoms or ligands and their influence on the reaction rate and product distribution. A variety of metal complexes of Rh, CO, Ir, Ru in homogeneous and heterogenized form have been proposed. However, Rh and Co were found to give better activity and selectivity. Wilkinson's catalyst, $HRh(CO)(PPh_3)_3$ is known to give very high activity, selectivity and requires mild operating conditions.

A detailed review of kinetics and mechanistic studies of hydroformylation of olefins is presented in this chapter. In the previous work, kinetics of hydroformylation of linear olefins has been studied using both Co and Rh catalysts but only a few reports on the kinetics of hydroformylation of styrene are known. Also, in most cases limited rate data and empirical rate equations are reported. It will be more appropriate to study the kinetics based on a mechanistic model derived using a molecular level description of the catalytic cycle.

The relevant literature on biphasic catalysis in hydroformylation has also been presented in Chapter 1. Synthesis of water-soluble catalyst is a key step in biphasic catalysis and hence a literature review on the synthesis of new water-soluble ligands has also been presented. Since many of the organic substrates are sparingly soluble in water, the reaction rates are often reduced drastically in a biphasic media. Reports on improvement of the reaction rates in a biphasic media, by using surfactants, use of tenside ligands, interfacial catalysis, use of co-solvents, cyclodextrins, fluorous biphasic systems and supported aqueous phase catalysis have also been thoroughly reviewed in this Chapter.

In Chapter 2 a detailed study on kinetics of hydroformylation of styrene using a homogeneous $HRh(CO)(PPh_3)_3$, in a batch pressure reactor in a temperature range of 333-353K has been presented. The reaction was found to be first order with respect to catalyst and H_2 partial pressure. The rate vs. partial pressure of CO showed negative order dependence with CO indicating a CO inhibited kinetics. Change in styrene concentration showed no effect on the rate of hydroformylation. A rate equation has been derived using a catalytic cycle based on molecular level description of elementary steps and assuming oxidative addition of hydrogen to acylrhodium intermediate as the rate-determining step. The kinetic parameters were estimated using a non-linear regression analysis. The following mechanistic model proposed was found to predict the data within ± 5% error at all temperatures.

$$r = \frac{k\,K_1\,K_2\,C_A\,C_B\,C\,C_D}{1 + K_1\,B + K_1\,K_2\,C_B C_D + K_1\,K_2\,K_3\,C_B^2\,C_D + K_1\,K_2\,K_3\,K_4\,C_B^3\,C_D} \qquad (1)$$

Where C_A is the concentration of H_2 in the reaction mixture, kmol/m^3; C_B is the concentration of CO in the reaction mixture, kmol/m^3; C is the catalyst concentration, kmol/m^3; C_D is the Styrene concentration, kmol/m^3; k is the Reaction rate constant, m^3/kmol/s and K_1,K_2,K_3,K_4 are the equilibrium constants for the elementary steps in the catalytic cycle. The activation energy was found to be 68.80 kJ/mol.

In Chapter 3 the results on kinetics of hydroformylation of styrene in a biphasic media using $HRh(CO)(TPPTS)_3$ have been presented. The effects of different parameters like concentration of catalyst precursor, TPPTS, styrene, partial pressures of CO and hydrogen were investigated in a temperature range of 363 K to 383 K. The rate was found to be first order with respect to catalyst loading up to a concentration of 1.21 $kmol/m^3$. At higher catalyst concentrations, the rate behaviour was not linear, and was likely to be limited by the transport of styrene form organic phase to aqueous phase. Rate was found to be first order with partial pressure of hydrogen, indicating that the addition of hydrogen to acyl rhodium species is the rate-limiting step. Unlike in the case of hydroformylation in homogeneous medium, rate was found to be first order with respect to styrene concentration and carbon monoxide partial pressure. The following rate model has been proposed:

$$r = \frac{\beta_1 C_A C_B C_D}{1 + \beta_2 C_B + \beta_3 C_B C_D} \tag{2}$$

Where $\beta_1; \beta_2; \beta_3$ are the lumped rate constants. Activation energy of the reaction was found to be 107.79 kJ/mol.

The effect of co-solvents on kinetics of biphasic hydroformylation was also investigated. This is important as the use of co-solvent enhances the reaction rate significantly. Effect of various co-solvents such as, N-methylpyrrolidone-2 (NMP), ethanol (ETOH), methylethyl ketone (MEK) and γ-butyrolactone (GBL), on the enhancement of reaction rate was studied. N-Methyl pyrrolidone-2 was found to be a better co-solvent than ethanol, due to its inert to the present system. In the presence of NMP as a co-solvent, the rate of reaction was found to increase by several times compared to that in the absence of co-solvent. The effect of catalyst and styrene concentration, partial pressures of H_2 and CO was studied at 373 K using $HRh(CO)(TPPTS)_3$ in the presence of NMP as a co-solvent. The rate was found to be first order with catalyst and hydrogen partial pressure and a 0.7th order with CO. The rate was found to be first order with styrene up to a concentration of 3.49 $kmol/m^3_{org}$ and then zero order beyond this concentration. The difference in the trends was explained based on the difference in solubility of styrene and CO in the presence of NMP. A rate equation similar to Eq 2 for the biphasic hydroformylation and found to represent the rate data. The rate parameters were found to be $\beta_1 = 74.08$; $\beta_2 = 0.83$; $\beta_3 = 709.15$ at 373 K.

Chapter 4 presents a study on kinetics of hydroformylation of styrene using $HRh(CO)(TPPTS)_3$ as a supported aqueous phase catalyst. The effects of concentration of catalyst, styrene, partial pressures of CO and hydrogen were investigated over a temperature range of 353 K to 373 K. The rate was found to be first order with respect to hydrogen partial pressure, 0.67th order with CO for SAPC system. Effect of styrene showed that rate varies with first order shifting to zero order with increase in concentration. Effect of water loading on the SAP catalyst was also studied and it was found that the rate increased with increase in water amount up to 40% (w/w) on silica and then decreased with increase in water content. The rate model of the form similar to Eq 2. was derived and was found to represent the data satisfactorily. Activation energy of the reaction was found to be 63. 48 kJ/mol.

Comparative study on activity and selectivity behaviour of homogeneous, Biphasic (with and without co-solvent) and SAP hydroformylation of styrene showed a 6.5 times drop in activity for biphasic system compared to that of the homogenous system. The activity was improved by 3 to 3.6 times, when the reaction was carried out in biphasic medium with NMP as a co-solvent and with SAPC system respectively. Further, the selectivity towards the desired-branched aldehyde was improved by 66-79% in these systems compared to that observed for aqueous-biphasic medium (58%). Kinetics of hydroformylation of styrene for homogenous, biphasic (with and without co-solvent) and supported aqueous phase catalyst has also been compared.

In conclusion, this thesis reports a detailed investigation of the hydroformylation of styrene using $HRh(CO)(PPh_3)_3$ a homogeneous, , $HRh(CO)(TPPTS)_3$ as biphasic (with and without co-solvent), as well as SAP catalyst systems. The proposed rate equations may be useful for selection of catalyst type as well as designing reactors.

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CHAPTER I

Literature Survey

1 INTRODUCTION

Since the evolution of life, majorities of biological reactions are catalytic, enzymes are nature's catalysts. Interestingly these reactions are so specific that they hardly produce any byproduct. Today chemical processing under stringent environmental regulations is forcing industry to optimize their processes, so that they produce negligible side products or effluents. Since the discovery of catalysis phenomenon, catalysts are serving the purpose of selective chemical processing, which is desirable for commercial viability. The world of catalysis has broadened and grown enormously to an extent that, today most of the industrial reactions are catalytic. The number of different chemical compounds produced worldwide at the present time is roughly in the range of 20, 000 to 30, 000 [Weissermel and Arpe (1993)]. These large number of substances are produced from only few basic chemical raw materials (see Figure 1.1).

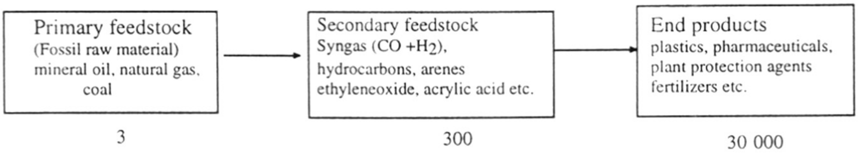


Figure 1.1 The raw material basis of the chemical industry

Catalysis plays a key role in production of such a wide range of products, which are having applications in food, clothing, drugs, plastics, agrochemicals, detergents, fuels etc. In addition, catalysis is playing an ever-expanding role in environmental protection not only by providing cleaner alternative routes for stoichiometric technologies [Sheldon (1992)] but also by conversion of polluting emissions to harmless streams. Thus, the importance of catalysis to society is obviously based on its great economic impact in the production of a broad range of commodity products that improve our standard of living and quality of life.

Generally catalysts are classified as homogeneous and heterogeneous, depending on the physical form in which they are used. Homogeneous catalysis using soluble metal complexes provides selective synthetic routes under mild operating conditions for valuable chemicals from basic organic precursors. Systematic progress in the field of co-ordination chemistry with improved techniques of catalyst characterization and simultaneous developments in process technologies has led to numerous new commercial processes based on homogeneous catalysis. Today homogeneous catalysis has emerged as a major synthetic tool, both in laboratory as well as in chemical industry. Some of the basic reactions catalyzed by transition metal complexes are hydrogenation, oxidation, hydroformylation, carbonylation, carbon-carbon bond formation reactions such as Heck reaction, telomerization, co-polymerization and ring opening metathesis. Some of the important commercial applications of homogeneous catalysis are: hydroformylation of olefins to aldehydes/alcohols, carbonylation of methanol to acetic acid, synthesis of L-dopa by asymmetric hydrogenation, oxidation of p-xylene to terephthalic acid, hydrocynation of butadiene to adiponitrile, ethylene oligomerization etc. [Parshall (1980)]. Being highly selective, homogeneous catalysis is assuming increasingly important role in highly efficient processes. Today, high process efficiency has become a need, since the natural resources are finite and the consumption is ever increasing. These facts along with the deteriorating climate, motivated a movement towards efficient catalytic alternatives to stoichiometric organic transformations.

Homogeneous catalysis has advanced considerably in the last few decades leading to the discovery of new catalytic complexes, their applications, novel techniques of characterization as well as new industrial processes. It is projected to be even more significant in 21^{st} century when chemical industry in particular and society in general, is seeking ways of global preservation and energy conservation. One of the most significant examples of industrial homogeneous catalytic process is the hydroformylation of olefins for Oxo alcohols manufacture. While many variations of the process are operating in practice, mainly differing by the catalyst used, there is a need to further improve the catalysts and processes to achieve high activity and selectivity as also the separation of catalyst from products. The aim of this thesis is to study hydroformylation of styrene as a model reaction system, using homogeneous, biphasic (with and without co-solvents) and supported aqueous phase Rh complex catalysts, in order to understand in detail the kinetics, mechanism and reaction engineering aspects. Hence the focus of this chapter is a detailed survey of the relevant literature on catalysis and kinetic modeling of both homogeneous and heterogenised (biphasic and SAPC) catalysts for hydroformylation.

1.1 Hydroformylation

Otto Roelen discovered hydroformylation or Oxo-reaction in 1938, which is considered as one of the land mark discovery in the area of homogeneous catalysis. Hydroformylation is best known in the context of the synthesis of linear aldehydes and alcohols from an olefin, carbon monoxide and hydrogen in the presence of a transition metal catalyst. Today hydroformylation is one of the largest applications of homogeneous catalysis in the industry, to produce a wide range of Oxo alcohols of high commercial value. More than six million tons of hydroformylation products are produced per year as precursors for detergent, perfumery and plasticiser products [Cornils (1980); Beller et al. (1995)]. A summary of the important industrial oxo processes is shown in Table1.1. Detailed review of the developments in the hydroformylation catalysis and its industrial applications has been discussed in very recent monographs by Beller et al. (1995) and Frohning and Kohlpainter (1996). The range of products derived through hydroformylation is shown in Figure 1.2

Table 1.1 Industrially Important oxo processes [Cornils and Herrmann (1996)]

Catalyst metal	Cobalt		Rhodium		
Variant	Unmodified	Modified	Unmodified	Modified	
Ligand	None	Phospines	None	Phospines	
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.

Currently, hydroformylation of specialty olefins has emerged as a versatile method in organic synthesis, especially in the context of the synthesis of branched aldehyde products that form the basis for fine chemicals, pharmaceuticals and natural products [Parshall and

Nugent (1988), Siegel and Himmele (1980)]. Some of the commercially proven examples are discussed in the following section.

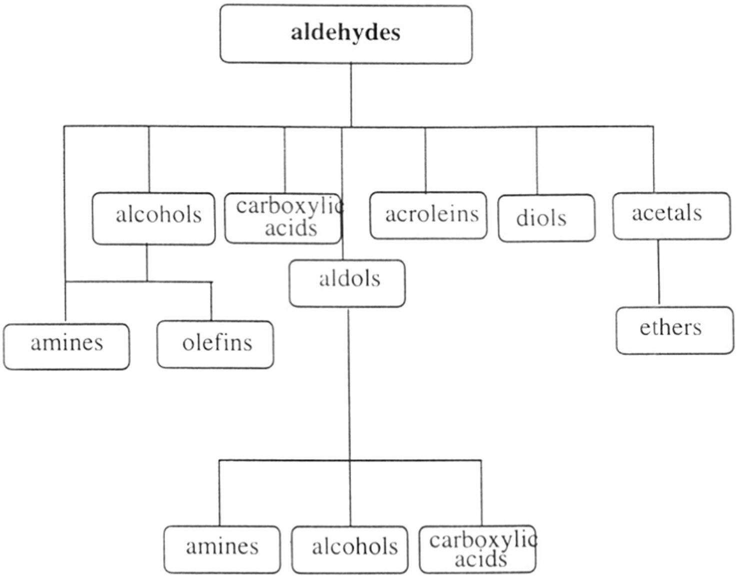


Figure 1.2: Bandwidth of compounds accessible through hydroformylation. [Frohning and Kohlpainter (1996)]

BASF and Hoffmann-La Roche have developed a process for Vitamin A, based on hydroformylation using rhodium catalyst as the key step, though the strategies differ significantly (see Figure 1.3). In these processes, the C_5 aldehyde, i.e. 2-methyl-4-acetoxy butanal (2) is prepared by hydroformylation of diacetoxybutene (4). The high selectivity towards the desired branched aldehyde (up to 80%) in the BASF process is achieved by using unmodified rhodium carbonyl catalyst at high-pressure conditions (60 MPa.) [Pommer (1960; 1977)]. The symmetry of 4 in Hoffmann-La Roche process does not lead to regioselectivity problems. Elimination of acetic acid and isomerization of the *exo* double bond (La Roche) yields the final product 2 in both processes [Himmele and Aquila (1974); Himmele et al. (1972); Fitton and Moffet (1978)]. Both these processes satisfy the market demand of about 3000 tons per annum of Vitamin A. This synthesis of α,β-unsaturated aldehydes by hydroformylation of 2-alkenyl acetates and subsequent

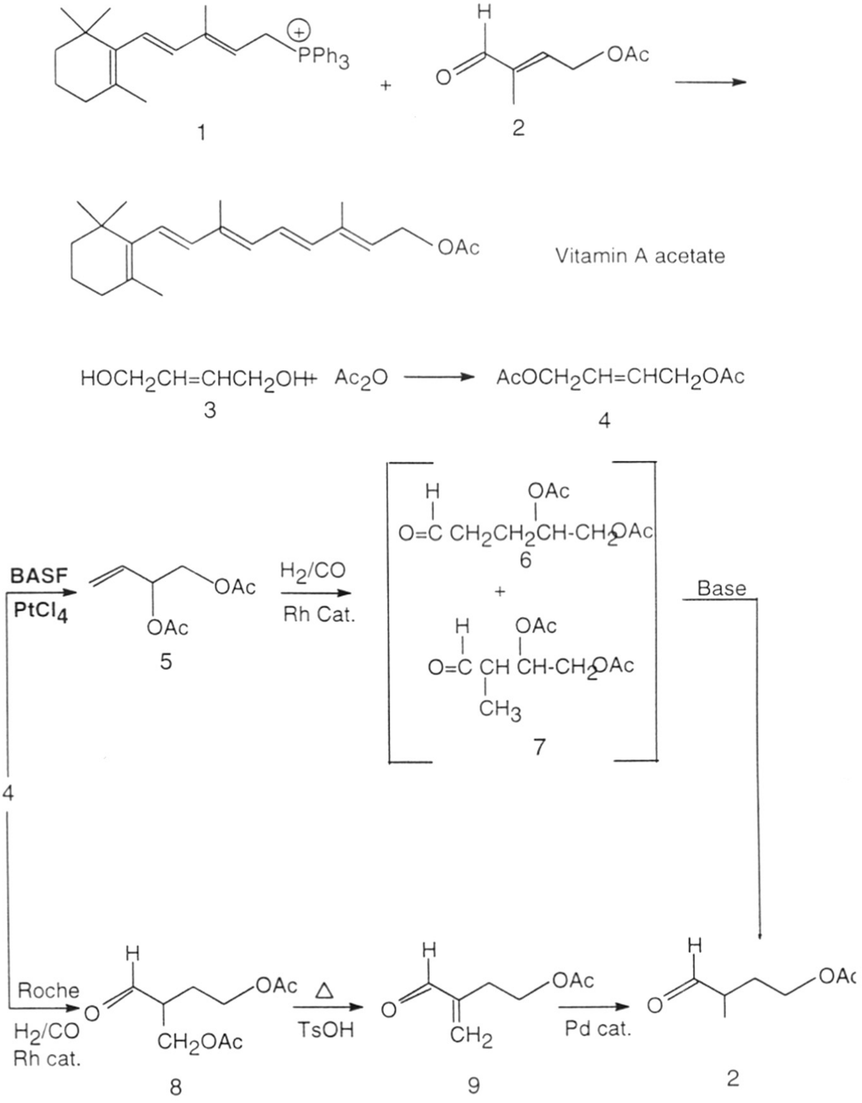
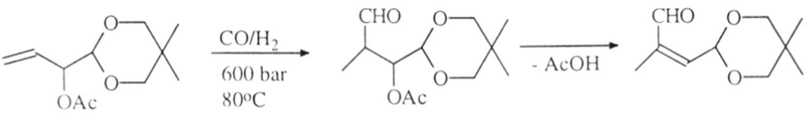


Figure 1.3: Synthesis of Vitamin A. (Parshall 1988)

elimination of acetic acid can also be used for the production of further intermediates which are of interest in terpene chemistry having great significance to perfumery applications [Siegel and Himmele (1980)]. Trans-2-Methyl-3-(5,5-dimethyl-1,3-dioxan-2-yl)acrylaldehyde (12) an important intermediate for the synthesis of carotinoids, can be obtained by similar way from the acetal (10) [Schuster et. al (1976)]



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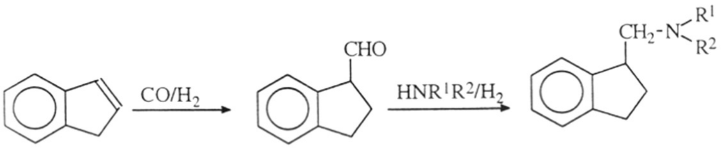
Pharmacologically active amines are readily accessible by hydroformylation of indiene (13) with rhodium catalysts and subsequent reaction of the resulting aldehydes with amines can produce β-arylethylamines (15) with interesting hypotensive properties [Himmele and Aquila (1970)].



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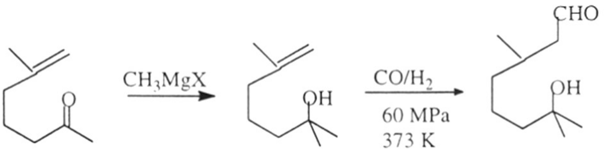
An industrial process for production of an important odorant hydroxycitronellal was developed wherein the said product (18) can be prepared by hydroformylation of 2,6-dimethyl-6-hepten-2-ol (17) [Himmele et al. (1969)].

Hydroformylation of vinyl acetate affords 2-formylethyacetate (19) in high yields. This ester, and also other 2-formylalkyl acetates, are important intermediates for a novel one step synthesis of furan carboxylic acid derivatives, which are of great industrial



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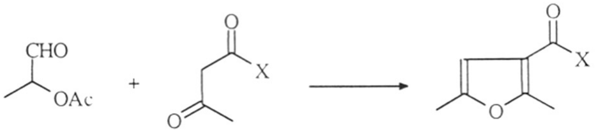
importance in seed disinfection [Distler et al. (1970)] and in wood preservation [Zeeth et al. (1974)]. Reaction of (19) with acetoacetamides (20) or acetoacetates (22) leads to 2,5-dimethyl-3-furancarboxamides (21) or the corresponding esters (23), in high selectivity.



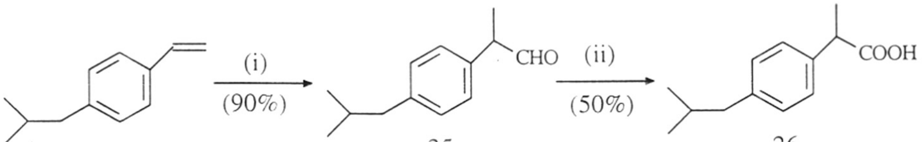
19

20 X = NH$_2$,
22 X = NR$_2$ or OR

21 X = NH$_2$,
23 X = NR$_2$ or OR

Hydroformylation of vinylarenes to 2-arylpropanals under mild conditions is of great significance, since these aldehydes can be easily oxidized to corresponding acids which are used as the largest selling anti-inflammatory class of drugs [Rieu et al.(1986); Jordano et al. (1984)]. In the conventional process, 2-arylpropionic acids are synthesized using Friedel Crafts reaction which generate large amount of waste and expensive raw materials such as 2-chloropropionic acid [Neibecker et al. (1989)]. The preparation of 2-arylpropionaldehydes by hydroformylation of easily available corresponding vinylarenes is a simple and environmentally attractive process. A typical example of this type is the synthesis of Ibuprofen (26) from p-isobutyl styrene (24) as given in Figure 1.4. p-isobutyl styrene is hydroformylated in presence of Rh(CO)$_2$Cl$_2$ at 353 K and CO/H$_2$ pressure of 10 MPa in benzene for two hours to yield p-isobutyl-2-phenylpropionaldehyde, which upon subsequent oxidation with KMnO$_4$/H$_2$SO$_4$ mixture at 288 K for 2.5 hours yields Ibuprofen.

[Arakawa (1977)]. Recently, Riley and co-workers (1987) have reported an efficient method for the oxidation 2-arylpropionaldehydes using manganese stearate as catalyst and m-chloro-peroxybenzoic acid as oxidizer.



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(i) CO + H_2, Rh $(CO)_2Cl_2$, PhH, 353 K, 10 MPa, 2h.
(ii) $KMnO_4/H_2SO_4$, 288 K, 2.5 h.

Figure 1.4: Synthesis of ibuprofen from p-isobutyl styrene.

Detailed literature on hydroformylation chemistry, kinetics, and variation of process aspects are discussed in the following sections.

1.2 Mechanism of Hydroformylation

Although the hydroformylation reaction is known for more than sixty years, its reaction pathway is still under investigation. Among the industrial hydroformylation catalysts major differences are observed between modified and unmodified systems. The catalyst used in the conventional cobalt catalyzed hydroformylation process is the hydridocarbonyl complex, $HCo(CO)_4$. This catalyst is stable only at higher temperatures and CO/H_2 pressures, and therefore the reaction conditions are usually very severe (20-35 MPa and 383-453 K). The discovery of rhodium catalyst for hydroformylation of olefins was a significant development in the oxo process technology. Schiller (1956) was the first to report the use of Rh carbonyls $HRh(CO)_4$ as a catalyst in hydroformylation reaction. The generally accepted hydroformylation mechanism for the unmodified cobalt and rhodium catalysts are shown in Figure 1.5, which involves seven elementary steps such as, (1) reaction of the metal carbonyl $Co_2(CO)_8$ with hydrogen to form the hydridometal carbonyl species $HCo(CO)_4$; (2) dissociation of CO to generate the unsaturated 16e species $HCo(CO)_3$; (3) coordination of the olefin $RCH{=}CH_2$ (18e); (4) formation of alkylmetal carbonyl species (16e); (5) coordination of CO (18e); (6) insertion of CO to form the acylmetal carbonyl $RCH_2CH_2COCo(CO)_3$ (16e); (7) cleavage of the acylmetal species by hydrogen to form the aldehyde and regeneration of the hydridometal carbonyl $HCo(CO)_3$. This mechanism was originally proposed by Heck and Breslow (1960, 1961) for unmodified cobalt catalysts, but the mechanism is valid for unmodified rhodium complexes as well.

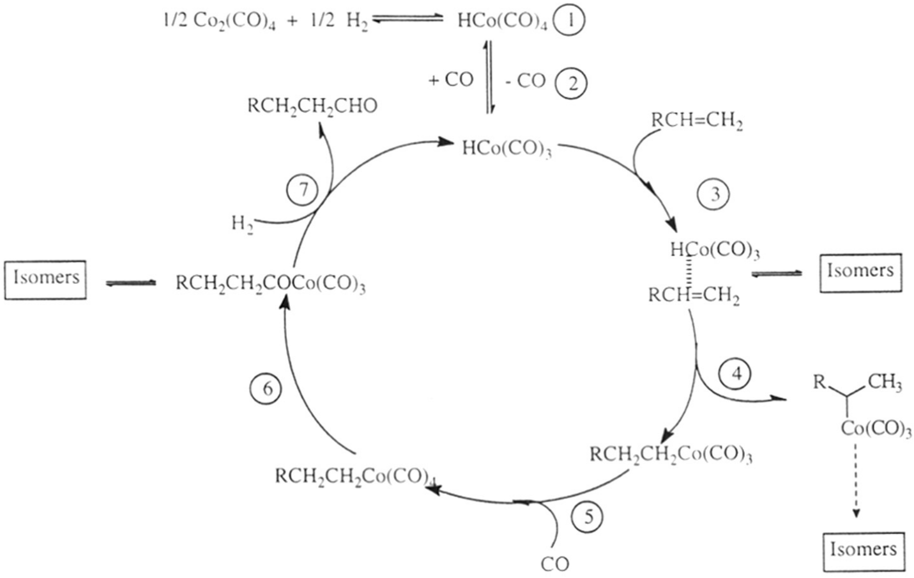


Figure 1.5 Catalytic cycle of hydroformylation with unmodified cobalt catalysts.

The potential importance of Rh catalyst was realized only after the discovery of $HRh(CO)(PPh_3)_3$ complex catalyst by Wilkinson and coworkers [Evans et al., (1968a), (1968b)]. This was a significant improvement over the conventional cobalt catalysts, which require severe operating conditions. Some of the key features of this catalyst are (i) Higher activity and selectivity (ii) higher n/i ratio (8-16) and (iii) requires mild operating conditions (333-393 K and 1-5 MPa as compared to 423-453 K and 20-30 MPa of cobalt process). This improvement in activity and selectivity was achieved by use of triphenylphosphine as a ligand. It is used commercially for the hydroformylation of propylene in the LP oxo process and also in the Union oil process. This was followed with numerous studies on the role of ligands, solvents and substrates in Rh catalysed hydroformylation. Wilkinson and coworkers investigated the mechanism of hydroformylation using $HRh(CO)(PPh_3)_3$ catalyst. According to them, $HRh(CO)_2(PPh_3)_2$ is the key intermediate even though several species might exist in solution in equilibrium [Evans et al., (1968a), (1968b), Pruett and smith, (1969)]. It has been shown from NMR studies that out of $HRh(CO)(PPh_3)_3$ and $HRh(CO)_2(PPh_3)_3$, only the latter reacts with ethylene at 298 K and 0.1 MPa [Evans et al. (1968a)]. Two different pathways involving associative and dissociative mechanism as proposed by Evans et al. (1968b) are shown in Figure 1.6. The dissociative pathway is initiated by dissociation of a phosphine ligand from $HRh(CO)_2(PPh_3)_2$ followed by the addition of olefin to give coordinately unsaturated square planar complex (step 9, Figure 1.6). The addition of olefin via π complex gives σ alkyl complex (species C_3, Figure 1.6). Alkyl migration or CO insertion leads to the formation of acyl complex which on oxidative addition of hydrogen give rise to a dihidride complex (species G, Figure 1.6). This is reported to be the rate controlling step in the mechanism. Finally, the dihydride complex reductively eliminates the products and the catalyst is regenerated. In the associative mechanism, the alkyl complex is formed, by the addition of olefin to the bisphosphine complex (species C, Figure 1.6). The catalytic cycle again operates through the above

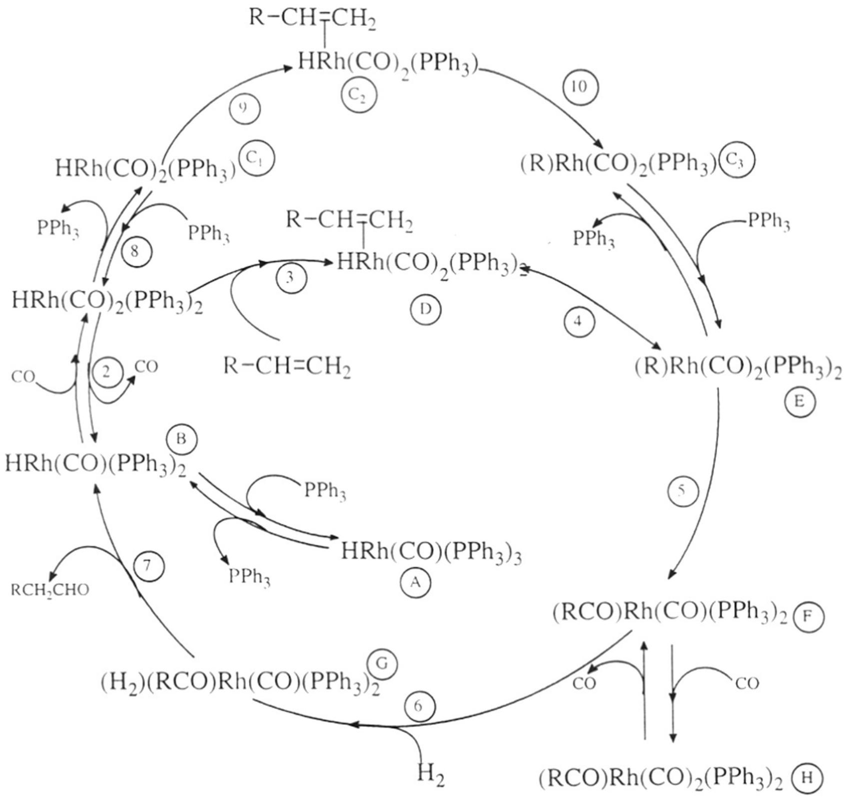


Figure 1.6 Mechanism for hydroformylation using modified rhodium catalysts (L= PPh_3)

steps giving the product and the regeneration of the catalyst. Brown and Wilkinson (1970) studied the kinetics of hydroformylation of 1-hexene using $HRh(CO)(PPh_3)_3$ complex catalyst at 298 K. They reported that rate was first order with respect to catalyst and hexene concentration and partial pressure of hydrogen and negative order with respect to partial pressure of carbon monoxide and the concentration of excess PPh_3. These results have been discussed in detail on the basis of mechanism proposed (Figure 1.6).

1.3 Heterogenization of Homogeneous Catalysts

One of the key challenges in the commercial development of homogeneous catalysis has always been the separation of the catalyst from the products. The separation process is often complicated by air and thermal sensitivity associated with many of these catalysts. Because of facile separation, heterogeneous catalysts find more applications in industry than homogeneous catalysis. In order to overcome this major limitation, the variation of application phase has been the subject of intense research in hydroformylation of olefins, to achieve an easy and economical separation of catalyst from the products, retaining all advantages of homogeneous catalysis. Development of new separation techniques has led to new technologies based on homogeneous catalysis. (e.g. Ruhrchemie - Rhone Pholenc process for propylene hydroformylation using water soluble Rh-triphenylphosphine trisulphonate catalyst). Some of the important developments in this regard are the use of (a) two immisicible liquids: catalysis in biphasic media. (b) Supported liquid phase catalysis (SLPC) or Supported aqueous phase catalysis (SAPC) (c) use of polymer supports etc. Figure 1.7 shows a schematic representation of the various developments in order to achieve an easy catalyst separation from the reaction mixture. The subject of different methods of heterogenizing aqueous biphasic catalysts has been thoroughly reviewed recently by Cornils and Herrmann (1996, 1998). Among the various approaches developed to heterogenize the homogeneous catalyst, water-soluble organometallic catalysts are so far the only commercially successful class for immobilizing them with the aid of immiscible aqueous liquid. In 1984, Ruhrchemie-Rhone Poulenc has commercialized a hydroformylation process utilizing a biphasic system in which the olefin and aldehyde products were contained in a separable organic layer and the catalyst consisting of a water soluble sulfonated triphenylphosphine salt complex with Rh, remains in aqueous phase. Similarly reverse concept is also employed wherein catalyst can remain in organic phase and products in aqueous phase. Some of the commercial applications of biphasic reactions are shown in Table 1.2.

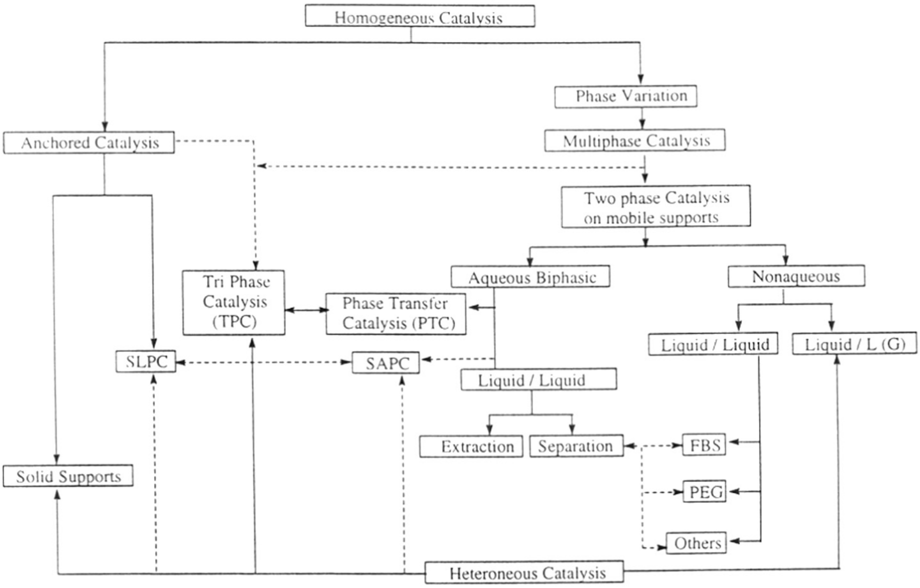


Figure 1.7 Different approaches to the variation of the application phase of oxo catalysis (FBS = fluorous biphasic system; PEG = poly ethylene glycol) [Beller et al. (1995)]

Although aqueous biphasic reactions have proved to be a successful solution in some cases, these reactions are impeded by mass transfer limitations of the organic substrates to the aqueous catalyst phase due to their limited solubility. In addition another constraint is the limited interfacial area [Davis (1992)]. Another strategy, which attracted lot of attention, was heterogenization of the transition metal catalysts by anchoring the

Table 1.2 Applications of biphasic catalysis

Sr. No.	Reaction	Catalyst	Catalyst Type	Reference
1.	Hydroformylation of i) Propylene to butyraldehyde	Rh- TPPTS Rh- BISBIS	Water Soluble Water Soluble	Kuntz (1987) Herrman et al. (1992)
	ii) 1-hexene to heptaldehyde	Rh- BISBIS	Water Soluble	Herman et al. (1992)
	iii) Allyl alcohol to 4-hydroxy butanal	HRh(CO)(PPh$_3$)$_3$	Organic soluble	Deshpande et al. (1992)
2.	Hydrogenation of α, β-unsaturated aldehyde	Rh- TPPTS Ru- TPPTS	Water Soluble	Grosselin et al. (1991)
3.	Oligomerisation of i) Ethylene to α-olefin (SHOP process)	Ni(C$_6$H$_5$)$_2$P-CH$_2$COOH	Organic phase	Bauer et al. (1972); Mason et al. (1973)
	ii) Terminal alkynes	Rh-water soluble phosphines	Water Soluble	Baidossi et al (1993)
4.	Carbonylation of i) p-isobutyl phenyl ethyl alcohol to ibuprofen	Pd-TPPTS	Water Soluble	Papadogianakis et al (1997)
	ii) Benzyl chloride to phenyl acetic acid	NaCo(CO)$_4$/PTC	Phase transfer catalysis	Cassar and Foa (1977)

ligands to various solids as well as polymer supports. However the efficiency of these catalysts is often hampered by the suppression of catalyst mobility stemming from the anchoring process and metal leaching was also recognized as significant problem [Hartley (1985)]. One innovative solution to this difficulty, which appears to offer the ideal solution is supported aqueous phase catalysis (SAPC), first demonstrated by Archancet et al. in 1989. In SAPC thin film of aqueous solution of catalyst is supported on the high surface area solid which appears to retain dynamic features of homogeneous catalysis at the same time effectively providing facile separation. This concept can also be viewed as technique to enhance rates of reaction in biphasic systems. Both biphasic catalysis and supported aqueous phase catalysis are elaborated in following sections.

1.3.1 Biphasic Catalysis

The basic principle of biphasic catalysis is accordingly that the homogeneous catalyst is in solution in one of the phases and the reactants and products are located in a second phase. which is immiscible with the catalyst phase. Generally biphasic catalytic reactions are classified as a) water-soluble metal complex catalysis or aqueous biphasic catalysis; b) organic soluble metal complex catalysis (reverse biphasic catalysis); c) organometallic phase transfer catalysis. Majority of organic reactants and products are water immisible and hence the concept of aqueous biphasic catalysis is an important technique for easy separation of catalysts from the products. In simple version, it can be depicted as in Figure 1.8.

In recent years, aqueous biphasic catalysis using water-soluble catalysts have been extensively studied to develop new routes and efficient process for a variety of products and the subject has been repeatedly reviewed by Kalck and Monteil (1992); Herrmann and Kohlpainter (1993); Beller et al. (1995); Joó and Kathó (1997), Joó et al. (1998) and Cornils and Herrmann (1998). 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 immisible with catalyst phase should have minimum solubility

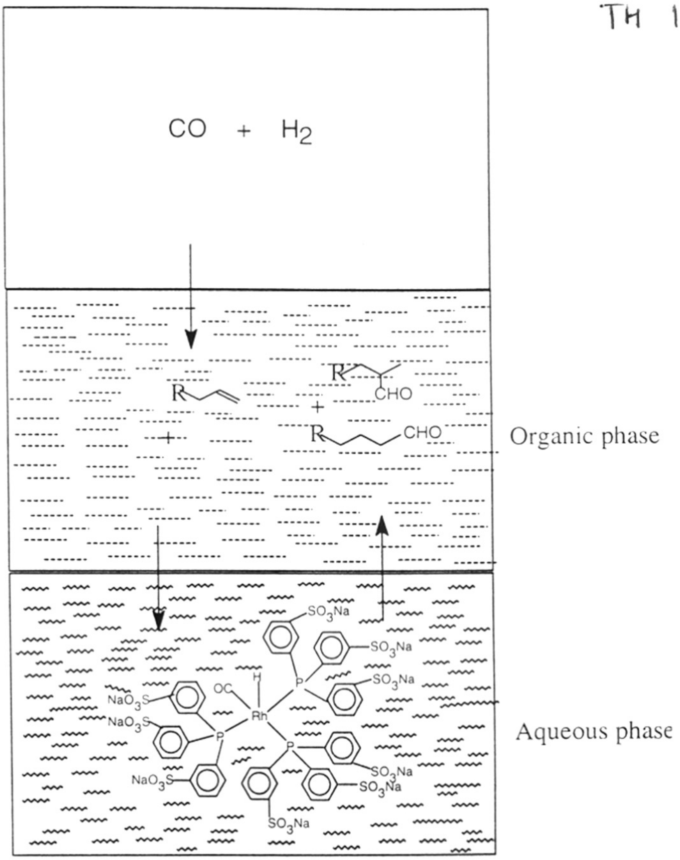


Figure 1.8 Schematic representation of hydroformylation of olefins in aqueous-biphasic media

in the catalyst phase to obtain reasonable reaction rates. Variety of reactions such as hydroformylation, carbonylation, dimerization, telomerization, hydrocyanation, aldolizations, Claisen condensations and the great diversity of C-C coupling reactions have been carried out using this concept [Cornils and Herrmann (1998)]. Aqueous biphasic processes will become more important in the future because of the operational simplicity of this version of homogeneous catalysis. Biphasic catalysis offers the following advantages over reactions carried out in homogeneous medium.

