KINETIC MODELING OF HYDROFORMYLATION OF OLEFINS USING HOMOGENEOUS AND BIPHASIC CATALYSIS

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BY

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FORM - A

CERTIFIED that the work incorporated in this thesis entitled - KINETIC MODELING OF HYDROFORMYLATION OF OLEFINS USING HOMOGENEOUS AND BIPHASIC CATALYSIS, submitted by Mr. Sunil S. Divekar was carried out by him under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

(Dr. R.V. Chaudhari)
Supervisor

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SSDivekar

Pune
(S.S. Divekar)

September, 1995

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DEDICATED

TO MY PARENTS

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List of Publications based on this work :

1) Deactivation of homogenous $HRh(CO)(PPh_3)_3$ catalyst in hydroformylation of 1-hexene
R. M. Deshpande, **S. S. Divekar**, R. V. Gholap and R. V. Chaudhari
J. Mol. Catal. **67**, 333, 1991.

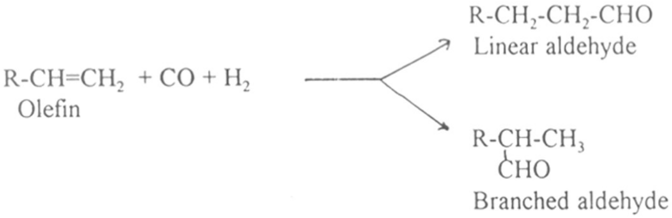
2) Solvent effect in kinetics of hydroformylation of 1-hexene using $HRh(CO)(PPh_3)_3$ catalyst
R. M. Deshpande, , **S. S. Divekar**, B. M. Bhanage and R. V. Chaudhari.
J. Mol. Catal. 77, L13 - L17, 1992

3) Kinetics of Hydroformylation of 1-decene using homogenous $HRh(CO)(PPh_3)_3$ Catalyst : A molecular level approach
S. S. Divekar, R. M. Deshpande and R. V. Chaudhari
Catal. Lett. **21,** 191-200, 1993

4) Selectivity in Hydroformylation of 1-decene by homogeneous catalysis
S. S. Divekar, R. M. Deshpande, B. M. Bhanage, R. V. Gholap and R. V. Chaudhari
J. Mol. Catal. **91**, L1-L6 1994

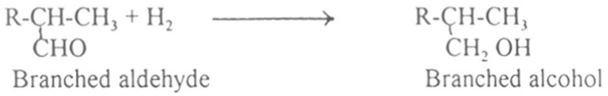
SUMMARY AND CONCLUSIONS

The hydroformylation of olefins is an example of one of the largest scale industrial applications of homogeneous catalysis, in which an olefin reacts with carbon monoxide and hydrogen in the presence of a soluble metal complex catalyst to give the corresponding aldehydes. These aldehydes act as intermediates for a variety of bulk and speciality chemicals. Generally, these aldehydes are further hydrogenated to alcohols (oxo alcohols) which find applications as solvents, surfactants, detergents and plasticizers. The important reactions which occur during hydroformylation process for oxo alcohols are :



$$\underset{\text{Olefin}}{R\text{-}CH{=}CH_2} + CO + H_2 \longrightarrow \begin{cases} \underset{\text{Linear aldehyde}}{R\text{-}CH_2\text{-}CH_2\text{-}CHO} \\ \underset{\text{Branched aldehyde}}{R\text{-}\underset{CHO}{CH}\text{-}CH_3} \end{cases} \qquad (1)$$

$$\underset{\text{Linear aldehyde}}{R\text{-}CH_2\text{-}CH_2\text{-}CHO + H_2} \longrightarrow \underset{\text{Linear alcohol}}{R\text{-}CH_2\text{-}CH_2\text{-}CH_2OH} \qquad (2)$$



$$\underset{\text{Branched aldehyde}}{R\text{-}\underset{CHO}{CH}\text{-}CH_3 + H_2} \longrightarrow \underset{\text{Branched alcohol}}{R\text{-}\underset{CH_2\,OH}{CH}\text{-}CH_3} \qquad (3)$$

A wide range of alcohols (C_4-C_{40}) are being produced commercially by this process and an approximate volume of production worldwide is about 6 million tpa. This process employs homogeneous transition metal complex catalysts consisting of cobalt or rhodium complexes. The major developments in hydroformylation technologies over the last five decades has been mainly due to breakthroughs in catalysis. A review of the technological developments of this subject is presented by Cornils (1980). Extensive research on the role of different catalysts, ligands, solvents and reaction mechanism has also been done in this area and a detailed account of this is given by Evans et. al. (1968), Pruett and Smith (1969), Cornils (1980) and Bahrmann et. al. (1990). The low pressure rhodium complex catalysts had a major impact on the new generation hydroformylation technology, however, this could not be applied for the production of higher alcohols due to difficulties in separation of the catalyst and the non-volatile products. To overcome these drawbacks, the use of water soluble catalysts in biphasic systems (Kuntz 1987, Kalck and Monteil 1992,) appear to be promising. The information on the reaction kinetics and mechanism of these biphasic systems is very limited in the literature. Also, there is a need for further work on understanding the kinetics and mechanism of hydroformylation using rhodium complex catalysts based on a molecular level approach and to develop rate equations which can be useful for predicting rate behavior and elucidating the different reaction mechanisms. Considering the industrial importance of the hydroformylation reactions, it was thought important to undertake investigations on the kinetics and mechanism of this reaction using both the homogeneous and biphasic catalytic systems. The following specific problems were chosen for the present thesis :

* Hydroformylation of olefins (C_6 - C_{10}) using homogeneous $HRh(CO)(PPh_3)_3$ complex catalyst : activity, selectivity and kinetic studies

* Hydroformylation of ethylene using homogeneous $HRh(CO)(PPh_3)_3$ complex catalyst : A kinetic study

* Hydroformylation of ethylene using Rh-TPPTS complex catalyst in an aqueous medium : Catalysis and Reaction Engineering studies

* Hydroformylation of ethylene using Rh-TPPTS complex catalyst in a biphasic (water-toluene) medium : Catalysis and kinetic modeling.

The hydroformylation reaction is also an interesting example of simultaneous absorption of two or more gases followed by a complex catalytic reaction. In such a case, the rate of reaction could also be influenced by gas to liquid mass transfer and phase equilibrium properties. The kinetics of hydroformylation has been studied previously for some cases (Deshpande and Chaudhari 1987, 1989), which showed a very complex dependence of the rate on CO, H_2 and olefin concentrations. A negative order with respect to CO appears to be a characteristic feature of the hydroformylation reaction. The role of mass transfer coupled with such complex kinetics is not yet well understood, hence, the present work would also be very useful from the reaction engineering point of view. The investigations on biphasic catalysis are important considering the great potential it has in separation of the homogeneous catalysts. This thesis is presented in 4 chapters, a brief summery of which is given below.

In chapter 1, pertinent literature including the historical background and the current developments in catalysis, reaction kinetics and reaction engineering aspects have been summarized. In homogeneous medium, mainly two types of catalysts are extensively used. In the early stages, cobalt carbonyls were used but due to the requirement of severe reaction conditions coupled with lower selectivity to the desired product, these catalysts were replaced by ligand modified cobalt catalysts. These catalysts have shown a real commercial success and are still applied for the direct manufacture of alcohols from the olefins.