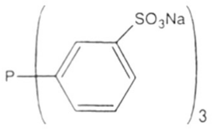
1. The most important advantage of catalysts used in biphasic media is the easy separation of catalysts and products by simple phase separation. This is directly related to recovery and recycle of the catalysts and thus improves process economics.
2. Contamination of catalysts with products is avoided.
3. For substrate inhibited kinetics, higher activity is achieved in such systems as the concentration of reactants in the catalyst phase can be controlled taking advantage of the solubility limitations.

1.3.1.1 Water Soluble Ligands

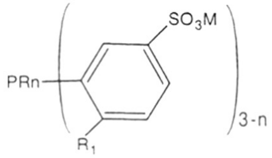
Since the discovery of the water-soluble ligand tris(sodium-m-sulfonatophenyl) phosphine (TPPTS), and its commercial application, catalysis in aqueous-organic two phase system has emerged as an important method for achieving easier separation of homogeneous metal catalysts [Cornils and Hermann (1998)]. 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 [Aharland et al. (1958)], it was only after the synthesis of TPPTS (trisulfonated triphenylphosphine) by Kuntz (1975), that the research on water-soluble lignads was initiated as major activity in the field of biphasic catalysis. A wide range of sulfonated mono phosphines so far reported in literature can be represented as structures 1 to 6 given in Figure 1.9 [Cornils and Herrmann (1998)].

Most important procedure to synthesize sulfonated phosphines is the direct sufonation of phosphines with oleum, originally introduced by Kuntz (1975) for the preparation of TPPTS. Extended series of TPPTS-type ligands, e.g., **1b, 1c, 1d, 1e, 5a, 5b,** and **4** have been synthesized in using the same procedure [Cornils and Herrmann (1998)]. Major disadvantage of this synthetic procedure is the formation of phosphine oxides (Bartik et al. (1992)]. Formation of oxides can be suppressed by using boric acid and sulfur trioxide complex [Herrmann et al. (1995)]. Alternative synthetic routes have been developed using either nucleophilic phosphination of sulfonated fluorobenzenes,e.g. F-C_6H_4-2-SO_3K. F-C_6H_4-4-SO_3K, F-C_6H_3-2,4-$(SO_3K)_2$, in superbasic media (DMSO/KOH) or Pd-catalyzed P-C coupling of sulfonated bromo- or alternatively by reaction of iodo-aromatic compounds with PH_3 or primary and secondary phosphines. Wide range of new water-soluble ligands (e.g. **2a, 2b, 2c, 3, 5c, 6a, 6b** and **6c** in Figure 1.9) are accessible by these improved synthetic procedures [Stelzer (1998)].

In several reports sulfonation was extended to new sophisticated bidentate ligands. The sulfonated diphosphines known so far are shown in Figure 1.10. Herrmann's group has developed a number of sulfonated bisphosphines such as BINAS, [Herrmann et al. (1995), Eckl et al. (1997)), BISBIS (Hermann et al. (1992)] which in combination with rhodium was used for hydroformylation catalysis. These ligands were tested for rhodium catalyzed biphasic hydroformylation of propene 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. In addition, the steric effect of the binapthyl unit was believed to cause higher l/b selectivities than TPPTS. Moreover, it was shown that substitution of the biphenyl unit of BISBIS by binapthyl unit in BINAS leads to significant enhancement of the catalytic activity, which was ascribed to electronic effects and large bite angle of the ligand.

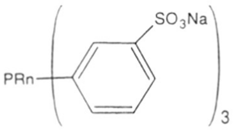


1a (TPPTS)



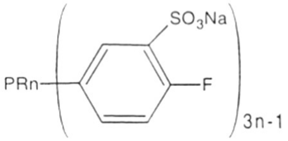
1b

R = Ph, n = 1, 2 (TPPDS TPPMS); R = Me; n = 1; R = C_6H_{13}; n = 1



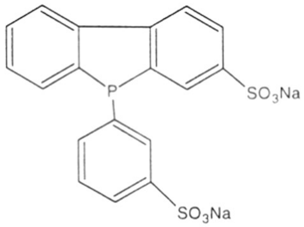
1c

R = Me, Et, Pr, Bu, Cy; R_1 = Me, OMe; n = 0-2

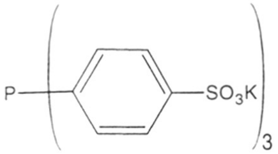


1d

R = 4-C_6H_4, n = 0-2



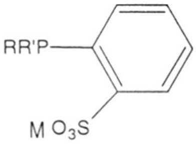
1e



2a

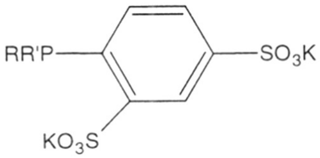
2b

R = R' = Ph, 3-Py; R = H
R' = Ph; R = 2-Py;
R' = 4-SO_3K-C_6H_4;;
M = Li, Na, K



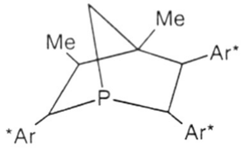
2c

R = R' = Ph; M = Li, K
R = H; R' = Ph; M = K, Na



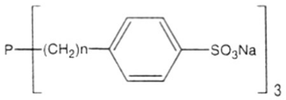
3

R = R' = Ph, 3-Py;
R = h; r' = Ph, Ar*
R = 2-Py, Ph; R' = Ar*
R=CH_2Ph, nBu; R' = Mes;
Ar* = 2,4-$(SO_3K)_2C_6H_3$

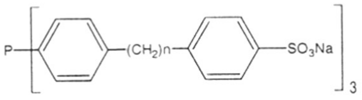


4

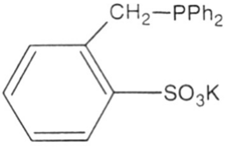
Ar* = 4-SO_3Na-C_6H_4
(NORBOS)



5a (n = 1-3, 6)



5b (n = 3,6)



5c

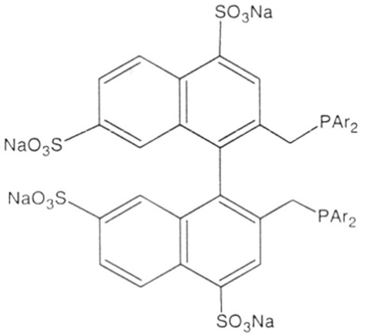
$R_2P-(CH_2)n-SO_3M$

6a (R = Ph; n = 2-4; M = Li, Na, K)
6b (R = Et; n = 2; M = Na)

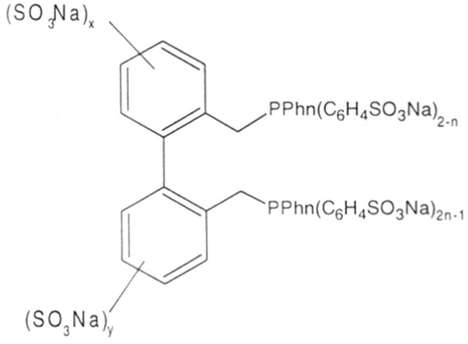
$\mathrm{Ph}\left[\mathrm{P}-(CH_2)_4-SO_3Na\right]_2$

6c

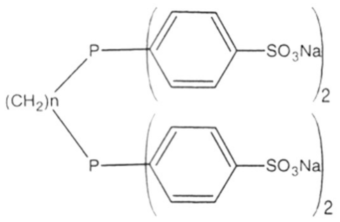
Figure 1. 9: Water-soluble phosphines containing sulfonated aryl and alkyl side chains.



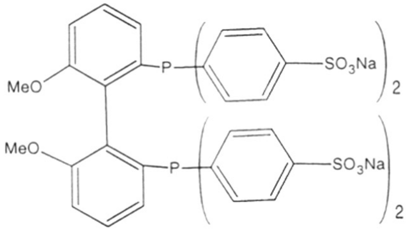
7 Ar = C6H4-*m*-SO3Na



8



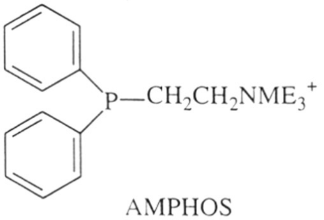
9 n = 2
10 n = 3



11

Figure 1.10 BINAS-8 (1), BISBIS (2), 1,2-bis[di(3-sulfonatophenyl)phosphino]ethane (3), 1,3-bis[di(3-sulfonatophenyl)phosphino]propane (4)

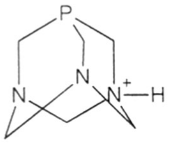
Although sulfonated aryl phosphine catalysts is the central activity of the research carried out in the area of aqueous catalysis, other types of water-soluble ligands have also been reported. One such ligand is AMPHOS (**12**), which on complexation with Rh led to water-soluble hydrogenation and hydroformylation catalysts [Smith et al.(1982)]. Hanson and co-workers have also investigated a number of quaternary-ammonium based systems with Rh for hydroformylation [Toth et al. (1990), Toth and Hanson (1990)].



AMPHOS

12

Some of the other examples of nitrogen containing water-soluble ligands are shown in Figure 1.11.



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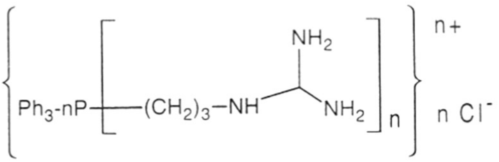
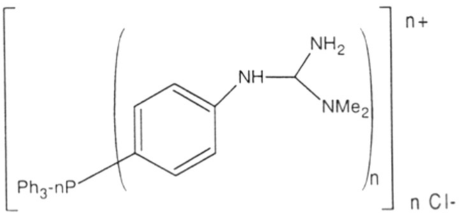


14 (n = 1,2)

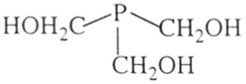


15 (n = 1-3)

Figure 1.11 Nitrogen containing cationic water-soluble ligands

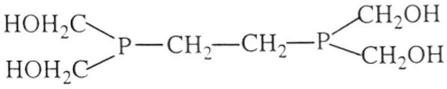
Aliphatic water-soluble phosphines for aqueous phase catalysis have also been reported. Pringle et al. (1995) synthesized tris (hydroxymethyl)phosphine, THMP (**16**), from PH_3 and formaldehyde. Pringle et al. have also shown that the addition of PH_3 to aldehydes and ketones provides a general route to a number of hydroxy-substituted aliphatic phosphines which can be used to prepare water-soluble catalyst systems.

Addition of formaldehyde to chelating phosphines such as 1,2-diphoshinoethane yield chelating ligands such as 12-bis[bis(hydroxymethyl)phosphino]ethane (17) [Pringle et al. (1995)].



THMP

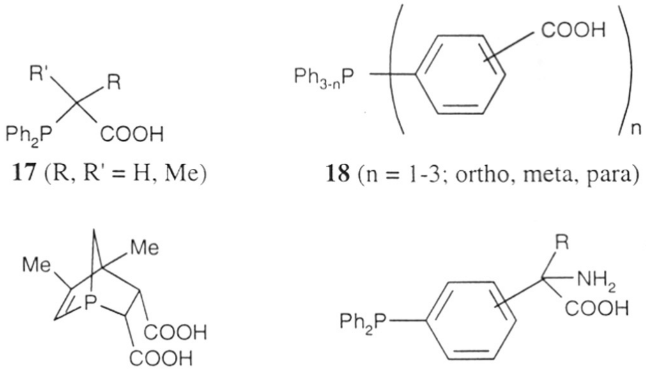
16



17

Daigle and Pepperman (1975) have used tris(hydroxymethyl)phosphine as a precursor to prepare another water-soluble phosphine, 1,3,5-triza-7-phosphaadamantane (PTA). [Daigle et al., (1975] (Coordination chemistry of PTA has been extensively developed by Darensbourg et. al (1991). Systems with PTA and Rh or Ru have been found to be active catalysts for hydrogenation of aldehydes and olefins in water and also for hydrogenation of unsaturated aldehydes [Darensbourg et al (1993)].

Water-soluble ligands containing carboxylic acid groups are also known. These ligands can be prepared by standard preperative methods comprising alkylation and arylation of alkali-metal organophosphides in organic solvents [Keim and Schulz (1994), Van Doorn and Meijboom (1989), Hoots et al. (1982)] or by using improved synthetic procedures such as nucleophilic phosphination of fluorobenzoic acids [Hingst et al. (1998)] or Pd-catalysed P-C coupling reaction of bromo and idobenzoic acids with primary or secondary phoshines [Herd et. al. (1996)]. Some of the examples of carboxylic acid containing water soluble are shown in Figure 1.12.



17 (R, R' = H, Me)

18 (n = 1-3; ortho, meta, para)

19

20 (R = H, Me; ortho, para)

Figure 1.12 Water-soluble ligands containing COOH group

In addition to these ligands there are several other water-soluble ligands reported in the literature. Stelzer (1998) has reviewed the different kinds of water soluble ligands recently.

1.3.1.2 Application of Biphasic Catalysis

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 (see Figure 1.13). 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, thus indicating bright prospects for future tailor-made oxo catalysts in biphasic operation, although commercial availability of these ligands is questionable at this stage.

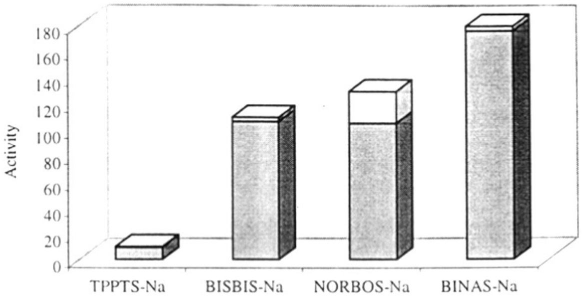
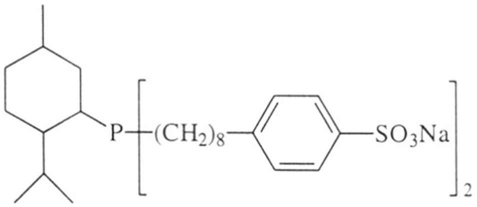


Figure 1.13 Comparison of Oxo catalyst $HRh(CO)L_3$, with TPPTS, BISBIS, NORBOS and BINAS

There are only very few reports on hydroformylation providing selectivity for branched isomer using water-soluble catalysts and styrene seems to be substrate of choice for such reactions. Hanson and co-workers (1995) have reported the synthesis of surface-active phosphines for hydroformylation of styrene under two-phase conditions. $P(menthyl)[(CH_2)_8C_6H_4\text{-}p\text{-}SO_3Na]_2$ (21) with $Rh(CO)_2(acac)$ was found to be more active than the catalyst formed with TPPTS. The TOF achieved with the surface-active phsophine was higher (245 h^{-1}) compared with the Rh/TPPTS system (100 h^{-1}) under identical conditions. Selectivity towards 2-phenylpropanal was found to be 74%, which was also slightly higher than that of TPPTS systems [Bartik et al. (1995)]. Although the phosphine is chiral, no optical activity was observed in the phenylisopropanal product. Though higher activities were achieved, one obvious problem with such systems is the formation of stable emulsion requiring longer process times for phase separation and catalyst recycle.



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Chen and Alper (1997) have reported a water soluble rhodium catalyst system bearing water-soluble polymers. Water-soluble polymer, poly(enolate-co-vinyl alcohol-co-vinyl acetate) (PEVV) was prepared by controlled oxidation of poly(vinyl alcohol-co-vinyl acetate). The average turnover frequencies were 5.46×10^{-5} kmol $(kg(Rh)s)^{-1}$ and 2.36×10^{-4} kmol $(kg(Rh)s)^{-1}$ for hydroformylation of 1-octene at 363 K and for 1-dodecene at 333 K respectively. The reactivity of Rh-PEVV compares well with the best TOF of 5.11×10^{-5} using PPh_3 ligand promoted $HRh(CO)(TPPTS)_3$ biphasic catalytic system for 1-octene at 373 K [Chaudhari et al. (1995)], indicating that the Rh-PEVV is a very effective biphasic catalyst. Styrene and its derivatives were also hydroformylated at 313 K, 4.14 MPa of H_2/CO = 1:1. High selectivity of 97% towards the branched aldehyde was achieved only at lower conversion (4%). Higher activity of the catalyst is possibly due to interfacial distribution of the catalyst during reaction. Water-soluble cationic (sugar substituted arene) rhodium complex has been reported by Son et al. (1998). The complex was synthesized by the reaction of an ethanol solution of $[Rh(COD)Cl]_2$ with $AgBF_4$ and then with phenyl-β-D-glucopyranoside and was found to be active for hydroformylation of styrene and its derivatives. Styrene was hydroformylated to 100% under optimum reaction conditions of 313 K and a pressure of 3.4 MPa with H_2: CO of 2:1 for 22 hours. Using this catalyst system selectivity of 94.6% was achieved for the branched aldehyde.

1.3.1.3 Attempts to Improve Reaction Rate.

Organometallic catalysis in aqueous/organic two-phase systems combines the inherent advantages of homogeneous catalysts (high activity and selectivity) with the facile catalyst separation, which is a great advantage of heterogeneous systems thus affording both economic and environmental benefits [Cornils and Herrmann (1996)]. However, application of aqueous biphasic catalysis is limited to compounds having some solubility but, in the case of compounds like octene, which have low solubility in water, Rh/TPPTS catalysts exhibit lower catalytic activity. Solubility of 1-hexene is 50 ppm at 298 K, where as the solubility of 1-decene is only 0.6 ppm at 298 K [Shaw et al. (1989)]. The reaction rates decreases dramatically with increasing C-number of the olefin due to this drastic decrease in the solubility. For example, 1-hexene is hydroformylated with conversions up to 22% under similar conditions [Bahrmann et al. (1985)], where as the highly water-immiscible 1-tetradecene gives only traces of C_{15}-aldehydes [Fell and Papadogianakis (1991)].

Several approaches have been suggested to increase the rates in aqueous-phase catalysis such as use of surfactants, use of tenside phosphines ligands, counter (inverse)-phase transfer catalysis using β-cyclodextrins, addition of promoter ligands e.g. PPh_3 [Chaudhari et al. (1995)], addition of co-solvents and use of fluorous biphasic systems.

1.3.1.3.1 Surfactants

A surfactant is composed of a nonpolar hydrophobic (lipophilic) region, usually an elongated alkyl group called the tail, and a polar hydrophilic (lipophobic) portion called the head. It therefore has both hydrophobic and hydrophilic properties. Addition of 2.5% of cationic detergent such as benzyltrimethylammonium (BTMA) to the catalyst phase under standard conditions, conversion could be increased by 45-60% [Bahrmann et al (1984)]. Different anions such as benzenemonosulfate, chloride, or sulfate do not have any effect, but variation of the chain length of alkyl group of the detergent ammonium cation $[RN(CH_3)_3]^+$ shows strongest effect in the typical detergent region with C_{14}. With higher alkyl chains (C_{16}-C_{20}) the effect is less pronounced and phase separation becomes difficult due to forming.

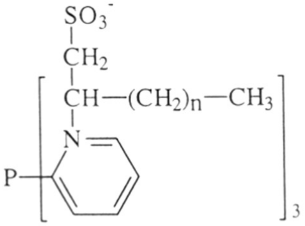
However, addition of anionic detergents such as sodium salts of fatty acids, alkylsulfonic acids, α-olefin sulfonates, fatty alcohol sulfates, fatty alcohol polyglycol ethers, alkylphenol ether sulfates, alkylphosphonic acids and salicyclic acid do not show any activating effects [Bahrmann and Bogdanovic (1998)]. Greatest difficulty with detergents is that they tend to produce foams and emulsions and in many cases phase separation is made impossible.

The enhancement of the activity can be ascribed to reduction of the surface tension, thereby achieving good dispersion wherein contact surface area is increased. Also hydrotropic transfer of substrate with micells is also believed to operate. Specifically cationic surfactants seem to enhance activity compared to their anionic counterparts because cationic suffactant produce Guy-Chapman field below surface thereby electrostatically attracting negatively charged catalyst. On the contrary, anionic surfactants repel anionic catalyst thus retarding the reaction. [Russell (1988)]

1.3.1.3.2 Tenside Ligands

Instead of adding surfactants to the reaction medium another approach to overcome the problem of solubility is to generate transition metal complexes from tenside phosphines which combine both the properties of an amphiphilic ligand and a surfactant in one molecule, and use them as catalysts in micellar systems. Papadogianakis and Sheldon (1998) have reviewed the applications of tenside ligands in biphasic catalysis in detail. The term tenside is synonymous with surfactant (surface-active agent), amphiphilic or amphiphatic. Wilkinson and co-workers have mentioned in 1978 that the water-soluble sulfonated phosphines may combine the properties of a ligand and a surfactant in the same molecule in their study of hydroformylation 1-hexene using rhodium and ruthenium catalysts modified with TPPMS (triphenylphosphine monosulfonate) in an aqueous/organic two-phase system. This reduction of the surface tension could also be because of aldehyde that is produced since aldehyde group is polar.

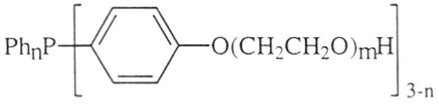
However, the first water-soluble system specifically designed to combine both functions of a ligand and surfactant in one molecule and applied in transition-metal-catalyzed conversions of highly water-insoluble substrates in micellar systems is zwitterionic tenside trisulfoalkylated tris(2-pyridyl)phosphine, **22** (n = 0, 3, 5, 7, 9, 11) [Fell and Papadogianakis (1991)]. Turnover frequencies (TOF) up to 340 h^{-1} were achieved in the micellar hydroformylation of 1-tertradecene to pentadecanals, using Rh/**22** catalyst at 398 K, where as only traces of pentadecanals were obtained under the same biphasic conditions using Rh/TPPTS catalysts.


n = 0, 3,5, 7, 9, 11

22

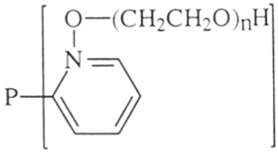
Rhodium complexes modified with the tenside chiral phosphine, used as a catalyst in the hydroformylation of styrene in an aqueous/organic two-phase system has been already discussed in section 1.3.1.2.

Another recent development in the field of hydroformylation of higher olefins is the use of rhodium catalysts modified with non-ionic surfactant phosphines **23** and **24**, which become organic soluble on heating above cloud point and on cooling back to room temperature become water-soluble again, providing for higher rates and a quantitative catalyst separation by simple phase separation [Yan et al (1994); Jin et al. (1996)].



n = 0, 1, 2; m = 3-25

23



n = 3-14

24

A catalyst which is capable of transferring between the aqueous phase and the organic phase in response to temperature changes are known as thermoregulated phase-transfer catalyst and a homogeneous catalytic process effected by a thermoregulated phase-transfer catalyst is called "thermoregulated phase-transfer catalysis" (TRPTC) [Jin et al (1997)]. This phenomena has been explained on the basis that, at temperature lower than the cloud point, a non-ionic phosphine-modified rhodium catalyst would remain in the aqueous phase, since at this temperature catalyst prefers hydration shell. On heating to a temperature higher than the cloud point, hydration shell is lost thereby transferring the catalyst into organic phase and thus catalyzing transformation of alkenes to aldehydes. As soon as the reaction is completed and the system cools to a temperature lower than the cloud point, the catalyst regains its hydrate shell and returns to the aqueous phase [Jin et al (1997)]. TRPTC has been successfully demonstrated for the hydroformylation of higher olefins in aqueous/organic two-phase media. Variety of olefins such as 1-hexene, 1-octene, 1-dodecene, styrene, cyclohexene, oleyl alcohol etc. have been converted to the corresponding aldehydes in the presence of nonionic phosphine-modified rhodium complexes as catalysts [Jin and Zheng (1998)]. An average turnover frequency of 250 h^{-1} for 1-dodecene and 470 h^{-1} for styrene been achieved. Highly water-insoluble oleyl alcohol also gave 72% of aldehyde where as Rh/TPPTS complex showed no reaction under identical conditions. It should be emphasized that the reaction site of TRPTC is the organic phase rather than the aqueous phase or the aqueous/organic interface. Thus even the reaction of extremely water-immiscible substrate could be conveniently carried out.

1.3.1.3.3 Interfacial Catalysis

The idea of interfacial catalysis to enhance the reaction rate in aqueous-biphasic catalysis was proposed by Chaudhari et al. (1995). This approach involves the addition of a ligand that is insoluble in the aqueous phase, i.e., catalyst phase but has a strong affinity for the metal complex catalyst. The two-phase hydroformylation of 1-octene with $HRh(CO)(TPPTS)_3$ was accelerated by a factor of 10-50 times by addition of triphenylphosphine (TPP) in the organic phase. At the phase boundary, complexes of the general formula $[HRh(CO)TPP)_{3-x}(TPPTS)_x]$ (confirmed by NMR spectroscopy) are formed via ligand exchange reactions, thus enriching the catalytic species at the interface. The authors have also studied the leaching of rhodium to the organic phase by recycling the organic phase after the reaction and found no activity for hydroformylation. Rhodium analysis of the organic phase showed only <5 ppm, under the conditions used. In another report, Kalck et al. (1998) have also studied the application of interfacial catalysis for hydroformylation of R-(+)-limonene using $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$. Addition of little amount of PPh_3 in the organic phase increased reaction rate significantly (60-70 times), however in this report it has been proved by infrared and NMR spectroscopies that the increased catalytic activity is due to the species, $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(PPh_3)_2]$, present in the organic bulk phase and not due to the mixed species $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)(PPh_3)]$ which may be formed at the interface. On further studies on hyroformylation of octene by interfacial catalysis by using $HRh(CO)(TPPTS)_3$ and PPh_3 system, [Kalk et al. (1999)] have shown that the main species responsible for the increase in reactivity is $HRh(CO)(PPh_3)_3$, which operates in the organic phase at the ratio of $Rh:TPPTS:PPh_3 = 1:6:1$, whereas that of Bhanage (1995) was 1:12:1. However the application of interfacial catalysis has a limitation that the promoter ligand TPP will stay in the crude aldehyde mixture after the phase separation and will have to be separated by a distillation step.

1.3.1.3.4 Co-solvents

An easy method to improve the solubility of higher olefins in the aqueous phase is the addition of co-solvents in to the aqueous phase and thus to improve the reaction rate. Biphasic reaction conditions can be achieved within a wide range of operating conditions with respect to co-solvents. The most common co-solvents are the lower alcohols. In a recent study it has been shown that ethanol is very effective in improving the reaction rate of hydroformylation of 1-octene in comparison with other co-solvents such as methanol, acetone, and acetonitrile [Monteil (1994)]. It is estimated that the solubility of 1-octene in a 50:50 mixture of ethanol and water is 10^4 times greater than water alone [Purwanto and

Delmas (1995)]. Hydroformylation of 1-octene using $Rh(CO)_2(acac)$ in water alone and 50% aqueous methanol has been reported by Ding et al. (1994, 1995). Generally the use of co-solvents in hydroformylation reaction with Rh/TPPTS systems has a limitation that it decreases the reaction selectivity and produce acetals as a side product when alcohols used as a co-solvent.

Kanagasabapathy et al. (1995) have reported the hydroformylation of tetradecene in methanol alone as a solvent. Since the sodium salt of TPPTS is not soluble in methanol, the authors have used $Ph_2P(CH_2)_4SO_3Na$ as the ligand. Good activities were observed although reaction selectivity to linear products was typically 70% and a relatively high proportion of alcohol products was observed. The addition of strong base such as LiOH minimizes the possible formation of acetals by the side reaction of the aldehydes and methanol.

1.3.1.3.5 Cyclodextrins

A different approach towards the improvement of the mass transfer of higher olefins into the aqueous TPPTS phase is the use of cyclodextrins (CD) suggested by Mortreux and co-workers. Cyclodextrins (CD) are the products of the α-D-glucopyranose polycondenstaion. They are cyclic oligomers built up from α-D-glucopyranosyl unities linked through 1-4' pyranoside bonds. They occur in nature in three main groups according to the number of glucopyranosyl units as α-cyclodextrins (with six sugar units), β-cyclodextrins (with 7 sugar units) and γ-cyclodextrins (with 8 sugar units).

The most remarkable property of the cyclodextrins is their capacity to form inclusion complexes in aqueous solutions with various molecules, including alkenes. It is assumed that this phenomenon does not depend on the chemical nature of the substrate.

The formation of the complex involves several equilibrium steps such as (i) approach of substrate to the CD, (ii) elimination of the water molecules out of the CD cavity, (iii) assimilation of these water molecules to the bulk, (iv) interaction of the CD with the substrate, (v) rebuilding of the hydrated structure round the final complex [Kalck et al. (1998)]. The CD's play the role of transfer agent due to their complexing properties, therefore the non-soluble substrate can be included in the CD which, then brings it into the catalyst containing aqueous phase. After the reaction, the dissociative equilibrium permits the substrate to leave CD cavity and to return into the organic phase and then is again ready to play the role of a phase transfer agent. Kalck and co-workers have carried out hydroformylation of 1-octene, 1-decene and limonene at 353 K and 1.5 MPa pressure of 1:1 $CO:H_2$, for 20 hours. The rate was found to increase 5 times in presence of β-CD. According to the authors the effect is due to the solubility of the alkylated cyclodextrins in both the organic phase and the aqueous phase.

1.3.1.3.6 Fluorous Biphasic Systems

The problem of low solubility of many organic compounds in the aqueous phase and thus the lower reaction rate could be overcome by using non-aqueous biphasic systems, provided the catalyst is preferentially soluble in the catalyst phase at the conditions under which the catalyst phase is separated from the product phase. Such a concept of performing chemical transformations, including transition-metal catalyzed reactions based on the limited miscibility of partially or fully fluorinated compounds with nonfluorinated compounds was recently demonstrated by Horváth and Rábai (1994). The fluorous biphasic systems consists of a fluorous phase containing a preferentially florous-soluble organometallic catalyst and a second phase, which may be any organic or inorganic solvent with limited solubility in the florous phase. The fluorous phase is defined as the fluorocarbon-rich phase of a biphasic system. The most effective fluorous solvents are perfluorinated alkanes, perfluorinated alkyl ethers and perfluorinated trialkyl amines. The organometallic complexes can be made fluorous soluble by attaching florocarbon moieties to ligands in appropriate size and number. The most effective fluorocarbon moieties are linear or branched perfluoroalkyl chains with high carbon numbers that may contain other heteroatoms (the "fluorous ponytails") [Horváth (1998)].

A fluorous biphasic reaction could proceed either in the florous phase or at the interface of the two phases, depending on the solubilities of the reactants in the florous phase. It is also possible that the fluorous biphase system can become one-phase system on increasing the temperature and separate upon cooling. The fluorous-soluble $P[CH_2CH_2(CF_2)_5CF_3]_3$-modified rhodium catalyst was found to be an excellent catalyst for the hydroformylation of 1-decene at 373 K under 1.1 MPa CO/H_2 (1:1) in perfluoromethylcyclohexane and the aldehydes can be easily separated from fluorous catalyst phase [Horváth and Rábai (1994)]. Comparative kinetic studies have shown that fluorous catalyst is about ten times slower than the triphenylphosphinie-modified rhodium catalyst. The n/i selectivity is similar for both the systems. Fluorous biphasic concept has also been applied to reactions such as hydrogenation, hydroboration, hydrosilyation, oligomerization and oxidation reactions [Horváth (1998)]. This concept has however the disadvantage that fluorous phase soluble organometallic compounds have to be specially synthesized.

1.3.1.4 Supported Aqueous Phase Catalysis (SAPC)

Comprehensive reviews of immobilization (heterogenization) techniques are available [Hartely (1985)]. In principle, immobilization may be achieved in one of several ways: physical adsorption or chemisorption of a metal complex onto a support; entrapment of metal complexes via in-situ synthesis of within zeolite; dissolution of a metal complex in a nonvolatile solvent; and dissolution of a metal complex in a nonvolatile solvent that is adsorbed on to the surface of a support, i.e., as supported liquid phase (SLP) [Rony and Roth (1974); Hjortkjaer et al. (1981)]. Except dissolution of metal complex in a non-volatile solvent, the other methods have not yet proved a commercially viable heterogeneous catalyst. This is because in general, the immobilized systems never approach the combined activity/selectivity performance levels of their homogeneous counterparts and tend not to retain the complexes for a sufficiently long time ("leaching") under the reaction conditions. Aqueous biphasic catalysis has been commercially applied for hydroformylation of propylene [Kuntz (1987)]. However the application of biphasic catalysis is limited by the less solubility of organic substrate in the aqueous phase and hence lowers the reaction rate, which is not commercially attractive. Arhancet et al. (1989) have introduced the concept of supported aqueous phase catalysis in order to overcome this limitation. The details of the catalysts will be discussed in Chapter 4 (section 4.1).

In the initial reports by Arhancet et al. (1989, 1990), SAP catalyst was prepared by depositing $HRh(CO)(TPPTS)_3$ with excess TPPTS on a controlled-pore glass, CPG-240 (mean pre size 24.0 nm) in a thin water film. The SAP catalysts were used for hydroformylation of olefins. A highly water insoluble oleyl alchol was hydroformylated at 373 K with 5 MPa CO + H_2 (CO:H_2, 1:1). Rhodium analysis of the organic phase after the reaction showed no detectable amounts, with a sensitivity of 1ppb and the organic filtrate after the reaction showed no activity towards hydroformylation, indicating no leaching of Rh from the SAP catalyst. The reactivity of the SAP catalyst towards the highly water immiscible oleyl alchol indicate that the reaction occurs at the organic-aqueous film interface. Experiments with SAP catalyst on various CPGs of different surface areas showed conversion proportional to the interfacial area thus further confirming that the reaction is taking place at the interface.

Horvath (1990) has carried out hydroformylation of different higher olefins using rhodium SAPCs and found that the TOFs are independent of olefin carbon number (TOFs for hydroformylation of heptanals, nonanal and undecanals were 0.12 s^{-1}, 0.12 s^{-1}, 0.11 s^{-1} respectively). This has been shown to be true also for carbon numbers as high as 17 [Arhancet (1991)]. Horvath has also studied the leaching of rhodium by performing a continuous-flow experiment in a trickle-bed reactor for 38 hours and showed that that on prolonged use water in the film is removed leading to loss of activity. It was concluded that mobility within the film is essential to have good activity. Also no metal leaching was observed proving that the catalyst remain immobilized and that the reaction occurs at the interface. It has also been shown that the SAPC can self assemble and remain more stable under reaction conditions than when they are dissembled [Arhancet (1991)]. These authors have also shown that the water content of $HRh(CO)(TPPTS)_3$-based SAPCs have a great influence on their performances. The activity increases with increasing water content up to a certain limit and then decreases. When hydroformylation was carried out for 25% of octene in cyclohexane, with varying water content from 2.9% to 31%, the activity was found to be maximum at about 8% water content [Arhancet (1990)]. Similar observations were reported by other researchers as well [Frémy et al (1995); (1996)]. The increased activity is due to the increased mobility of the organometallic complex with in the film. Bunn et al. (1994) have used ^{31}P NMR spin lattice relaxation time measurements to study the mobility of the complex within the aqueous film. It was concluded that the mobility at the optimal loading of water was near to that of the organometallic complex in aqueous solution. The loss of activity when the water content become large, may be attributed to the loss in contact between the reactants and the organometallic complex catalyst, which is situated deep in the aqueous phase [Davis (1998)].

Yuan et al. (1994) investigated the effect of codeposition of alkali metal salts on the surface of the beads prior to hydration. The resulted SAP catalyst were reported to benefit in terms of both activity and n:b ratios in the hydroformylation of terminal olefins when the ratio of KCl : Rh was in the range 2-10 : 1. Addition of salt is excepted to assist CO insertion into metal-alkyl bonds by stabilizing the polar transition state thereby increasing the steady state concentration of the acyl intermediate, which leads to an increase in turnover frequency.

Tóth et al., (1997) synthesized HexDPPS in order to make the ligand more surface active, with the reasoning that the lipophilic chain should bring the metal closer to the interface. However the SAPC formed from this ligand proved to be less active, yet showed similar n:b ratios, no leaching and was recyclable, reinforcing the previous conclusion that the TPPTS analogues act at the interface.

Frémy et al. (1995; 1996) reported that hydroformylation using SAP catalysis can proceed with higher turnover frequencies than that of the analogous homogeneous reaction. Methyl acrylate, a polar substrate, was subjected to the hydroformylation reaction with silica as a support and proved to yield average turnover frequencies over ten times greater that those observed for the analogous biphasic and homogeneous reactions. This effect is ascribed to the beneficial interactions between methyl acrylate, supported solvent and surface hydroxyl groups.

The use of alternative supported hydrophilic layers in the hydroformylation reaction has been investigated by Naughton and Drago (1995), who after studying the catalytic properties of their system proposed the term supported homogeneous film catalysis (SHFCS). High boiling liquid or liquid polymer films containing the hydrophilic rhodium catalyst $HRh(CO)(TPPTS)_3$ on the surface of silica were synthesized in an analogous manner to that described previously by Davis and co-workers. Polyethylene glycol was selected for its ability to form films, non-volatile nature, insolubility in substrate and product, and its ability to dissolve and retain the catalyst. It was concluded that the supported PEG thin film catalyst behave as a supported homogeneous catalyst. The hydroformylation of 1-hexene in the PEG 600 film show activities of 25 TON/min with n/b ratio of 6: 1 which was close to that of homogeneous catalysts under identical conditions. These catalysts are active for higher olefins (e.g. 1-octene and 1-octadecene) as well. The polymer film is insoluble at moderate concentrations and has low solubility in aldehyde rich solutions. Unlike homogeneous catalysts, the SHFCs do not need an external solvent for the hydroformylation reaction.

Hydroformylation using SAP catalysts containing Cobalt-TPPTS [Guo I., (1991a)] and Pt-TPPTS [Guo I., (1991b)] metals have also been reported. Application of supported aqueous phase catalysis have also been extended to other reactions such as hydrogenation, Wacker oxidation, Heck reaction, Suzuki reaction and allylic substitutions. A detailed review of these reactions are available in a recent review by Anson et al (1998).

1.4 Kinetics of Hydroformylation

About 250 papers and patent applications appear annually in the area of hydroformylation, most of them dealing with the new phosphine ligands and their transition metal complexes with catalytic activity and selectivity studies towards different olefins [Frohning and Kohlpainter (1996)]. When compared to this 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.