A major breakthrough was the use of low pressure rhodium complex catalyst modified with trialkyl or triaryl phosphines as ligands. These catalysts require mild operating conditions (pressure = 2 MPa and temperature = 373 K) and give very high n/iso ratio (16 - 20) of the aldehyde products. Their application was, however, limited only to the hydroformylation of lower olefins such as propylene because of the ease of less volatile product separation. Though, rhodium catalysts are also very active and selective for higher olefins, their use in practice has not emerged due to the difficulties in separation of the high boiling products from the catalysts.

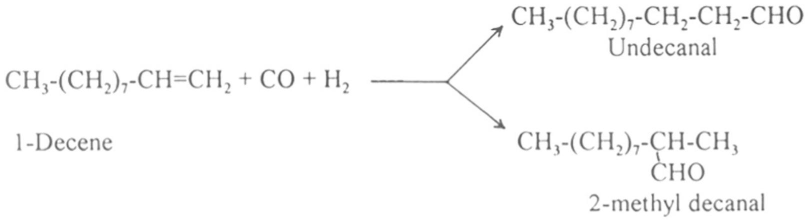
To overcome these problems associated with the catalyst recycle /recovery, water soluble catalysts have been proposed. As the majority of the substrates and products are organic moeities, these can be separated from the catalyst by simple phase separation. The literature on the synthesis of water soluble ligands, preparation of water soluble complexes and their applications has been reviewed.

There are only a few reports on kinetics of hydroformylation of olefins in homogeneous as well as biphasic media. These studies are mainly limited to the development of empirical rate equations. The literature on all these studies along with some reports on molecular level approach to kinetic modeling have been presented.

Chapter 2 presents an experimental study on the activity and selectivity of $HRh(CO)(PPh_3)_3$ catalyst for on hydroformylation of 1-hexene and 1-decene and a detailed study on the kinetics of hydroformylation of 1-decene. The reactions were carried out in a 3×10^{-4},m^3 high pressure stirred autoclave reactor provided with automatic temperature control and sampling arrangements.

It was found that the $HRh(CO)(PPh_3)_3$ catalyst was deactivated at higher temperatures during the hydroformylation of 1-hexene. It was noted that the addition of excess phosphine retards catalyst deactivation, which, however could not be prevented completely. Solvents were also found to play an important role in the deactivation of the catalyst. It was observed that, while in benzene as a solvent the maximum conversion achieved was ~ 31%, in butyraldehyde and n-heptanol it increased to 52 and 64% respectively for identical time runs. The effect of 1-hexene concentration on the activity of $HRh(CO)(PPh_3)_3$ complex catalyst has also been studied in various solvents. The rate of reaction versus olefin concentration showed a maximum indicating substrate inhibited kinetics at higher olefin concentrations. This maximum rate was found to be strongly dependent on the solvent type used. This variation was probably due to formation of inhibiting species and their stabilisation due to the solvent.

The hydroformylation of 1-decene was studied using a homogeneous $HRh(CO)(PPh_3)_3$ complex catalyst with the aim of understanding the role of solvents and ligands on the selectivity and the intrinsic kinetics of the reaction. The stoichiometric reaction is :



$$\underset{\text{1-Decene}}{CH_3\text{-}(CH_2)_7\text{-}CH{=}CH_2 + CO + H_2} \longrightarrow \begin{cases} \underset{\text{Undecanal}}{CH_3\text{-}(CH_2)_7\text{-}CH_2\text{-}CH_2\text{-}CHO} \\ \underset{\text{2-methyl decanal}}{CH_3\text{-}(CH_2)_7\text{-}\underset{\displaystyle CHO}{CH}\text{-}CH_3} \end{cases} \qquad (4)$$

The main products formed were undecanal and 2-methyl decanal. The linear aldehyde, undecanal finds major applications in perfumery industry, therefore, the selectivity to the linear aldehyde (often expressed as n/iso ratio) is an important requirement from the practical point of view.

In this work, the effect of solvents like benzene, toluene, ethanol, butanol, heptanol, methyl ethyl ketone and acetone on the selectivity has been investigated. It was observed that if the aromatic solvents like benzene, toluene are used, the n/i ratio decreases with conversion of 1-decene whereas with higher alcohols as solvents an n/iso ratio higher than that aromatic and ketonic solvents was obtained under the identical reaction conditions and at similar conversion levels. In benzene as a solvent the n/iso ratio was found to decrease with conversion of 1-decene at $P/Rh < 4$. For $P/ Rh > 4$, the n/i ratio remains constant and was shown to be independent of the conversion of 1-decene and P/Rh ratio itself.

For the purpose of kinetic study, experiments on hydroformylation of 1-decene were carried out at different concentrations of 1-decene, catalyst, P_{CO} and P_{H2} in a temperature range of 323 - 343 K. The rate was found to vary with a 1.2th order with the catalyst concentration and a 1.5th order with hydrogen concentration. The rate showed first order dependence at lower 1-decene concentration whereas it was zero order at higher concentrations of 1-decene. The rate shows a negative order kinetics at higher carbon monoxide concentrations. Based on the observed rate data, the following rate equation has been proposed :

$$R = \frac{k\,(A^*)^{1.5} \times B^* \times C^{1.2} \times D}{(1 + K_B\,B)^3\,(1 + K_D\,D)} \tag{5}$$

where, R is the rate of reaction, in kmol/m^3 sec, k is the reaction rate constant in m$^{11.1}$/kmol$^{3.7}$ sec, A^*, B^* are the dissolved concentrations of H_2 and CO in benzene in kmol/m^3 respectively, C and D represent the catalyst and 1-decene concentrations in kmol/m^3 respectively. K_B and K_D are the apparent equilibrium constants for species B and D respectively, in m^3/kmol. The activation energy was calculated to be 49.20 kJ/mol. The rates predicted using equation (5) were found to be in excellent agreement with the experimental data.

A molecular level approach to the kinetic modeling is also discussed for the present case and various rate equations were derived assuming different elementary steps to be rate controlling in the fundamental hydroformylation reaction mechanism. A rate model derived, assuming, hydrogen addition to the acyl rhodium complex to be rate controlling, showed a good agreement between predicted and the experimental rate data. This model is given below :

$$R = \frac{k' K_1 K_2\, A^* \times B^* \times C \times D}{1 + K_2 B^* + K_1 K_2 B^* D + K_1 K_2 K_3 (B^*)^2 D + K_1 K_2 K_3 K_4\,(B^*)^3 D} \tag{6}$$

where, K_1 to K_4 are the equilibrium constants for the elementary reactions in the catalytic cycle and k' is the reaction rate constant (m^3/kmol s). This model explains the negative order kinetics with respect to CO, quantitatively. It should also be noted that there is a close similarity (analogy) between the empirical model and the one developed on the basis of the mechanism.

In chapter 3, the kinetics of hydroformylation of ethylene using a homogeneous $HRh(CO)(PPh_3)_3$ complex catalyst is presented. The reactions were carried out in stirred autoclave reactor provided with automatic temperature control and sampling arrangements. The stoichiometric reaction is :

$$\underset{\text{Ethylene}}{CH_2{=}CH_2} + CO + H_2 \longrightarrow \underset{\text{Propionaldehyde}}{CH_3\text{-}CH_2\text{-}CHO} \tag{7}$$

Propionaldehyde was formed as the only product and the mass balance of ethylene, carbon monoxide and hydrogen consumed and the propionaldehyde formed were in good agreement (>97%) as per the above stoichiometry. The aim of this work was to investigate the rate behavior with respect to the various reaction conditions. This particular reaction involves simultaneous absorption of three gases followed by a catalytic reaction in the liquid phase, and hence it was first ensured that the rate data were in a kinetically controlled regime. This was confirmed by experiments at different agitation speeds.