1.4.1 Unmodified Co and Rh catalysts

For the high-pressure oxo 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 [Cornils (1980)]. 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 $HCo(CO)_3$ (see Scheme 1.4). 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 dervied by Natta and Ercoli is generally accepted (eq. 1) [Natta et al. (1954), (1955)]

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

Gohalp et al. (1992a) 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 (entry No. 4 in table 1.3), 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 (1955) 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. (1992b) studied the kinetics of isomeric aldehyde formation in hydroformylation of propene (see entry No. 5 in Table 1.3). The activation energies required for the formation of n- and isobutanal were determined to be 54 and 82 kJ/mol respectively.

1.4.2 Ligand modified Oxo Catalysts

Brown and Wilkinson (1970) 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 observed trends have been explained based on the mechanism shown in Figure 1. 15. 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 unreactive 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.

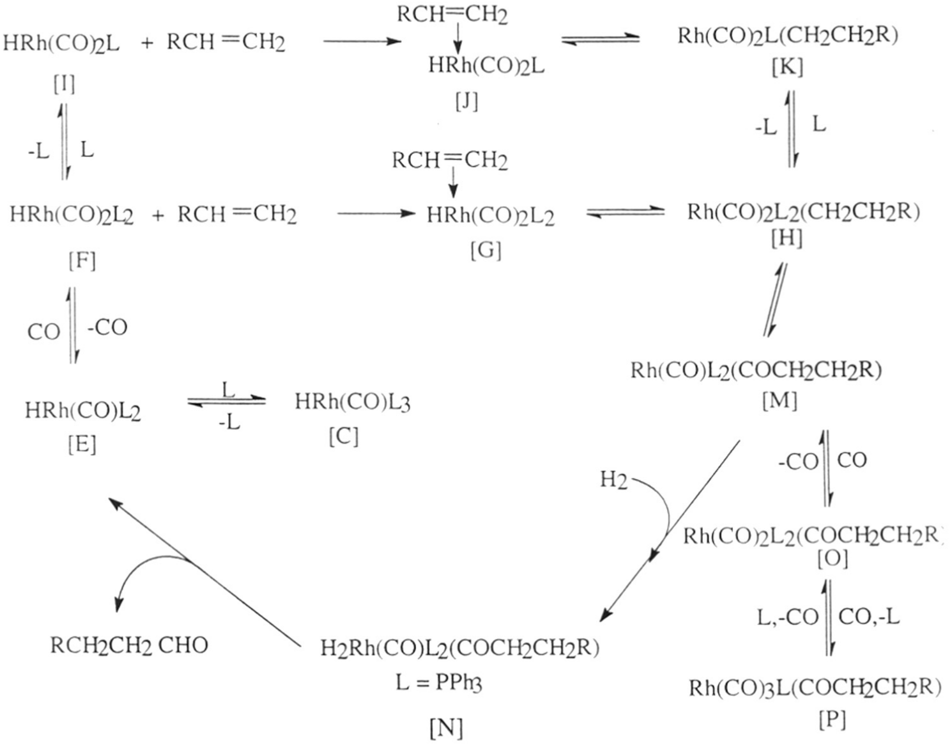


Figure 1.14 Mechanism of hydroformylation of olefins [Evans et al. (1968b)]

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 [Deshpande R.M., Chaudhari R.V (1988); (1989a); (1989b); (1991); Divekar et al. (1993); Bhanage et al (1997)]. 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 (table 1.3 entry No.15), which was found to predict the observed trends satisfactorily [Deshpande and Chaudhari (1988)]. The activation energy was found to be 115 kJ/mol. In similar way, kinetics of allyl alcohol, vinyl acetate, decene and dodecene was also studied and the activation energy for the corresponding reactions were found to be 94 kJ/mol [Deshpande and Chaudhari (1989a)], 73.6 kJ/mol [Deshpande and Chaudhari (1989b)], 48.5 kJ/mol [Divekar et al (1993)] and 57 kJ/mol [Bhanage et al (1997)] respectively. The kinetics of hydroformylation of vinyl acetate using $[Rh(CO)_2Cl]_2$ complex catalyst in ethanol as a solvent has also been reported by Deshpande and Chaudhari (1991) at 353 K and a rate equation proposed (see table 1.3 entry No. 17). In all these studies empirical rate models were developed based on the observed trends.

Kalck et al (1992) have studied the hydroformylation of terminal olefins using a $[Rh(\mu\text{-}S^tBu)(CO)(PPh_3)]_2$ catalyst. Preliminary kinetic studies show that CO has an inhibiting effect but surprisingly the reaction is also inhibited by high pressure of hydrogen. Kinetics of hydroformylation of 1-heptene using $[Rh(nbd)Cl]_2$ (nbd = norbornadiene) was studied by Royo et al. (1982). A rate equation of the form (eq. 2) has been proposed.

$$\text{Rate} = k'C^{1/2}\, C_{Rh}{}^{1/4}(P_{H_2}/P_{co})^{1/2} \qquad 1.2$$

Solvents have a significant effect on the rate of hydroformylation reaction. Polar solvents e.g. alcohols, lead to higher rates than nonpolar solvents such as toluene or hexane. It was observed that in hydroformylation of 1-octene with alcohols as solvents, the reaction rate passes through a maximum at a PPh_3: Catalyst (L/Rh) ratio of 4: 1

(catalyst = $HRh(CO)(PPh_3)_3$). With benzene or toluene as solvents the reaction rate is highest without excess PPh_3, passes through a minimum at ratios <4 and is not influenced by high excess of PPh_3 [Deshpande et al (1993)].

In general the trends observed for kinetics of hydroformylation using phosphine-modified rhodium catalysts on different parameters can be summarized as follows. [Cornils (1996)]

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

Kinetics of hydroformylation of styrene using Rh-1,2,5-triphenyl-1H-phosphole system is reported by Bergounhou et al.(1995), in which a first order dependence of the rate with catalyst, styrene and hydrogen and a negative first order with respect to CO has been observed. In all these studies, empirical rate equations were used to represent the kinetics. It will be more appropriate to study the kinetics based on a mechanistic model derived using a molecular level description of the catalytic cycle. Such an approach to kinetic modeling of hydroformylation of 1-decene using $HRh(CO)(PPh_3)_3$, has been reported by Divekar et al.(1993), however, in this study, only the dependence of the rate on CO has been explained. In a recent paper, by van Rooy (1995), kinetics of hydroformylation of octene, cyclohexene and styrene has been studied using Rhodium-[tris(2-tert-butyl-4-menthylphenyl) phosphite] catalyst. The rate data for 1-octene has been explained using a rate equation derived, assuming the oxidative addition of hydrogen to acylrhodium intermediate complex as the rate-determining step. For cyclohexene hydroformylation, addition of cyclohexene to the starting rhodium hydride complex is considered as a rate-determining step. Kinetics of hydroformylation of styrene was found to be more complex and the rate expression for octene or cyclohexene was not found to be suitable for this system. Feng and Garland (1999) have reported detailed kinetics of the regioselective synthesis in hydroformylation of styrene using unmodified homogeneous rhodium catalyst. Quantitative high-pressure in-situ infrared spectroscopic measurements showed the disappearance of the precursor $Rh_4(CO)12$ resulted in the formation of two observable intermediates, namely the major isomer (±)-$PhCH(CH_3)CORh(CO)_4$ and the minor isomer (±)-$PhCH_2CH_2CORh(CO)_4$. Rate equations were developed to explain the observed regioselectivity. None of these studies have attempted evaluation of rate parameters using a mechanistic model.

In a very recent report, Kiss and co-workers (1999) have evaluated rate parameters based on refined Wilkinson mechanism for hydroformylation of ethene with triphenylphosphine modified rhodium catalyst. The following kinetic model developed fits all experimental observations and was used to predict reaction rates and selectivities over a wide range of reaction conditions.

Table 1.3 A summary of the studies on kinetics of hydroformylation.

Note: A = P_{H2}; B = P_{CO}; C = Concentration of the catalyst; D = Concentration of Olefin; P = PPh_3; R = Rate of reactio; k = Rate Constant

Serial No.	Catalyst	Olefin	Range of condition		Remarks	Rate model	Reference
			Temp. K	Press. MPa.			
1	$Co_2(CO)_8$	Methyl oleate	383-403	7.1-21.3	R independent of (A+B)	-	Nata and Beti, (1945)
2	$Co_2(CO)_8$	Propene	383-393	12-33	R α C,D R independent of (A+B)	$R = \frac{kACD}{B}$	Natta and Ercoli, (1952)
3	$Co_2(CO)_8$	Cyclohexene	383-393	12-38	R α C,D R independent of (A+B)	$R = \frac{kACD}{B}$	Natta et. al., (1954)
4	$Co_2(CO)_8$	Propylene	383-423	3.5-10	Empirical rate mode	$R = \frac{kA^{0.6}BC^{0.8}D}{(1+K_B B)^2}$	Gholap et. al. (1992a)
5	$Co_2(CO)_8$	Propylene	383-423	3.5-19	R_N, R_{iso} are the rate of formation os n- and iso-aldehyde	$R_N = \frac{kA^{0.55}BC^{0.75}D^{0.87}}{(1+K_{NB}B)^2}$ $R_{ISO} = \frac{kA^{0.32}BC^{0.62}D}{(1+K_{isoB}B)^2}$	Gholap et. al. (1992b)
6	$Rh_4(CO)_{12}$	Heptene	348	15.2	R independent of D	$R = \frac{kAC}{B}$	Heil and Marko, (1968)
		Cyclohexene			R ∝ A, C, D	$R = KA^{1/2}C^{1/4}D$	Csontos et. al., (1974)

Table 1.3 (cont.)

Serial No.	Catalyst	Olefin	Range of condition		Remarks	Rate model	Reference
			Temp. K	Press. MPa.			
7	$Rh_4(CO)_{12}$	Hexene	423	B<90 B<90	R α A, B, $C^{1/4}$, D R α A, B, $C^{1/4}$, D 1/R α B	--	Gankin et. al (1967a), (1967b), (1968)
8	Polymer immobilized Rh-complex	Ethylene	373			$R = \frac{kACD}{B^{0.5}}$	Arai et. al., (1975)
9	Rh/activated carbon	Ethylene	393		Power law model	R = k ABCD	Takahashi et. al., (1992)
10	$Rh(CO)Cl(PPh_3)_3$ /SLPC	Propylene	373			$R = k\,DBA\exp\left(\frac{-E}{RT}\right)$	Hjortkjaer et. al,, (1981)
11	$Rh(CO)Cl(PPh_3)_2$	Olefins	343-323	3.5-7	R α D, (A+B)		Marko (1974)
12	$HRh(CO)(PPh_3)_3$	cyclododecene	373		R α A, B, D		Ushakov et. al., (1979)
13	$HRh(CO)(PPh_3)_3$	Hexene	298	0.65	R α A, B, D R α 1/B	$R = \frac{kACD}{B}$	Brown and Wilkinson, (1970)
14	$HRh(CO)(PPh_3)_3$	Hexene	363		R α A, B, D R α 1/B	$R = \frac{kACD}{B}$	Strohmeier and Michel, (1981)

Table 1.3 (cont.)

Serial No.	Catalyst	Olefin	Range of condition		Remarks	Rate model	Reference
			Temp. K	Press. MPa.			
15	$HRh(CO)(PPh_3)_3$	Hexene	303-323	2.2	Critical conc. of catalyst is needed	$R = \dfrac{kAC(C_0 - C_c)D}{(1 + K_B B)^{2.5}(1 + K_D D)^2}$	Deshpande and Chaudhari, (1988)
16	$HRh(CO)(PPh_3)_3$	Allyl alcohol	363-383	5.4	R α $A^{1.5}$, B, D R α 1/B	$R = \dfrac{kA^{1.5}BCD}{(1 + K_B B)^3(1 + K_D D)^2}$	Deshpande and Chaudhari, (1991)
17	$[Rh(CO)_2Cl]$	Vinyl acetate	353			$R = \dfrac{kABCD}{(1 + K_C C + K_D D^2}$	Deshpande and Chaudhari, (1991)
18	$HRh(CO)(PPh_3)_3$	Polybutadiene	350-390	2.17		$R = \dfrac{kAC^{\alpha}D^{\beta}}{B}$	Mills et. al., (1990)
19	Rh(CO)12(acac)/ tris(2-ter-butyl-4-methyl phenyl phosphine	Octene, Cyclohexene	323-363			$R = \dfrac{kAC}{(K_B B)}$ $R = \dfrac{K_I kCD}{(K_I + B)}$	van Rooy et. al. (1995)
20	$HRh(CO)(PPh_3)_3$	1-Decene	323-363	2.72	R α $A^{1.2}$, C, D R α 1/B	Mechanistic model	Divekar et. al. (1993)
21	$[RhCl(1,5\text{-}COD)]_2$ /TPPTS	Octene	333-343		Biphasic Catalysis	$R = \dfrac{kABCD}{(1 + K_B B)^2(1 + K_A A)}$	Purwanto and Delmas, (1995)

$$\mathrm{TOF} = \frac{k_1K_1K_{11}\dfrac{P_{C2H4}}{[PPh_3]} + k_2K_2K_{21}\dfrac{P_{C2H4}}{P_{CO}}}{1 + K_1K_{11}\dfrac{P_{C2H4}}{[PPh_3]} + K_2K_3\dfrac{[PPh_3]}{P_{CO}} + K_2K_{21}\dfrac{P_{C2H4}}{P_{CO}}} \qquad 1.3$$

Where K_0, K_1, K_2, K_3, K_{11} and K_{21} are equilibrium constants and k_1 and k_2 are rate constants. The rate was found to be first order with respect to rhodium and also with ethene at higher PPh_3 concentration (> 50 mmol/l). Both CO and PPh_3 inhibit the reaction above a threshold value, below, which a positive fractional order was observed. Hydrogen has little effect on the rate of hydroformylation in the region where ethene concentration has a first order dependence, however it has a first order dependence when ethene saturation occurs. This phenomenon is linked to a shift in the rate-determining step of the reaction. Activation energy at a constant PPh_3/CO ratio was found to be between 75 - 78.7 kJ/mol and the rate determining step in the ethene first order regime was found to be olefin addition or olefin insertion.

1.4.3 Kinetics using water-soluble catalysts

There are only limited data on the kinetics of hydroformylation of olefins using water-soluble catalysts. Chaudhari and Bhanage (1998) have reviewed the subject recently. The specific review on the kinetics of hydroformylation of olefins using biphasic catalysis will be discussed in chapter 3 (section 3.1).

1.5 Hydroformylation of Styrene

Hydroformylation of styrene is a convenient model reaction to study the catalysis and kinetic modeling. Several different catalyst systems have been employed in the hydroformylation of styrene and a summary of literature on styrene hydroformylation is given in Table 1.4. The stoichiometry of the reaction is as shown below (Figure 1.15).

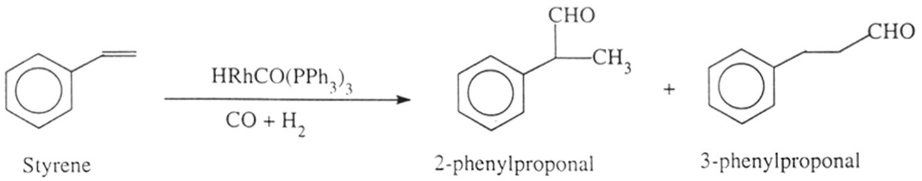


Figure 1. 15 Hydroformylation of styrene

The reaction has been attempted by using ruthenium [Owaki, (1976)], Cobalt [Lai and Ucciani, (1978)], rhodium [Takesada, and Wakamatsu (1970); Takeda et al. (1979); Arakawa (1977)], Iridium [Shimizu et al. (1986)] and Pt catalysts [Muller et al (1990)], but high activities and selectivities to the branched aldehydes were achieved with rhodium-phosphine systems only. The rhodium-triphenylphosphine-catalyzed hydroformylation of styrene proceeds under mild conditions (298 K, 0.1 MPa) and selectivities to 2-phenyl propanal up to 94% can be achieved [Cerriotti et al. (1984a), (1984b)]. Neibecker et al. (1989) have reported that rhodim-phosphole and rhodium-phosphanorboranadiene systems show even better activity than triphenylphosphine systems (Four times more active than triphenylphosphine) with very high selectivity towards branched aldehyde and without any hydrogenation or other side reaction under mild reaction conditions. It was also found that 1,2,5- triphenylphosphole as a ligand is independent of 1,2,5- triphenylphosphole/Rh ratio above 2, unlike PPh_3, where the activity decreases with increase in P/Rh ratio [Bergounhou et al. (1988)]. Rhodium catalysts with bulky phosphite ligands are more active for sterically hindered less reactive alkenes. For example phosphite-modified rhodium catalysts with tris (o-t-butylphenyl) phosphite and tris(hexafluoroisopropyl) phosphite are thirty times higher active than that of triphenylphosphine towards unreactive olefins such as 2-methyl-1-hexene, limonene, cyclohexene and methylene cyclohexene. The high rates observed are attributed to the steric and electronic properties of these phosphite ligands and their ability to stabilize unsaturated rhodium species [van Leeuwen and Roobeek (1983)].

In a very recent report Faraone and co-workers have reported bimetallic, binuclear complexes of IrPd, IrHg, IrCu, IrTl bridged by a short-bite ligand, 2-Diphenyl phosphino pyridine. These catalysts were active towards hydroformylation of styrene, however they have a low chemoselectivity (38-46% hydrogenated product) [Francio et al.(1998)]. Mixed mononuclear rhodim (I) complexes have been studied by Gladiali et al. (1991) Rhodium complexes such as $RhH(CO)(PPh_3)_2(PPh_2Py)$ and $RhH(CO)(PPh_3)(PPh_2Py)_2$ were prepared by *in situ* addition of 2-diphenylphosphino pyridine (PPh_2Py) to $RhH(CO)(PPh_3)_3$ at a variable ligand to metal ratio (Figure 1.16). ^{31}P NMR showed that in solution PPh_2Py can easily displace one or two moles of PPh_3 from Wilkinson complex giving rise to mixed mononuclear phosphine-rhodium complexes.

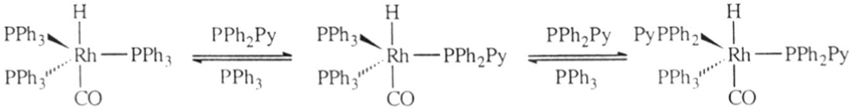


Figure 1.16 Substitution of (PPh_2Py) to $RhH(CO)(PPh_3)_3$ at a variable ligand to metal ratio.

These catalysts showed improved activity towards hydroformylation of styrene. The favorable effect of PPh_2Py was considered to be due to the presence of basic nitrogen in the pyridine [Gladiali et al. (1991)]. In another report Abu-Gnim and Amer have shown the influence of (P-N) bidentate ligand on rhodium-catalysed hydroformylation of styrene. While the catalysts with $[RhCl(COD)]_2$, (COD = 1,5, cyclooctadiene) and

]

diphenylphosphinomethane such as $Ph_2PCH_2PPh_2$ (dppm), $Ph_2P(CH_2)_3PPh_2$ (dppp) and $Ph_2P(CH_2)_4PPh_2$ (dppb) showed no activity towards hydroformylation. The catalysts with mixed bidentate ligands such as PPh_2Py, $Ph_2P(CH_2)_2Py$ (Py=2-pyridyl), $Ph_2PCH_2N(CH_3)_2$, $Ph_2PCH_2CH_2N(CH_3)_2$ and $Ph_2PCH_2CH_2CH_2N(CH_3)_2$ showed better results (353 K and 4.081 MPa of H_2/CO (1:1) for 1 hour, giving 76% of expected aldehydes with 94% selectivity towards branched aldehydes) than diphos and the monophosphine (Ph_2PCH_3 and PPh_3) complexes (styrene at 353 K and 4.081 MPa of H_2/CO (1:1) for 5 hours, gave only 43% of excepted aldehydes) (Abu-Gnim and Amer (1993)). It has also been shown that rhodium complexes of mixed aminophosphine oxide ligands e.g. $Ph_2P(O)CH_2NMe_2$ show high activity and selectivity for formation of branched aldehydes under mild reaction conditions (353 K and 4.081 MPa $CO + H_2 = 1:1$) [Abu-Gnim and Amer (1994)]. Electron withdrawing substituents on the ligand has shown a favorable effect on the regioselectivity of hydroformylation of vinyl arenes. Very high selectivities (branched/linear ratio was increased to 13.3 from 3.5) can be obtained by using a perfluro analogue of dppe i.e. 1,2-(bis(pentaflurophenyl)phosphino)ethane, as phosphine ligand in Rh complex catalyst [Chan et al. (1995)].

Table 1.4 Literature on hydroformylation of styrene

No.	Catalyst	Substrate	Reaction conditions			Conversion	Selectivity		References
			Temp. K	Press. MPa	Others		iso	n	
1	$[Rh(NBD)BF_4]$ + 1,2-bis[bis(pentafluorophenyl)phosphino]ethane	Sub. Styrenes	328	1.36	24h in benzene, $CO/H_2=1$	100%	13-24	1%	Chan et al. (1995)
2	$\{RhCl\ (COD)\}_2$ + $Ph_2P(O)CH_2NMe_2$	Styrene	353	4.08	1.5, hrs. in $CHCl_3$ $CO/H_2=1$	100%	91%	9%	Abu-Gnim & Amer (1994)
3	Rh(SOX)(COD) + dppp	Styrene	333	0.1	7h, in toluene, P/Rh=2 $CO/H_2=1$	TOF 194	93-96%	4-7%	Chen et al. (1994)
4	Cationic complex of Rh containing bis(dioxaphospholane)	Aryl olefins	343	10.2	16,h. in THF, $CO/H_2=1$	>3000/Rh/hr.	92%	8%	Kwok & Wink (1993)
5	$Rh(CO)_2(acac)$ + 1 or 2	Styrene and vinyl acetate	313	4	30,h. in benzene $CO/H_2=1$	TOF 9.7, 4.6 per Rh atom per hour.	95-97%	5-3%	Yamamoto et al. (1994)

Table contd. in the next page

Table 1.4 Literature on hydroformylation of styrene (contd.)

No.	Catalyst	Substrate	Reaction conditions			Conversion	Selectivity		References
			Temp. K	Press. MPa	Others		iso	N	
6	$[Rh(NBD)(III)]^+ ClO_4$	Styrene	323	4	13h, in benzene, $CO/H_2=1$	100%	89	11%	Miyazawa et al. (1990)
7	$\{RhCl\ (COD)\}_2$ + $Ph_2P(CH_2)_2Py$	Styrene	353	4.081	1.0, hrs. in $CHCl_3$	100%	91%	9%	Abu-Gnim & Amer (1993)
8	$RhH(CO)(PPh_3)_3$	Sulphur substituted vinyl arenes	308	8	48h, in toluene, $CO/H_2=1$	100%	94%	6%	Browning et al. (1993)
9	$Rh\text{-}P(OPh\text{-}o\text{-}Bu^t)^3$ on styrene copolymer	Styrene & cyclooctene	353	2	P/Rh =5, $CO/H_2=1$	K_{obs} = 7.01 l/mol/s	-	-	Jongsma et al. (1993a).
10	$Rh\text{-}P(OPh\text{-}o\text{-}Bu^t)^3$ on styrene copolymer grafted on silica	Styrene	353	2	Active for ten days in benzene	K_{obs} (init.)= $30x10^{-3}$ l/mol/s	65%	35%	Jongsma et al. (1993b)
11	$\{RhCl\ (COD)\}_2$ + $Ph_2P(O)CH_2NMe_2$	Styrene	353	4.081	1.5, hrs. in CHCl3	100%	91%	9%	Abu-Gnim & Amer (1994)

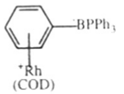
Table contd. in the next page

Table 1.4 Literature on hydroformylation of styrene (contd.)

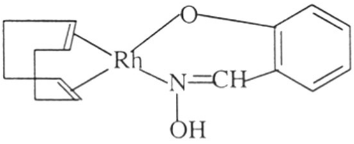
No.	Catalyst	Substrate	Reaction conditions			Conversion	Selectivity		References
			Temp. K	Press. MPa	Others		iso	n	
12	$Ph_2P(CH_2)_2Py$ + $RhH(CO)(PPh_3)_3$	Styrene	353	0.8	2, h. in C_6H_6	98%	70%	30%	Gladiali, et al. (1991)
13	$SiO_2/SnCl_2/PtCl(OH)$-$(PPh_3)_2$	Styrene	363	10	3, h. in $CHCl_3$	3.1%	75%	25%	Homs et al. (1992)
14	Cis-$[PtCl_2(PPh_3)_2]$ $/SnCl_2$	Styrene	363	10	4, h. in $CHCl_3$	40%	46%	54%	Muller et al. (1990)
15	Rh-Phosphle and Rh-phosphanorboranadiene	Aryl olefins	313	2	6,h. in toluene,	98%	84%	16%	Neibecker et al. (1989)
16	Rh-(1,2,5-triphenylphosphle)	Styrene	313	2	3,h. in toluene P/Rh = 2	92%.	83%	17%	Bergounhou et al. (1988)
17	$PPN[HRu(CO)_4]$	Styrene	423	30	In DMF	98%	43.6%	4.1%	Hayashi et al. (1988)
18	Rh complexes of α,α & β,β-TREDIP	Styrene	293	0.1	20, h. in CH_2Cl_2	100%	98%	2%	Brown et al (1986)

Table contd. in the next page

Table 1.4 Literature on hydroformylation of styrene (contd.)

No.	Catalyst	Substrate	Reaction conditions			Conversion	Selectivity		References
			Temp. K	Press. MPa	Others		iso	n	
19	P(menthyl)[$(CH_2)_8$-C_6H_4-p-$SO_3Na]_2$ /Rh(acac)$(CO)_2$	Styrene	393	1.4	2-8h, in toluene-water system, P/Rh = 3	70-80%	67%	33%	T. Bartik et al. (1995)
20	Co_{4-n} $Rh_n(CO)_{12}$ + xL, (n=0,2,4; X = 0-9) where L is trisubstituted phosphine or phosphite	Styrene	298	0.1	48h, in toluene, P/Rh=2	18-43 mol of Aldehyde/ mol cluster/h	86%	14%	Ceriotti et al. (1984a), (1984b)
21	Rh-poly(enolate-co-vinyl alcohol-co-vinyl acetate) Water-soluble	Styrene	313	4.14	22,h. in THF,	13%	94%	6%	Chen & Alper (1997)
22		Styrene and sub. styrene	320	1.36	22,h. in $CHCl_3$	89%.	97%	3%	Amer & Alper (1990)

Laio and co-workers (1994) have studied the hydroformylation of styrene by (1,5-cyclooctadiene)salicylaldoximatorhodium, {Rh(SOX)(COD)} (I), under atmospheric pressure in presence of phosphine ligands such as $P(OPh)_3$, dppm, dppe, dppp. Rh(SOX)(COD) complex containing an anionic chelate ligand having N and O as donating atoms was found to be very effective catalyst in the presence of phosphine ligands under atmospheric pressure (at 333 K and 0.1 MPa pressure an initial turnover frequency of 0.74 min^{-1}, with 96% towards 2-phenylpropanal). The activity of Rh(SOX)(COD) complex was attributed to chelating effect of the salicylaldoximate ligand bond to rhodium atom [Chen et al. (1994)].

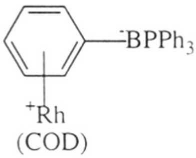


Rh(SOX)(COD)

I

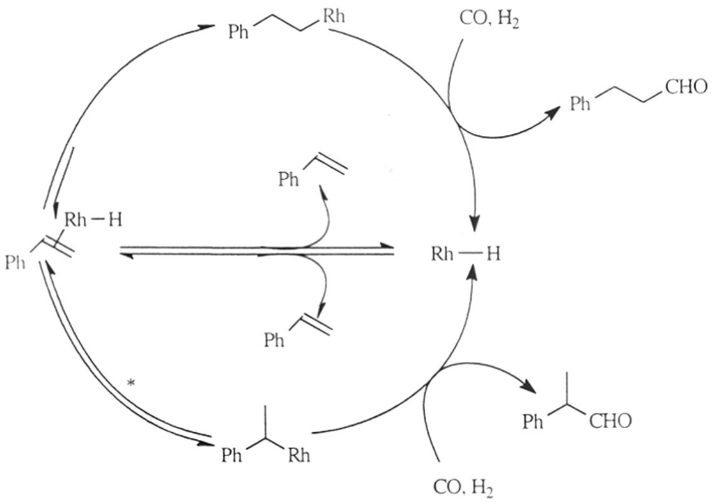
Yamamoto and co-workers have reported the synthesis of a new bidentate ligand of the type (2R*, 5R*)-2,5-bis(diphenylphosphinomethyl)bicyclo[2.2.1]heptane. Rhodium cationic complex of this ligand was highly regioselective (92-98% for branched) for hydroformylation of styrene and vinylarenes under mild reaction conditions (2-4 MPa and 298-323 K), however synthesis of this ligand requires nine steps from cyclopentanone [Miyazawa et al. (1990); Yamamoto et al. (1994)].

Like numerous neutral and several cationic rhodium complexes [Kwok and Wink (1993)], zwitterionic rhodium complexes have been reported for hydroformylation of styrene [Amer and Alper (1990)]. Zwitterionic complex of the type II was found to be highly active and selective under mild reaction conditions. Styrene was hydroformylated at 320 K and CO/H_2 pressure of 1.36 MPa to achieve 89% conversion with 97.3% selectivity to 2-phenylpropanal. The high selectivity was attributed to the presence of a formal positive charge on the metal, which could direct the regioselectivity of the process that cationic rhodium hydride and alkyl intermediates may be more susceptible to olefin coordination (and metal hydride addition) and carbonyl insertion, respectively. In addition, the anionic triphenylboron substitutent attached to the coordinated arene ring may exert steric and/or electronic effects, subject to the stereochemistry of the intermediate, which also has the olefin reactant, bound to rhodium. Several other substituted styrenes and aryl olefins have been tested and found to have high selectivity towards branched aldehyde.



I I

Reaction parameters such as temperature and gas pressure have strong influence on the regioselectivity of hydroformylation of styrene [Lazzaroni et al. (1989)]. The branched isomer, which prevails in all cases, decreases with increasing reaction temperature and decreasing gas pressures. This has been explained with the help of deuteroformylation experiments. It has been shown that the formation of the linear and branched alkyl rhodium intermediates from styrene and the catalytic complex is not reversible at room temperature, whereas at higher temperature, mainly the branched alkyl complex gives back styrene via β-hydride elimination. As a consequence, when the hydroformylation is carried out at 293 K the isomeric ratio of the aldehydes obtained reflects the regioselectivity in the formation of the alkyl rhodium species very much in favor of the branched isomer.



* Reversible only at high temperatures

Figure 1.17 Reaction cycle showing effect of temperature on the regioselectivity

At higher temperatures, the partial dissociation of the branched alkylrhodium intermediate via β-hydride elimination decreases the fraction which can further react to give the corresponding acylrhodium intermediate, and thus altering the ratio in favor of the linear isomer (see Figure 1.17). It has also been proven that β-hydride elimination from the branched alkyl metal occurs to a larger extent at low CO and H_2 pressures. β-hydride elimination from the linear one, on the contrary, occurs only to a small extent even at low pressure. The very high selectivity towards the branched isomer is observed when no side reactions, such as β-hydride elimination, take place (i.e. at room temperature) is probably due to the polarization of rhodium-carbon bond with a partial negative charge on the carbon atom and a positive on the rhodium atom (Figure1.18). The intermediate leading to the branched isomer, in which the phenyl ring is adjacent to the negative charge, exert a stabilizing effect by delocalization charge with the phenyl ring [Fuchikami and Ojima (1982)].

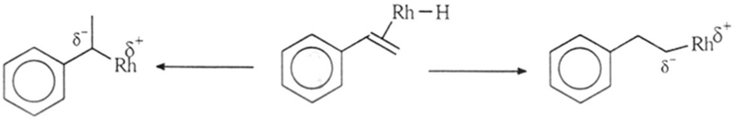


Figure 1.18 Possible polarization of Rh-C bond.

1.5 Scope and Objective

Majority of the hydroformylation literature is related to the electronic and steric properties of organometallic complex catalysts with different central metal atoms or ligands and their influence on reaction and product distribution. There are very few reports on the kinetic modeling. Similarly, for the newly developed biphasic and heterogenised homogeneous catalysts, understanding of the kinetics is further required. Also a systematic comparison of the homogeneous, biphasic, heterogenised homogeneous catalysts (SAPC) under identical conditions is lacking. Hydroformylation of olefins is an interesting example of a complex gas-liquid catalytic reaction involving simultaneous absorption of two or more gases with the reaction taking place in the liquid phase. For biphasic hydroformylation, an additional complication due to the presence of two immisible liquid phases also arises. In such a reaction, it is important to understand the role of gas-liquid and liquid-liquid mass transfer on the overall rate behavior.

Considering the importance of hydroformylation reaction, the present study focuses on both catalysis and engineering aspects of this reaction using styrene as a model substrate. The following specific problems were chosen for the present work.

1. Kinetics of hydroformylation of styrene using a homogeneous $HRh(CO)(PPh_3)_3$ catalyst: A molecular level approach.

2. Hydroformylation of styrene using water-soluble Rh-TPPTS catalyst in a biphasic system: kinetic modeling and reaction engineering studies (with and without co-solvents).

3. Hydroformylation of styrene using supported aqueous phase catalysis (SAPC): studies on activity, selectivity and reaction kinetics.

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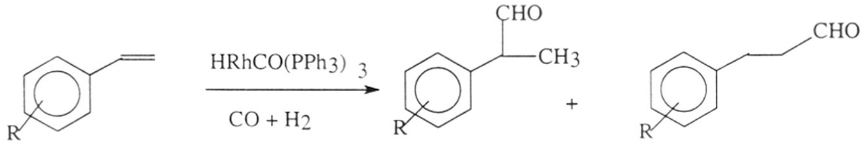
CHAPTER II

Kinetics of Hydroformylation of Styrene using Homogeneous Rh Complex Catalysts: A molecular level approach

2. 1 Introduction

Hydroformylation of olefins is a well-known synthetic tool for the preparation of a wide range of organic molecules of high commercial value [Cornils and Herrmann (1996)]. In recent years, new applications for high value added intermediate products for fine chemicals and pharmaceuticals are emerging [Parshall (1988)]. An important example of the latter class is the hydroformylation of styrene or its derivatives to obtain aryl propionaldehydes, which on subsequent oxidation can give aryl propionic acid derivatives (e.g. Ibuprofen from p-isobutyl styrene), [Shimasaki et. al. (1979), Miekus et. al (1982), Arakawa (1977), Rieu et. al. (1986)]. The stoichiometric reaction is :



Detailed literature on the chemistry of hydroformylation of styrene has been presented in Chapter 1(section 1.5). Hydroformylation of olefins is an example of a complex reaction system, which involves simultaneous dissolution of two or more gases, followed by a catalytic reaction. A knowledge of the kinetics and development of rate equations is important in understanding the mechanistic features of such complex reactions. Kinetic modeling of hydroformylation of olefins has been studied extensively for a variety of substrates (e.g vinyl acetate, allyl alcohol, hexene, decene and dodecene) by Chaudhari and Co-workers (1988, 1989a, 1989b, 1997). Kinetics of hydroformylation of styrene using Rh-1,2,5-triphenyl-1H-phosphole system is reported by Bergouniou et al. (1995), in which a first order dependence of the rate with catalyst, styrene and hydrogen and a negative first order with respect to CO has been observed. In all these studies, empirical rate equations were used to represent the kinetics. It will be more appropriate to study the kinetics based on a mechanistic model derived using a molecular level description of the catalytic cycle. Such an approach to kinetic modeling of hydroformylation of 1-decene using $HRh(CO)(PPh_3)_3$, has been reported by Divekar et al.(1993), however, in this study, only the dependence of the rate on CO has been explained. In a recent paper, by van Leeuwen (1995), kinetics of hydroformylation of octene, cyclohexene and styrene has been studied using Rhodium-[tris(2-tert-butyl-4-menthylphenyl) phosphite] catalyst. The rate data for 1-octene has been explained using a rate equation derived by assuming the oxidative addition of hydrogen to acylrhodium intermediate complex as the rate determining step. For cyclohexene hydroformylation, addition of cyclohexene to the starting rhodium hydride complex is considered as a rate determining step. Kinetics of hydroformylation of styrene was found to be more complex and the rate expression for octene or cyclohexene was not found to be suitable for this system. None of these studies have attempted evaluation of rate parameters using a mechanistic model.

In-situ IR spectroscopic and kinetic studies of regioselective rhodium carbonyl ($Rh_4(CO)_{12}$) as a catalyst precursor for hydroformylation of styrene has been studied very recently by Feng and Graland (1999). In all the experiments, the decomposition of the ($Rh_4(CO)_{12}$) was observed under reaction conditions, resulting in the formation of two observable acyl intermediates, namely, the major isomer (±)-$PhCH(CH_3)CORh(CO)_4$ and the minor isomer (±)-$PhCH_2CH_2CORh(CO)_4$. These species then undergo hydrogenolysis to give the major branched and the minor linear aldehydes. Based on the observable catalytic intermediates a condensed dual-cycle catalytic mechanism has been proposed (Figure 2.1).

In this chapter, the kinetics of hydroformylation of styrene using a homogeneous $HRh(CO)(PPh_3)_3$ complex catalyst has been studied and a detailed analysis of the rate equation based on a mechanistic model discussed. The dependence of rate on catalyst and styrene concentrations, and partial pressures of CO and H_2 on the initial rate of hydroformylation has been studied in a temperature range of 333 K to 353 K, and the kinetic parameters evaluated.

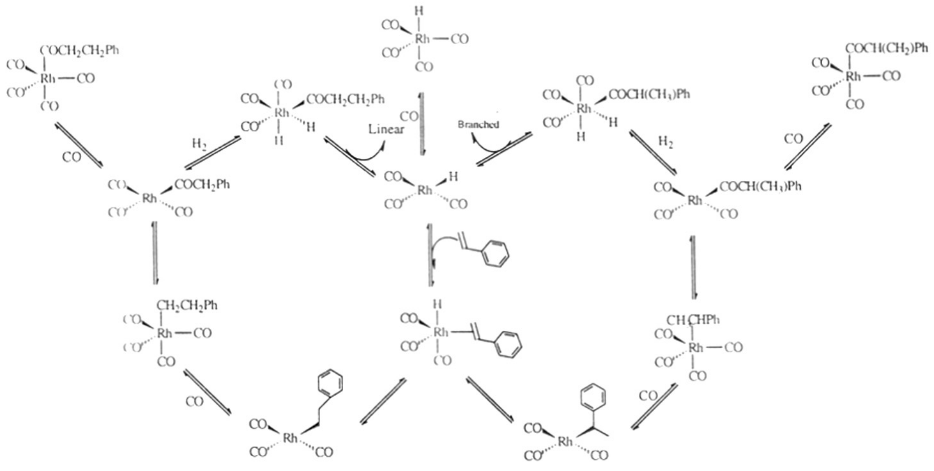


Figure 2.1 Condensed dual-cycle catalytic mechanism for the unmodified rhodium-catalyzed hydroformylation of styrene to give 2ppd and 3ppd

2.2 Experimental

2.2.1 Materials

Rhodium trichloride ($RhCl_3.3H_2O$), from Aldrich, U.S.A, riphenylphosphine (PPh_3) Loba India, and styrene Fluka AG, Switzerland was used as received without further purification. Hydrogen and nitrogen supplied by Indian Oxygen Ltd. Bombay, and carbon monoxide (> 99.8% pure) from Matheson Gas Co., U.S.A. were used directly from cylinders. The syngas mixture [(H_2 + CO) with 1:1 ratio] was prepared by mixing H_2 and CO in a reservoir vessel. The solvents, toluene and ethanol were freshly distilled and dried prior to use.