The effect of concentration of catalyst, ethylene, carbon monoxide and hydrogen on the rate of the reaction has been studied in a temperature range of 333 - 373 K. The rate was found to vary linearly with the catalyst and hydrogen concentrations and independent of ethylene concentration. The rate showed a negative order with respect to carbon monoxide concentration. Based on these data, a rate equation has been proposed and kinetic parameters evaluated. The activation energy was found to be 9.4×10^{-4}, kJ/kmol.

In Chapter 4, hydroformylation of ethylene using Rh-TPPTS complex catalyst in an aqueous medium and biphasic water-toluene media is reported. The reactions were carried out in a $5x10^{-5}$, m^3 capacity microclave reactor. In both the media, the only product formed was propionaldehyde and the mass balance of ethylene, carbon monoxide, hydrogen consumed and the propionaldehyde formed was > 95%.

In the preliminary studies, the role of solvents, co-solvent and aqueous phase hold-up has been studied. The use of a co-solvent like ethanol in biphasic media was found to increase the rate of reaction. This could be due to the increase in the solubility of the reactants in the reaction medium on addition of the cosolvent. The aqueous catalyst phase hold-up was varied between 0 to 1 and it was observed that the activity of the catalyst initially increases with increase in aqueous phase hold up and then it decreases.

For the purpose of kinetic studies the reaction conditions were selected such that the reaction is not controlled by mass transfer. The effect of concentration of various reactants like ethylene, carbon monoxide and hydrogen and catalyst concentration on the rate of reaction has been studied at a temperature of 313 K. The rate was found to vary linearly with the catalyst and hydrogen concentration. It showed zero order dependence with respect to ethylene and a negative order kinetics with respect to carbon monoxide concentrations. The observed rate dependencies were used to propose rate equation and the kinetic parameters were evaluated. The general trends were similar to that for homogeneously catalysed hydroformylation using $HRh(CO)(PPh_3)_3$ in toluene medium.

The hydroformylation of ethylene in biphasic medium (toluene - water) was studied using water soluble Rh-TPPTS catalyst. The kinetics was studied at 353 K. The effect of concentration of various parameters like catalyst, ethylene, carbon monoxide and hydrogen on the rate of reaction has been investigated. The rate was found to vary linearly with the catalyst and hydrogen concentration. It was found to be independent of ethylene concentration. The rate shows a negative order kinetics with respect to carbon monoxide concentration, as is typical in hydroformylation reactions.

References

Bahrmann H., Bach H., Ullmann's Encyclopedia of Industrial Chemistry Elvers B., Hawkins S. and Schulz G (Eds), 5th Ed., (VCH, Weinheim) **A18** 321 (1991).

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

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

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

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

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

Kuntz E., Chemtech 570 (1987).

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

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CHAPTER 1

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INTRODUCTION
AND
LITERATURE SURVEY

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1.1 INTRODUCTION

The 21st century will see the introduction of a number of advanced catalytic processes that deliver environmentally safer, more efficient and lower cost solutions to the chemical, petroleum and pharmaceutical industries. Catalysis has played an important role in the induction of a variety of complex chemical transformations leading to the development of new chemical technologies. The catalysts are generally categorized as heterogeneous or homogeneous, depending on their mode of application.

Homogeneous liquid phase processes have several advantages over their heterogeneous counterparts, viz,

1 Usually operate under mild conditions.
2 Highly selective
3 Heat and mass transfer resistances can be easily eliminated leading to a better control of temperature
4 Catalyst and ligand concentration easily regulated.
5 Conservation of energy and raw materials due to high activity, caused by total utilization of reactant molecules
6 Fine tuning possible by changing ligand environment around the metal to achieve specific reactions / selectivity
7 Mechanistic aspects can be better understood

The homogeneous catalysts consisting of transition metal complexes are commercially used in many processes e.g., carbonylation, hydroformylation, oxidation, polymerization etc. Some of the industrial processes based on homogeneous catalysis are summarized in Table (1.1). These catalysts have already indicated their potential to develop new alternative, and cleaner / environment friendly technologies in recent years e.g.

* Monsanto's Acetic Acid Process via Methanol Carbonylation
* Low Pressure Oxo process for n-Butyraldehyde by hydroformylation of Propylene
* Shell Higher Olefin Process (SHOP) via oligomerisation of ethylene and
* Stereoselective synthesis of l-Dopa via asymmetric hydrogenation of A → B (see also Table (1.1))

Inspite of these advantages, the application of these catalysts in industry is limited due to the following disadvantages.

* Separation of the products and catalyst is difficult.
* Expensive catalyst recovery and recycle processes necessary.

TABLE 1.1

INDUSTRIAL APPLICATIONS OF HOMOGENEOUS CATALYSIS

Serial No	Process	Company	References
1	Oxidation of ethylene to acetaldehyde	Wacker-Werke	Jira, (1969)
2	Carbonylation of —		
	i) Methanol to acetic acid	Monsanto BASF	Roth et. al. (1971)
	ii) Ethylene to propionic acid	BASF	Weissermal and Arpe (1993)
	iii) Acetylene to acrylic acid	BASF	Weissermal and Arpe (1993)
	iv) Methyl acetate to acetic anhydride	Halcon, Eastman Chem.	Coover and Hart (1992); Agreda et. al. (1992)
	v) Methanol to dimethylcarbonate	ENICHEM	Haggin (1987)
	vi) p-isobutyl phenyl ethyl alcohol to ibuprofen	Boots-Hoechst	Elango et. al. (1990)
3	Hydroformylation of		
	i) propylene to butyraldehyde	Ruhrchemie Rhone-Poulenc	Cornils (1980) Jenck et. al. (1984)
4	ii)ethylene to Propionaldehyde and then condensation with formaldehyde to MMA	BASF	Schwaar (1991)
5	Hydrocyanation of butadiene to adiponitrile	Du Pont	Ludecke (1976)
6	Polymerisation of ethylene to HDPE/LDPE	Union Carbide	Carrick (1966)
7	Oligomerisation of Ethylene	Shell Chemical Company	Bauer et. al. (1972), Mason (1973)
8	Asymetric hydrogenation of A to B	Monsanto	Chem. Week. (1974)
9	Dimerisation of ethylene to 1-butene	IFP	Hennico (1990)

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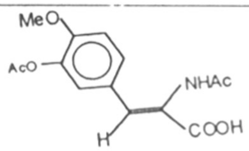

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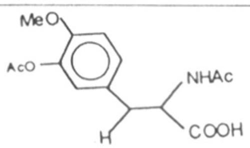


* Product contaminations.

In recent years, several new developments have taken place in this direction to overcome these drawbacks. These include the heterogenization of the homogeneous catalysts in different ways (Cornils 1980) : (a) Anchoring of the metal complex catalysts to polymeric or mineral/inert supports (b) Supported liquid phase catalysts (SLPC) and (c) Water soluble catalysts in two phase systems. Of these, the polymer bound and supported liquid phase catalysts have not found industrial applications due to problems such as leaching of the expensive metal catalyst, deactivation and low activity etc. (Cornils 1980; Pittman and Hirao 1978).

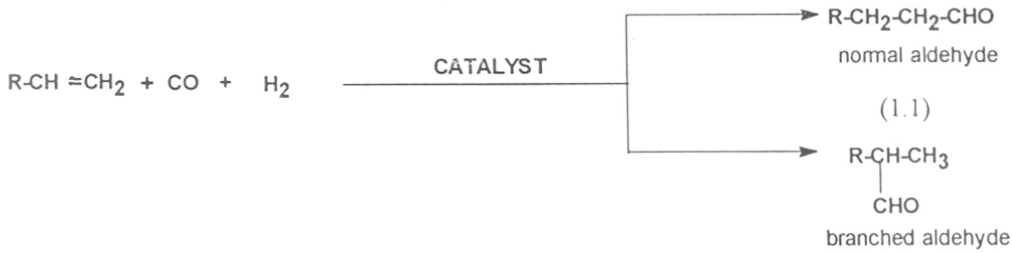
The recent development of water soluble metal complexes has made it feasible to operate gas-liquid catalytic reactions in a biphasic mode to achieve easy separation of the catalyst and products. In this approach, the catalyst exists in the aqueous phase leaving the products in the organic phase; thus simplifying the post reaction separations. This technology has been successfully utilized in the commercial oxo process by Ruhrchemie, Germany for the manufacture of n-butyraldehyde via propylene hydroformylation (Herrmann and Kohlpaintner, 1993). In this process a Rh complex with sulfonated triphenyl phosphine ligand (TPPTS) is used, which has very high solubility in water. The water soluble catalysts are stable, highly active and enable the hydroformylation process to be operated at pressures and temperatures comparable to the Low Pressure Oxo Process, thereby saving operating and investment cost.

The limitation of this approach is the poor solubility of the organic substrates in water. This leads to very poor rates of reactions. To overcome these problems, use of surfactants and cosolvents has been suggested. But these extra added reagents have to be separated after the reaction and very often lead to side reactions affecting selectivity.

The important aspects of the homogeneous catalysis include the understanding of the role of ligands, promoters and solvents on the activity and selectivity of the catalyst, as also the kinetics and mechanism. The hydroformylation reaction involves simultaneous absorption of two or three gases followed by a complex chemical reaction and hence, a study of mass transfer and reaction kinetics becomes inevitable. In biphasic catalysis, the effect of solvents, co-solvents, phase hold up, catalyst recycle, role of promoters, salts etc. have to be considered in addition to those discussed above. The mass transfer phenomenon and kinetic studies are also important for the purpose of reactor design. Therefore, it was thought important to investigate the above aspects of the hydroformylation reaction using homogeneous and biphasic catalysts. The relevant literature on hydroformylation of olefins is presented in the following sections.

1.2 HYDROFORMYLATION REACTION

The hydroformylation of olefins is the largest scale example of homogeneous catalysis in industry, in which an olefin, carbon monoxide and hydrogen react to produce an aldehyde product. The reaction stoichiometry is :



Scheme 1 : Stoichiometric reaction of hydroformylation of olefins

The major products formed in the reaction are normal and branched aldehydes as shown is eq. (1.1). The hydroformylation process is often combined with a hydrogenation step to produce alcohols in one or two steps from olefins. Some parallel and side reactions are also known to occur under oxo conditions (Cornils 1980) as shown in Fig. 1.1 As the normal (straight chain) aldehydes find major applications in industry, selectivity to the linear aldehyde becomes important i.e. a higher n/iso ratio. The reaction is highly exothermic and the heat of the reaction is of the order of 125, kJ/mole.

1.3 APPLICATIONS

Annually, 5.9 million tons of oxo alcohols are produced via the hydroformylation processes (Chin 1986). The most important industrial application of hydroformylation technology is the manufacture of n-butyraldehyde from propylene. n-Butyraldehyde is further hydrogenated to n-butanol or 2-ethyl hexanol via aldol condensation and hydrogenation. 2-ethyl hexanol is a raw material for the manufacture of phthalate esters, which are finally used as plasticizers in PVC. The alcohols in C_3-C_{20} range are used as solvents, intermediates for the production of plasticizers, lubricants, detergents and surfactants (see Table (1.2)). Several other intermediates and commercially attractive products can be obtained from these aldehydes and alcohols.

Since 1980, the chemical industries worldover have been shifting the emphasis of their businesses towards fine chemicals and away from commodity chemicals and polymers (Parshall and Nugent, 1988). Hydroformylation of olefinic substrates can be extended to develop new routes for some of the industrially important small volume, high value added organic chemicals.

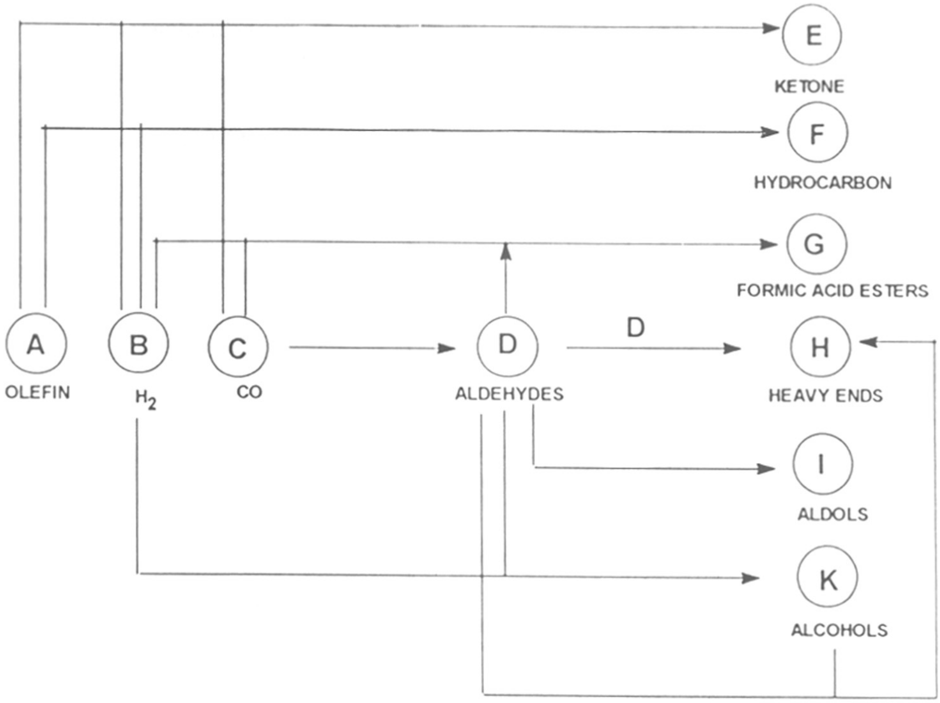


Fig. 1.1 : Some parallel and side reactions under oxo conditions (Cornils 1980)

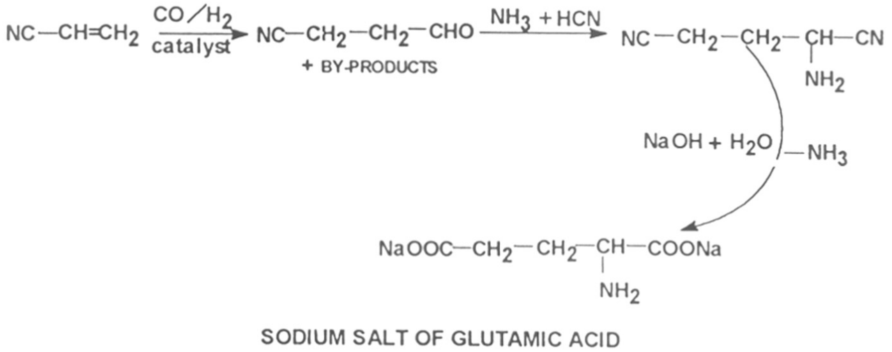
TABLE 1.2

COMMERCIAL OXO PRODUCTS AND APPLICATIONS

(Kirschenbaum et al 1977; Stewart 1982/83)

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

With the development of water soluble homogeneous catalysts, this technology can be applied for the production of even non-volatile products. Some of the new processes via hydroformylation are: *(a) Synthesis of a Vitamin A intermediate* : Vitamin A is generally produced by multistep stoichiometric reactions but recently, catalytic routes have been developed. A key step in the synthesis of Vitamin A is the hydroformylation of the 1,4-diacetoxy 2-butene intermediate with rhodium catalysts (Parshall and Nugent 1988). The hydroformylation step applied in the synthesis is shown in Fig. 1.2. *(b)* Hydroformylation of acrylonitrile to β-cynopropionaldehyde followed by the Strecker reaction yields sodium glutamate. The reaction sequence is shown below (Cornils 1980) in scheme 2.