2.2.2 Preparation of Hydridocarbonyltris(triphenylphosphino)rhodium(I)

To prepare $HRhCO(PPh_3)_3$, a method described by Ahmad et al (1974) was used. To a refluxing solution of triphenylphosphine (13.1gm) in 100 ml distilled ethanol, was added in rapid succession a solution of rhodium trichloride trihydrate (1.15g) in 100 ml ethanol, 50ml of aqueous formaldehyde (40% w/v) and then a solution of potassium hydroxide (3 g) in 100 ml hot ethanol. The mixture was refluxed for 15 minutes and allowed to cool to room temperature. The yellow crystals obtained were filtered, washed with ethanol, water and hexane, in succession and finally dried under vacuum. Yield: 3.8 g . The product thus obtained was characterised by IR and NMR.

2.2.3 Experimental set up

All the Hydroformylation experiments were carried out in a 50 ml micro reactor, supplied by Parr Instrument Company, USA. The reactor was provided with arrangements for sampling of liquid and gaseous contents, automatic temperature control and variable agitation speed. The reactor was designed for a working pressure of 3000 psi and temperature up to 250 °C. A safety rupture disk was also fitted to the reactor. The consumption of CO and H_2 at a constant pressure was monitored by observation of the pressure drop in the gas reservoir, from which (CO + H_2) mixture was supplied through a constant pressure regulator at 1:1 ratio. The pressure in the reservoir was recorded using a pressure transducer to follow the consumption of CO + H_2 as a function of time. A schematic diagram of the experimental set up is shown in Figure 2.2.

2.2.4 Experimental procedure

In a typical experiment, known quantities of the catalyst and styrene, along with the solvent were charged into the autoclave and the reactor was flushed with nitrogen. The contents were then flushed with a mixture of CO and H_2 and heated to a desired temperature. A mixture of CO and H_2, in the required ratio, was introduced into the autoclave, a sample of liquid withdrawn, and the reaction started by switching the stirrer on. The reaction was then continued at a constant pressure by supply of CO + H_2 (1:1) from the reservoir vessel. Since, the major products formed were isomeric aldehydes, supply of CO + H_2 at a ratio of 1:1 (as per stoichiometry) was adequate to maintain a constant composition of CO and H_2 in the autoclave, as introduced in the beginning. This was confirmed in a few cases by analysis of the CO content in the gas phase at the end of the reaction. All the reactions for kinetic studies were carried out for short duration such that the conversion in the liquid phase was minimum, to ensure differential conditions. In each kinetic run, samples were withdrawn at regular intervals of time and analysed for reactants and products in order to check the material balance. The reproducibility of the experiments was found to be in a range of 5-7%. Following this procedure, the effect of the catalyst and styrene concentrations, partial pressure of H_2 and CO and temperature on the rate of hydroformylation was studied.

2.2.5 Analytical methods

The quantitative analysis of the hydroformylation reactants and products was carried out using gas chromatographic technique by external standard method. For this purpose, a Varian 3600 gas chromatograph with a 10% OV-17 column of 8 feet long was used. The two aldehyde products, 2-phenyl propionaldehyde (2ppd) and 3-phenyl propionaldehyde (3ppd) were identified by IR, GCMS and ^{1}H NMR.

The optimised conditions for analysis are as follows:

Flame ionization detector temperature	573 K
Injection temperature	523 K
Column temperature programmed between	393-413 K
Rate of heating	20 K/min
Carrier gas (N_2)	20 ml/min

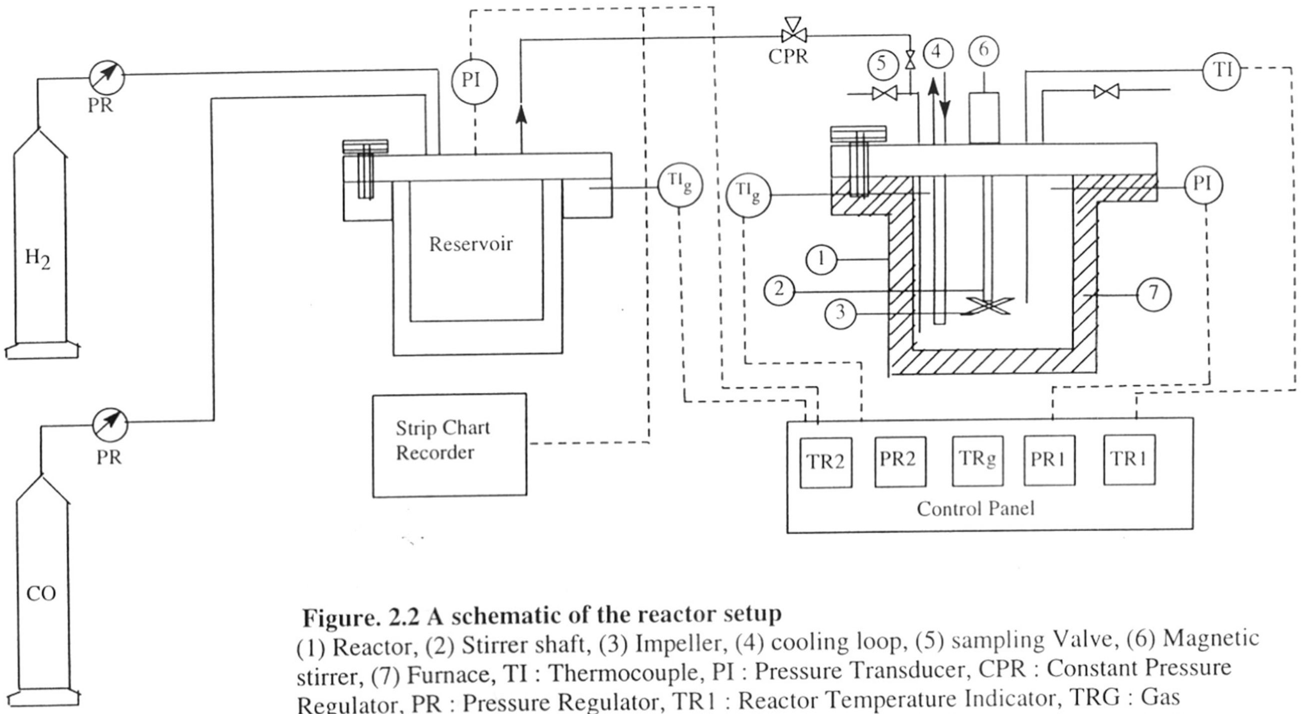


Figure. 2.2 A schematic of the reactor setup
(1) Reactor, (2) Stirrer shaft, (3) Impeller, (4) cooling loop, (5) sampling Valve, (6) Magnetic stirrer, (7) Furnace, TI : Thermocouple, PI : Pressure Transducer, CPR : Constant Pressure Regulator, PR : Pressure Regulator, TR1 : Reactor Temperature Indicator, TRG : Gas Temperature Indicator, PR1: Reactor Pressure Indicator, PR2: Resorvoir Pressure Indicator, TR2 : Reservoir Temperature Indicator

2.3 Results and Discussion

The main objective of this work was to investigate the kinetics of hydroformylation of styrene using a homogeneous HRhCO)$(PPh_3)_3$ complex catalyst. It was therefore, necessary to first check the material balance and reproducibility of the experiments. For this purpose, a few experiments were carried out in which the amount of styrene consumed, products formed, and CO + H_2 consumed were compared for experiments with high conversion of styrene. A typical concentration-time profile is shown in Figure 2.3.

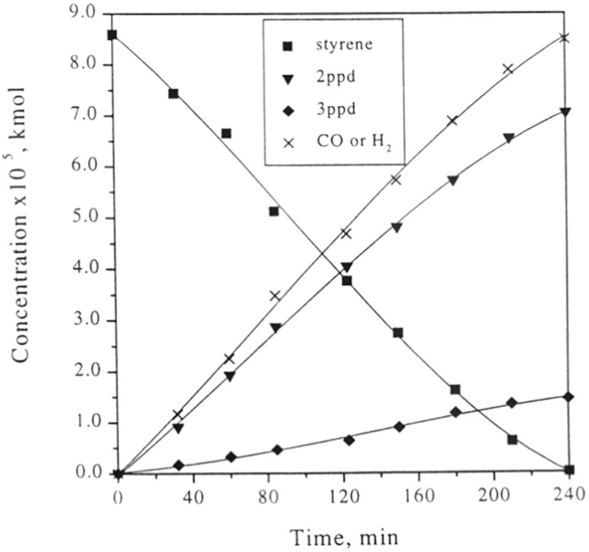


Figure 2.3 Concentration-time profile of a batch reactor: Styrene hydroformylation at 373 K
Reaction conditions:
$HRh(CO)PPh_3$: 1.01 kmol/m^3; Styrene: 3.45 kmol/m^3; P_{H2}: 2.07 MPa; P_{CO}: 2.04 MPa; Agitation speed: 900 rpm; Solvent: Toluene; Total volume: 2.5 X 10^{-5} m^3

In general, it was observed that the material balance of CO, H_2 and styrene consumed was consistent with the amount of total aldehyde products formed. Also, in the range of conditions covered in this work, the only products formed were 2-phenyl propionaldehyde and 3-phenyl propionaldehyde. No hydrogenation or isomerization products were observed. In order to study the kinetics it was important to ensure that reactions were carried out under kinetic regime.

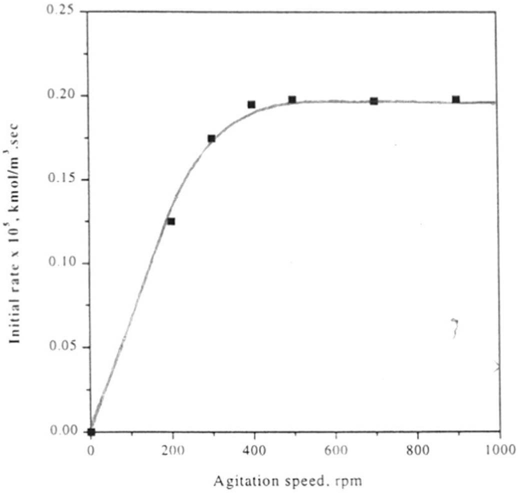


Figure 2.4 Concentration-time profile of a batch reactor: Styrene hydroformylation at 353 K
Reaction conditions:
HRh(CO)PPh$_3$: 1.01 kmol/m^3; Styrene: 3.45 kmol/m^3; P$_{H2}$: 2.07 MPa; P$_{CO}$: 2.04 MPa; Agitation speed: 900 rpm; Solvent: Toluene; Total volume: 2.5 x 10^{-5} m^3

The experiments at different agitation speeds showed that the rate of the reaction was independent of the agitation speed beyond 400 rpm, indicating kinetic regime. All the reactions were therefore carried out at an agitation speed of 900 rpm to ensure kinetic regime.

2.3.1 Solubility Data

For interpretation of kinetic data, knowledge of the concentration of the gaseous reactants in the reaction medium is essential. The solubility of CO and H$_2$ in toluene, styrene and styrene/toluene mixtures was determined experimentally at 333, 343 and 353 K, using a method described by Purwanto et al (1996). The solubility of H$_2$ and CO measured in 6.0 x 10^{-4} m^3 capacity stirred autoclave supplied by Parr Instrument Company, USA designed for 25 MPa pressure. The equipment was provided with automatic temperature control and a pressure recording system. The temperature of the liquid in the reactor was controlled within ±1 K. A pressure transducer having a precession of ±1 kPa was used to measure the autoclave pressure.

In a typical experiment for the measurement of solubility of H_2 and CO, a known volume (300 ml) of solvent was introduced in to the autoclave and the contents were heated to a desired temperature. After the thermal equilibrium was attained, the void space in the reactor was carefully flushed with a solute gas and pressurised to the level required. The contents were then stirred for about ten minutes to equilibrate the liquid phase with the solute gas. In general, it required, about 5 minutes to saturate the liquid phase. The change in the pressure in the autoclave was recorded on-line as function of time till it remained constant, indicating the saturation of the liquid phase. From the initial and final pressure readings, the solubility was calculated in mole fraction as

$$X_a = {(P_i - P_f)V_g M_s}/{RTV_L \rho_s} \qquad 2.1$$

Where X_a represents the mole fraction of the solute gas in the liquid phase at the partial pressure of the solute gas prevailing at P_f, P_i and P_f are the initial and final pressure readings in the autoclave, V_g and V_L are the volumes of the gas and liquid phases, respectively, R is the gas constant, T is the temperature, M_s is the molecular weight of the solvent and ρ_s is the molar density of the liquid. Following this procedure, the solubility data were obtained for hydrogen and CO in toluene, styrene and toluene-styrene mixtures at 333-353 K. The Henry's law constant, H was calculated as

$$H = {P_f}/{X_a} \qquad 2.2$$

The results are presented as Henry's law constant in Table 2.1 and 2.2, which indicate that the increase in styrene concentration in toluene decreases the solubility of both CO and H_2 only marginally (5-7%).

Table 2.1 Henry's constants of CO in toluene, styrene, and toluene-styrene mixture

gas, solvent	H_B MPa m^3/kmol at 333 K		H_B MPa m^3/kmol at 343 K		H_B MPa m^3/kmol at 353 K	
	Expt.	Predicted	Expt.	Predicted	Expt.	Predicted
CO in toluene	11.90	11.86	11.70	11.73	11.53	11.59
CO in 10% styrene in toluene	12.01	12.02	11.85	11.87	11.70	11.72
CO in 20% styrene in toluene	12.20	12.16	11.99	12.01	11.87	11.85
CO in 40% styrene in toluene	12.82	12.47	12.41	12.29	12.41	12.11
CO in 80% styrene in toluene	13.10	13.13	12.93	12.91	12.72	12.69
CO in styrene	13.60	13.47	13.32	13.22	13.10	12.98

Table 2.2 Henry's constants of hydrogen in toluene, styrene, and toluene-styrene mixture

gas, solvent	H_A MPa m^3/kmol at 333 K		H_A MPa m^3/kmol at 343 K		H_A MPa m^3/kmol at 353 K	
	Expt.	Predicted	Expt.	Predicted	Expt.	Predicted
H_2 in toluene	29.30	29.27	28.10	28.06	26.80	26.96
H_2 in 10% styrene in toluene	29.58	29.61	28.40	28.36	27.22	27.24
H_2 in 20% styrene in toluene	30..01	29.98	28.65	28.70	27.50	27.54
H_2 in 40% styrene in toluene	31.60	31.55	30.10	30.12	28.58	28.82
H_2 in 80% styrene in toluene	32.42	32.39	30.92	30.89	29.55	29.52
H_2 in styrene	33.22	33.23	31.83	31.65	30.50	30.20

The Henry's constant for carbon monoxide in toluene and styrene were also calculated using the correlation proposed by Reid and Prausnitz (1987) based on the theory of regular solution. The correlation used was:

$$-\ln{}_{A} = \ln\left(f_A^L / f_A\right) + \left\{\phi_S^2 V_A \left(\delta_S - \delta_A\right)^2 / RT\right\} \qquad 2.3$$

The use of this Eq. (1) requires a knowledge of three parameters of the solute viz: fugacity of hypothetical liquid, f_A^L (atm), solubility parameter δ, $(J/m^3)^{1\backslash 2}$ and molar volume V_A, (m^3/mol). The fugacity of hypothetical liquid solute (f_A^L) depends upon the critical temperature and critical pressure of the gases and was calculated from a correlation between fugacity and temperature (Eq 2.4), as reported by Yen and Mcketta (1962)

$$f_a^L = P_c \exp\left\{7.224 - 5.534\left(T_c/T\right) - 2.598\ln\left(T/T_c\right)\right\} \qquad 2.4$$

The regular solution theory also states that the solubility parameters for gas (δ_A) and molar volume of solutes are independent of temperature and were obtained from the work of Prausnitz and Shair (1961) ($6.4 \times 10^3\ J^{0.5}m^{-1.5}$ for CO and $7.835 \times 10^3\ J^{0.5}m^{-1.5}$ for H_2). The solubility parameter (δ_s) for toluene and styrene was calculated from the heat of vaporisation as proposed by Hildebrand and Scott (1948)

$$\delta_S = \left(\Delta H - RT / V_A\right)^{1/2} \qquad 2.5$$

The solubility values of CO and H_2 in pure toluene and pure styrene were further used for calculating the solubilities of these gases in a mixture of solvents (toluene/styrene) by using the method described by Hildebrand et.al. (1948), and given by following expression:

$$\left(\ln \chi_A\right)_{mix} = \phi_1 \ln\left(\chi_{A1}\right) + \phi_2 \ln\left(\chi_{A2}\right) - V_A \beta_{12} \phi_1 \phi_2 \qquad 2.6$$

where β_{12} = $(\delta_{S1}-\delta_{S2})^2/RT$; X_{A1}, X_{A2} and ϕ_1, ϕ_2 are the mole fraction of a gas in pure toluene and styrene and the volume fraction of solvent respectively. δ_{S1} and δ_{S2} are the solubility parameters for toluene and styrene. The results predicted for pure toluene, styrene and styrene/toluene mixtures were found to be in good agreement with the experimental values (within $\pm 3\%$) and are shown in Table 1 and 2. These data were used in the calculation of the concentrations of dissolved CO and H_2 the liquid medium for interpretation of the kinetics.

2.3.2 Initial Rate Data

In order to study the kinetics of the hydroformylation of styrene using $HRh(CO)(PPh_3)_3$ in toluene, several experiments were carried out in the range of conditions as shown in the Table 3. The initial rates of hydroformylation were calculated from observed data on the consumption of CO + H_2 as a function of time.

Table 2. 3 Range of conditions for kinetic study

Concentration of catalyst ($kmol/m^3$)	0.131 - 1.01
Concentration of styrene ($kmol/m^3$)	0.92 - 6.89
Partial pressure of hydrogen, MPa	1.03 - 4.12
Partial pressure of carbon monoxide, MPa	0.3 – 4.12
Temperature, K	333 - 353
Solvent	Toluene
Reaction volume, m^3	2.5×10^{-5}

The rate was calculated from the slope of CO or H_2 vs. time plots. These were essentially initial rates of reaction, calculated under low conversion (<10%) conditions. The results showing the dependence of the rates on different parameters and a kinetic model are discussed in the following sections.

The rate of hydroformylation of styrene was observed to be linearly dependent on catalyst precursor $[HRh(CO)(PPh_3)_3]$ concentration and hydrogen partial pressure.

These results are shown in Figures 2.5 and 2.6. A first-order dependency on hydrogen indicates that the oxidative addition of H_2 to the acylrhodium intermediate species is the rate-determining step. Similarly, the first order dependence with respect to catalyst is consistent with increase in the active Rh species concentration with increase in the catalyst precursor concentration.

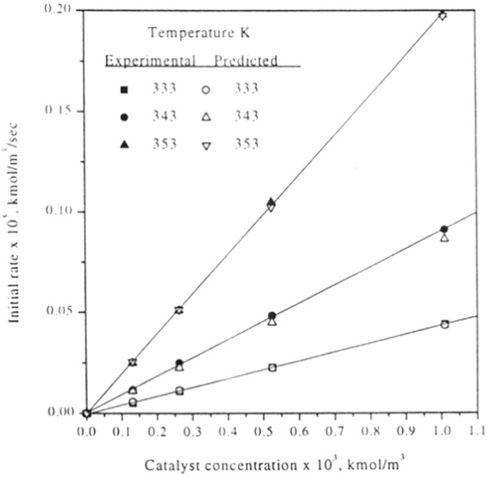


Figure 2.5 Effect of catalyst concentration on the rate of hydroformylation of styrene
Reaction conditions:
Styrene: 3.45 kmol/m^3; P_{H2}: 2.04 MPa; P_{CO}: 2.04 MPa; Agitation speed: 900 rpm; Solvent: Toluene; Total volume: 2.5 x 10^{-5} m^3; Reaction time: 120 min.

The rate of hydroformylation of styrene versus partial pressure of CO plot (Figure 2.7) shows a typical substrate inhibited kinetics As per the mechanism of hydroformylation proposed by Evans et al. (1968) (see Figure 2.9), the inhibition of the rate of hydroformylation with increase in partial pressure of CO 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 {Deshpande and Chaudhari (1988, 1989a, 1989b)].

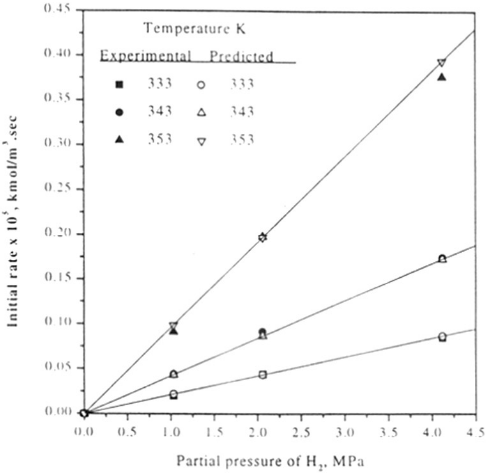


Figure 2.6 Effect of hydrogen partial pressure on rate of hydroformylation of styrene
Reaction conditions:

Styrene: 3.45 kmol/m^3; Catalyst: 1.01 kmol/m^3; CO partial pressure: 2.04 MPa; Agitation speed: 900 rpm; Solvent: Toluene; Total volume: 2.5 x10^{-5} m^3; Reaction time: 120 min.

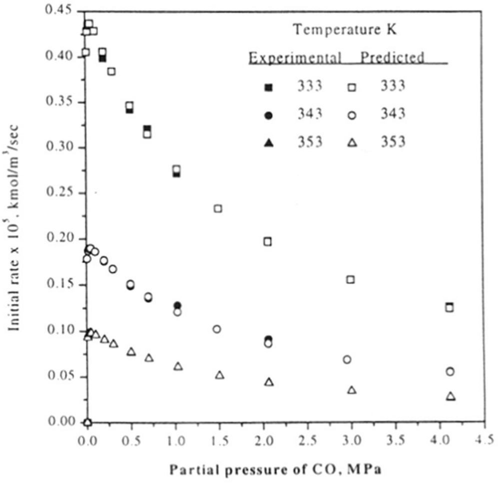


Figure 2.7 Effect of Carbon monoxide partial pressure on rate of hydroformylation of styrene
Reaction conditions:
Styrene: 3.45 kmol/m^3; Catalyst: 1.01 kmol/m^3; CO partial pressure: 2.04 MPa; Agitation speed: 900 rpm; Solvent: Toluene; Total volume: 2.5 x 10^{-5} m^3; Reaction time: 120 min.

The rate of hydrformylation was found to be zero order with styrene in the range of concentrations (0.92 to 6.89 kmol/m^3) studied. The results are shown in Figure 2.8. Unlike the previous reports [Deshpande and Chaudhari (1989a), Bhanage et al. (1997)] wherein the kinetics was found to be first order tending to zero order with 1-dodecene, and a negative order in case of allyl alcohol, here the rate was found to be independent of styrene concentration. According to the simplified reaction scheme (Figure 10), the rate of hydroformylation was found to be zero order with respect to styrene in the addition of olefin to form the olefin-Rh complex is an equilibrium reaction. The equilibrium may be attained even at lower concentration of styrene leading to zero order dependence. Zero order dependence of styrene was also observed by Lazzaroni (1990) with $Rh_4(CO)_{12}$ catalyst at 90°C and 18 MPa total pressure of (CO + H_2). However in some reports, a substrate inhibited kinetics with respect olefin has been observed (Deshpande and Chaudhari (1989b))

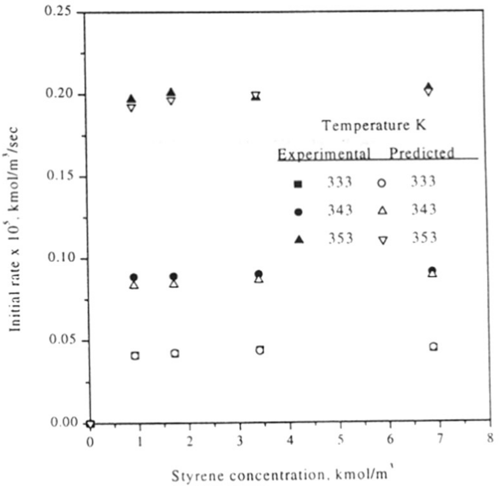


Figure 2.8 Effect of styrene concentration on rate of hydroformylation of styrene
Reaction conditions :
Catalyst: 1.01 kmol/m^3; H_2 partial pressure: 2.04 Mpa; CO partial pressure: 2.04 MPa; agitation speed: 900 rpm; Solvent: Toluene; Total volume: 2.5 x 10^{-5} m^3; reaction time: 120 min.

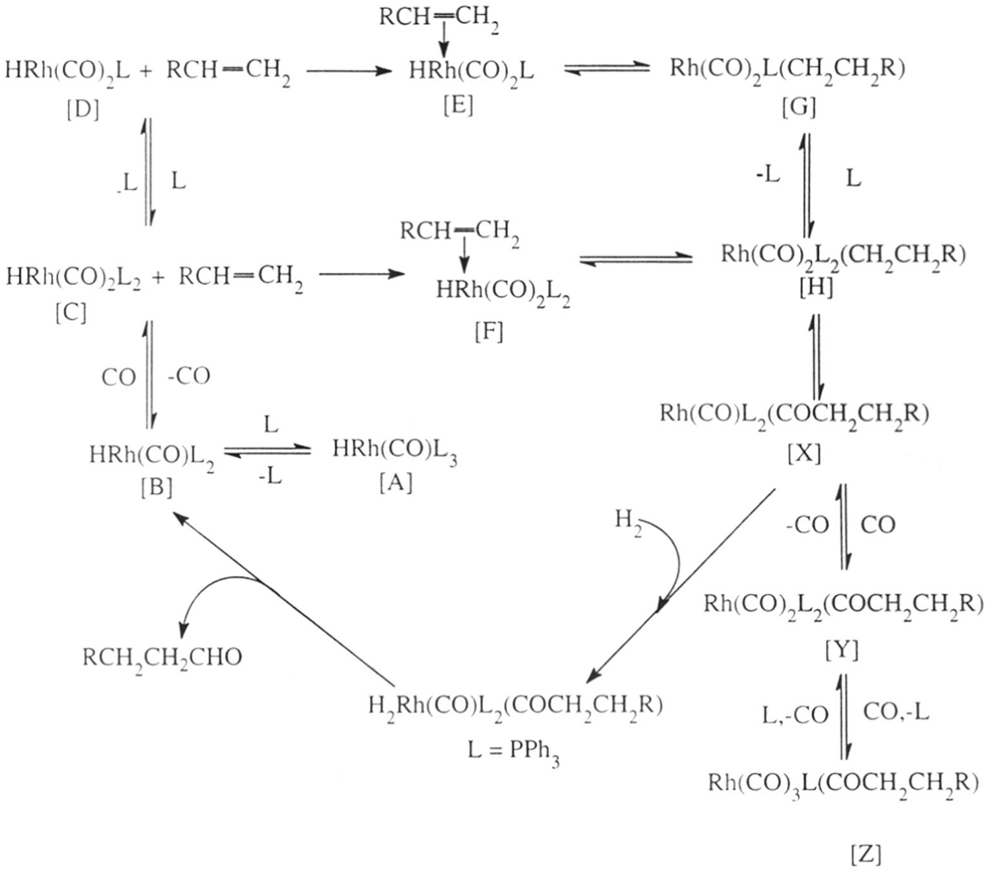


Figure 2.9 Mechanism of hydroformylation proposed by Evans et al.(1968)

2.3.3 Kinetic Model

In most of the earlier kinetic studies on hydroformylation of olefins, empirical rate models have been used. It will be more appropriate to derive a rate equation, based on a catalytic cycle. For this purpose, the mechanism described by Evans et al.(1968) (Figure. 2.9) was considered. The elementary steps involved in the catalytic cycle, can be simplified as shown in equations 2.7 to 2.11.

$$\underset{C_1}{\mathrm{HRh(CO)L_2}} + \underset{B}{\mathrm{CO}} \overset{K_1}{\rightleftharpoons} \underset{C_2}{\mathrm{HRh(CO)_2L_2}} \qquad 2.7$$

$$\underset{C_2}{\mathrm{HRh(CO)_2L_2}} + \underset{D}{\mathrm{RCH{=}CH_2}} \overset{K_2}{\rightleftharpoons} \underset{C_3}{\mathrm{Rh(CO)L_2(COCH_2CH_2R)}} \qquad 2.8$$

$$\underset{C_3}{\mathrm{Rh(CO)L_2(COCH_2CH_2R)}} + \underset{A}{\mathrm{H_2}} \xrightarrow{k} \underset{C_1}{\mathrm{HRh(CO)L_2}} + \mathrm{RCH_2CH_2CHO} \qquad 2.9$$

$$\underset{C_3}{\mathrm{Rh(CO)L_2(COCH_2CH_2R)}} + \underset{B}{\mathrm{CO}} \overset{K_3}{\rightleftharpoons} \underset{C_4}{\mathrm{Rh(CO)_2L_2(COCH_2CH_2R)}} \qquad 2.10$$

$$\underset{C_4}{\mathrm{Rh(CO)_2L_2(COCH_2CH_2R)}} + \underset{B}{\mathrm{CO}} \overset{K_4}{\rightleftharpoons} \underset{C_5}{\mathrm{Rh(CO)_3L(COCH_2CH_2R)}} \qquad 2.11$$

Figure 2.10 Simplified hydroformylation mechanism used for rate model derivation.

The detailed description of the mechanism is given in Chapter 1 (section 1.2). Assuming that the oxidative addition of hydrogen to the acylrhodium species is rate determining step. The rate of reaction will be

$$r = kC_3C_B \qquad 2.12$$

In order to derive the rate equation all the intermediate catalytic species have to be expressed in terms of C_3. From elementary steps 2.7, 2.8, 2.10, 2.11it can be shown that,

$$C_1 = {}^{C_3}\!/_{K_1K_2C_BC_D} \qquad 2.13$$

$$C_2 = {}^{C_3}\!/_{K_1C_B} \qquad 2.14$$

$$C_4 = K_3C_3C_B \qquad 2.15$$

$$C_5 = K_4C_3C_B \qquad 2.16$$

The total concentration of the catalyst added to the reaction mixture, C, is the sum of all these intermediate species, and therefore

$$C = C_1 + C_2 + C_3 + C_4 + C_5 \qquad 2.17$$

Substituting for C_1 to C_5 in terms of C_3

$$C = {}^{C_3}\!/\!_{K_1K_2C_BC_D} + {}^{C_3}\!/\!_{K_1C_B} + C_3 + K_3C_3C_B + K_4C_3C_B \qquad 2.18$$

Rearranging for C_3

$$C_3 = \frac{K_1\,K_2\,C_B\,C_C\,C_D}{1 + K_1\,B + K_1\,K_2\,C_B\,C_D + K_1\,K_2\,K_3\,C_B^{\,2}C_D + K_1\,K_2\,K_3\,K_4\,C_B^{\,3}\,C_D} \qquad 2.19$$

Substituting for C_3 in R, (eq. 2.4)

$$r = \frac{k\,K_1\,K_2\,C_A\,C_B\,C_CC_D}{1 + K_1\,B + K_1\,K_2\,C_BC_D + K_1\,K_2\,K_3\,C_B^{\,2}\,C_D + K_1\,K_2\,K_3\,K_4\,C_B^{\,3}\,C_D} \qquad 2.20$$

Where, K_1, K_2, K_3, K_4 are the equilibrium constants of various steps given above, and k is the reaction rate constant. In order to estimate the rate parameters, a non-linear least square regression analysis was used to fit the rate data using Eq. (2.21) and obtain the best-fit parameters. For this purpose, an optimization program based on a Marquart's method was used. The model parameters were estimated by minimizing the objective function ϕ_{min}., defined as :

$$\phi_{min} = \sum_{i=1}^{n}(R_{exp} - R_{pre})^2 \qquad 2.21$$

where R_{exp} and R'_{pre} are the observed and predicted rates respectively and n is the number of points. The model was further subjected to residual analysis, in which the relative residuals (RR%) of the model predictions were considered. RR% is defined as

$$RR\% = \frac{R_{exp} - R_{pre}}{R_{exp}} \times 100 \qquad 2.22$$

The RR% values for the model were scattered and did not show any regular trend with respect to any parameter, thus confirming the validity of the model. The error between the predicted and observed rate data was found to be ± 5%.

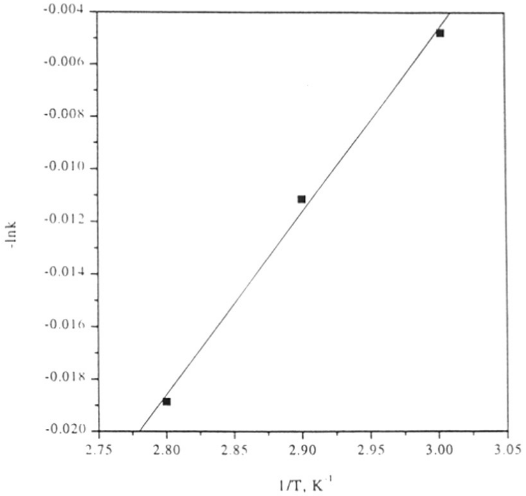


Figure 2.11 Temperature dependence of rate constant

The rate and equilibrium parameters determined for different temperatures are presented in Table 2.4. From the temperature dependence of the rate constants (Figure 2.11), the activation energy was found to be 68.80 kJ/mol.

Table 2.4 Rate constants evaluated from the rate model

Temperature K	k, m^3/kmol/s	K_1, m^3/kmol	K_2, m^3/kmol	K_3, m^3/kmol	K_4, m^3/kmol
333	1.61248	469.11	7.548	8.7372	0.05855
343	3.0482	404.5	7.515	8.539	0.05513
353	6.5915	337.695	7.4765	8.3575	0.05356

2.4 Conclusion

Kinetics of hydroformylation of styrene using a homogeneous $HRh(CO)(PPh_3)_3$ catalyst was studied in a batch pressure reactor in a temperature range of 333-353 K. The reaction was found to be first order with respect to catalyst and H_2 partial pressure. The rate vs partial pressure of CO showed negative order dependence with CO indicating a CO inhibited kinetics. Change in styrene concentration showed no effect on the rate of hydroformylation. A rate equation has been derived using a catalytic cycle based on molecular level description of elementary steps and assuming oxidative addition of hydrogen to acylrhodium intermediate as the rate determining step. The kinetic parameters were estimated using a non-linear regression analysis. The mechanistic model proposed was found to predict the data within $\pm$ 5% error at all temperatures. The activation energy was found to be 68.80kJ/mol.

Nomenclature

C_A = Concentration of H_2 in the reaction mixture, kmol/m^3

C_B = Concentration of CO in the reaction mixture, kmol/m^3

C = Catalyst concentration, kmol/m^3

C_D = Styrene concentration, kmol/m^3

f_A = Fugacity of pure gas at atmospheric pressure, MPa

f_A^L = Fugacity of hypothetical liquid solute at atmospheric pressure, MPa

H = Henry's constant, m^3.MPa/kmol

k = Reaction rate constant, m^3/kmol/s

K_1,K_2,K_3,K_4 = Equillibrium constants for the elementary steps in the catalytic cycle, m^3/kmol

M_s = Molecular weight of the solvent

P_I = Initaial pressure reading, MPa

P_f = Final pressure reading, MPa

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

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

R = Gas constant, J/K.mol

T = Temperature, K

V_g = Volume of the gas phase, m^3

V_L = Volume of liquid phase, m^3

X_A = Mole fraction of gas A

$X_{A,mix}$ = Mole fraction of gas in the solvent mixture

X_{A1} = Mole fraction of gas in pure styrene

X_{A2} = Mole fraction of gas in pure toluene

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

Greek Symbols

δ_A = Solubility parameter for the solute gas, (J/m^3)$^{1/2}$

ϕ_s = Volume fraction of solvent

ν_A = Molar volume of gas A, m^3/mol

δ_S = Solubility parameter for solvent, (J/m^3)$^{1/2}$

δ_A = Solubility parameter of solute (J/m^3)$^{1/2}$

β_{12} = $(\delta_{s1}-\delta_{s2})^2/RT$

ρ_s = Molar density of the liquid, kmol/m^3

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CHAPTER III

Hydroformylation of Styrene in a Biphasic Media: Kinetics and Reaction Engineering Studies

3.1 Introduction

Being in the same phase as the reactants, homogeneous catalysts have a definite advantage of maximum catalyst utilization. Furthermore, they can be easily modified by ligand variation and their structure and reaction pathways can be characterised in detail by a range of spectroscopic techniques thereby simplifying catalyst optimisation. They are also generally active under mild conditions with high selectivity. As described earlier (Chapter 1 section 1), these catalysts are used for various commercial applications, but the difficulties in separating the catalyst from the product mixtures create economic barrier for broader applications. The emergence of biphasic catalysis has extended the scope of homogeneous catalysis by simplifying the catalyst recovery from the product mixture and subsequent recycle. This simple approach involves design of ligands or engineering soluble supports in certain solvents, such as water, fluorocarbon, special mixtures of organic solvents, supercritical CO_2 and ionic liquids. In these systems, the catalyst remains in one phase and the reactants and products in another phase and the separation of the catalyst can be easily achieved by simple phase separation. This methodological advance in homogeneous catalysis was stimulated by the discovery of sulfonated triphenyl phosphine (TPPTS) by Kuntz (1975) and its successful commercial utilisation for the oxo process [hydroformylation of propylene to n-butyraldehyde (300 000 tpa)] by Ruhrchemie/Rhône-Poulenc in 1984. These fundamental advances in facilitating catalyst separation have sparked renewed interest in developing water soluble catalysts for efficient synthesis of a wide range of chemicals in pharmaceutical and fine chemical industries [Catalysis Today (1998), Cornils and Hermann (1998)].

Though several publications have appeared in the literature related to biphasic catalysis for a wide range of reactions, only a limited information is available on the kinetics and engineering aspects. The kinetics and reaction engineering aspects are important for transforming the catalytic chemistry into economically feasible production process. As a first step, it is required to investigate the intrinsic kinetics and develop rate equations, which can be used for analysis of reaction engineering issues. The relevant literature on biphasic hydroformylation using water-soluble catalysts is presented in detail in Chapter 1 (section 1.3.1), mainly on the type of catalyst systems and different concepts of two-phase catalysis. A brief report on previous studies on kinetics of biphasic hydroformylation is summarised here.