Scheme 2 : Hydroformylation of acrylonitrile as a key step in the manufacture of glutamic acid

1.4 INDUSTRIAL OXO PROCESSES

The industrially important oxo processes can be divided into five main types. The major advancement in this technology has been mainly due to breakthroughs in catalysis. An overview of the catalyst systems, reaction conditions and expected products is summarized is Table (1.3). (Bahrmann et. al. 1991). The cobalt catalysts are extensively studied and described in the literature (Cornils 1980). Since, their industrial importance is constantly declining they are dealt with only briefly here.

1.4.1 Cobalt processes

1.4.1.1 Unmodified cobalt process

Before 1975, most commercial oxo processes were based on unmodified cobalt catalyst. However, since the successful introduction of modified cobalt and rhodium catalyst, its importance has declined. The cobalt carbonyl in the form of $HCo(CO)_4$ as a catalyst was used in many industrial hydroformylation processes. Typical reaction conditions are 110-180°C and

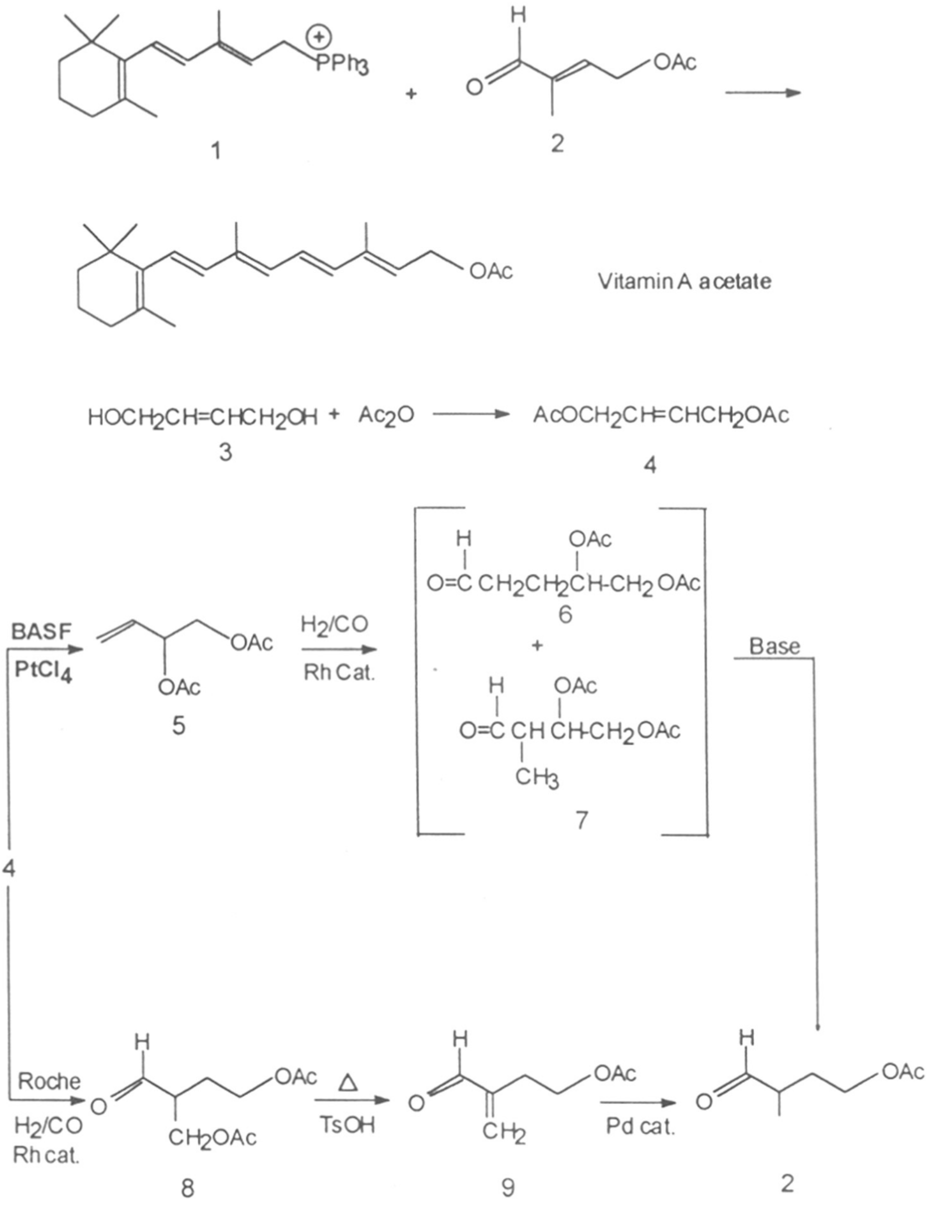


Fig. 1.2 : **BASF and Roche route for the synthesis of Vitamin A (Parshall 1988)**

Table 1.3

Comparison of the various oxo processes (Bahrmann and Bach 1991)

Catalyst	$[RhH(CO)(PR_3)_3]$		$[RhH(CO)_4]$	$[Co\ H(CO)_3(PR_3)]$	$[CoH(CO)_4]$
	R= C_6H_5	R= 3-$C_6H_4SO_3Na$			
Hydroformylation conditions					
Pressure. MPa	1.5-2	1-10	20-30	5-10	20-35
Temperature. K	358-388	323-403	373-414	433-473	383-453
Results					
Selectivity for aldehydes	high	high	high	low	medium
n/i ratio	92:8	95:5	50:50	88:12	80:20
Hydrogenation	low	low	low	high	medium

200-300, atm pressure. This process is used to produce C_6-C_{13} and detergent grade alcohols even today. The n/iso ratio is observed to be 3-4 : 1.

Higher pressure of CO is required because of the instability of the catalyst at lower pressures. This process has several drawbacks besides the severity of the operating conditions. The hydrogenation of propylene to propane, condensation of aldehydes to form acetal derivatives are major side reactions (Sheldon 1983).

1.4.1.2 Modified cobalt process

The one step oxo process developed by Shell Chemical Company is the sole commercial process which uses a cobalt hydridocarbonyl trialkylphosphine complex ($HCo(CO)_3PR_3$) catalyst. This requires lower operating pressures in the range of 40-50, atm. and temperature of 180 - 200° C. This process gives improved n/iso ratio and has been used to manufacture the oxo alcohols directly. In both these cobalt catalyzed processes, the separation of products from the catalyst and the recovery of the cobalt in a form suitable for reuse is complex and a relatively expensive operation.

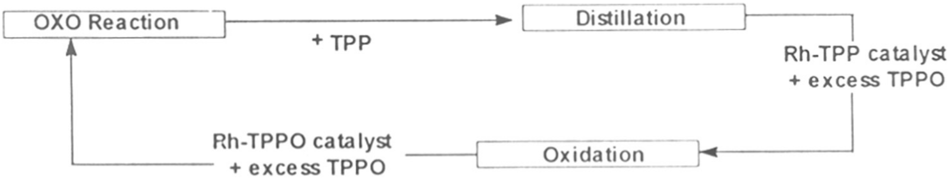
1.4.2 Rhodium processes

1.4.2.1 Low pressure oxo process

The development of a low pressure oxo process (LPO) based on rhodium - triphenylphosphine complex catalyst has been a major breakthrough in the oxo technology. Around 1976, the first plant was started using the process developed jointly by Union Carbide, Davy Mckee and Johnson Matthey (Stewart 1982/83). This process utilizes a homogeneous Rh complex catalyst ($HRh(CO)(PPh_3)_3$ and requires less than 20 atm pressure and 85-100°C temperature. The n/i ratio obtained is as high as 10:1, and also the side reactions leading to isomerization, hydrogenation and condensation are negligible. This process is mainly used for the conversion of propylene to n-butyraldehyde and about 13 commercial plants are operating or under construction throughout the world based on this process.

1.4.2.2 Mitsubishi Kasei (MKC) process

This process has been mainly developed for the manufacture of isononyl alcohol (INA) by hydroformylation of octenes (Onoda 1991). Non modified Rh carbonyl was used as a catalyst. After the reaction, a quantitative amount of triphenylphosphine is added to the reaction product and aldehydes are separated by distillation leaving the Rh-phosphine catalyst in high boiling residue without any decomposition. However, this recovered Rh catalyst showed very low activity and it was further discovered that triphenylphosphine oxide (TPPO), when added as a ligand, accelerates the oxo reaction of octene. Therefore, triphenylphosphine and/ or Rh-triphenylphosphine complex are first oxidized by an oxidant to triphenylphosphine oxide and/or its Rh complex, which gives the same activity as a fresh Rh carbonyl catalyst. The above mentioned results are summarized in the following Fig. 1.3.



(TPP : Triphenylphosphine, TPPO : Triphenylphosphineoxide)

Fig. 1.3 : New catalyst system for OXO reaction of octenes (Onoda 1991)

1.4.2.3 Water soluble Rhodium complex process

Another breakthrough in the hydroformylation technology after the highly successful low pressure process is based on a water soluble rhodium complex catalyst (Bahrmann et. al 1991). As with the LP Oxo process, this process developed by Ruhrchemie / Rhone Poluenc has found its greatest importance in the hydroformylation of propylene and a commercial plant of 30,000, TPA butyraldehyde has been set up, based on this process (Bach et. al. 1984).

The water soluble catalyst brings with it, all the advantages of homogeneous as well as heterogeneous catalysts. As the catalyst operates in the aqueous phase, the product is separated by simple phase separation, minimizing the loss of noble metal complex catalyst. Thus, the catalyst regeneration / recycle step can be simplified. This catalyst also has potential for application to the hydroformylation of higher olefins.

1.5 Catalysis and chemistry of hydroformylation

The use of rhodium and cobalt complexes as oxo catalysts has been extensively studied and important developments have been reviewed by Cornils (1980) and Pruett (1979). These are summerised in Table 1.4. Catalysts consisting of Mn, Ru, Cr, Cu and Mo have also been claimed to be active for this reaction. The activity of these metals for hydroformylation is reported as follows :

Rh > Co > Ru > Mn > Fe > Cr, Mo, W, Ni,
10^3-10^4 1 10^{-2} 10^{-4} 10^{-6} 0

TABLE 1.4

A SUMMARY OF CATALYSIS SCREENED FOR THE HYDROFORMYLATION REACTION

Sr. No.	Catalytic system	Olefin	Range of condition		Remark	Reference
			Temp. K	Press. MPa		
1.	$HCo(CO)_4$ and $Co_2\ (CO)_8$	1-octene	373	6.08	Catalytic species are characterised using insitu IR technique	Van Boven et. al. 1975
2.	$Co_2(acac)_2(H_2O)_2$	cyclohexene	403-423	7.09-1.01	H_2/CO 4 to 1	Bannerjee et. al. 1981
3.	$HCO(CO)_4$ and $Co_2\ (CO)_8$	1-octene cyclohexene	353	9.12 bar	Reaction mechanism using various insitu spectroscopic techniques.	Mirbach 1984
4.	$Co_4(CO)_8/PPh_3.$ $p(C_6H_4\text{-}Me\text{-}4)_3.p(CH_2Ph)_3$	hexene	-	-	deactivation by P-C cleavage	Dubois et. al. 1984
5.	$HCO(CO)_4$	Polyiso-butene	428	19.25	Mechanistic model proposed and the kinetic parameters are evaluated	Serio et. al. 1991
6.	Co/SiO_2 + alkaline earth oxide	Ethylene	463	1.1	Effect of alkaline earth oxide on selectivity	Takeuchi et. al. 1991
7.	$Co_2(CO)_8$	1-hexene	373	10.1	Reaction mechanism and influence of polar solvents on rate	Guertler 1993

(table continued....)

Sr. No.	Catalytic system	Olefin	Range of condition		Remark	Reference
			Temp. K	Press. MPa		
8.	$Rh(CO)_3(PPh_3)_2BPh_4$	hexene	353	9.12	n/i = 3	Monsanto Co. 1974
9.	$Rh(PPh_3)_2NO$	allyl acetate	373	4.05	-	Hayashi et al 1978
10.	Rh carbonyl complexes	ethylene	308	2.03-10.1	Catalytic intermediates using IR	King et. al 1979
11.	$Rh(CO)Cl(PPh_2NRR')_2$	olefins	-	-	R α amine type	Grimbolt et. al. 1980
12.	$HRh(CO)(PPh_3)_3$	Propylene	-	-	Deactivation & recovery of the catalyst	Gregorio et. al. 1980
13.	$Rh(COD)(acetate)/Ph_2PCH_2CH_2PPh_2$	1,3 butadiene	393	1.22	-	Van Leuven 1981
14.	$HRh(PPh_3)_4$ $[Rh(CO)_2Cl]_2$	styrene styrene	443 403	6.28 6.28	- -	Hayashi 1981
15.	$[Rh(CO)_2Cl]_2$/PEG 1600	hexene	413	10.13	$CO/H_2=0.5$ 97.9% n-alcohol	Jap. Patent 1981
16.	$Rh(PPh_2CH_2)_2P(O)Ph_2$	hexene	353	-	CO/H_2 0.125 n/i 33.8	Abatjoglou 1983

(table continued....)

Sr. No.	Catalytic system	Olefin	Range of condition		Remark	Reference
			Temp. K	Press. MPa		
17.	$H_2Rh(OOCOH)(P(CHMe_3)_3)_3$	hexene	-	-	Using paraformaldehyde	Okano et. al. 1982
18.	$[Rh(pz)(COD)]_2$ $[Rh(pz)(PPh_3)(CO)]_2$	heptene, hexene	353	5.07	76% sel.	Uson 1982
19.	$HRh(CO)(PPh_3)_3$	Allyl alcohol	333	0.138	4-hydroxy butyraldehyde is major product. Activity & selectivity of the catalyst	Abatjoglou & Bryant 1985
20.	$Rh(AA)(CO)(PPh_3)$ $AA=\beta$diketone or 8-hydeoxyquinoline	1-hexene	358	12.8	Effect of ligand on activity and selectivity	Janecko et. al. 1984
21.	$HRh(CO)(PPh_3)_3$ & $Rh_6(CO)_{16}$	1-hexene	323-398	2.07	Regioselectivity as a function of conversion	Hanson & Davis 1987.
22.	Rh-phosphine	Terpenes	833-413	3.45	Activity and selectivity	Chalk, 1988
23.	$HRh(CO)(PPh_3)_3/$ SiO_2	Propylene	363-393	0.3-1.01	Influence of ligand structure on activity & selectivity	Hjortkjaer et. al. 1990
24.	$HRh(CO)(C_{60}(PPh_3)$	Propylene	363	1.11	di-n-butyl phthate solvent. Activity and regiaselectivity.	Claridge et. al. 1994.