The kinetics of hydroformylation reaction is known to be very complex with rate inhibition at certain concentrations of CO and olefins for the homogeneous systems (see Chapter 2). For water-soluble catalysis, very few published reports on intrinsic kinetics are known. The kinetics of hydroformylation 1-octene and ethylene has been reported by Bhanage (1995) and Deshpande et al. (1998) respectively, in a biphasic media using $[Rh(COD)Cl]_2$ -TPPTS as a catalyst precursor, in the absence of any co-solvents. In case of 1-octene, the rate was found to be first order with respect to catalyst concentration, hydrogen partial pressure and substrate concentration and 0.7^{th} order with CO in a temperature range of 363-373 K. A rate model (Eq. 3.1) based on the hydroformylation mechanism assuming addition of hydrogen to acyl rhodium species as the rate-determining step was found to explain the observed trends satisfactorily.

$$r = \frac{k K_1 K_2 K_3 A B C D}{1 + \alpha B} \qquad 3.1$$

Where A = partial pressure of hydrogen [MPa]; B = partial pressure of carbon monoxide [MPa]; C = Concentration of catalyst $[kmol/m^3]_{aq}$; D = Concentration of olefin $[kmol/m^3]_{aq}$; k = reaction rate constant; K_1; K_2; K_3; α = constants

In the case of ethylene hydroformylation, the rate was found to be first order with respect to catalyst concentration and hydrogen partial pressure. The rate passes through a maxima for both CO and ethylene partial pressures at 313 K. An empirical rate equation (Eq 3.2) was proposed to explain the observed trends.

$$r = \frac{3450\,A\,B\,D}{(1+278B)^2 + (1+3829D)^2} \qquad 3.2$$

The solubility of higher olefins like hexene, octene and higher homologues in water is very poor and hence results in very low rates of reaction [Chaudhari et al. (1994), Wachsen et al. (1998)]. The use of co-solvents to enhance the solubility of the organic substrates has been reported in the literature. Ethanol, as a co-solvent increases the concentration of 1-octene in water by two orders of magnitude [Hablot (1991)]. This results in significant increase in the reaction rate while retaining the biphasic nature of the system [Hablot et al. (1993)]. Kalck and co-workers (1994) have studied hydroformylation of 1-octene using water-soluble dinuclear complex $[Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2]$ as a precursor. Several co-solvents such as acetone, acetonitrile, methanol and ethanol have been used to enhance the rate of hydroformylation. Ethanol as a co-solvent was found to enhance the reaction rate dramatically by a factor of 25.

Purwanto and Delmas (1995), have reported the kinetics of hydroformylation of 1-octene using $[Rh(COD)Cl]_2$ -TPPTS catalyst in the presence of ethanol as a co-solvent in a temperature range 333- 353 K. The reaction rate showed a first order dependence with respect to catalyst and 1-octene concentrations. The rate varied with 0.6-0.7th order with partial pressure of hydrogen, but passed through a maxima with increase in partial pressure of carbon monoxide. An empirical rate equation of the form Eq. 3.3 was found to explain the observed trends satisfactorily. In this case, the aqueous phase was continuous and the organic phase was in the form of a dispersed phase. Ethanol as a co-solvent has a limitation of forming acetals with the aldehyde products at higher temperature.

$$r = \frac{k\ A\,B\,C\,D}{(1 + K_B\ B)^2 + (1 + K_A A)} \qquad 3.3$$

Deshpande et al. (1996) have further studied kinetics of hydroformylation of 1-octene using the same system in a lower temperature range, 323-343 K and at higher pH (10) in order to reduce the formation of acetals. An empirical rate equation of the form Eq 3.4 was proposed. A semi-empirical equation of the form Eq. 3.5 was also derived based on a mechanism assuming addition of olefin to $HRh(CO)_2(TPPTS)_2$ as the rate-controlling step and was found to fit the data in good agreement.

$$r = \frac{k\ A\,B\,C\,D}{(1 + K_B\ B)^3 + (1 + K_A A)} \qquad 3.4$$

$$r = \frac{k\ A\,B\,C\,D}{1 + K_A A\,B + K_B B^2} \qquad 3.5$$

Kinetics of hydroformylation of 1-hexene using ethylene glycol as a co-solvent in a biphasic medium using Rh-TPPTS catalyst has been reported by Nair et al. (1998). The rate was found to be 0.5 and 0.7 order with hydrogen and carbon monoxide partial pressure and 1.6th order with hexene concentration. A simple power law model (Eq 3.6) was proposed and was found to explain the trends satisfactorily at 353 K. In this study, a reduced selectivity towards the aldehyde products was observed due to the condensation of heptanals with ethylene glycol leading to the formation of acetal derivatives.

$$r = kA^m B^n D^p \qquad 3.6$$

Though, the use of alcohols as co-solvents appears to be an attractive and easy method to enhance the reaction rates in biphasic hydroformylation, due to their reactive nature, the selectivity towards aldehyde products is often reduced and hence may not be of commercial interest. It will be most desirable to explore better unreactive co-solvents that will enhance the reaction rate.

Bhanage (1995) has also studied the kinetics of hydroformylation of 1-octene in a biphasic media using $[Rh(cod)Cl]_2$-TPPTS system in the presence of added PPh_3 in the organic phase at 373 K. A rate enhancement of 10-50 times was observed when a little amount of PPh_3 (Rh : TPPTS : PPh_3 = 1: 6 : 0.5) was added in the organic phase [Chaudhari et al. (1995)]. The detailed description of the rate enhancement phenomena has been given in the Chapter 1 (section 1.3.1.3). The rate was found to increase with PPh_3, up to a concentration of 6.6×10^{-3} kmol/m^3 without any exchange of Rhodium to the organic phase. Effect of $[Rh(COD)Cl]_2$ concentration showed a positive order dependence on the reaction rate, however Rh was found to leach to the organic phase at very low concentration (below 1.5×10^{-3} kmol/m^3) of $[Rh(cod)Cl]_2$. Effect of TPPTS showed negative order dependence on the reaction rate. Other parameters such as H_2, CO, and 1-octene concentration on the initial rate showed a first order, substrate inhibited kinetics and a fractional order respectively. An empirical rate equation (Eq 3.7) was proposed to explain the observed trends.

$$r = \frac{k\ A\,B\,D}{(1 + K_B\ B)^2 + (1 + K_D D)} \qquad 3.7$$

In all the previous reports, kinetics of hydroformylation was studied using $[Rh(cod)Cl]_2$-TPPTS system, which forms $HRh(CO)(TPPTS)_3$ in-situ under hydroformylation conditions. Deshpande et al.(1997) has observed a two to five fold increase in the rate of hydroformylation of 1-octene in toluene-water system with ethanol as a co-solvent, when the pH was changed from 7 to 10. This enhancement in rate was explained on the basis of faster dissociation of $Rh_2Cl_2(TPPTS)_4$ to the active monomer $HRh(CO)(TPPTS)_3$ at pH 10. The dissociation rate was expected to be less at pH 7. This was further confirmed by addition of equimolar quantities of triethyl amine (in relation to the amount of chloride present) at pH 7. In this case, a similar enhancement in reaction rate was observed as at pH 10. These observations clearly indicate that it will be more appropriate to use $HRh(CO)(TPPTS)_3$ directly than preparing it in-situ form $[Rh(cod)Cl]_2$-TPPTS system. Kalck and co-workers have also found that it is better to use $HRh(CO)(TPPTS)_3$ directly than preparing it in-situ from $Rh_2(\mu\text{-}S^tBu)_2(CO)_2(TPPTS)_2$ dimer due to the loss of thiol and significant amount of $Rh_2(\mu\text{-}S^tBu)_2(CO)_4$ in to organic phase, in the case of biphasic hydroformylation of 1-octene.

In order to further understand the kinetics of biphasic hydroformylation, a detailed study on kinetics of hydroformylation of styrene using $HRh(CO)(TPPTS)_3$ in a temperature range of 363-383 K was undertaken. Particularly, the goal was to develop rate equations based on mechanistic models and compare the kinetic trends with and without co-solvents. The effect of agitation speed and catalyst phase hold up on the rate of reaction has been studied to understand the role of mass transfer and to ensure that the experiments carried out are in the kinetic regime. The effect of catalyst concentration, TPPTS concentration, partial pressure of CO and H_2 and substrate concentration has been investigated. The solubilities of H_2 and CO in both the liquid phases have been determined experimentally and in some cases, solubility data given in literature was used. The liquid-liquid equilibrium profiles for styrene-water-toluene has been predicted using UNIFAC approach [Fredenslund (1975); Joulia et al. (1987)]. Both, empirical and mechanistic models have been formulated and tested with experimental data. The best model has been selected on the basis of least average error and its relevance to the mechanism of the reaction.

Effect of various co-solvents on the rate of hydroformylation of styrene using biphasic Rh-TPPTS catalyst was also undertaken with an objective to select an inert co-solvent to achieve higher rate. In addition, experiments were also carried out, to understand the effect of various parameters such as catalyst and substrate concentration, H_2 and CO partial pressures, agitation speed and aqueous phase holdup, in the presence of co-solvent and the results compared with those obtained in aqueous biphasic medium without co-solvent.

3.2 Experimental

3.2.1 Materials

Rhodium trichloride ($RhCl_3.3H_2O$), from Aldrich, USA, styrene from Fluka AG, Switzerland, Triphenyl phosphine (PPh_3) from Loba Chemie, India, Sulphuric acid, dimethyl formamide, acetyl acetonate and Sodium hydroxide from SD fine chemicals, India, were used as received. Oleum of 65% (w/w of SO_3 in H_2SO_4) strength was prepared by distillation of 20% oleum solution. Distilled degassed water was used in all operations. Solvents, toluene, water, ethanol, methylethylketone, γ-buterolactone, 1-methyl N-pyrrolidone-2 were freshly distilled and degassed prior to use. Hydrogen, nitrogen supplied by Indian Oxygen Ltd. Bombay, and carbon monoxide (> 99.8 % pure) from Matheson Gas Co., U.S.A. were used directly from cylinders. The syn gas with 1:1 ratio of H_2:CO was prepared by mixing H_2 and CO in a reservoir. All operations were performed under argon atmosphere

3.2.2 Synthesis of TPPTS

Sulfonated phosphines are useful ligands for preparing water-soluble catalysts, which can be used in biphasic mode. Triphenyl phosphine trisulfonate (TPPTS) forms complexes with most of the transition metals, just like triphenyl phosphine (TPP) [Herrmann et al. (1990)] and hence can be widely used for a variety of reactions. Moreover it has a higher solubility in water (1.1 kg/l) as compared to other phosphines

[Kuntz (1987)]. For the synthesis of TPPTS a procedure standardized by Bhanage (1995) was used.

3.2.2.1 Sulfonation Reactor

For synthesis of triphenyl phosphine trisulphonate (TPPTS), a double-jacketed one-litre glass reactor equipped with a high-speed half moon stirrer with provision for monitoring bulk liquid temperature was used. This reactor was designed so that operations under argon atmosphere were possible. The temperature was controlled by circulation of a constant temperature fluid (50% ethanol-water mixture v/v) using a cryostat.

3.2.2.2 Reaction Charge

- SO_3/TPP =12 (molar ratio)
- SO_3/(SO_3 + H_2SO_4 + TPP) = 34% (w/w)
- H_2SO_4/ (SO_3 + H_2SO_4 + TPP) = 56%(w/w)

Reaction temperature : 22°C; Agitation : mechanical stirrer

3.2.2.3 Procedure for preparation of TPPTS

200 g of 98% pure sulfuric acid was introduced into the reactor. The acid was cooled under constant stirring to 12-15°C by means of a cryostat. 50 g of triphenyl phosphine (TPP) (190.75 mmol) was introduced slowly at 15°C over a period of 30-45 min. This gave a homogeneous yellow coloured solution of TPP in sulfuric acid. 280 g (141.48 ml, d=1.98 at 35°C) of 65% oleum (SO_3 content: 2.275 mol) was transferred into the addition funnel from the oleum receiver. This oluem was then introduced in the sulfonation reactor containing TPP solution in sulfuric acid, over a period of 40-45 min maintaining a maximum temperature of 15°C with good stirring. The temperature of the reaction mixture was then raised to 22°C and was maintained for 76 hrs. This step of keeping the reaction mixture at 22°C is critical for optimum yield of TPPTS. [A cryostat was used for this purpose]. Thereafter, the temperature of the reaction was

lowered to ~ 10°C and 50 g of distilled water was introduced while maintaining the temperature at 10°C. This addition is necessary to quench the excess SO_3 present after the reaction is complete. The addition of water is highly exothermic, and hence temperature was maintained at < 10°C while addition of water. This gave a solution of sulfonated triphenyl phosphine in sulphuric acid. This reaction mixture was further diluted to approximately 800 ml under cooling (10°C). This diluted solution was then transferred into a neutralization reactor under Argon atmosphere. The reactor was similar to the reaction vessel but of a larger capacity (approx. 3 liters). A 50% (w/w) degassed sodium hydroxide solution was added to this reactor maintaining 10°C temperature. At neutralization point, the solution turns yellow, under slightly alkaline conditions the colour of the solution was distinct yellow. Neutralization was carried out to a point where the solution was colourless (slightly acidic). [Note: Na_2SO_4 precipitated out much before neutralization was complete and the reaction mixture obtained was in a slurry form]. The neutralized mixture was then filtered and the filtrate was evaporated under reduced pressure at 80-90°C till the volume reduced to about 250 ml from the initial two liters. 1.5 liters of methanol was added to the above solution and the mixture was refluxed under argon atmosphere for 2 hours. TPPTS dissolved in methanol completely, which was filtered hot, with residue comprising only sodium sulphate. The filtrate was evaporated under reduced pressure. The solid TPPTS obtained was weighed and stored under argon atmosphere. The yield was found to be 80-85%. ^{31}P NMR analysis was comparable with that observed in the literature [Bartik et al. (1992)] showed approximately 90% TPPTS and 10% OTPPTS formation. No further purification of TPPTS was undertaken for use as a ligand for the preparation of water-soluble catalyst precursors.

3.2.3 Preparation of $Rh(CO)_2(acac)$

$Rh(CO)_2(acac)$ was prepared by a method used by Varshavskii and Cherkasova (1967). Acetylacetonate (12 ml) was added to a solution of 3 g of rhodium trichloride in 60 ml dimethyl formamide, with stirring. The solution was refluxed for thirty minutes and then cooled. It was diluted to twice the volume with distilled water. Addition of water resulted in a voluminous crimson precipitate. The precipitate was filtered and washed with alcohol and ether. The complex was recrystallised from hexane solution. The red-green crystals of needle shape 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:

	Theoretical %	**Experimental %**
C	23.25	23.31
H	2.71	2.68

3.2.4 Preparation of $HRh(CO)(TPPTS)_3$

A TPPTS solution of 400 mg (0.704, mmol) in 1 ml water was added to 50 mg acetylacetonato dicarbonyl Rhodium (I), $[Rh(CO)_2(acac)]$, 0.194 mmol in a small two neck flask kept under argon. The solution was maroon coloured after dissolution of $Rh(CO)_2(acac)$. Syngas (H_2/CO 1:1) was introduced to the flask at room temperature and atmospheric pressure. The colour of solution changes from maroon to yellow in 5 min. After 6 h, the solution was filtered under positive flow of argon to remove small amounts of rhodium metal and 8 ml of absolute alcohol saturated with H_2/CO (1:1) was added to yield a yellow precipitate. The solid collected was washed with absolute alcohol, and vacuum dried. 380 mg of $HRh(CO)(TPPTS)_3$ was obtained. The complex was characterised by ^{31}P NMR and IR and was found to be comparable to that reported in the literature [Horváth (1989)].

3.2.5 Reactor Set Up for hydroformylation

All the hydroformylation experiments were carried out in a 50 ml microclave reactor supplied by Parr Instrument Company USA, details of which has been described in Chapter 2.

3.2.6 Experimental Procedure

In a typical experiment, a known quantity of catalyst HRh(CO)(TPPTS)$_3$ and 3 mols of excess TPPTS were added to a known volume (10ml) of water. This comprises of the catalyst phase. This solution was charged into the reactor alongwith a known quantity of styrene in toluene, which comprises the organic phase. The contents were flushed with nitrogen and then with a mixture of CO and H_2. Heating was started to attain a desired temperature, and then a mixture of CO and H_2, in a required ratio was introduced into the autoclave up to the desired pressure. A sample of the liquid phase mixture was withdrawn, and the reaction started by switching the stirrer on. The reaction was then continued at a constant pressure of CO + H_2 (1:1) by supply of syngas from the reservoir vessel through a constant pressure regulator. Since, in this study the major products formed were isomeric aldehydes, supply of CO + H_2 at a ratio of 1:1 (as per stoichiometry) was adequate to maintain a constant composition of H_2 and CO in the reactor as introduced in the beginning. This was confirmed in a few cases by analysis of CO content in the gas phase at the end of reaction.

3.2.7 Analytical methods

HRh(CO)(TPPTS)$_3$, TPPTS and other sulfonated derivatives were analysed, using IR, ^{1}H NMR and ^{31}P NMR and the data obtained were compared with that reported in the literature [Bartik et al. (1992), Kalck and Monteil (1992)]. NMR spectra were recorded on a Brüker AC 200 (200.13 MHz). The external reference for

^1H spectra was tetramethylsilane (TMS) and 85% H_3PO_4 for ^{31}P spectra were used. IR spectra were obtained on a Perkin Elmer 282B spectrometer.

The quantitative liquid phase analysis of the reactants and products was carried out by an external standard method using a Varian 3600 gas chromatograph. A 10% OV-17 packed column of 8 feet length was used. Synthetic standards were used for calibration of GC analysis. The optimised conditions for analysis were as follows.

Flame ionization detector temperature	573 K
Injection temperature	523 K
Column temperature programmed between	393-433 K
Rate of heating	30 K/min
Carrier gas (N_2) flow rate	20 ml/min

3.3 Solubility and liquid-liquid equilibrium data

For kinetic study, a knowledge of the solubility of H_2 and CO in organic phase and aqueous phase is required. The solubility data for H_2-water and CO-water systems were used from previous literature reports. Solubility at 383 K, was obtained by extrapolating solubility values up to 373 K. These data for different temperatures are presented in Table 3.1.

The solubility of styrene in the aqueous phase was calculated using the UNIFAC approach [Fredenslund (1975); Joulia et al. (1987)]. Applicability of this method has already been demonstrated wherein the comparison of the experimental data with the predictions shows a good agreement [Hablot et al. (1992)]. The validity of this method has also been demonstrated by Purwanto et al. (1996) for prediction of liquid-liquid equilibrium data for 1-octene-ethanol-water system at 323 K. The liquid-liquid solubility data for styrene in toluene -water mixture has been presented in Table 3.2. It was observed that the solubility of styrene in the aqueous phase increases with increasing concentration of styrene in the organic phase, however, with increase in temperature, the change in the solubility was marginal.

Table 3.1 Solubility of H_2 and CO in water

Temperature, K	H_A ,* MPa m^3/kmol	$H_B \times 10^3$,** MPa m^3/kmol
363	135.32	159.74
373	124.22	161.03
383	119.33	162.07

*Wiebe and Gaddy (1934); ** Dean (1972)

Table 3.2 Liquid-Liquid equilibrium data for styrene-water-toluene system using UNIFAC method

Temperature, K	Styrene in organic phase, kmol/m^3	Styrene in aqueous phase x 10^4, kmol/m^3	Ratio of aqueous to organic conc., $M_D \times 10^3$
363	0.4964	7.16052	1.44248
373	0.4961	7.18183	1.44765
383	0.4957	7.24547	1.46166

The Henry's constants for hydrogen (H_A) and carbon monoxide (H_B) given in Table 3.1 and the partition coefficients for styrene in Table 3.2 were used to evaluate concentrations of H_2 and CO and styrene in the aqueous phase required for rate analysis. The solubility of CO and H_2 at 363-383 K in toluene, styrene, and toluene-styrene mixtures was experimentally determined and calculated using the method described in Chapter 2 (section 2.3.1) and are given in Table 3.3 and 3.4.

Table 3.3: Henry's constants of CO in toluene, styrene, and toluene-styrene mixture

Gas, Solvent	H_B MPa m^3/kmol at 363 K		H_B MPa m^3/kmol at 373 K		H_B MPa m^3/kmol at 383 K	
	Expt.	Predicted	Expt.	Predicted	Expt.	Predicted
CO in Toluene	11.44	11.46	11.34	11.36	11.23	11.24
CO in 10% Styrene in toluene (v/v)	11.57	11.59	11.47	11.46	11.30	11.34
CO in 20% Styrene in toluene (v/v)	11.70	11.71	11.58	11.57	11.45	11.44
CO in 40% Styrene in toluene (v/v)	11.93	11.95	11.75	11.79	11.66	11.64
CO in 80% Styrene in toluene (v/v)	12.45	12.48	12.25	12.29	12.02	12.09
CO in Styrene	12.74	12.75	12.56	12.55	12.30	12.34

Table 3.4: Henry's constants of hydrogen in toluene, styrene, and toluene-styrene mixture

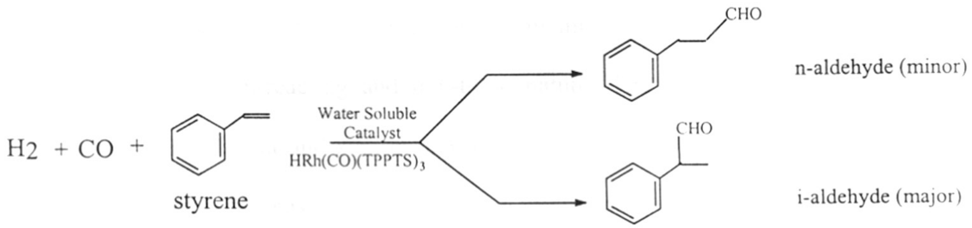
Gas, Solvent	H_A MPa m^3/kmol at 363 K		H_A MPa m^3/kmol at 373 K		H_A MPa m^3/kmol at 383 K	
	Expt.	Predicted	Expt.	Predicted	Expt.	Predicted
H_2 in Toluene	25.95	25.94	25.01	25.04	24.22	24.20
H_2 in 10% Styrene in toluene (v/v)	25.20	25.21	25.30	25.27	25.40	24.41
H_2 in 20% Styrene in toluene (v/v)	25.45	26.48	25.50	25.52	25.60	24.63
H_2 in 40% Styrene in toluene (v/v)	27.01	27.05	26.05	26.02	25.05	25.08
H_2 in 80% Styrene in toluene (v/v)	28.20	28.27	27.10	27.12	26.08	26.07
H_2 in Styrene	28.95	28.93	27.70	27.72	26.60	26.61

3.4 Results and Discussion

The objective of this work was to investigate the kinetics of hydroformylation of styrene using water-soluble $HRh(CO)(TPPTS)_3$ catalyst in a two-phase system, initially without adding any co-solvent and then in the presence of a co-solvent. For this purpose the effect of different parameters such as catalyst concentration, hydrogen and carbon monoxide partial pressures and styrene concentration on the initial rate of hydroformylation was studied in a temperature range of 363-383 K. The results are discussed in the following sections. The effect of co-solvents on the rate enhancement of biphasic hydroformylation has also been discussed.

3.4.1. Preliminary experiments

Several preliminary experiments on hydroformylation of styrene using water soluble $HRh(CO)(TPPTS)_3$ catalyst were carried out in a temperature range of 363-383 K to assess material balance and product distribution. The stoichiometric reaction is:



$$A_{(g)} \; + \; B_{(g)} \; + \; D_{(l)} \longrightarrow P_{(l)}$$

The results of a typical experiment carried out for 373 K and 4.14 MPa total pressure of CO/H_2 (1:1) is shown in Table 3.5.

It was observed that 30% conversion of styrene was achieved in 60 minutes and material balance of CO or H_2 and styrene consumed was in good agreement with the total amount of aldehydes formed. In the range of conditions investigated, the only products formed were the isomeric aldehydes, 2-phenylpropanal (2PPD) and 3-phenylpropanal (3PPD) which were isolated and characterised by IR and ^{1}H, NMR. No hydrogenation products were observed in these studies.

Table 3.5 Mass Balance in a Batch Experiment

Sr. No	Time, min	Amount of styrene, x 10^5, kmol	CO/H_2 consumed x 10^6, kmol	Total aldehydes x 10^6, kmol	2PPD, %	3PPD, %
1	0	1.75	0	0	0	0
2	15	1.58	1.72	1.73	56.60	43.40
3	40	1.35	4.0	3.98	56.55	43.45
4	60	1.24	5.12	5.14	55.62	44.38

Reaction conditions:
$HRh(CO)(TPPTS)_{3(aq)}$: 0.681 kmol/m^3; $TPPTS_{(aq.)}$: 2.02 kmol/m^3; Styrene $_{(org.)}$: 1.16 kmol/m^3; P_{CO}: 2.04 MPa; P_{H2}: 2.04 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3.

Toluene was selected as the organic solvent mainly because of the ease of separation, low volatility, non-reacting and non-toxic nature. The major advantage of biphasic catalysis is the efficient and simple recycle of aqueous catalyst phase. This is achieved by a simple physical phase separation of two immiscible liquid phases. For the recycle experiments, the aqueous phase catalyst was used in several successive experiments with fresh charge of the organic phase each time. The catalyst was recycled five times without loss of activity as shown in Figure. 3.1. The rates as well as the selectivity behavior towards aldehyde products were found to be unaffected in recycle experiments indicating the reusability of the catalyst. The initial rates of hydroformylation were calculated from the observed CO or H_2 consumption-time profile. Under the conditions chosen for the kinetic study, no side reactions were found to occur and hence, these data represent the overall hydroformylation of styrene to the corresponding aldehydes.

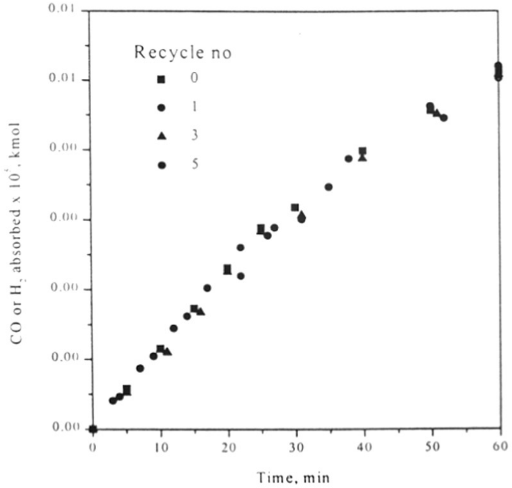


Figure 3.1 Catalyst recycle experiments

Reaction conditions:
$HRh(CO)(TPPTS)_{3(aq)}$: 0.681 kmol/m^3; $TPPTS_{(aq.)}$: 2.02 kmol/m^3; Styrene $_{(org.)}$: 1.16 kmol/m^3; P_{CO}: 2.04 MPa; P_{H2}: 2.04 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3; Temperature 373 K.

Since, the CO and H_2 were consumed in a 1:1 ratio, the rate of reaction of either gas would equal to half of the total gas absorption. For calculating the initial rate of reaction, the H_2 or CO consumption-time profiles observed under different conditions were fitted to a second order polynomial by a linear regression procedure.

$$y = a + bt + ct^2 \qquad 3.8$$

Here, y represents the H_2 or CO consumed in kmol, a, b, c, are polynomial coefficients and t represents the time in minutes. Initial rate can be calculated by differentiating above equation with respect to t, at t = 0

$$\left.\frac{dy}{dt}\right|_{t=0} = b \qquad 3.9$$

Moreover, the initial rate per unit volume of reaction mixture was calculated as

$$r_i = \frac{b}{\text{volume of reaction charge} \times 60} \qquad 3.10$$

Where, r_i represents the initial rate in kmol/m^3/s. A typical H_2 or CO consumption-time profile is shown in Figure 3.2

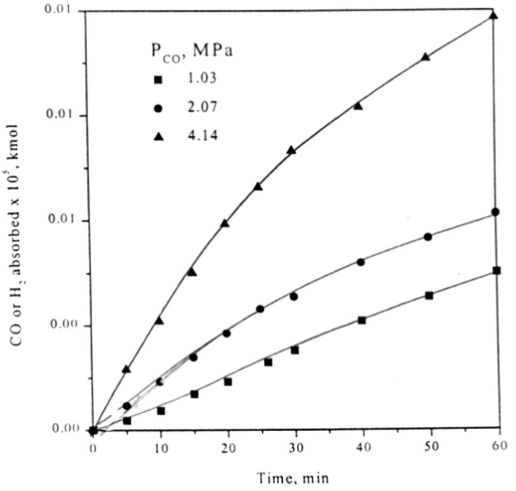


Figure 3.2 Typical CO or H_2 consumption-time profile: Effect of CO partial pressure on the initial rate of hydroformylation

Reaction conditions:
$HRh(CO)(TPPTS)_{3(aq)}$: 0.681 kmol/m^3; $TPPTS_{(aq.)}$: 2.02 kmol/m^3; $Styrene_{(org.)}$: 1.16 kmol/m^3; P_{H2}: 2.04 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3, Temperature: 373 K; Reaction time: 60 min.

3.4.2. Physical description of the system

Hydroformylation of styrene in a biphasic media is a multiphase reaction since, it involves three phases (gas-liquid-liquid) containing two gaseous reactants H_2 and CO with styrene as a liquid reactant in the organic media and the catalyst in the aqueous medium. The overall reaction rate depends on transport of H_2 and CO to the liquid phase, followed by transport of dissolved H_2, CO and styrene from organic phase to aqueous phase and reaction in the aqueous catalyst phase. A schematic of biphasic hydroformylation reaction is shown in Figure 3.3

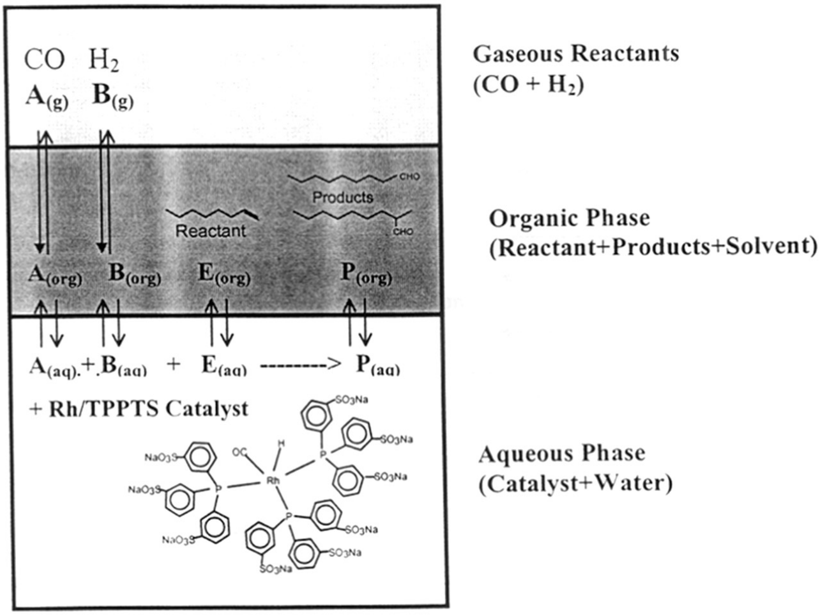


Figure 3.3 Schematic of biphasic hydroformylation of olefins

The factors affecting the rate behaviour of gas-liquid-liquid catalytic reactions have been discussed by Chaudhari et al. (1995). The overall performance of such reactions would depend on a number of parameters such as reaction kinetics, gas-liquid and liquid-liquid mass transfer, solubility of gases in organic and aqueous phases, liquid-liquid equilibrium and the complex hydrodynamics of the dispersed liquid droplets. The various parameters/steps governing the rate of gas-liquid-liquid reactions are shown in Figure 3.4. In order to understand the rate behaviour, detailed analyses of these phenomena with relevant experimental studies are necessary.

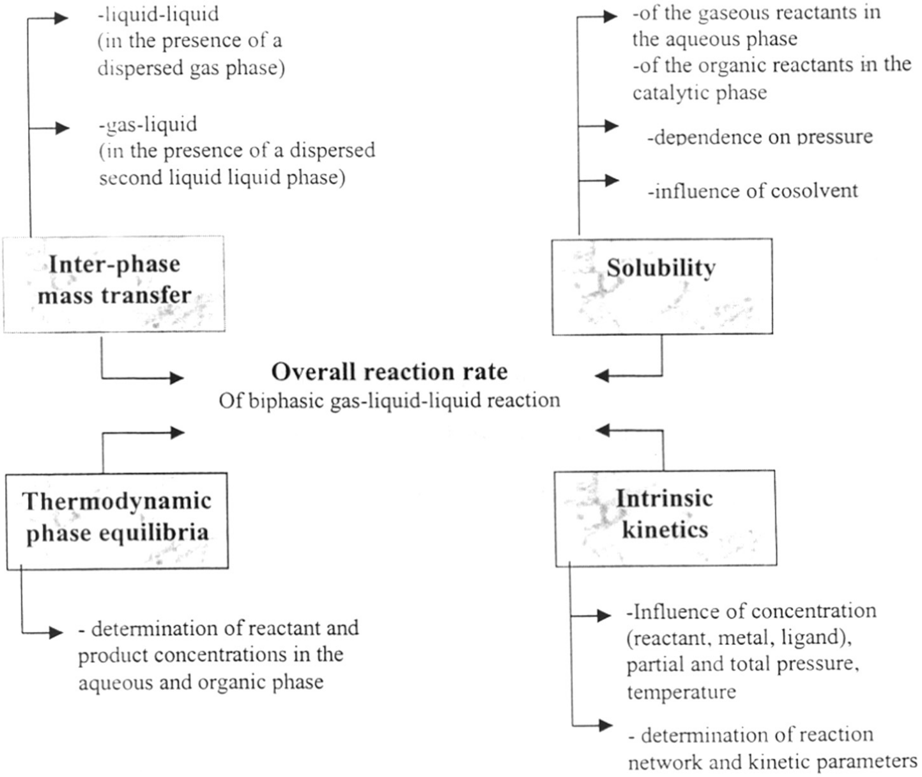


Figure 3.4 Parameters/steps in gas-liquid-liquid reactions [Claus and Baerns (1998)]

3.4.3. Mass transfer effects in Gas-Liquid-Liquid systems

For investigation of intrinsic kinetics of multiphase reactions, it is important to ensure that the rate data obtained are in the kinetic regime. A careful consideration to the significance of mass transfer must be given for kinetic analysis of a complex multiphase reaction involving gas-liquid-liquid system. For a gas-liquid-liquid reaction system, the overall rate would depend on the gas-liquid, liquid-liquid mass transfer and the intrinsic kinetics of the reaction in the aqueous phase.

3.4.3.1 Experimental observations

A few experiments were carried out to investigate the effect of catalyst phase hold up, agitation speed and catalyst concentration on the rate of reaction. These experiments were important to understand the role of mass transfer and ensure the kinetic regime. The experiments were carried out in a temperature range of 363-383 K Rh complex concentration of 0.681 $kmol/m^3_{aq}$, TPPTS concentration of 2.01 $kmol/m^3_{aq}$ and at styrene concentration of 1.16 $kmol/m^3_{org}$. The partial pressures of hydrogen and carbon monoxide were maintained at 2.04 MPa. Figure 3.5 shows that the rate of reaction increases with agitation speed, up to 700 rpm. But for agitation speed greater than 700 rpm, the rate of reaction does not change. This observation indicates that the mass transfer effects are important below 700 rpm.

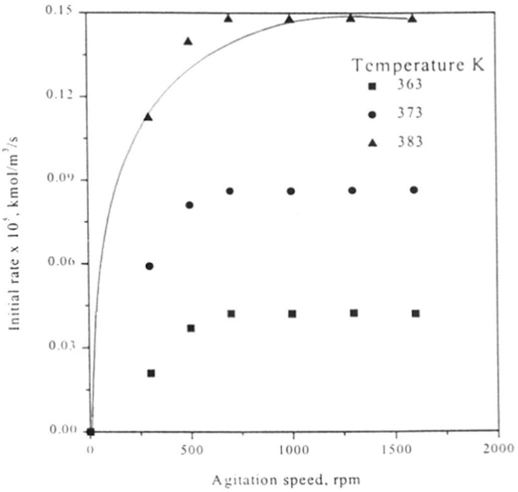


Figure 3.5 Effect of agitation speed on initial rate of hydroformylation

Reaction conditions:
$HRh(CO)(TPPTS)_3$: 0.681 kmol/m^3; $TPPTS_{(aq.)}$: 2.02 kmol/m^3; Styrene $_{(org.)}$: 1.16, kmol/m^3; PCO: 2.07 MPa; P_{H2}: 2.07 MPa; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3, Reaction time: 60 min.

Figure 3.6 shows the effect of aqueous catalyst phase hold-up (ε) on the initial rate of hydroformylation of styrene at various agitation speeds. It was observed that the phase inversion takes place at aqueous phase hold up of about 0.5. For aqueous phase hold-up less than 0.5, the aqueous phase is the dispersed phase, as shown schematically in Figure 3.8 (a). In this case, the liquid-liquid interfacial area is determined by aqueous phase hold-up (ε). For aqueous phase hold-up greater than 0.5, the organic phase is the dispersed phase, as shown schematically in Figure 3.8 (b). In this case, the liquid-liquid interfacial area will be determined by the organic phase hold-up (1-ε).

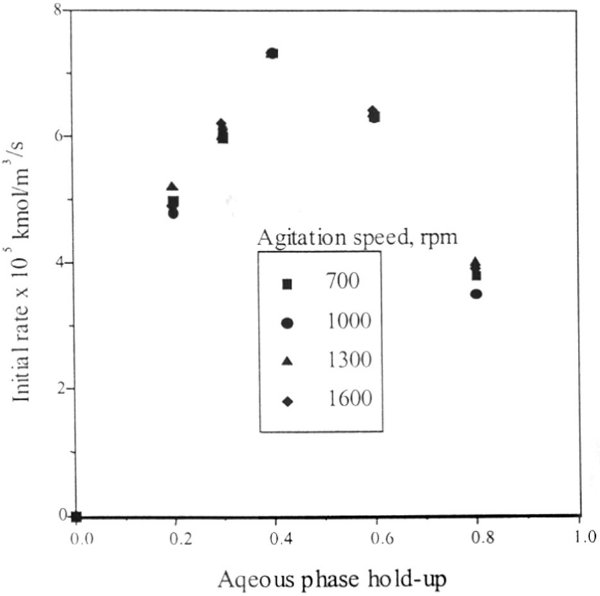
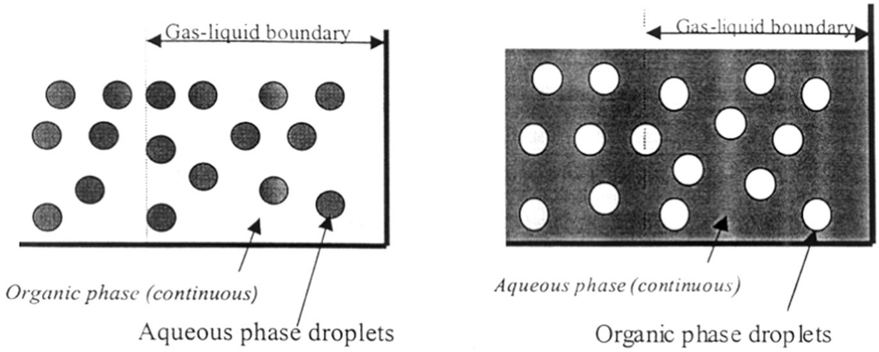


Figure 3.6 Effect of aqueous phase aqueous phase hold up on initial rate of hydroformylation
Reaction conditions:
$HRh(CO)(TPPTS)_3$: 0.681 kmol/m^3; $TPPTS_{(aq.)}$: 2.02 kmol/m^3; Styrene $_{(org.)}$: 1.16 kmol/m^3; PCO: 2.07 MPa; P_{H2}: 2.07 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water; Total volume: 2.5 x10^{-5} m^3, Reaction time: 60 min.

At agitation speed of 1300 rpm, a plot of initial rate vs. aqueous (catalyst) phase hold-up (Figure 3.6) shows that the rate first increases with increase in aqueous phase hold up and then passes through a maximum. In kinetic regime, the rate per unit volume of the aqueous phase is expected to remain constant with increase in aqueous phase hold up and agitation speed. However, in the case where the reaction occurs essentially at liquid-liquid interface, it would depend on the liquid-liquid interfacial area, which is governed by both agitation speed and hold up of the dispersed phase. The results at aqueous phase hold up less than 0.5 indicate kinetic regime. For higher aqueous phase hold up the decreasing rate indicate mass transfer limitation but this observation is not consistent with the observation of negligible agitation effect. In order to understand this effect requires further studies, however for the kinetic modeling the data below aqueous phase hold up of 0.5 (at 0.4) were used, wherein kinetic regime prevails certainly.

Effect of catalyst concentration is described on a latter, section (3.4.4.1) and hence not discussed here.

3.4.3.2 Physical description of models



(a) Aqueous phase dispersed $(0<\varepsilon<0.5)$

(b) Organic phase dispersed $(0.5<\varepsilon<1.0)$

Figure 3.7 Schematic presentation of two different physical situations prevailing in the reactor depending upon the phase hold up

The gas-liquid-liquid reactions can be classified into two categories depending on which phase is dispersed and where the reaction occurs. For the present case, wherein aqueous catalyst phase is the reaction phase, we have

- *Model A: aqueous phase is dispersed in organic phase ($\varepsilon < 0.5$) and*
- *Model B : organic phase is dispersed in aqueous phase ($\varepsilon > 0.5$)*

The important steps involved in a gas-liquid-liquid catalytic reaction are [Chaudhari et al. (1995)] given in Table 3.6.

Table 3.6. Important steps in an aqueous biphasic catalytic reaction

Case I: Aqueous droplets containing the dissolved catalyst dispersed in continuous organic liquid phase	Case II: Organic liquid phase dispersed in a continuous aqueous phase which contains the catalyst
Step	
(a) Transport of a gaseous reactants (A) and (B) from the bulk gas phase to gas/organic liquid interface	Transport of a gaseous reactants (A) and (B) from the bulk gas phase to gas/aqueous liquid interface.
(b) Transport of (A) and (B) through the gas/organic liquid interface into the bulk of the organic liquid	Transport of (A) and (B) through the gas/aqueous catalyst interface into the bulk of the aqueous catalyst phase.
(c) Transport of both dissolved (A) and (B) and liquid reactant (D) from organic phase to the organic/aqueous interface	Transport of liquid reactant D from the organic droplets to the organic/aqueous interface
(d) Transport of (A), (B) and D from the organic/aqueous interface to the aqueous phase catalyst	Transport of D from the organic/aqueous interface to the aqueous catalyst phase.
(e) Homogeneously catalysed reaction of dissolved (A), (B) and D to product (P) in the bulk aqueous phase.	Homogeneously catalysed reaction of dissolved (A), (B), D to product (P) in the aqueous phase.
(f) Transport of water-immiscible product P from the aqueous to the organic phase.	Transport of water-immiscible product P from the aqueous to the organic liquid phase.

3.4.3.3 Gas-liquid mass transfer effect

The significance of gas-liquid mass transfer resistance was analyzed by comparing the initial rate of reaction and maximum possible rate of gas-liquid mass transfer. The gas-liquid mass transfer resistance is negligible if a factor α_l defined as follows is less than 0.1 for the experimental conditions used.

$$\alpha_{l,A} = \frac{R_{exp}}{k_L a_B C_{A,org}} \qquad 3.11$$

$$\alpha_{l,B} = \frac{R_{exp}}{k_L a_B C_{B,org}} \qquad 3.12$$

The gas-liquid mass transfer coefficient (k_La_B) used in above equations was estimated by using a correlation proposed by Chaudhari et al (1987) for a reactor similar to that used in this work for agitation speed of 1300 rpm (at which the kinetic experiments were performed). The equilibrium solubilities for the gases given in Table 3.2 were used. The factor α_l was calculated for both hydrogen and carbon monoxide and found to be in a range of 6×10^{-3} to 2.29×10^{-3} and 2.87×10^{-2} to 1.08×10^{-2}, respectively. Since the values of α_l are very much less than 0.1 for both the gaseous reactants, gas-liquid mass transfer resistance can be assumed to be negligible.

3.4.3.4 Liquid-liquid mass transfer effect

The significance of liquid-liquid mass transfer resistance can be analyzed using a similar approach as used to analyze gas-liquid mass transfer, by comparing the initial rate of reaction with maximum rate of liquid-liquid mass transfer. Since the solubility of styrene in the aqueous phase is very less that that of hydrogen and carbon monoxide (Table 3.1 and 3.2), the liquid-liquid mass transfer is analysed for transport of styrene across the liquid-liuqid interface. The liquid-liquid mass transfer resistance is negligible if a factor α_2 defined as follows is less than 0.1.

$$\alpha_{2,D} = \frac{R_{exp}}{K_{ll}\, C_{D,aq}} \qquad 3.13$$

The overall liquid-liquid mass transfer coefficient for the transport of styrene from the organic phase to the aqueous phase, in terms of external and internal mass transfer coefficients can be written as

$$\frac{1}{k_{ll}} = \frac{1}{k_{l,aq}} + \frac{1}{k_{l,org}\, m_D} \qquad 3.14$$

Assuming that the dispersed phase is also moving with the same velocity as that of the continuous phase (i.e if there is negligible relative macro motion between the drops and the continuous phase) then $k_{l,aq}$ can be calculated by using Sherwood number, $sh = 2.0$, as follows.

$$k_{l,aq} = \frac{2\, D_{D,aq}}{d_{32}} \tag{3.15}$$

For micro droplets, Mehra (1988) has shown that $k_{aq} \sim k_{org}/3$ and the controlling resistance is decided by partition coefficient if styrene, m_D, if the diffusivities of styrene, $D_{D,aq} = D_{D,org}$. The diffusivities of styrene in aqueous (D_{Daq}) and in organic phase (D_{Dorg}) have been calculated at various temperatures using Wilke and Chang (1955) and are given in Table 3.7. Since the values of m_D are much greater than unity [m_D= 695 $(\text{kmol/m}^3)_{org}/(\text{kmol/m}^3)_{aq}$], the controlling resistance clearly lies in the aqueous phase. So the concentrations prevailing in the bulk organic phase are assumed to prevail at the liquid-liquid interface. Hence, the overall mass transfer coefficient given by Eq. (3.14) becomes

$$K_{ll} = a_{ll} \times k_{l,aq} \tag{3.16}$$

The drop diameter (d_{32}) (Figure A3) and specific interfacial area (a_{ll}) (Figure A2) were estimated as discussed in Appendix I. For agitation speed of 1300 rpm at which all experiments have been carried out, the values of α_2 were less than 0.1. The α_2 values calculated for catalyst loading experiments (at catalyst phase hold up of 0.4, and agitation speed of 1300 rpm) are shown in Table 3. 8. At the standard catalyst loading of 0.681 kmol/m^3, the α_2 were found to be less than 0.1 in the range of 363 to 383 K, indicating kinetic regime. At higher $HRh(CO)(TPPTS)_3$ concentration (1.25 and 2.5 kmol/m^3), α_2 values were found to be higher than 0.1 indicating marginal deviation from kinetic regime and hence a slight shift from first order dependence at higher Rh complex concentration (Figure 3.8).

Table 3.7 Diffusivities of styrene in aqueous and organic phase

Temperature, K	$D_{D,\ aq}$ x 10^9 m^3/s	$D_{D,\ org}$ x 10^9 m^3/s
363	3.1521	4.5667
373	3.7186	5.2137
383	4.4825	6.4488

Table 3.8 α_2 values at different catalyst loading

$HRh(CO)(TPPTS)_3$ concentration $kmol/m^3$	α_2 values at different temperatures		
	363 K	373 K	383 K
0.327	0.0149	0.0248	0.0397
0.681	0.0299	0.0494	0.0688
1.250	0.0559	0.0848	0.1073
2.510	0.0929	0.1335	0.1496

3.4.4. Kinetics of Hydroformylation of Styrene

In order to investigate the kinetics of hydroformylation of styrene using $HRh(CO)(TPPTS)_3$ complex catalyst in biphasic media, several experiments were carried out in the range of conditions given in Table 3.9.

Table 3.9 Range of conditions used for the kinetic studies

Concentration of catalyst $HRh(CO)(TPPTS)_3$, $(kmol/m^3)_{aq}$	0.33-2.51
Concentration of TPPTS $(kmol/m^3)_{aq}$	2.01
Concentration of Styrene $(kmol/m^3)_{org}$	0.58 – 2.33
Partial pressure of hydrogen, MPa	1.03 - 4.14
Partial pressure of carbon monoxide, MPa	1.03 – 4.14
Temperature, K	363 - 383
Solvent	Toluene-Water
Aqueous phase hold up, ε	0.4
Agitation speed, rpm	1300
Reaction volume, m^3	2.5×10^{-5}

3.4.4.1 Effect of catalyst concentration

For studying the effect of catalyst concentration on initial rate of hydroformylation, three cases were considered at constant catalyst phase hold up of 0.4.

a) Variation of $HRh(CO)(TPPTS)_3$ concentration (0.33-2.51 $kmol/m^3_{aq}$) without any excess TPPTS,

b) Variation of both $HRh(CO)(TPPTS)_3$ (0.33-2.51 $kmol/m^3_{aq}$) and TPPTS (0.49-3.79 $kmol/m^3_{aq}$) concentration keeping the Rh : TPPTS ratio constant and

c) Variation of $HRh(CO)(TPPTS)_3$ concentration (0.33-2.51 $kmol/m^3_{aq}$) with excess, but at a constant TPPTS concentration of 2.02 $kmol/m^3_{aq}$.

The results are shown in Figures 3.8, 3.9 and 3.10 respectively. The effect of catalyst concentration carried out without any excess of TPPTS at 363 K showed that the rate passed through a maximum. Similar trend was observed for catalyst concentration, keeping Rh : TPPTS ratio (1 : 6) constant (Figure 3.10) at 363 and 373 K showed. These trends are unusual, since it is excepted to show a linear dependence as per the mechanism. This observation could not be explained with the available data

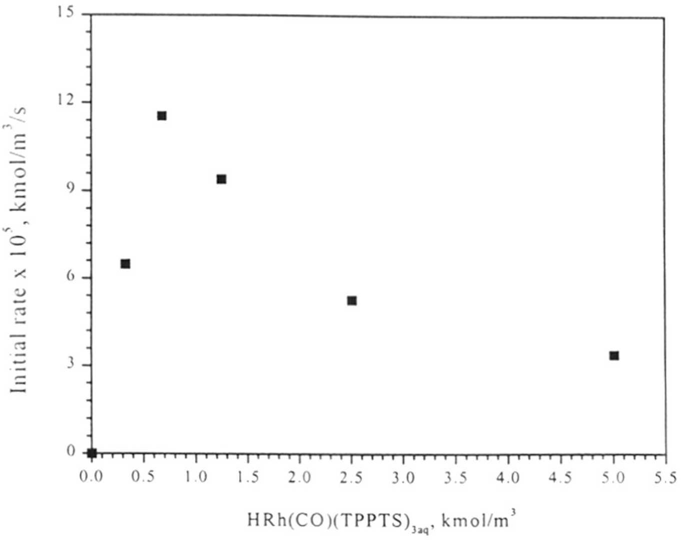


Figure 3.8: Effect of catalyst concentration on the initial rate of hydroformylation using without excess TPPTS at 363 K.

Reaction conditions:

Styrene$_{(org.)}$: 1.16 kmol/m^3; P_{H2}: 2.07 MPa; P_{CO}: 2.07 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3, Reaction time: 60 min.

The effect of catalyst concentration studied as in case (c) at various temperatures (363-383 K) showed that the rate varied linearly with catalyst concentration up to 1.2 kmol/m^3, at 363 K and 373 K. However, at 383 K, the reaction rate was not linear with increase in catalyst loading. Moreover, with further increase in catalyst concentration (>1.0 kmol/m^3), there was only marginal increase in the reaction rate at all temperatures studied and indicate mass transfer limitations at higher catalyst concentrations. In order to check the role of mass transfer effects a quantitative analysis of mass transfer effects was carried out as described in section 3.4.3. It was found that the α_2 values were higher than 0.1 (Table 3.7) at higher Rh complex concentration, which indicated that marginal effect of liquid-

liquid mass transfer of styrene across the aqueous-organic interface is likely to be the limiting factor.

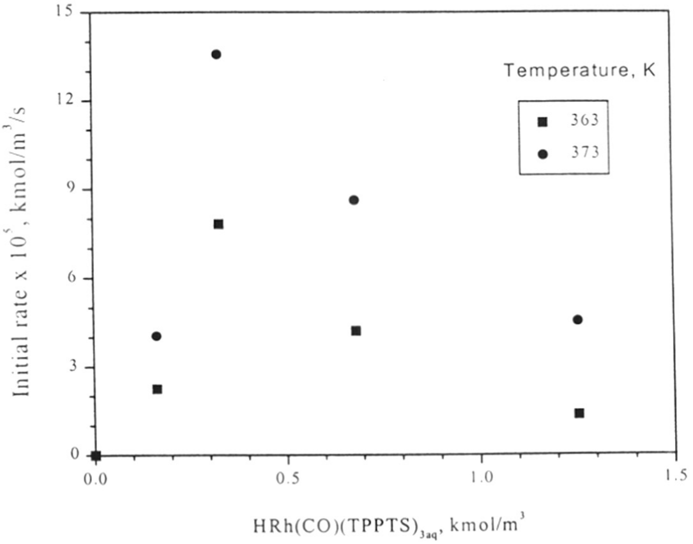


Figure 3.9: Effect of catalyst concentration (Rh:TPPTS=1:6) on the initial rate of hydroformylation

Reaction conditions:

Rh : TPPTS = 1: 6; Styrene$_{(org.)}$: 1.16 kmol/m^3; P_{H2}: 2.07 MPa; P_{CO}: 2.07 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Reaction time: 60 min. Total volume: 2.5x10^{-5} m^3

3.4.4.2 Effect of TPPTS concentration

The concentration of TPPTS in the aqueous phase plays a significant role in biphasic catalysis. The effect of TPPTS concentration in aqueous phase on the rate was studied in the range of 0.49 to 2.02 kmol/m$^3_{(aq)}$ concentration at constant HRh(CO)(TPPTS)$_3$ (i.e. in the Rh to TPPTS ratio of 1:3 to 1:6) at 363 K. The results are presented in Figure 3.11. It has been observed that rate of the reaction decreases with increase in TPPTS concentration. This effect is similar to the PPh_3 effect in homogeneous catalytic hydroformylation using HRh(CO)(PPh$_3$)$_3$ catalyst [Brown and Wilkinson (1970)].

Similar trends have been reported in hydroformylation of 1-octene using $[Rh(cod)Cl]_2$/TPPTS catalyst system in biphasic medium [Bhanage (1995)]. As shown in Figure 3.12, the formation of species C_2 from C_1 is likely to be reduced leading to loss of active catalytic species and hence a drop in activity [Evans et al. (1968)] is observed.

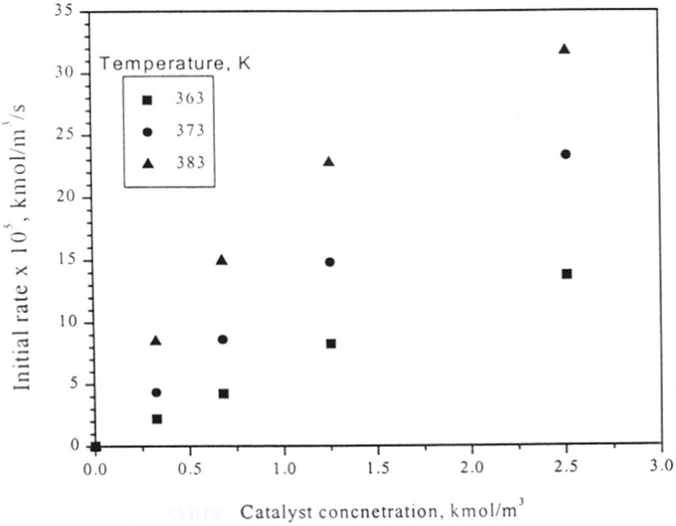


Figure 3.10 Effect of catalyst concentration on the initial rate of hydroformylation styrene using $HRh(CO)(TPPTS)_3$.

Reaction conditions:
Styrene: 1.16 kmol/$m^3_{(org.)}$; TPPTS: 2.02 kmol/$m^3_{(aq.)}$;P_{CO}: 2.07 MPa; P_{H2}: 2.07 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3, Reaction time: 60 min.

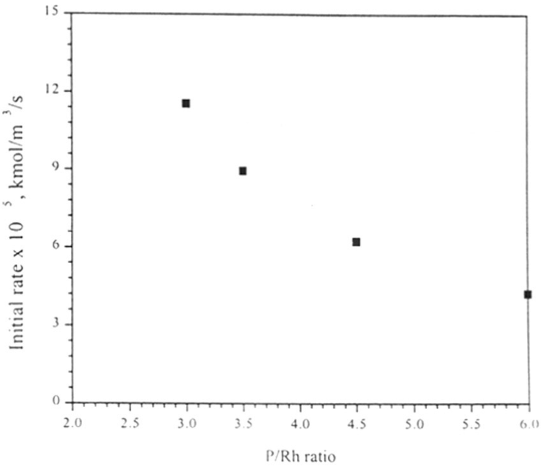


Figure 3.11 Effect of P/Rh ratio on initial rate of hydroformylation of styrene using $HRh(CO)(TPPTS)_3$ at 363K.

Reaction conditions:
Styrene$_{(org.)}$: 1.16 kmol/m^3; P_{H2}: 2.07 MPa; P_{CO}: 2.07 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total volume: 2.5×10^{-5} m^3, Reaction time: 60 min.

3.4.4.3 Effect of partial pressure of hydrogen (P_{H2})

The effect of partial pressure of hydrogen on the rate of hydroformylation of styrene was investigated at a constant CO partial pressure of 2.07 MPa, styrene concentration of 1.16 kmol/m^3, 0.681 kmol/m^3 of $HRh(CO)(TPPTS)_3$ and TPPTS concentration of 2.02 kmol/m^3. The results are shown in Figure 3.13. The rate of reaction was found to be first order with P_{H2}. As per the reported mechanism of hydroformylation of olefins, the oxidative addition of hydrogen to the acyl carbonyl rhodium species is the rate limiting step, leading to increase in rates at higher partial pressures of hydrogen.

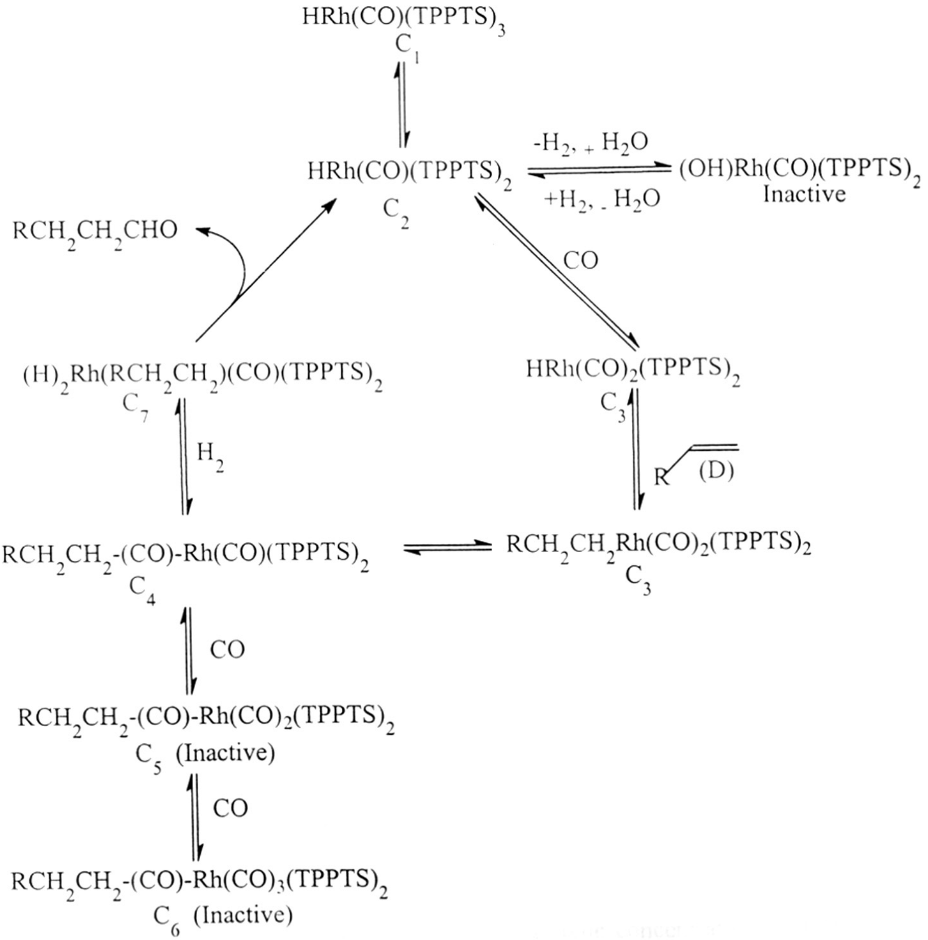


Figure 3.12 Mechanism for hydroformylation of olefins using water soluble $HRh(CO)(TPPTS)_3$

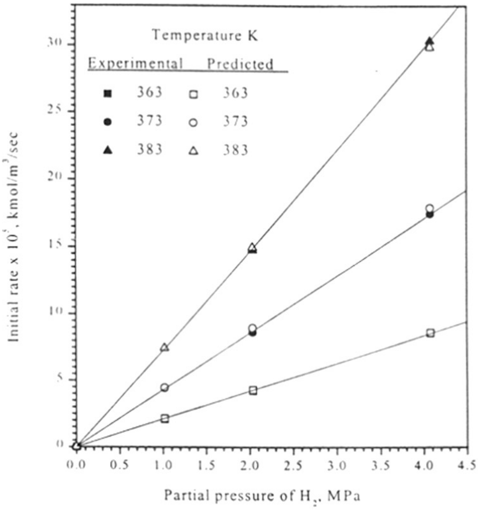


Figure 3.13 Effect of hydrogen partial pressure on the initial rate of hydroformylation styrene using $HRh(CO)(TPPTS)_3$

Reaction conditions:
$HRh(CO)(TPPTS)_{3(aq)}$: 0.681 $kmol/m^3$; $TPPTS_{(aq.)}$: 2.02 $kmol/m^3$; $Styrene_{(org.)}$: 1.16 $kmol/m^3$; P_{CO}: 2.04 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3, Reaction time: 60 min.

3.4.4.4 Effect of partial pressure of CO (P_{CO})

The effect of P_{co} on the rate of hydroformylation of styrene was studied at a constant hydrogen partial pressure of 2.07 MPa, styrene concentration of 1.16 $kmol/m^3$, $HRh(CO)(TPPTS)_3$ complex concentration of 0.681 $kmol/m^3$ and TPPTS concentration of 2.02 $kmol/m^3$. The results are shown in Figure 3.14. Interestingly the rate was found to be first order with CO partial pressure unlike in homogeneously catalysed hydroformylation of styrene in organic medium using $HRh(CO)(PPh_3)_3$ catalyst (see Chapter 2, section 2.3.2) where the rate passes through a maxima. This is because, the solubility of CO in organic medium is much higher than the solubility in the aqueous phase used in the biphasic system (Concentration of CO varies from 6.45 x 10^{-3} $kmol/m^3$ to 2.55 x 10^{-2} $kmol/m^3$ in the aqueous medium whereas in the organic medium it varies from 3.26 x 10^{-2} kmol/m^3 to 0.137 kmol/m^3). This increased concentration of CO leads to formation of inactive dicarbonyl acyl Rh species [$(RCO)Rh(CO)_2(PPh_3)_2$] (see reaction mechanism, Figure 2.9 in Chapter 2), which results in rate inhibition.

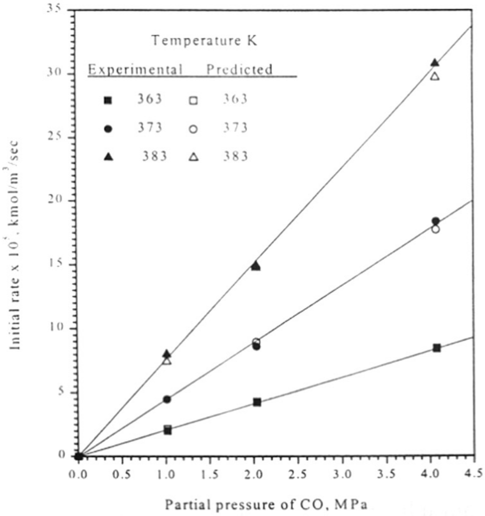


Figure 3.14 Effect of carbon monoxide partial pressure on the initial rate of hydroformylation styrene using $HRh(CO)(TPPTS)_3$

Reaction conditions:
$HRh(CO)(TPPTS)_{3(aq)}$: 0.681 kmol/m^3; $TPPTS_{(aq.)}$: 2.02 kmol/m^3; $Styrene_{(org.)}$: 1.16 kmol/m^3; P_{H2}: 2.07 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total liquid volume: 2.5 x10^{-5} m^3; Reaction time: 60 min.

In the present case, the concentration of dissolved CO in the aqueous phase was much less than that in the organic phase and hence, the formation of inactive dicarbonyl and tricarbonyl species is expected to be minimized. Therefore, this difference in trends is not truly due to any change in the reaction mechanism. In an earlier study by Bhanage (1995), also observed first order dependence at lower partial pressures of CO, and zero order at higher partial pressures of CO in case of 1-octene hydroformylation. Deshpande et al. (1996) have observed CO inhibition at higher partial pressures of CO (~0.5 MPa) for hydroformylation of 1-octene in biphasic system in presence of a co-solvent ethanol. The addition of ethanol to the aqueous phase increases solubility of CO and results into formation of inactive dicarbonyl and tricarbonyl Rh acyl species (see Figure 3.12) at higher partial pressures of CO.

3.4.4.5 Effect of styrene concentration

The effect of concentration of styrene on the rate of hydroformylation of styrene was studied at a total pressure of 4.14 MPa ($CO:H_2 = 1:1$), $HRh(CO)(TPPTS)_3$ complex concentration of 0.681 $kmol/m^3$ and TPPTS concentration of 2.02 $kmol/m^3$. The results are shown in Figure 3.15. Here, the rate was found to be first order with respect to styrene concentration. Interestingly this observation is different from that observed in the homogeneous hydroformylation of styrene using $HRh(CO)(PPh_3)_3$ wherein a zero order dependence was observed (Figure 2.8 in chapter 2). The addition of styrene to the active dicarbonyl species is an equilibrium reaction (Eq 2.8 in the simplified catalytic mechanism shown in Figure 2.10 in Chapter 2) and the equilibrium has been attained under the concentration range of styrene studied and hence a zero order. In the present situation the concentration of styrene in the aqueous phase is very much less than that in the case of single phase homogeneous reactions. Here again, the addition of styrene to the active catalytic species in the catalytic cycle is an equilibrium reaction, however it is very likely that the equilibrium is not attained under the styrene concentration in the range available in the aqueous medium. (Concentration of styrene varies from 8.37×10^{-4} $kmol/m^3$ to 3.41×10^{-3} $kmol/m^3$ in the aqueous medium where as that in the organic medium it varies from

0.92 to 6.89 kmol/m^3). Hence this effect is not considered for the calculation for the CO and H_2 dissolved in water.

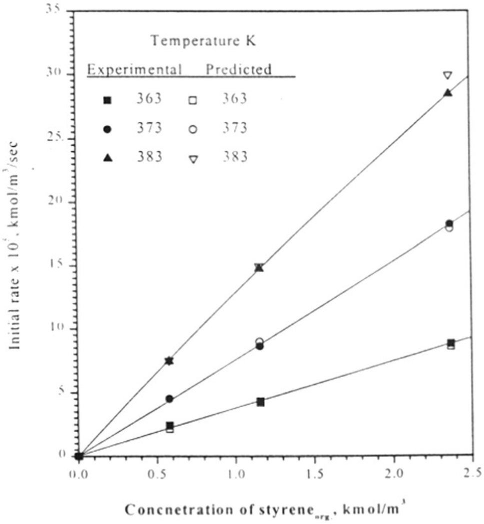


Figure 3.15 Effect of styrene concentration on the initial rate of hydroformylation styrene using $HRh(CO)(TPPTS)_3$

Reaction conditions:

$HRh(CO)(TPPTS)_{3(aq)}$: 0.681 kmol/m^3; $TPPTS_{(aq.)}$: 2.02 kmol/m^3; P_{H2} : 2.07 MPa; P_{CO}: 2.07 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3, Reaction time: 60 min.

3.4.4.6 Kinetic Modeling

For the purpose of kinetic modeling, only those experiments were chosen wherein the criteria given in Eqs. 3.11, 3.12 and 3.13 were satisfied. Mainly the data at higher aqueous phase hold up and higher catalyst concentrations were excluded. Experiments were carried out at a constant catalyst concentration of 0.681 kmol/m^3 of the $HRh(CO)(TPPTS)_3$ complex and 2.20 kmol/m^3 of TPPTS and at aqueous phase hold up of 0.4.

The mechanism of hydroformylation is well known (see Figure 3.12), and hence, it was more appropriate to consider the molecular level approach for kinetic modeling of water soluble catalytic hydroformylation instead of the empirical rate forms considered earlier [Purwanto and Delmas (1995)]. The mechanism shown in Figure 3.12 can be simplified as given below.

$$\underset{C_1}{\mathrm{HRh(CO)(TPPTS)_3}} \xrightleftharpoons{K_1} \underset{C_2}{\mathrm{HRh(CO)(TPPTS)_2}} + \underset{L}{\mathrm{TPPTS}} \tag{i}$$

$$\underset{B}{\mathrm{CO}} + \underset{C_2}{\mathrm{HRh(CO)(TPPTS)_2}} \xrightleftharpoons{K_2} \underset{C_3}{\mathrm{HRh(CO)_2(TPPTS)_2}} \tag{ii}$$

$$\underset{C_3}{\mathrm{HRh(CO)_2(TPPTS)_2}} + \underset{D}{\mathrm{Olefin}} \xrightleftharpoons{K_3} \underset{C_4}{\mathrm{HRh(acyl)(CO)(TPPTS)_2}} \tag{iii}$$

$$\underset{C_4}{\mathrm{HRh(acyl)(CO)(TPPTS)_2}} + \underset{A}{\mathrm{H_2}} \xrightarrow{k} \underset{C_2}{\mathrm{HRh(CO)(TPPTS)_2}} + \underset{P}{\mathrm{aldehyde}} \tag{iv}$$

The intra-molecular rearrangement steps were considered as fast. Since, CO inhibition was not observed in the present investigation, the steps involving formation of dicarbonyl and tricarbonyl species were assumed to be negligible and hence not considered in deriving the rate models. Herrmann et al. (1990) have shown that $\mathrm{HRh(CO)(TPPTS)_3}$ in aqueous medium can form $\mathrm{HO\text{-}Rh(TPPTS)_2(CO)}$, a species in equilibrium with the $\mathrm{HRh(CO)(TPPTS)_3}$. However, it has also been shown that under hydroformylation conditions, the hydroxy species is quantitatively reconverted to $\mathrm{HRh(CO)(TPPTS)_3}$ and does not interfere the hydroformylation reaction. In this work the following cases were considered for deriving the rate models.

- ***Model I: Addition of hydrogen as rate limiting step***

The step no. (iv) i.e. the addition of H_2 to acyl rhodium carbonyl species (C_4) was considered as a rate determining step, as shown below:

$$C_1 \overset{K_1}{\rightleftharpoons} C_2 + C_L \qquad 3.17$$

$$C_2 + B \overset{K_2}{\rightleftharpoons} C_3 \qquad 3.18$$

$$C_3 + D \overset{K_3}{\rightleftharpoons} C_4 \qquad 3.19$$

$$C_4 + A \xrightarrow{k} C_2 + P \qquad 3.20$$

The rate of reaction is then given by

$$r = k\, C_4\, C_A \qquad 3.21$$

The concentration of C_4 is unknown, but the total concentration of the catalyst $HRh(CO)(TPPTS)_3$ is known and is given as:

$$C = C_1 + C_2 + C_3 + C_4 \qquad 3.22$$

where C is the amount of catalyst $HRh(CO)(TPPTS)_3$ charged. The concentrations of C_1 to C_4 can be expressed in terms of C_4 through the equilibrium constants K_1, K_2, K_3 for the Eqs. 3.17, 3.18 and 3.19 and hence, C_4, which is substituted in equation Eq 3.21 to give the following rate equation:

$$r = \frac{k\, K_1 K_2 K_3\, C C_A\, C_B\, C_D}{C_L + K_1 + K_1 K_2 C_B + K_1 K_2 K_3 C_B C_D} \qquad 3.23$$

At constant concentration of the catalyst, Eq 3.23 becomes

$$r = \frac{\beta_1\, C_A C_B C_D}{1 + \beta_2\, C_B + \beta_3 C_B C_D} \qquad 3.24$$

$\beta_1 = kK_1K_2K_3C/K'_1$; $K'_1 = K_1 + C_L$; C_L = Conc. of dissociated TPPTS from Rh complex
$\beta_2 = K_1K_2/K'_1$; $\beta_3 = K_1K_2K_3/K'_1$

$C_A = P_A \times H_{A(aq)}$; $C_B = P_B \times H_{B(aq)}$; $C_E = m_D\, C_{D,\,org}$

- ***Model II: Addition of olefin as rate limiting step***

In certain cases, addition of olefins to the active Rh species (C_2) also has been found to be the rate determining step [Moser et al. (1987); Deshpande et al. (1996)]. In this form of the rate model, addition of olefin to the species HRh $(CO)_2(TPPTS)_2$ (step (iii) in simplified mechanism) was considered as a rate limiting step.

The rate is then given by:

$$r = kC_3C_D \qquad 3.25$$

Substituting for C_3 in terms of C, we obtain

$$r = \frac{k\,K_1\,K_2\,C\,C_A\,C_B\,C_D}{1 + C_P + K_3\,C_AC_L + K_1\,K_3C_A + K_1\,K_2\,K_3\,C_AC_B} \qquad 3.26$$

C is the catalyst concentration; $C_A = P_A \times H_{A(aq)}$; $C_B = P_B \times H_{B(aq)}$; $C_E = m_D\, C_{D,\,org}$

Where, H_A and H_B represent the Henry's Constants and P_A and P_B represent the partial pressures of H_2 and CO; of respectively; m_E represent the partition coefficient of styrene in toluene-water system

The presence of product concentration term in the denominator indicates an influence of product concentration in the reaction rate, which was not observed experimentally, hence this model was not considered for the analysis of rate data.

Rate model (Eq 3.24) based on H_2 addition to the acyl species as a rate-determining step was used to estimate the rate parameters, using a non-linear least square regression analysis to fit the rate data and to obtain the best-fit parameters. For this purpose, an optimization program based on Marquart's method was used. The model parameters were estimated by using the same procedure as described in Chapter 2 (section 2.3.3). The RR values for the model were scattered and did not show any regular trends with respect to any parameter, thus confirming the validity of the model. The agreement of experimental and predicted rates with different parameters such as hydrogen and carbon monoxide partial pressures and styrene concentration are shown in Figure 3.13, 3.14 and 3.15 respectively. The error between the predicted and observed rate data was found to be ± 5%.

The rate and equilibrium parameters, k and K_3 calculated from β_1 and β_3 for different temperatures are presented in Table 3.10, however it was not possible to separate K_1, K_2 and C_L. From the temperature dependence of the rate constants (Figure 3.16), the activation energy was found to be 102.79, kJ/mol.

Table 3.1 Rate constants evaluated from the rate model

Temperature	k, m^3/kmol/s	β_2	K_3, m^3/kmol	ϕ_{min} x 10^{11}
363	0.58	0.80	402.57	1.50
373	1.68	0.42	523.37	14.74
383	3.42	0.21	831.21	39.80

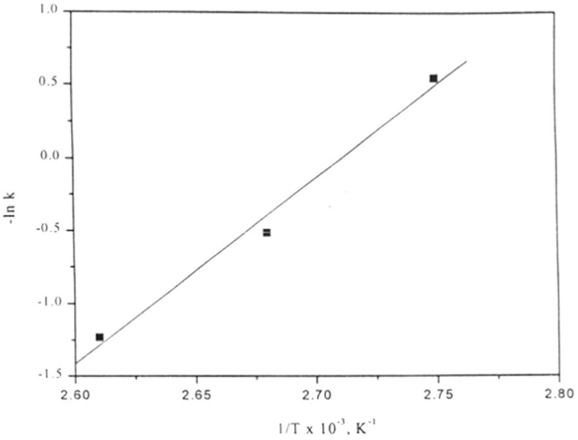


Figure 3.16 Temperature dependence of rate constant

Even though the rate model derived is complex in nature, with C_A and C_B terms in the denominator, it explains the trends observed, because the second and third terms in the denominator varied from 0.01-0.02 and from 0.007-0.01respectively. Therefore, the overall denominator becomes nearly equal to 1 reducing the rate equation to

$$r = \beta C_A C_B C_D \qquad 3.27$$

The first order dependence of C_A, C_B and C_D can be easily explained using the above equation.

3.5 Effect of co-solvents

One of the major disadvantages of biphasic catalysis using water-soluble catalysts has been the poor rate of reaction, especially for higher olefins, which have very low solubility in the aqueous phase. Several approaches have been proposed to enhance the reaction rates in biphasic medium as discussed in detail in Chapter 1 (section 1.3.1.3).

Abatjoglou et al. (1993) of Union Carbide has used N-methylpyrrolidone (NMP) in a process for separation of the catalyst from the aldehyde mixture in a non-aqueous hydroformylation reaction. They have demonstrated that when a mixture of monosulfonated triphenylphosphine sodium salt (TPPMS-Na) ligand, NMP (as the polar organic solubilizing agent) and a mixture of unrefined nonanal aldehyde, nonanal dimer and 1-octene (in the ratio of 6:3:1 by weight) along with little amount of rhodium dicarbonyl acetyacetonate complex (0.378g) becomes one phase on heating to 100°C. It was found that the mixture separated into two liquid phases while cooling. It was found that 92% by weight of rhodium and 94% (by weight) of the TPPMS-Na was separated to the polar NMP phase and more than 90% of the organic products were retained in the non-polar organic phase. When the same experiment was repeated with 10% of water, almost all rhodium and TPPMS-Na was extracted into the polar phase and there was no loss of organic reagents into the NMP phase. This result has motivated us to apply the use of NMP as a co-solvent in the hydroformylation of styrene using water soluble $HRh(CO)(TPPTS)_3$ catalyst in a biphasic medium. However, several other aspects e.g. formation of side products, product selectivity and increase in the reaction rates need to be investigated and compared with other co-solvents.

In the present study, hydroformylation of styrene using several co-solvents such as N-methylpyrrolidone-2 (NMP), ethanol (ETOH), methylethyl ketone (MEK) and γ-butyrolactone (GBL) was carried out and results are shown in Figure 3.17. In order to compare the enhancement in the reaction rate, an experiment was also done at the same conditions without using a co-solvent at 373 K. NMP, ETOH and GBL was miscible with water in any proportion and a 50% (v/v) co-solvent-water mixture was used as the aqueous phase in the reactions. In case of MEK, only 30% (v/v) of MEK was used as the co-solvent due to solubility limitation of MEK in water. The results in Figure 3.17 indicated that NMP showed similar rate enhancement (7.3 times) as that of ethanol (8 times). In this study NMP was selected as the co-solvent for the further studies, since it showed 100% selectivity towards the aldehyde products. In case of ethanol as a co-solvent only 80% selectivity to aldehydes was observed and the remaining 20% was acetals, formed by the condensation of ethanol and aldehyde products.