Cobalt or rhodium complexes clearly offer the best activity for the hydroformylation reactions (Sheldon 1983). A brief summary of studies on catalysis is given here.

1.5.1 Cobalt catalyst

The investigations on the cobalt catalyzed processes revealed that the actual catalytic species was the soluble complex $HCo(CO)_4$ (Wender 1950; Wender 1953; Adkins and Krsek 1949). The catalyst is generated by treating finely divided cobalt or a cobalt (II) salt (e.g. cobalt acetate) with syngas at elevated temperatures and pressures. The transformation sequence is as follows ,

$$Co^{II} \xrightarrow[CO]{H_2} Co(0) \longrightarrow Co_2(CO)_8 \xrightarrow{H_2} HCo(CO)_4$$

Scheme 3 : Various steps involved in the catalyst ($HCo(CO)_4$) generation

The most widely accepted mechanism for the hydroformylation with cobalt catalyst was proposed by Heck and Breslow (1961), as seen in Fig 1.4. The first step in this mechanism is the attack of hydrogen on the $Co_2(CO)_8$ complex to form $HCo(CO)_4$. This complex further dissociates into $HCo(CO)_3$ and CO (eq. (1), in Fig. 1.4). The acyl cobalt complex is formed through various addition, insertion steps (see Fig. 1.4). The slowest step in the mechanistic cycle is the formation of $HCo(CO)_4$ from $Co_2(CO)_8$. The main $HCo(CO)_4$ generating step was found to be via H_2 attack on $RCOCo(CO)_4$, and not on $Co_2(CO)_8$. Thus, the regeneration of the catalyst is the key step in this mechanism.

The formation of the branched product probably results from several steps. These include i) isomerization of olefin, ii) isomerisation of π complex via allylic intermediate, iii) isomerisation of the acylcobalt complex. The nature of active catalytic species and its direction of addition (Markownikow vs anti-Markownikow) to the olefin also plays an important role in deciding the selectivity pattern (Piacenti et. al. 1976; Bianchi et. al. 1977; Taylor and Orchin 1971). Thus, Markownikow addition of $HCo(CO)_3$ to the olefin resulted in 70% of branched aldehyde whereas with $HCo(CO)_4$ it yields only 30% branched aldehyde (Orchin and Rupilius 1972).

The hydrogenation of initial olefin or an aldehyde to hydrocarbon or oxo alcohol respectively are the main side reactions catalyzed by $Co_2(CO)_8$ or $HCo(CO)_4$ (Cornils 1980). The formation of alcohol increases with increase in temperature, hydrogen partial pressure, catalyst

$$Co_2(CO)_8 + H_2 \rightleftharpoons 2\,H\,Co(CO)_4 \tag{i}$$

$$HCo(CO)_4 \rightleftharpoons HCo(CO)_3 + CO \tag{ii}$$

$$\begin{tikzcd} R\text{-}CH{=}CH_2 + HCo(CO)_3 \arrow[r, shift left] & R\text{-}CH{=}CH_2 \arrow[l, shift left] \arrow[r] \arrow[d] & R\text{-}CH_2\text{-}CH_2Co(CO)_3 \\ & HCo(CO)_3 & \end{tikzcd} \tag{iii}$$

$$R\text{-}CH_2\text{-}CH_2Co(CO)_3 + CO \rightleftharpoons R\text{-}CH_2\text{-}CH_2Co(CO)_4 \tag{iv}$$

$$R\text{-}CH_2\text{-}CH_2Co(CO)_4 \rightleftharpoons R\text{-}CH_2\text{-}CH_2COCo(CO)_3 \tag{v}$$

$$R\text{-}CH_2\text{-}CH_2COCo(CO)_3 + CO \rightleftharpoons R\text{-}CH_2\text{-}CH_2COCo(CO)_4 \tag{vi}$$

$$\begin{tikzcd} & R\text{-}CH_2\text{-}CH_2CHO + Co_2(CO)_8 \quad \text{(vii)} \\ R\text{-}CH_2\text{-}CH_2COCo(CO)_4 \arrow[ur, "H\,Co(CO)_4"] \arrow[dr, "H_2"'] & \\ & R\text{-}CH_2\text{-}CH_2CHO + H\,Co(CO)_4 \quad \text{(viii)} \end{tikzcd}$$

$$R\text{-}CH_2\text{-}CH_2COCo(CO)_4 + H\,Co(CO)_3 \longrightarrow R\text{-}CH_2\text{-}CH_2CHO + Co_2(CO)_7 \tag{ix}$$

$$Co_2(CO)_7 + CO \rightleftharpoons Co_2(CO)_8 \tag{x}$$

Fig. 1.4 : Mechanism of cobalt carbonyl catalysed hydroformylation of olefins

concentration and residence time. However, these variants may also lead to other secondary (ester and heavy end formation) and parallel (olefin hydrogenation) reactions.

1.5.2 Rhodium catalyst

The potential advantage of Rh-based hydroformylation catalysts over those involving cobalt were first disclosed by Schiller (1956) and it was shown that Rh was a much more active metal as a catalyst for (100 to 100000 times) hydroformylation than cobalt (Cornils 1980). It operates under much milder temperature and pressure conditions. The unmodified Rh catalyst operates at 70-150°C and a total pressure of 50-150, atm ($CO/H_2=1$). The active catalytic species is reported to be $HRh(CO)_3$, analogous to the cobalt complex and the overall mechanism is also similar to that reported for the cobalt. These catalysts have a high activity for isomerization of olefins but have no hydrogenation activity. The selectivity to linear isomer is poor (n/i -~1).

The major breakthrough in the development of the rhodium catalyst for oxo technology was by Slaugh and Mullineaux (1961), who discovered the use of trialkylphosphine and arsine complexes of rhodium as alkene hydroformylation catalysts. Similar results were independently reported by Osborn et. al., (1965) wherein a catalyst system based on a rhodium-phosphine complex was developed. The catalyst generated from $HRh(CO)(PPh_3)_3$ precursor was shown to be active at ambient conditions. This catalyst was used for the hydroformylation of a variety of olefinic substrates (Evans et. al. 1968b; Pruett 1979) at 25-120°C and 1-20, atm pressure.

This newly developed catalyst has many advantages over the conventional cobalt catalysts such as :

* High activity and selectivity to aldehyde products (Osborn et.al. 1965; Slaugh and Mullineaux 1966)

* Higher n/i ratio (Fell 1977)

* Operates at milder operating conditions (Brown and Wilkinson 1970).

This catalyst was found to be suitable for commercial scale application and a process was jointly developed for the hydroformylation of propylene by Union Carbide, Davy Mckee and Johnson Matthey (Stewart 1982/1983). This process with $HRhCO(PPh_3)_3$ as a catalyst operates at temperatures of 60-120°C and pressures of 28-31, atm in the presence of a hydrogen rich syngas with excess triphenylphosphine as a solvent (Cornils 1980).