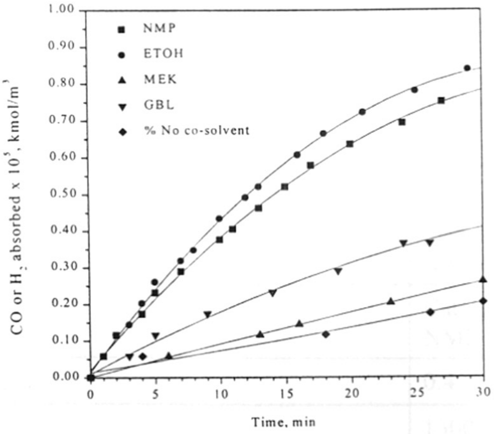


Figure 3.17 Effect of various co-solvents on the rate of hydroformylation styrene at 373K

Reaction conditions:
$HRh(CO)(TPPTS)_{3(aq)}$: 0.681 kmol/m^3; $TPPTS_{(aq.)}$: 2.02 kmol/m^3; Styrene $_{(org.)}$: 1.16 kmol/m^3; P_{CO}: 2.04 MPa; P_{H2}: 2.04 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water-co-solvent; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3, Reaction time: 30 min.

3.5.1 Kinetics of styrene using NMP as a co-solvent

Preliminary experiments showed that the mass balance of H_2, CO and styrene consumed and the total amount of aldehydes formed were in good agreement with stoichiometry of hydroformylation. A 50% (v/v) NMP-water was used as the catalyst phase for all the kinetic experiments. In a typical experiment $HRh(CO)(TPPTS)_3$ complex concentration of 0.68 $kmol/m^3$, TPPTS concentration of 2.02 $kmol/m^3$, styrene concentration of 1.16 $kmol/m^3$ and total pressure of 4.14 MPa of 1:1 $CO:H_2$, at catalyst phase hold up of 0.4 were used.

Table 3.11 Range of conditions used for the kinetic studies

Concentration of catalyst $HRh(CO)(TPPTS)_3$, ($kmol/m^3$)	0.33-2.51
Concentration of TPPTS ($kmol/m^3$)	2.01
P/Rh ratio (for all experiments except catalyst concentration effect)	6
Concentration of Styrene ($kmol/m^3$)	0.58 – 4.65
Partial pressure of hydrogen, MPa	1.03 - 4.14
Partial pressure of carbon monoxide, MPa	1.03 – 4.14
Temperature, K	373
Organic phase	Toluene, styrene and reaction products
Aqueous Phase	Catalyst and water-NMP
Aqueous phase hold up, ε	0.4
Agitation speed, rpm	1300
Reaction volume, m^3	2.5×10^{-5}

The main objective of the experiments with co-solvents was to study the rate enhancement, formation of side products, selectivity pattern of the products in the biphasic medium with NMP as a co-solvent and compare the results with those obtained in normal aqueous biphasic medium. Hence, experiments were done at a temperature of 373 K. Visual observations of the reaction mixtures in a glass reactor at 373 K showed that, the reaction mixture does not become homogeneous. The effect of catalyst phase recycle was also investigated and showed comparable activity in the recycle experiments (Figure 3.18). Some more experiments were carried out with recycle of the organic phase separated after the reaction with addition of fresh styrene showed no activity for hydroformylation. This confirmed negligible leaching of rhodium catalyst in the organic phase. In the range of conditions investigated, the only products formed were the isomeric aldehydes (2PPD and 3PPD), that were confirmed by comparing GC analysis of standard samples. No hydrogenation or isomerization or condensation products were observed in these experiments. The results of a typical experiment showed 70-75% conversion in 30 minutes, with an improved selectivity towards the desired branched isomeric aldehyde 2PPD up to 80-85% (The selectivity towards 2PPD was only 55-60% under biphasic conditions without co-solvent)

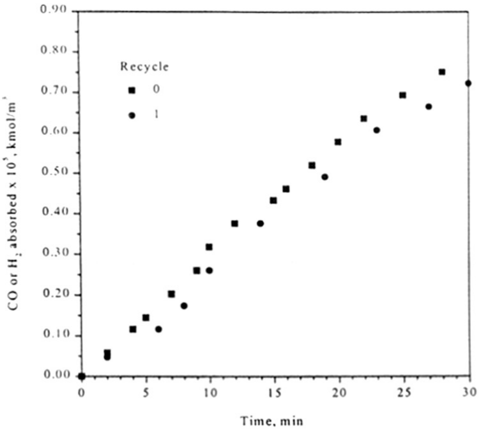


Figure 3.18 Effect of recycle using NMP as co-solvent on the rate of hydroformylation styrene at 373K

Reaction conditions:
HRh(CO)(TPPTS)$_{3(aq)}$: 0.681 kmol/m^3; TPPTS$_{(aq.)}$: 2.02 kmol/m^3; Styrene $_{(org.)}$: 1.16, kmol/m^3; P$_{CO}$: 2.04 MPa; P$_{H2}$: 2.04 MPa; Agitation speed: 1300 rpm; Solvent: toluene-50% NMP-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5}, m^3, Reaction time: 30, min

Experiments at various agitation speeds showed that the rate is independent of agitation speed beyond 700 rpm. Therefore, all experiments were carried out at 1300 rpm in order to ensure kinetic regime. Experiments at different catalyst phase hold up showed a continuous increase in the rate as shown in Figure 3.19. Such a trend is expected with increase in catalyst phase hold up, because the total amount of the catalyst present in the system increases.

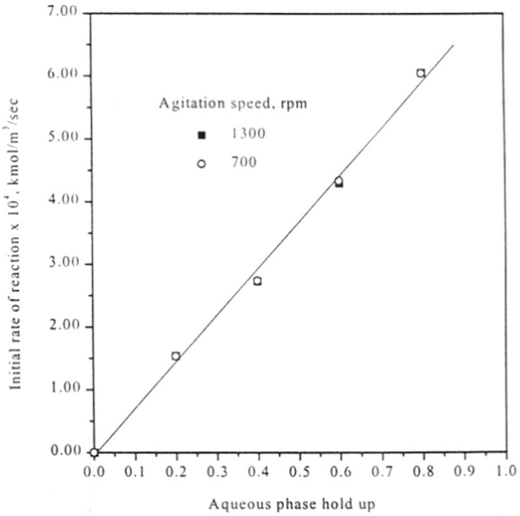


Figure 3.19 Effect of aqueous phase hold up on the initial rate of hydroformylation styrene using NMP as a co-solvent at 373K

The effect of catalyst concentration on the rate of hydroformylation is shown in Figure 3.20. The experiments were carried out at various catalyst concentrations (0.33-2.51 kmol/m^3). The other experimental conditions are described in Table 3.11. The rates showed a first order dependence with respect to catalyst loading indicating chemically controlled regime. However, under similar conditions (at a temperature of 373 K), the rate of reaction for experiments without using a co-solvent (see Figure 3.7) were not increased with first order dependence, specially at catalyst loading greater than 1.21 kmol/m^3. This was essentially because of likely transport limitation of styrene across the liquid-liquid interface ($\alpha_2 > 0.1$, see Table 3.7). But when co-solvent was added to such a system, the solubility of styrene in the aqueous phase significantly increases (22.7 times) and the reaction operates in a chemically controlled regime.

The effect of hydrogen partial pressure on the rate of reaction for a range of 1.03-4.14 MPa is shown in Figure 3.21. A first order dependence of reaction rate was observed with respect to hydrogen partial pressure and indicates that the addition of hydrogen to acyl rhodium is the rate determining step. Similar results were observed for hydrogen partial pressure in case of hydroformylation experiments without co-solvents and effects have already been discussed.

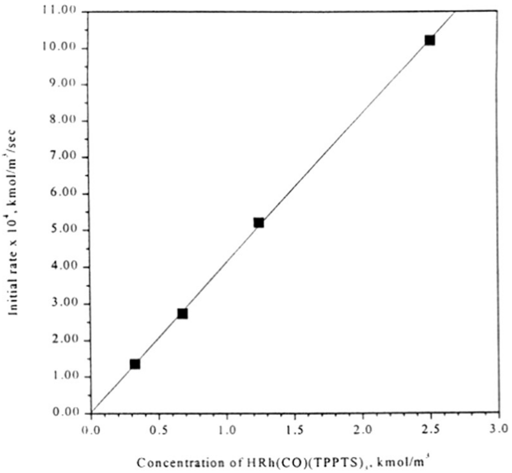


Figure 3.20 Effect of catalyst concentration on initial rate of hydroformylation of styrene using NMP as a co-solvent at 373K

Reaction conditions
Styrene $_{(org.)}$: 1.16 kmol/m^3; TPPTS: 2.02 kmol/m^3, P_{CO}: 2.04 MPa; P_{H2}: 2.04 MPa; Agitation speed: 1300 rpm; Solvent: toluene-50% NMP-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3, Reaction time: 30 min.

The experiments were done with CO partial pressure varying from 1.03 to 4.14 MPa and the results are shown in Figure 3.22. Effect of partial pressure of CO showed a fractional order dependence on the reaction rate unlike the first order dependence observed in case of hydroformylation experiments without any co-solvent (Figure 3.14). This is because of the increased solubility of CO in NMP-water mixture than in pure water. Purwanto and Delmas (1995) and Desphande et al. (1996) have observed a strong inhibition in rate of hydroformylation of 1-octene in presence of ethanol as a co-solvent at higher partial pressures of CO (~ 0.5 MPa). Homogenous hydroformylation of styrene using $HRh(CO)(PPh_3)_3$ also showed a inhibition in the reaction rate and has been discussed in detail in Chapter 2 (section 2.3.2). In the present case, the difference in the reaction trends is due to the difference in solubility of CO in the catalyst phase. CO inhibition was not observed because of the lower concentration available in the catalyst phase may not be sufficient to form the inactive di and tri carbonyl species. Here, a fractional order dependence was observed unlike the first order with CO, in the normal biphasic system (Figure 3.14) in the absence of a co-solvent. This is due to the enhanced solubility of CO in the catalyst phase in presence of NMP as co-solvent. At increased concentration of CO a fraction order is expected as the rate equation developed (Eq 3.24) based on the hydroformylation mechanism

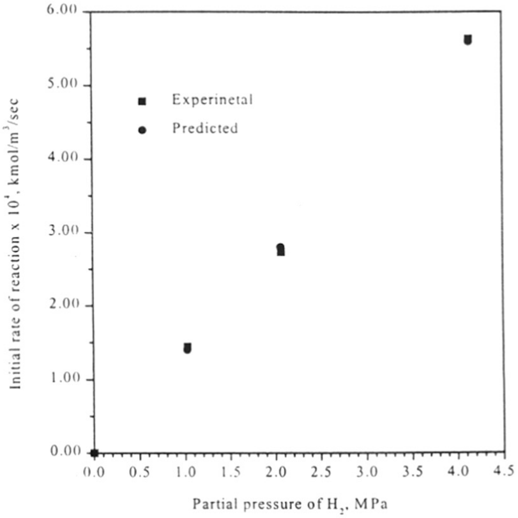


Figure 3. 21 Effect of hydrogen partial pressure on initial rate of hydroformylation of styrene using $HRh(CO)(TPPTS)_3$

Reaction conditions:
$HRh(CO)(TPPTS)_{3(aq)}$: 0.681 kmol/m^3; $TPPTS_{(aq.)}$: 2.02 kmol/m^3; $Styrene_{(org.)}$: 1.16 kmol/m^3; $P_{CO:}$ 2.04 MPa; Agitation speed: 21.67 Hz; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3, Reaction time: 60 min; Temperature 373 K.

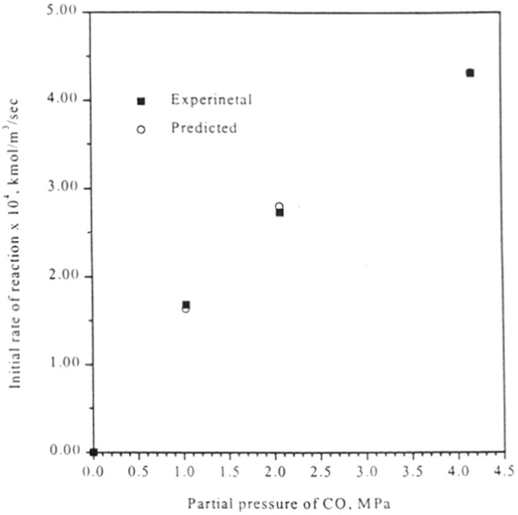


Figure 3.22 Effect of carbon monoxide partial pressure on initial rate of hydroformylation of styrene using $HRh(CO)(TPPTS)_3$

Reaction conditions:
$HRh(CO)(TPPTS)_{3(aq)}$: 0.681 kmol/m^3; $TPPTS_{(aq.)}$: 2.02 kmol/m^3; $Styrene_{(org.)}$: 1.16 kmol/m^3; P_{H2}: 2.04 MPa; Agitation speed: 21.67 Hz; Solvent: toluene-water; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3, Reaction time: 60 min. Temperature 373 K.

Effect of styrene concentration in the range of 0.58 to 4.65 kmol/m^3, on the initial rate of hydroformylation is shown in Figure 3.23. The rate of reaction was found to be varying with first order dependence and then tends to zero order with respect to styrene concentration after a particular concentration. In homogeneous hydroformylation of styrene a zero order dependence was observed (see Figure 2.8 of Chapter 2) because the concentration of styrene in the reaction medium was in the regime of zero order dependence of styrene concentration in the present case. In the biphasic system without co-solvent a first order dependence was observed due to the very low concentration of styrene in the aqueous phase (in comparison with a system with co-solvent) and the particular styrene concentration in reaction phase may not have reached under conditions studied.

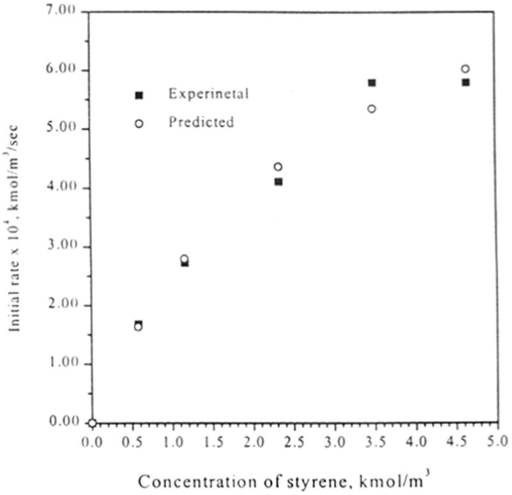


Figure 3.23 Effect of styrene concentration on the initial rate of hydroformylation styrene using $HRh(CO)(TPPTS)_3$

Reaction conditions:
$HRh(CO)(TPPTS)_{3(aq)}$: 0.681 kmol/m^3; $TPPTS_{(aq.)}$: 2.02 kmol/m^3; $P_{H2:}$ 2.04 MPa; $P_{CO:}$ 2.04 MPa; Agitation speed: 1300 rpm; Solvent: toluene-water-NMP; Aqueous phase hold-up: 0.4; Total volume: 2.5 x10^{-5} m^3, Reaction time: 60 min.; Temperature 373 K.

In order to predict the reaction rate using a rate model, knowledge of solubility of H_2, CO and styrene in 50% NMP-water was essential and hence was determined experimentally at 373 K [see chapter 2 (section 2.3.1)]. The partition coefficient of styrene in toluene water-NMP system was also determined experimentally. The Henry's constants for H_2 and CO in 50% NMP-water was found to be 6.26 MPa m^3/kmol and 7.78 MPa m^3/kmol respectively. Partition coefficient for styrene was found to be 3.28475 x 10^{-2}. The kinetic model derived for the biphasic hydroformylation assuming hydrogen addition as the rate-determining step (Eq 3.24) was used to predict the reaction rates. Using these values in the rate model, Marquate's optimization method was used to predict the observed rates and found to represent the data exceedingly well (see Figure 3.21-3.23). The optimized constants were found to be as $\beta_1 = 74.07616$; $\beta_2 = 0.8277128$; $\beta_3 = 709.152$; with a ϕ_{min} of 1.05×10^{-8}.

3.6 Conclusions

The kinetics of hydroformylation of styrene has been investigated in a biphasic media using HRh(CO)(TPPTS)$_3$. The effect of different parameters like concentration of catalyst precursor, TPPTS, styrene, partial pressures of CO and hydrogen were investigated in a temperature range of 363 K and 383 K. The rate was found to be first order with respect to catalyst loading up to a concentration of 1.21 kmol/m^3. At higher catalyst concentrations, the rate was found to be limited by the transport of styrene form organic phase to aqueous phase. Rate was found to be first order with partial pressure of hydrogen, indicating that the addition of hydrogen to acyl rhodium species is the rate-limiting step. Unlike in the case of hydroformylation in homogeneous medium, rate was found to be first order with respect to styrene concentration and carbon monoxide partial pressure. This trend was explained on the basis of lower ranges of concentrations of CO and styrene in the present case. The following rate model based on a mechanistic approach has been proposed which was found to represent the data satisfactorily.

$$r = \frac{\beta_1 C_A C_B C_D}{1 + \beta_2 C_B + \beta_3 C_B C_D}$$

Activation energy of the reaction was found to be 107.79 kJ/mol.

Effect of various co-solvents on the enhancement of reaction rate has been studied. N-Methyl pyrrolidone-2 was found to be a better co-solvent than ethanol, due to its unreactive nature with the aldehyde products. In presence of NMP as a co-solvent, the rate of reaction was found to increase by seven times than that in the absence of co-solvent. In order to compare the reaction trends in presence of NMP, effect of catalyst and styrene concentration, partial pressures of H_2 and CO have been studied at 373 K. The rate was found to be first order with catalyst and hydrogen partial pressure. CO showed a fractional order dependence unlike the substrate inhibited kinetics showed in presence of ethanol as a co-solvent [Deshpande et al. (1996)]. The rate was found to be first order with styrene up to a concentration of 3.49 $kmol/m^3{}_{org}$ and then zero order beyond this concentration. The difference in reaction trends was due to the difference in solubility of styrene and CO in presence of a co-solvent and not due to the change in mechanism. A rate equation used for the biphasic hydroformylation based on the same mechanism found to explain the observed reaction rates exceedingly well.

Notations

a_{ll}	specific liquid-liquid interfacial area (m^2/m^3)
b	slope as defined in Eq 3.9
C	total concentration of the catalyst in aqueous phase, $kmol/m^3$
C_1, C_2, C_3, C_4 C_5, C_6, C_7	concentration of species $HRh(CO)(TPPTS)_3$, $HRh(CO)(TPPTS)_2$, $HRh(CO)_2(TPPTS)_2$,$Rh(alkyl)(CO)(TPPTS)_2$, $Rh(acyl)(CO)_2(TPPTS)_2$, $Rh(acyl)(CO)_3(TPPTS)_2$, $(H_2)Rh(acyl)(CO)(TPPTS)_2$[defined by eqns. (3) to (6) or (11) to (14)], respectively, $kmol/m^3$
C_L, C_P	concentration of ligand and products in aqueous phase, $kmol/m^3$
$C_{A.org}$, $C_{B.org}$, $C_{D.org}$	concentration of H_2, CO, and styrene in organic phase, respectively ($kmol/m^3$)
$C_{A.aq}$, $C_{B.aq}$, $C_{D.aq}$	concentration of H_2, CO, and styrene in aqueous phase, respectively ($kmol/m^3$)
$C_{A.org}$, $C_{B.org}$, $C_{D.org}$	Equilibrium concentration of H_2, CO, and styrene in the bulk organic phase, respectively ($kmol/m^3$)
d_{32}	sauter mean diameter (m)
d_{max}	maximum stable drop diameter (m)
D	impeller diameter (m)
D_A, D_B, D_E	diffusivity of H_2, CO and 1-octene, respectively, in aqueous phase (m^2/s)
H_A	Henry's constant for hydrogen-toluene system, $m^3.MPa/kmol$
H_B	Henry's constant for carbon monoxide-toluene system, $m^3.MPa/kmol$
p_A	partial pressure of hydrogen, MPa
p_B	partial pressure of carbon monoxide, MPa
k	reaction rate constant as defined in the text
$k_{l,aq}$	liquid-liquid mass transfer coefficient (aqueous phase)
$k_{l,org}$	liquid-liquid mass transfer coefficient (organic phase)
k_o	overall mass transfer coefficient defined by eqn. (2)
k_{ll}	mass transfer coefficient defined by Eq 3.14
K_{ll}	overall mass transfer coefficient defined by Eq 3.16

K_1, K_2, K_3	equilibrium constants
K_B	constant defined by equation (17), m^3 /kmol
k_La_B	gas-liquid mass transfer coefficient (1/sec)
m_D	liquid-liquid partition coefficient for styrene, $(kmol/m^3)_{aq}$/ $(kmol/m^3)_{org}$
N	agitator speed (rps)
R_{exp}	reaction rate, experimental, kmol/m^3/sec
r_i	initial rate, kmol/m^3/sec
R_{pre}	reaction rate, predicted, kmol/m^3/sec
RR%	relative residual percentage
sh	Sherwood Number ($k_{l,aq}\, d_{32}/D_D$) (-)
We	Weber number ($\rho_c N^2 D^3/\sigma$)

Greek letters

$\alpha_{1,A}$	as defined in Eq 3.11
$\alpha_{1,B}$	as defined in Eq 3.12
$\alpha_{2,E}$	as defined in Appendix I
β_1, β_2, β_3	lumped constants in rate model.
ϕ_{min}	minimised sum of square of errors between experimental and predicted rates
ε	aqueous phase hold up

Subscripts

1, 2, 3, 4, 5, 6, 7	species $HRh(CO)(TPPTS)_3$, $HRh(CO)(TPPTS)_2$, $HRh(CO)_2(TPPTS)_2$, $Rh(acyl)(CO)(TPPTS)_2$, $Rh(acyl)(CO)_2(TPPTS)_2$, $Rh(acyl)(CO)_3(TPPTS)$ and $(H)_2Rh(acyl)(CO)(TPPTS)_2$, respectively
A	hydrogen
B	carbon monoxide
C	catalyst
D	styrene
L	ligand
P	product
org	in organic phase
aq	in aqeuos phase

Appendix I

Estimation of drop diameter and liquid-liquid interfacial area

The knowledge of liquid-liquid interfacial area is crucial in analysis of the rate processes, especially when liquid-liquid mass transfer is controlling. The liquid interfacial area is normally evaluated by the expression

$$a_{ll} = \frac{6\,\varepsilon}{d_{32}} \qquad \text{A1}$$

The Sauter mean diameter, d_{32}, cannot be evaluated through simple analysis. Therefore, the interfacial area is evaluated based on the maximum stable drop diameter, d_{max}, existing near the impeller, which has a theoretical basis (Lagisetty *et al.*, 1986; Kumar *et al.*, 1991; Kumar *et al*, 1998). The d_{max} evaluated from the theoretical basis is then multiplied with an empirical factor (equal to 0.6) to obtain d_{32} (Calabrese *et al.*, 1986). The value of d_{max} depends on characteristics of the reactor geometry, flow field and physical properties of the system.

Kumar *et al.* (1991) have studied the drop breakage in batch turbulent stirred

$$\frac{d_{\max}}{D} = C_1\,(1 + C_2\,\varepsilon)^{1.2}\,We^{-0.6} \qquad \text{A2}$$

vessel and have experimentally shown that with increase in the dispersed phase hold-up, the value of d_{max} first increases, passes through a maximum and then decreases. Lagisetty *et al.* (1986) have proposed following expression, based on turbulent breakage mechanism, for dispersed phase with low viscosity:

The values of C_1 and C_2 used by Lagisetty et al. (1986) were 0.125 and 4.0, respectively for the reactor geometry used in their experiments to determine the d_{max}. It was observed that the d_{max} values obtained experimentally by Lagisetty et al. (1986), for toluene-water system were in good agreement with those predicted by above expression up to ε value of about 0.5.

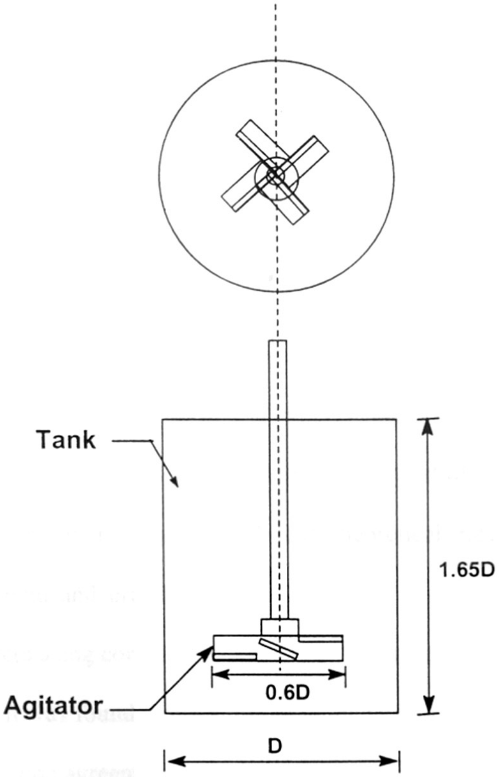


Figure A1: Details of reactor used for hydroformylation reactions

For our experiments on hydroformylation, the system (toluene +water) was same as used by Lagisetty *et al.* (1986). So above correlation was directly used for determining the d_{max} and liquid-liquid interfacial area. The reactor geometry used in our hydroformylation experiments is shown in Figure A1. The details of reactor configuration and physical properties of both the phases used in eqn. (1), at reaction temperature (373, K), are given in Table 3. The d_{max} values are calculated at various agitation speeds used in the hydroformylation experiments. For aqueous phase hold up less than 0.5, the aqueous phase is the dispersed and the organic phase is the continuous phase. However, for aqueous phase hold up greater than 0.5, eqn. (1) is used to calculate the drop diameter considering organic phase as dispersed phase and water as the continuous phase. The specific liquid-liquid interfacial area increases up to the phase inversion point and decreases thereafter with further increase in aqueous phase hold up.

Buwa *et al.* (1999) have used such analysis to study the mass transfer effects for biphasic hydroformylation 1-octene. They have observed that the theoretical rates of hydroformylation of 1-octene obtained using d_{32} and a_{ll} (predicted by using above correlation) were three times higher than that of experimentally observed rates of reactions. However, when they use value of C_1 in eqn. (1) as 0.3 instead of 0.125, they have found good agreement between their experimental and theoretical rates. The disagreement between the experimental and predicted rates of reaction can be because of the under-predicted drop diameters using correlation (eqn. (1)). A similar approach has been used for the present study and it was found that a value of C_1 equal to 1.5 was found to predict the experimental rates in good agreement.

Table 3: Physical properties of the system and impeller specifications

1.	**Viscosity of toluene**	**2.84×10^{-4} kg/m s**
2.	**Viscosity of water**	**2.85×10^{-3} kg/m s**
3.	**Density of toluene**	**0.797×10^{3} kg/m^3**
4.	**Density of water**	**0.959×10^{3} kg/m^3**
5.	**Interfacial tension**	**3.881×10^{-3} N/m**
6.	**Vessel diameter**	**2.540×10^{-2} m**
7.	**Impeller diameter**	**1.905×10^{-2} m**
8.	**Number of blades**	**4**

The reactor used in our hydroformylation experiments (as well as used by Buwa *et al.* (1999)) was unbaffled (See Figure 1) and the ratio of impeller diameter to tank diameter was also slightly different than the stirring vessel used by Lagisetty *et al.* (1986). These factors are known to affect the drop size distribution. Lagisetty *et al.* (1986) have observed that the C_1 in eqn. (1) is dependent only on the geometry of the vessel and the agitator, and not on the rheological properties of the dispersed phase. The value of C_1 (=0.125) determined by Lagisetty *et al.* (1986) was obtained by fitting their experimental data. Calabrese *et al.* (1986) and Chen and Middelman (1967) have obtained C_1 to be about 0.85. Coulaloglou and Tavlarides (1976) have estimated C_2 to be 4.47 to best fit their experimental data. Since, the geometry of reactor used for hydroformylation experiments was different than both the standard vessel used by Lagisetty *et al.* (1986) and Buwa et al. (1999), the constant C_1 was calculated by fitting the experimental rate data.

The new value of C_1 (=0.1875) was found to be within the range reported in the literature (0.125-0.85). as also observed by Buwa *et al.* (1999). The predicted drop diameters and specific liquid-liquid interfacial areas using C_1 as 0.1875 for different agitation speeds are shown in Figures 2 and 3, respectively.

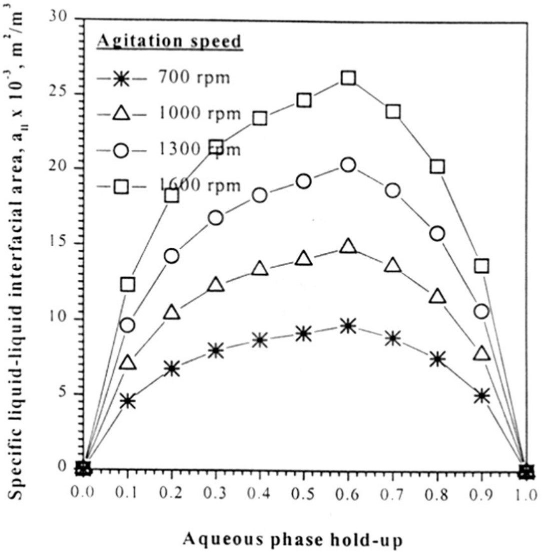


Figure A2: Predicted specific liquid-liquid interfacial area as a function of aqueous phase hold up

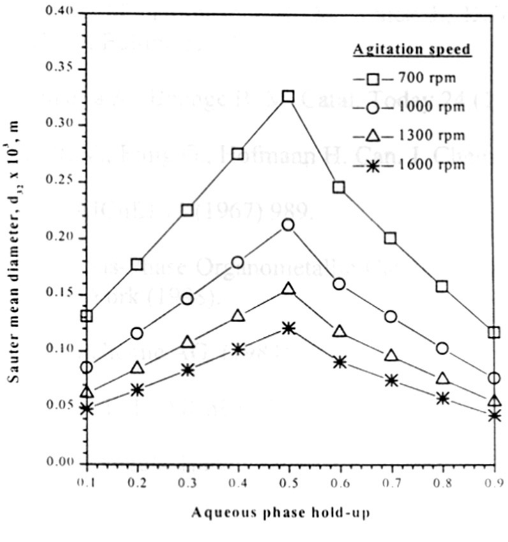


Figure A3: Predicted sauter mean drop size as function of aqueous phase hold up

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CHAPTER IV

Activity, Selectivity and Kinetics of Hydroformylation of Styrene using Supported Aqueous Phase Catalysis

4.1 Introduction

Supported Aqueous Phase Catalysis (SAPC) is a novel method for rendering the water-soluble homogeneous catalytic system into its heterogeneous analogue. The catalytic material consists of a thin film of water containing a metal complex catalyst spread over a high-surface-area inorganic support, such as silica or controlled-pore glass. A schematic representation of the SAP catalyst is shown in Figure 4. 1.

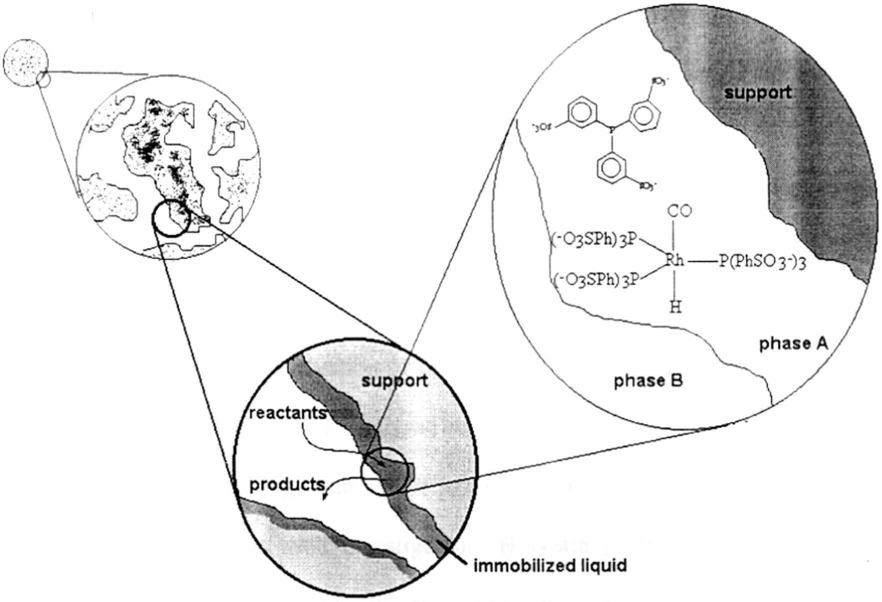


Figure 4.1: A schematic representation of the SAP catalyst (Archanct (1990))

The catalyst is used in place of the homogeneous catalyst in a gas-liquid-solid reaction wherein SAPC is suspended in a liquid medium consisting of a reactant and solvent. Catalyst recovery is accomplished by simple filtration. Two advantages of this technique are the higher rate of reaction compared to biphasic catalytic reactions using water-soluble complexes as catalyst and the easy separation of catalyst due to its heterogeneous (solid state) nature. By distributing the catalyst phase over a large surface area, the amount of catalyst available at the organic/aqueous interface is markedly increased. In systems where the organic substrate is sparingly soluble in the aqueous catalyst phase, this technique serves to increase the availability of the catalyst at the aqueous/organic interface by providing a large surface area.

A detailed review on previous work on hydroformylation of olefins using SAP catalyst is presented in Chapter 1 (section 1.3.2). After the first demonstration of SAP catalysts for hydroformylation, it has also been applied to many other transition metal catalysed reactions such as, asymmetric hydrogenation [Wanand Davis (1994)], Wacker oxidation [Archncets et al. (1991)], Heck reaction [Kiji et al. (19995)], allylic substitution [Choplinet et al. (1998)], and Suzuki coupling [Anson et al. (1998)] etc. In all these cases SAPC showed high selectivity like their homogeneous counterparts, at the same time allowing easy separation and recycle. Though in some cases, low levels of transition metal leaching was observed [Anson et al. (1998)]. SAPC has potential applications in commercial production of fine chemicals which are otherwise prepared by homogeneous transition metal catalysed reactions. Many important features like, life of SAPC, metal leaching, stability of aqueous film and water loss and catalyst deactivation have not been well investigated. Horvatth (1990) has shown that on continuous testing, the activity of SAPC decreased significantly indicating deactivation due to loss of water content from the catalyst film. Inspite of its potential applications, no attempt to study the kinetics of SAP catalysed reactions have been made previously.

The objective of this work was to compare the activity, selectivity and recycle studies of SAP catalysts with homogeneous and biphasic counterparts for hydroformylation of styrene and to investigate the kinetics of the reaction to develop a rate equation. For this purpose, the effect of different parameters such as catalyst loading, hydrogen and carbon monoxide partial pressures and styrene concentration on the initial rate of hydroformylation was studied using $HRh(CO)(TPPTS)_3$ in the form of

SAPC in a temperature range of 353-373 K. Water content on the SAP catalyst is known to have significant effect on the rate of reaction, and hence the effect of water loading on the initial rate was also investigated.

4.2 Experimental

4.2.1 Materials

Rhodium trichloride ($RhCl_3.3H_2O$), from Aldrich, USA, styrene from Fluka AG, (Switzerland), dimethyl formamide, acetyl acetonate and Silica of particle size range of 60-120 mesh from SD fine chemicals, (India), were used as received. Solvents, cyclohexane, water and ethanol, were freshly distilled and degassed prior to use. Hydrogen and nitrogen supplied by Indian Oxygen Ltd. Bombay, and carbon monoxide (> 99.8 % pure) from Matheson Gas Co., U.S.A. were used directly from cylinders. The syn gas with 1:1 ratio of H_2 : CO was prepared by mixing H_2 and CO in a reservoir.

4.2.2 Preparation of Supported Aqueous Phase Catalyst (SAPC)

$Rh(CO)_2(acac)$, TPPTS, and $HRh(CO)(TPPTS)_3$ were prepared by the method described in Chapter 3 (section 3.2.2). In order to obtain reliable kinetic data, it was important to ensure that SAP catalyst used was uniform in nature with respect to water and rhodium content. In order to ensure uniformity, the catalyst prepared from a single batch was used. SAP catalyst was prepared by incipient wetness method as described in the literature [Santos et al (1998), Arhancet et al (1990)]. To a degassed solution of 500 mg of $HRh(CO)(TPPTS)_3$ in 40ml of water in a two necked 250 ml RB flask, 20 g of silica (S_{BET} = 464 m^2/g, pre-treated under high vacuum at 150°C with stirring and frequent flush of argon gas using a two way valve for 1 hr) was added. The mixture was in the form of slurry and was stirred for 1 h at room temperature under argon atmosphere. Majority of the water was removed under high vacuum with frequent shaking. The final product was free flowing pale yellow powder. The weight of the final product was 25.2437 g (special care was taken to avoid handling loses). The increase in weight corresponds to the film of water coated on the silica and it was found to be 23.7% w/w of silica. SAP catalyst thus obtained was stored under argon in gas tight bottle and used for kinetic studies.

4.2.3 Reactor Set Up for hydroformylation

All the hydroformylation experiments were carried out in a 50 ml microclave reactor supplied by Parr Instrument Company USA, details of which have been described in Chapter 2 (section 2.2.3).

4.2.4 Experimental Procedure

In a typical experiment, a known quantity of SAP catalyst alongwith a 25 ml solution of styrene in cyclohexane were added to the reactor. The contents were flushed with nitrogen and then with a mixture of CO and H_2. Heating was started to attain a desired temperature, and then a mixture of CO and H_2, in a required ratio was introduced into the autoclave up to the desired pressure. A sample of the liquid phase mixture was withdrawn, and the reaction continued by switching the stirrer on. The reaction was then continued at a constant pressure of CO + H_2 (1:1) by supply of syngas from the reservoir vessel through a constant pressure regulator. Since, in this study the major products formed were isomeric aldehydes, supply of CO + H_2 at a ratio of 1:1 (as per stoichiometry) was adequate to maintain a constant composition of H_2 and CO in the reactor as introduced in the beginning. This was confirmed in a few cases by analysis of CO in the gas phase at the end of reaction.

4.2.5 Analytical methods

Analysis of $HRh(CO)(TPPTS)_3$, TPPTS, and the quantitative determination of the reaction products were carried in the same manner as described in the Chapter 3 (section 3.2.7). The SAP catalyst was prepared by a method described previously and thus obtained catalyst was characterised by AAS for Rh content (1.22×10^{-8} kmol of Rh per gram of SAP catalyst), thermogravimetric analysis for water content (23.0 %) and BET measurement for surface area (S_{BET}: 463.9 m^2/g).

4.3 Solubility data

For kinetic study, a knowledge of solubility of H_2 and CO in cyclohexane is required and since this data were not available in the temperature range studied, it was determined experimentally and also predicted theoretically as described in Chapter 2 (section 2.3.1). Solvent parameter, δ_s, required for the theoretical prediction of solubility of CO and H_2 in cyclohexane was obtained by back calculating from the experimentally observed solubility of CO in cyclohexane at 373 K. Solvent parameter, δ_s was found to be 18000 $J^{1/2}m^{-3/2}$. This value was further used to predict the solubility of CO in cyclohexane at other temperatures and for hydrogen solubility at all temperatures (353-373 K) within an average error of ±2%. The results are presented in Table 4.1.

Table 4.1: Henry's constants of CO and H_2 in cyclohexane.

Gas, Solvent	H_B MPa m^3/kmol at 353 K		H_B MPa m^3/kmol at 363 K		H_B MPa m^3/kmol at 373 K	
	Expt.	Predicted	Expt.	Predicted	Expt.	Predicted
CO in Cyclohexane	10.49	10.43	10.05	10.08	9.71	9.73
H_2 in Cyclohexane	18.32	18.27	16.98	16.22	14.25	14.50

4.4 Results and Discussion

4.4.1. Preliminary experiments

Hydroformylation of styrene using SAPC consisting of water-soluble $HRh(CO)(TPPTS)_3$ on silca support was investigated initially to examine product distribution, solvent choice and recyclability, before undertaking kinetic study.

Initially when toluene, was used as a solvent for hydroformylation using SAPC, the reaction mixture was found to be yellow in colour due to leaching of Rh from the catalyst. This was further confirmed by recycle of the recovered SAPC catalyst, which showed a significant decrease in activity (see Figure 4.2). Analysis of Rh content in toluene after the reaction (equivalent to 70% of Rh loading SAPC) confirmed this conclusion.

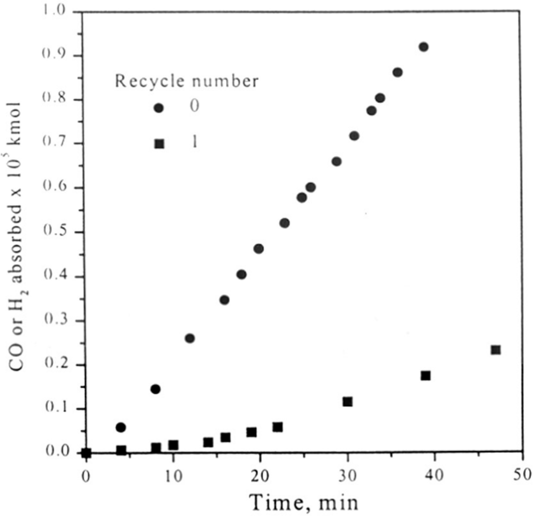


Figure 4.2 Effect of SAP catalyst recycle using toluene as a solvent

Reaction conditions:

SAP Catalyst (2.5% w/w of $HRh(CO)(TPPTS)_3$ on silica): 20 kg/m^3; water content: 27.3% (w/w of SiO_2); styrene: 0.69 kmol/m^3; P_{CO}: 2.04 MPa; P_{H2}: 2.04 MPa; agitation speed: 1300 rpm; Solvent: cyclohexane; Total volume: 2.5 x10^{-5} m^3; Temperature: 373 K.

With cyclohexane as a solvent, no rhodium leaching was observed and the SAP catalyst showed consistent activity on recycle for four successive experiments (see Figure 4.3). However, a progressive drop in the activity of the SAP catalyst after several recycles of the catalyst were observed by other investigators [Santos et al (1998), Horváth (1990)]. This effect is correlated to the leaching of water, in to the organic phase and not due to the leaching of the metal. In the present case Rh analysis in cyclohexane was below detectable levels by AAS methods (less than 5 ppm). For all the further experiments cyclohexane was used as the solvent. Archant et al. (1989, 1990) also used cyclohexane as a solvent in their first report on the SAP catalysis and found no leaching of rhodium. For the recycle experiments, the SAP catalyst was used in several successive experiments with fresh charge each time. After each reaction the product mixture was removed from the reactor and the catalyst was washed with degassed cyclohexane 3-4 times to remove the adhered reactants and products to the catalyst.

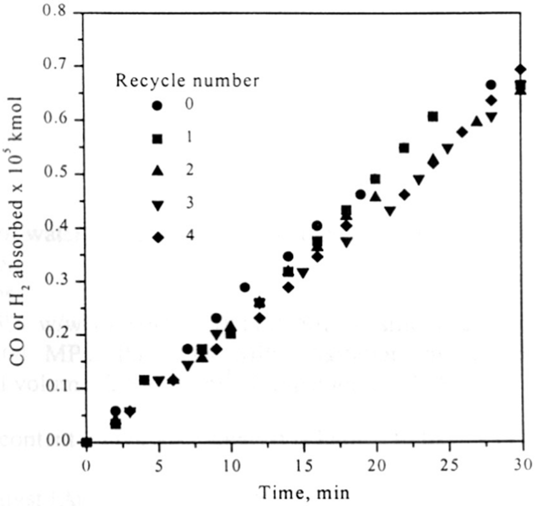


Figure 4.3 SAP catalyst recycle experiments using cyclohexane as a solvent.

Reaction conditions:
SAP Catalyst (2.5% w/w of $HRh(CO)(TPPTS)_3$ on silica): 20 kg/m^3; water content: 27.3% (w/w of SiO_2); styrene: 0.69 kmol/m^3; P_{CO}: 2.04 MPa; P_{H2}: 2.04 MPa; agitation speed: 1300 rpm; solvent: cyclohexane; total volume: 2.5 x10^{-5} m^3; temperature: 373 K.

In order to further confirm, that there was no metal leaching, the organic phase after the reaction was recycled with additional styrene. In these experiments, no further styrene conversion was found even after six hours, indicating absence of active catalyst in the organic medium. Such an indirect test to check the presence of metal in the organic phase was also employed by Arhancet et al. (1990) in hydroformylation of oleyl alcohol using a SAP catalyst.

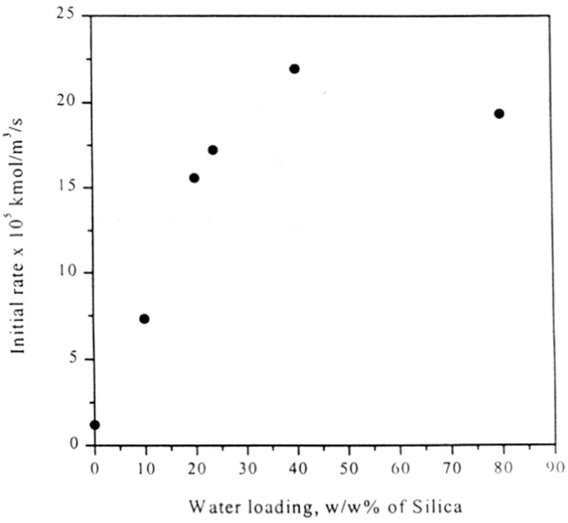


Figure 4.4 Effect of water content on SAPC catalyst on the rate of hydroformylation of styrene.
Reaction conditions:
SAP Catalyst (2.5% w/w of $HRh(CO)(TPPTS)_3$ on silica): 20 kg/m^3; Styrene: 0.69 kmol/m^3; P_{CO}: 2.04 MPa; P_{H2}: 2.04 MPa; Agitation speed: 1300 rpm; Solvent: cyclohexane; Total volume: 2.5 x10^{-5} m^3; Temperature: 373 K.

The water content on the SAP catalyst is known to have a dramatic effect on the activity of the catalyst [Arhancet et al. (1991)]. The effect of water content on the rate of hydroformylation of styrene was studied at 373 K and the results are shown in Figure 4.4. The rate was found to increase up to 40% w/w of water on silica and then started decreasing. This phenomenon can be correlated to a possible mobility of the complex on the surface of silica, as also discussed earlier by (Harvoth 1990). When the reaction was carried out in the absence of water, the activity was drastically reduced and it was found that only 5% conversion of styrene took place in 45 minutes. The experiments were carried out by varying the water content from 10-80% on the SAP catalyst. For this purpose the required amount of water, silica and HRh(CO)(TPPTS)$_3$ was added separately to the reactor along with the reaction mixture (except for 23.7% data, on the Figure 4.4, which is the standard catalyst used for kinetic experiments). The SAPC prepared in this way is believed to be consisting of an aqueous rhodium complex self assembled on silica surface, similar to that obtained by preparation following the method described by Davis and co-workers (Archancet et al. (1990))

The main objective of this study was to investigate the kinetics of hydroformylation of styrene using the SAP catalyst. Before studying the kinetics it was necessary to ensure the mass balance of the reaction products and reactants consumed. The results of a typical experiment carried out for 373 K and 4.14 MPa total pressure of CO/H$_2$ (1:1) are shown in Table 4.2. It was observed that 57.14% conversion of styrene was achieved in 60 minutes and material balance of CO or H$_2$ and styrene consumed was in good agreement with the total amount of aldehydes formed. In the range of conditions investigated, the only products formed were the isomeric aldehydes, 2-phenylpropanal (2ppd) and 3-phenylpropanal (3ppd) which were isolated and characterised as described in Chapter 2 (section 2.2.5).

Table 4.2 Table showing mass balance

Sr. No	Time, min	Amount of styrene, x 10^5, kmol	CO/H$_2$ consumed x 10^6, kmol	Total aldehydes x 10^6, kmol	2ppd, %	3ppd, %
1	0	1.75	0	0	0	0
2	15	1.36	3.76	3.74	66.60	33.40
3	40	0.90	8.38	8.35	66.55	33.45
4	60	0.75	10.11	10.09	66.62	33.38

Reaction conditions:
SAP Catalyst (2.5% w/w of HRh(CO)(TPPTS)$_3$ on silica): 20 kg/m^3; Water content: 27.3% (w/w of SiO$_2$); styrene: 0.69 kmol/m^3; P_{CO}: 2.04 MPa; P_{H2}: 2.04 MPa; Agitation speed: 1300 rpm; Solvent: cyclohexane; Total volume: 2.5 x10^{-5} m^3; temperature: 373 K.

Under the conditions chosen for kinetic study, no side reactions were found to occur and hence, these data represent the overall hydroformylation of styrene to corresponding aldehydes. Since, CO and H_2 are consumed in a 1:1 ratio, the rate of reaction of either gas would equal to half of the total gas absorption. The initial rate of reaction was calculated, from the H_2 or CO consumption-time profiles as described in the Chapter 3 (section 3.4.1). A typical H_2 or CO consumption-time profile is shown in Figure 4.5

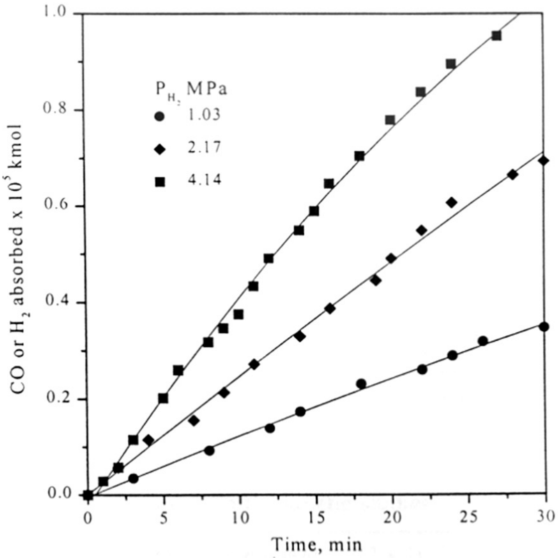


Figure 4.5 Typical CO or H_2 consumption-time profile: Effect of H_2 partial pressure on the initial rate of hydroformylation of styrene using SAP catalyst.

Reaction conditions:

SAP Catalyst (2.5% w/w of HRh(CO)(TPPTS)$_3$ on silica): 20 kg/m^3; Water content : 27.3% (w/w of SiO_2); styrene: 0.69 kmol/m^3; P_{CO}: 2.04 MPa; P_{H2}: 2.04 MPa; Agitation speed: 1300 rpm; Solvent: cyclohexane; Total volume: 2.5 x10^{-5} m^3; Temperature: 373 K.

In order to ensure that the rate data are obtained in the kinetic regime, experiments were carried out at varying agitation speed at a catalyst concentration of 20 kg/m^3 and at styrene concentration of 0.69 kmol/m^3 and hydrogen and carbon monoxide partial pressures of 2.14 MPa at 373 K. It was found that the rate was independent of agitation speed beyond 700 rpm, indicating that the mass transfer effects are unimportant above 700 rpm (Figure 4.6).

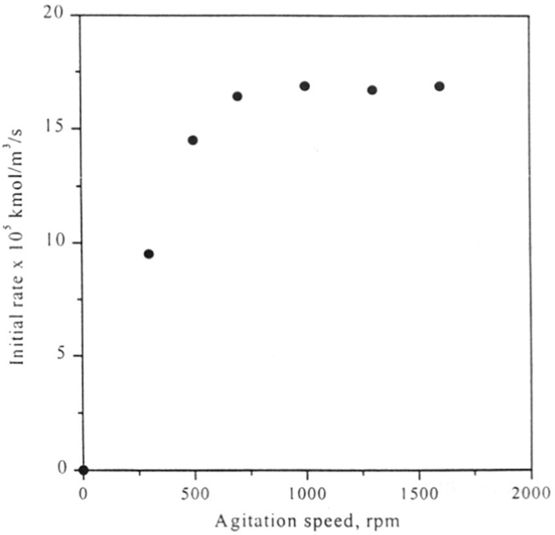


Figure 4.6 Effect of agitation speed on initial rate of hydroformylation
Reaction conditions:
SAP Catalyst (2.5% w/w of $HRh(CO)(TPPTS)_3$ on silica): 20 kg/m^3; Water content: 27.3% (w/w of SiO_2); Styrene: 0.69 kmol/m^3; P_{CO}: 2.04 MPa; P_{H2}: 2.04 MPa; Solvent: cyclohexane; Total volume: 2.5 x10^{-5} m^3, Temperature: 373 K.

Table 4.3 Range of conditions used for the kinetic studies

Amount of SAP catalyst (kg/m^3) (Rh content: 1.22 x 10^{-8} kmol/g)	20 - 40
Concentration of Styrene (kmol/m^3)	0.35 - 1.4
Partial pressure of hydrogen (MPa)	1.03 - 4.14
Partial pressure of carbon monoxide (MPa)	1.03 - 4.14
Temperature (K)	363 - 383
Solvent	Cyclohexane
Agitation speed (rpm)	1300
Reaction volume (m^3)	2.5 x 10^{-5}

4.4.2. Kinetics of Hydroformylation of Styrene

In order to investigate the kinetics of hydroformylation of styrene using HRh(CO)(TPPTS)$_3$ complex as SAPC several experiments were carried out in the range of conditions given in Table 4.3.

4.4.2.1 Effect of catalyst concentration

The effect of catalyst loading on the reaction rate was studied in a temperature range of 353-373 K and the results are shown in Figure 4.7, at various temperatures. It was found that the rate was having a first order with catalyst loading. The effect of agitation speed at catalyst concentration of 20 kg/m^3 showed no dependence on the rate beyond 700 rpm, indicating kinetic regime (Figure 4.5). To study the kinetics further experiments were carried out at a constant catalyst concentration of 20 kg/m^3.

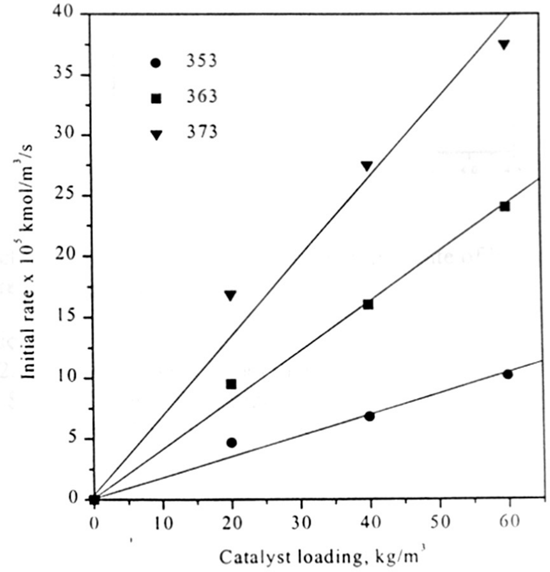


Figure 4.7 Effect of SAP catalyst loading on initial rate of hydroformylation of styrene using SAP catalyst.

Reaction conditions:
Water content: 27.3% (w/w of SiO$_2$); Styrene: 0.70 kmol/m^3; P_{CO}: 2.04 MPa; P_{H2}: 2.04 MPa; Solvent: cyclohexane; Agitation speed: 1300 rpm; Total volume: 2.5 x10^{-5} m^3.

4.4.2.3 Effect of partial pressure of hydrogen (P_{H2})

The effect of partial pressure of hydrogen on the rate of hydroformylation of styrene was investigated at a constant CO partial pressure of 2.07 MPa, styrene concentration of 0.7 kmol/m^3, SAP catalyst loading of 20 kg/m^3 and the results are shown in Figure 4.8. The rate of reaction was found to be first order with P_{H2}. This observation is consistent with that observed in the, homogeneous and biphasic (with and without co-solvent) systems.

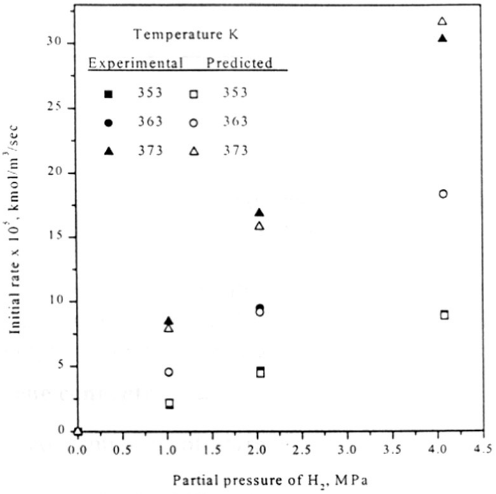


Figure 4.8 Effect of hydrogen partial pressure on initial rate of hydroformylation styrene using SAP catalyst

Reaction conditions:
SAP Catalyst (2.5% w/w of $HRh(CO)(TPPTS)_3$ on silica): 20 kg/m^3; Water content: 27.3% (w/w of SiO_2); Styrene: 0.70 kmol/m^3; P_{CO}: 2.04 MPa; Solvent: cyclohexane; Agitation speed: 1300 rpm; Total volume: 2.5 x10^{-5} m^3.

4.4.2.3 Effect of partial pressure of CO (Pco)

The effect of P_{co} on the rate of hydroformylation of styrene was studied at a constant hydrogen partial pressure of 2.07 MPa, styrene concentration of 0.7 kmol/m^3, SAP catalyst loading of 20 kg/m^3. The results are shown in Figure 4.9. The rate was found to have a 0.67th order with CO partial pressure.

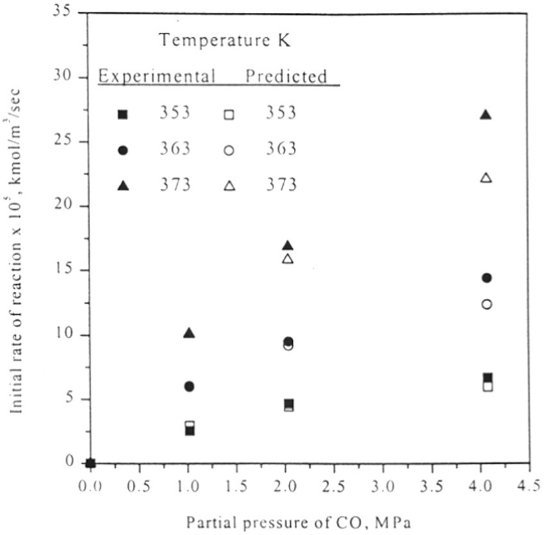


Figure 4.9 Effect of carbon monoxide partial pressure on initial rate of hydroformylation of styrene using SAP catalyst

Reaction conditions:

SAP Catalyst (2.5% w/w of $HRh(CO)(TPPTS)_3$ on silica): 20 kg/m^3; Water content: 27.3% (w/w of SiO_2); Styrene: 0.70 kmol/m^3; P_{H2}: 2.04 MPa; Solvent: cyclohexane; Agitation speed: 1300 rpm; Total volume: 2.5 x10^{-5} m^3.

4.4.2.4 Effect of styrene concentration

The effect of concentration of styrene on the rate of hydroformylation was studied at a total pressure of 4.14 MPa (CO: H_2 = 1:1), SAP catalyst loading of 20 kg/m^3. The results are shown in Figure 4.10. Here, the rate was found to be first order at lower concentrations up to (0.35 kmol/m^3) tending to zero order at higher styrene concentrations. As per the mechanism shown in Figure 4.11, the addition of styrene to the active dicarbonyl species is an equilibrium reaction (step (iii) in the simplified catalytic mechanism). In the present case the reaction is expected to take place at the aqueous-organic interface, and it is possible that at lowest concentration of styrene (0.35 kmol/m^3), the liquid film is not saturated with styrene and it gets saturated with styrene beyond 0.7 kmol/m^3. Based on arguments similar to that discussed in Chapter 3 (section 3.5.1) for co-solvent effect, the observed trends of first order going to zero order can be explained.

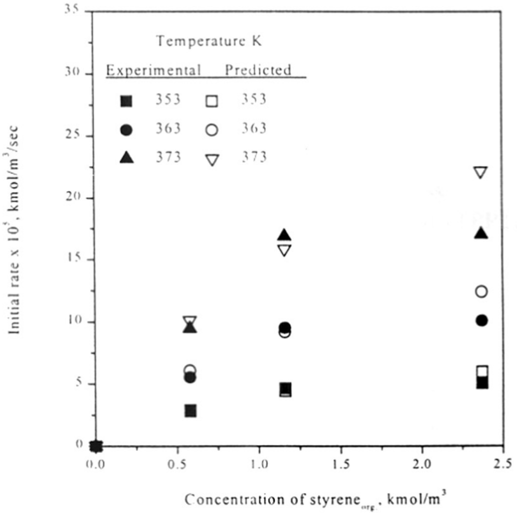


Figure 4.10 Effect of styrene concentration on initial rate of hydroformylation of styrene using SAP catalyst

Reaction conditions:

SAP Catalyst (2.5% w/w of $HRh(CO)(TPPTS)_3$ on silica): 20 kg/m^3; Water content: 27.3% (w/w of SiO_2); P_{H2}: 2.04 MPa; P_{CO}: 2.04 MPa; Solvent: cyclohexane; Agitation speed: 1300 rpm; Total volume: 2.5 x10^{-5} m^3.

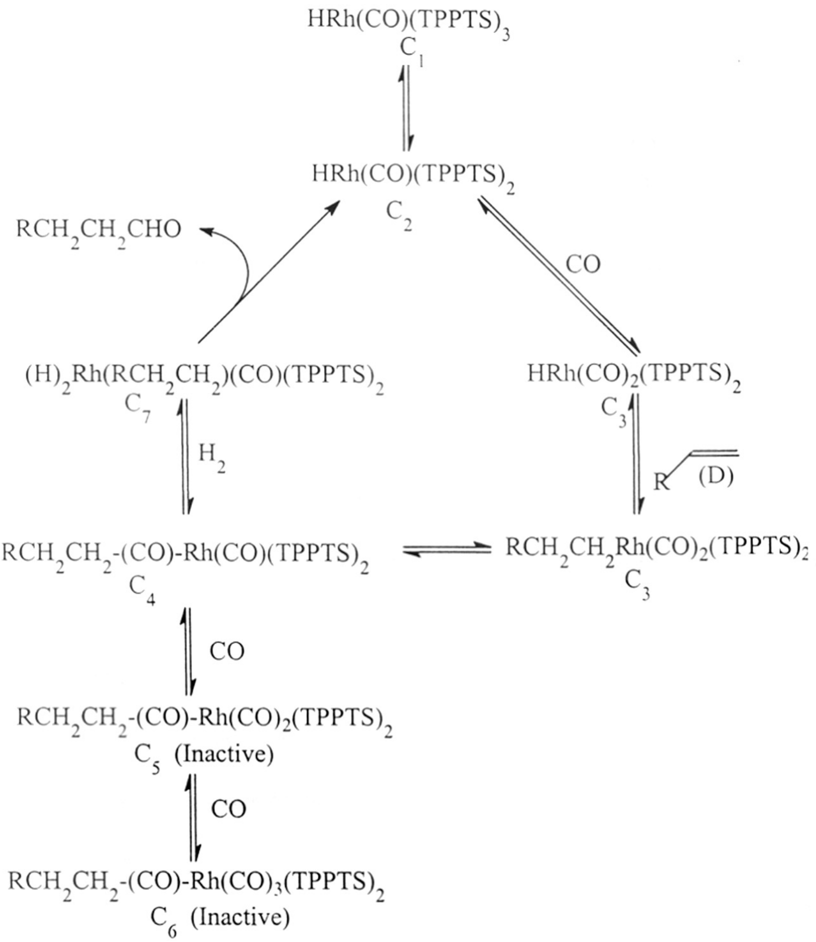
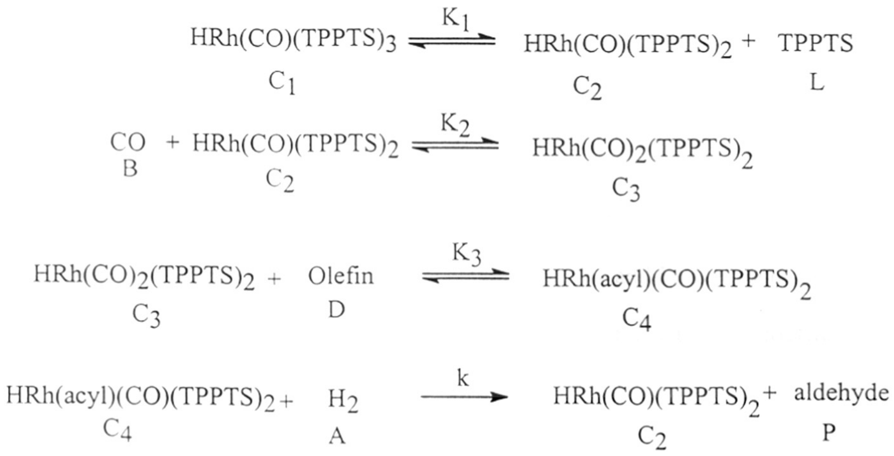


Figure 4.11 Mechanism for hydroformylation of olefins in SAPC media

4.4.2.5 Kinetic Modeling

The mechanism of hydroformylation is well known for water-soluble catalytic hydroformylation (Figure 3.12 of Chapter 3) and hence, it is more appropriate to consider the molecular level approach for kinetic modeling instead of using empirical rate forms. The mechanism shown in Figure 4.11 can be simplified as given below.



$$\underset{C_1}{HRh(CO)(TPPTS)_3} \xrightleftharpoons{K_1} \underset{C_2}{HRh(CO)(TPPTS)_2} + \underset{L}{TPPTS}$$

$$\underset{B}{CO} + \underset{C_2}{HRh(CO)(TPPTS)_2} \xrightleftharpoons{K_2} \underset{C_3}{HRh(CO)_2(TPPTS)_2}$$

$$\underset{C_3}{HRh(CO)_2(TPPTS)_2} + \underset{D}{Olefin} \xrightleftharpoons{K_3} \underset{C_4}{HRh(acyl)(CO)(TPPTS)_2}$$

$$\underset{C_4}{HRh(acyl)(CO)(TPPTS)_2} + \underset{A}{H_2} \xrightarrow{k} \underset{C_2}{HRh(CO)(TPPTS)_2} + \underset{P}{aldehyde}$$

The intra-molecular rearrangement steps were considered as fast. Since, CO inhibition is not observed in the present investigation, the steps involving formation of dicarbonyl and tricarbonyl species were assumed to be negligible and has not been considered while deriving the rate models.

Assuming addition of H_2 to acyl rhodium carbonyl species as the rate-determining step, a rate model was derived in a similar manner described in Chapter 3 (section 3.4.4.6).

$$r = \frac{\beta_1 C_A C_B C_D}{1 + \beta_2 C_B + \beta_3 C_B C_D} \qquad 4.1$$

$\beta_1 = kK_1K_2K_3C/K'_1$; $K'_1 = K_1 + C_L$; C_L = Conc. of dissociated TPPTS from Rh complex
$\beta_2 = K_1K_2/K'_1$; $\beta_3 = K_1K_2K_3/K'_1$

$C_A = P_A \times H_A$; $C_{B(org)} = P_B \times H_{B\,(org)}$; $C_D = m_D C_{D,(org)}$

Similarly, rate equation, assuming addition of olefin to the species HRh $(CO)_2(TPPTS)_2$ as a rate limiting step, can be derived (Eq 4.2). However this rate equation was not considered, since the equation represented product-inhibited kinetics which was not observed experimentally.

$$r = \frac{k\,K_1\,K_2\,C\,C_A\,C_B\,C_D}{1 + C_P + K_3\,C_A C_L + K_1\,K_3 C_A + K_1\,K_2\,K_3\,C_A C_B} \qquad 4.2$$

C is the catalyst concentration; $C_A = P_A \times H_{A(aq)}$; $C_B = P_B \times H_{B(aq)}$; $C_E = m_D\,C_{D,\,org}$

Where, H_A and H_B represent the Henry's constants and P_A and P_B represent the partial pressures of H_2 and CO; of respectively; m_D represent the partition coefficient of styrene in toluene-water system.

Rate model (Eq 4.1), based on H_2 addition to the acyl species as the rate-determining step was used to estimate the rate parameters. Analysis of rate data and the estimation of best-fit parameters was done using the same method described in Chapter 2 (section 2.3.3). The error between the predicted and observed rate data was found to be ± 5% except for the highest concentration of styrene and highest CO partial pressure. The results of both model predictions and experimental observations are shown in Figures 4.8–4.10.

Table 4.4 Rate constants evaluated from the rate model

Temperature K	$k \times 10^5$ $m^3/kmol/s$	$\beta_2 \times 10^2$	K_3, $m^3/kmol$	$\phi_{min} \times 10^{10}$
353	4.04	3.32	206.83	1.68
363	7.45	2.33	280.69	10.13
373	12.88	1.35	376.96	56.64

The rate constant k and equilibrium constant K_3 was calculated from β_1 and β_3 at different temperatures and are presented in Table 4.4, however, K_1 and K_2 and C_L could not be separated from the lumped constants. From the temperature dependence of the rate constants (Figure 3.16), the activation energy was found to be 63.48, kJ/mol.

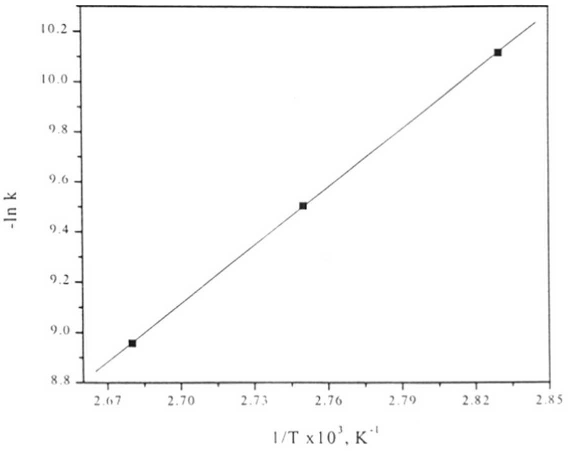


Figure 4.12 Temperature dependence of rate constant

4.5 Comparison of SAPC, biphasic and homogeneous systems

4.5.1 Activity selectivity studies

The objective of the present study was also to compare the activity and selectivity behavior of the SAP catalyst, for hydroformylation of styrene with homogeneous and biphasic (with and without co-solvents) catalysts. For this purpose, experiments were carried out under identical conditions with equivalent amount of rhodium loading (in case of homogeneous and biphasic experiments), using cyclohexane as a solvent and a total pressure of 4.14 MPa ($CO:H_2$ = 1:1), styrene concentration of 0.7 kmol/m^3 and at a temperature of 373 K. The activities (in TOFs, h^{-1}) were calculated at conversions of styrene <15%, for each catalyst system and are presented in Figure 4.13. The activity in biphasic medium was 6.5 times lower than that for the homogeneous system. The reduction in activity is expected due to the lower solubility of styrene, CO and H_2 in the aqueous phase. Addition of a co-solvent (50% v/v of NMP as co-solvent) to the aqueous phase is expected to increase the solubility of styrene in the aqueous phase and hence the activity was found to increase by 3 times as compared to the biphasic system without co-solvents.

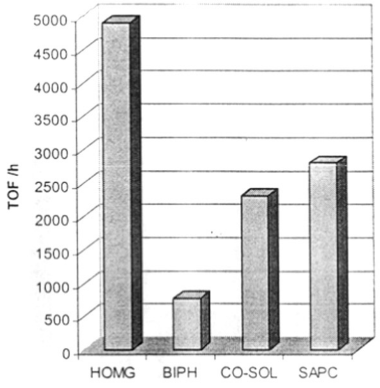


Figure 4.13 Comparison of Homogenous, Biphasic (with and without co-solvent) and SAP catalysts for hydroformylation of styrene

The activity of SAPC was found to be 3.64 times higher than that in the biphasic medium. The improvement in activity is due to the dispersion of the catalyst over a large surface area, which in turn increases the amount of catalyst available at the aqueous/organic interface. Use of a co-solvent or SAPC enhances the activity of aqueous biphasic catalyst significantly, retaining the advantage of easy catalyst separation. In addition, both SAPC and biphasic hydroformylation in presence of NMP as a co-solvent improved the selectivity towards the desired branched aldehyde, compared to that observed for the aqueous biphasic catalysts (see Figure 4.14).

4.5.2 Comparison of Kinetic studies

The objective of this study was also to have a comparison of kinetics of hydroformylation of styrene in homogeneous, biphasic (with and without co-solvent) and SAPC systems. For this purpose the data obtained in Chapter 2, Chapter 3 and Chapter 4 were used. The dependence of different parameters such as catalyst concentration, hydrogen partial pressure, carbon monoxide partial pressures and styrene concentration on the initial rate of hydroformylation of styrene along with the rate-determining steps and the activation energies in different systems are presented in Table 4.5.

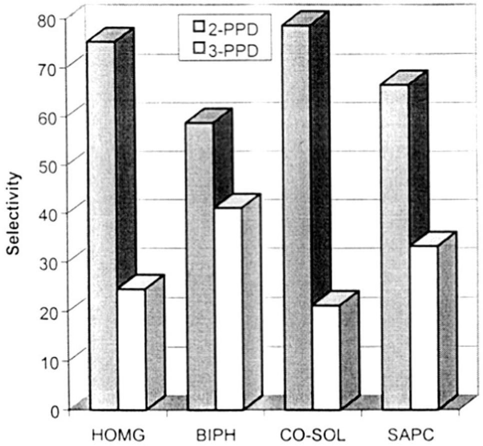


Figure 4.14 Selectivity behaviour of Homogenous, Biphasic (with and without co-solvent) and SAPC systems for hydroformylation of styrene.

The rate was found to be almost first order with catalyst concentration (except at 383 K for biphasic system without co-solvents, due to mass transfer limitations) and first order with hydrogen partial pressure in all the four systems studied. First order dependence with hydrogen indicated that in all the four systems, the addition of hydrogen to the acyl rhodium species is the rate-determining step as indicated by the mechanism considered in the respective systems. CO showed a positive order at lower partial pressures of CO and CO inhibited kinetics at higher partial pressures of CO in homogeneous systems. It showed a first order dependence in biphasic medium without any

Table 4.5 Comparison of kinetics of hydroformylation of styrene for homogeneous, biphasic (with and without co-solvent) and SAP catalyst systems

System	Reaction order				Activation Energy kJ/mol
	Catalyst	H_2	CO	Styrene	
Homogeneous	First	First	Positive order at lower P_{CO} and negative order at higher P_{CO}	Zero	68.80
Biphasic	0.9 at T = 363, 373 and 0.65 at T= 383	First	First	First	102.79
Biphasic with co-solvent	First	First	0.7	First to zero	----
SAPC	First	First	0.67	First to zero	63.48

co-solvent and 0.7th order in presence of NMP as a co-solvent and 0.67th order in case of SAPC. Styrene showed a zero order dependence in homogenous system, first order in biphasic system without any co-solvent and first order going to zero order in both biphasic system with a co-solvent and in SAPC systems. The differences in trends have been explained on the basis of solubility differences of CO and styrene in the respective systems (homogeneous (Chapter 2), biphasic systems with and without co-solvent (Chapter 3) and SAPC (present Chapter). Rate models derived based on the well-known hydroformylation mechanism, assuming hydrogen addition to the rhodium acyl species as the rate-determining step was found to explain the observed trends exceedingly well. Activation energies were calculated based this mechanistic model.

4.6 Conclusions

The kinetics of hydroformylation of styrene has been investigated using $HRh(CO)(TPPTS)_3$ as supported aqueous phase catalyst. The effect of concentration of catalyst, styrene, partial pressures of CO and hydrogen were investigated over a temperature range of 353 K to 373 K. The rate was found to be first order with respect to hydrogen partial pressure indicating that the addition of hydrogen to rhodium acyl species is the rate-determining step. Unlike CO inhibition observed in the homogeneous medium, a positive 0.70th order dependence was observed for SAPC, indicating that the inactive acyl Rh di and tri carbonyl species are not likely to be significant under the conditions investigated. Effect of styrene showed a first order going to zero order dependence. Effect of water loading on the SAP catalyst was also studied and it was found that the rate increased up to 40% w/w water on silica and then found to decrease with increase in water content. The following form of rate model, assuming hydrogen addition to the acyl rhodium species as the rate-determining step, based on the well-known mechanism of hydroformylation was found to represent the data satisfactorily.

$$r = \frac{\beta_1 C_A C_B C_D}{1 + \beta_2 C_B + \beta_3 C_B C_D}$$

Activation energy of the reaction was found to be 63. 48 kJ/mol.

Comparative study on activity and selectivity behavior of homogeneous, Biphasic (with and without co-solvent) and SAPC hydroformylation of styrene showed a 6.5 times drop in activity of biphasic system than that of homogenous system. The activity was improved by 3 to 3.6 times, when the reaction was carried out in biphasic medium with NMP as co-solvent and with SAPC system respectively than the aqueous biphasic medium. Further the selectivity towards the desired-branched aldehyde was improved by 66-79% in these systems than that observed in aqueous-biphasic medium (58%). By using biphasic hydroformylation of styrene in presence of co-solvent and as well as for SAPC, the activity and selectivity of aqueous biphasic systems can be improved to almost that observed in the homogenous medium, with retaining the advantage of easy catalyst separation. Kinetics of hydroformylation of styrene in homogenous, biphasic (with and without co-solvent) and supported aqueous phase medium was also compared.

Notations

C	total concentration of the catalyst in aqueous phase, $kmol/m^3$
C_1, C_2, C_3, C_4 C_5, C_6, C_7	concentration of species $HRh(CO)(TPPTS)_3$, $HRh(CO)(TPPTS)_2$, $HRh(CO)_2(TPPTS)_2$,$Rh(alkyl)(CO)(TPPTS)_2$, $Rh(acyl)(CO)_2(TPPTS)_2$, $Rh(acyl)(CO)_3(TPPTS)_2$, $(H_2)Rh(acyl)(CO)(TPPTS)_2$[defined by eqns. (3) to (6) or (11) to (14)], respectively, $kmol/m^3$
C_L, C_P	concentration of ligand and products in aqueous phase, $kmol/m^3$
H_A	Henry's constant for hydrogen-toluene system, $m^3.MPa/kmol$
H_B	Henry's constant for carbon monoxide-toluene system, $m^3.MPa/kmol$
p_A	partial pressure of hydrogen, MPa
p_B	partial pressure of carbon monoxide, MPa
k	reaction rate constant as defined in the text
K_1, K_2, K_3	equilibrium constants
m_D	liquid-liquid partition coefficient for styrene, $(kmol/m^3)_{aq}/ (kmol/m^3)_{org}$

Greek Letters

Greek letters

$\beta_1, \beta_2, \beta_3$	Lumped constants in rate model.
ϕ_{min}	Minimised sum of square of errors between experimental and predicted rates
δ_s	solvent parameter

Subscripts

1, 2, 3, 4, 5, 6, 7	species $HRh(CO)(TPPTS)_3$, $HRh(CO)(TPPTS)_2$, $HRh(CO)_2(TPPTS)_2$, $Rh(acyl)(CO)(TPPTS)_2$, $Rh(acyl)(CO)_2(TPPTS)_2$, $Rh(acyl)(CO)_3(TPPTS)$ and $(H)_2Rh(acyl)(CO)(TPPTS)_2$, respectively
A	hydrogen
B	carbon monoxide
C	catalyst
D	styrene
L	ligand
P	product
org	in organic phase
aq	in aqeuos phase

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