1.5.3 Mechanism

The widely accepted mechanism of hydroformylation using $HRh(CO)(PPh_3)_3$ is the one based on the work of Wilkinson and co-workers (Evans et. al. 1968a; Evans et. al. 1968b) and Pruett and Smith (1969). Extensive dissociation of $HRh(CO)(PPh_3)_3$ occurs on dissolution in a solvent (e.g. benzene). The equilibrium steps are reported to be as follows (Evans et. al. 1968b).

$$\underset{1}{[HRh(CO)(L)_3]} \underset{+\,L}{\overset{-\,L}{\rightleftharpoons}} \underset{2}{[HRh(CO)(L)_2]} \underset{+\,L}{\overset{-\,L}{\rightleftharpoons}} \underset{3}{[HRh(CO)(L)]} \qquad (1.2)$$

$$L = PPh_3$$

Under the hydroformylation conditions, this equilibrium is also accompanied by a competition of CO and PPh_3 for the free coordination sites on the rhodium atom (Pruett and Smith 1969) resulting in the formation of species 4 and 5 as shown below.

$$\underset{1}{[HRh(CO)(L)_3]} \underset{-\,L}{\overset{+\,CO}{\rightleftharpoons}} \underset{4}{[HRh(CO)_2(L)_2]} \underset{-\,L}{\overset{+\,CO}{\rightleftharpoons}} \underset{5}{[HRh(CO)_3(L)]} \qquad (1.3)$$

$$L = PPh_3$$

Two basic (dissociative and associative) mechanisms based on whether the rhodium atom is complexed with one or two phosphines have been proposed by Wilkinson (Evans et. al. 1968b). In the dissociative mechanism as shown in Fig. 1.5, dissociation of a phosphine ligand from the bis(phosphine) complex (4) is followed by the addition of olefin to the co-ordinatively unsaturated square planar complex (6). The addition of olefin via π complex gives σ-alkyl complex (7). Alkyl migration or CO insertion leads to the formation of an acyl complex (8) which on oxidative addition of hydrogen give rise to the dihydride complex (9). This is reported to be the rate controlling step in the mechanism. Finally, the dihydride complex reductively eliminates the product and the catalyst is regenerated. In the associative mechanism, the alkyl complex $RRh(CO)_2(PPh_3)_2$, is formed by the addition of olefin to the bis(phosphine) complex (4). The mechanistic cycle again operates through the above mentioned steps to give the product and the catalyst is regenerated.

Recently, a modified dissociative mechanism has also been suggested by many workers based on the isolation and characterization of the catalytic intermediates (Horvath et. al. (1989);

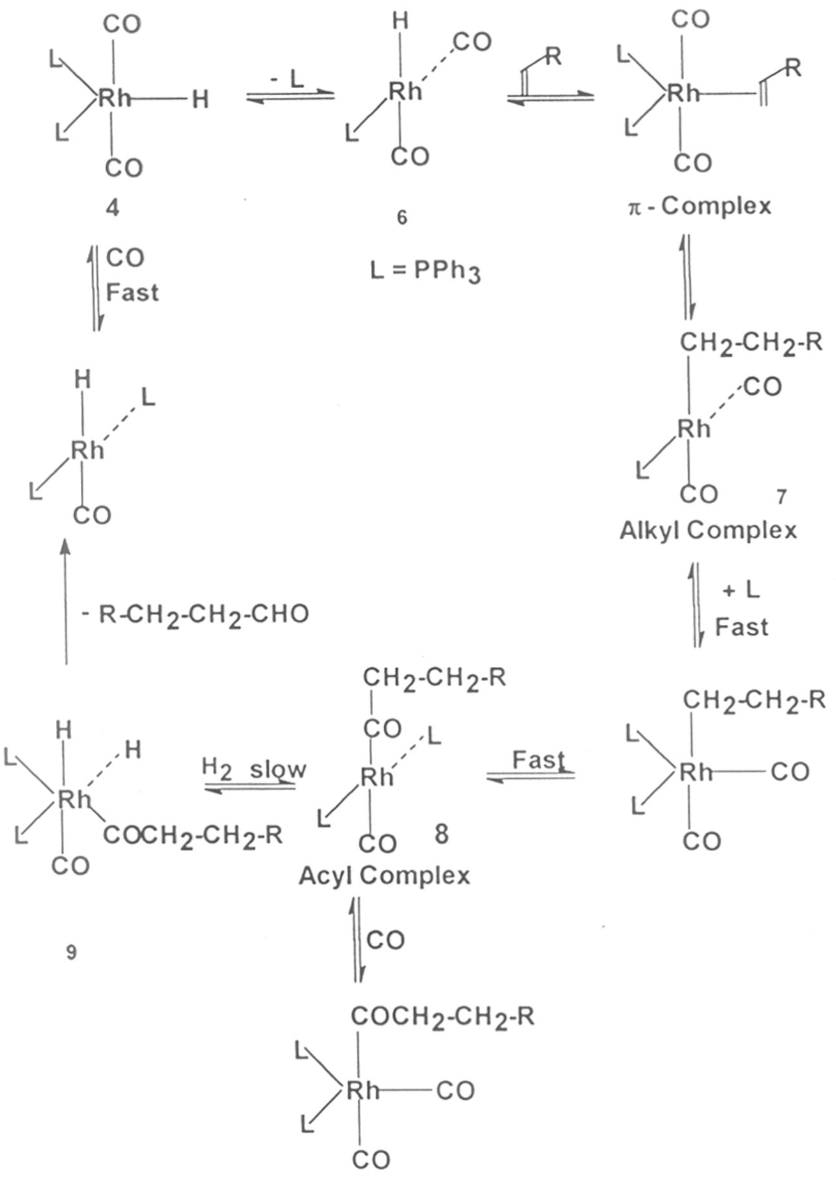


Fig. 1.5 : Mechanism (dissociative) of hydroformylation using $HRh(CO)(PPh_3)_3$ complex catalyst (Bahrmann 1991)

Oswald et. al. (1980) ; Russel (1988) ; Gregorio et. al. (1980) ; Cavalieri et. al. (1980)). The active catalytic species in are probably unsaturated square planar rhodium complexes containing one or two coordinated phosphine ligands. As shown in Fig.1.6, the complex (2) yields predominantly the n-aldehyde, whereas, the complex (6) gives the branched aldehyde.

1.6 KINETICS AND MECHANISM

Kinetic studies of a catalytic reaction are important to understand the mechanistic aspects of the reaction besides being useful in the reactor design. The hydroformylation of olefins involves the reaction of two or three gases with a complex catalytic reaction and in such a case detailed investigations of the intrinsic kinetics is most desirable. Only a few attempts to study such industrially important reactions have been made in the past. The relevant literature is summarized in Table (1.5) and important studies are described here.

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

The kinetics of hydroformylation of propylene using $Co_2(CO)_8$ catalyst in toluene as a solvent has been reported in a temperature range of 383-423, K (Gholap et. al. (1992a)). The rate increases with increase in the concentration of catalyst, propylene and hydrogen while it was inhibited at higher partial pressures of carbon monoxide. An empirical rate equations has has been developed, based on the observed trends (see Table (1.5)). In a subsequent report these authors have investigated the kinetics of formation of normal and branched butyraldehyde. The rate equations for formation of each aldehyde isomer have also been proposed (Gholap et. al. 1992b) (see Table (1.5)).

The hydroformylation of 1-octene, cyclohexene and styrene has been reported using $Rh_4(CO)_{12}$(acac) as a catalyst precursor and tris (2-tert-butyl-4-methyl phenyl) phosphine as the ligand in toluene meidum (van Rooy et. a! !995).

For 1-octene and styrene hydroformylation, the rate determining step was reported to be the oxidative addition of H_2 to the acylrhodium complex. A negative order dependence with CO concentration was observed. The following rate equation was proposed

$$r = \frac{k\,(H_2)\,(Rh)}{K_1\,(CO)} \qquad (1.4)$$

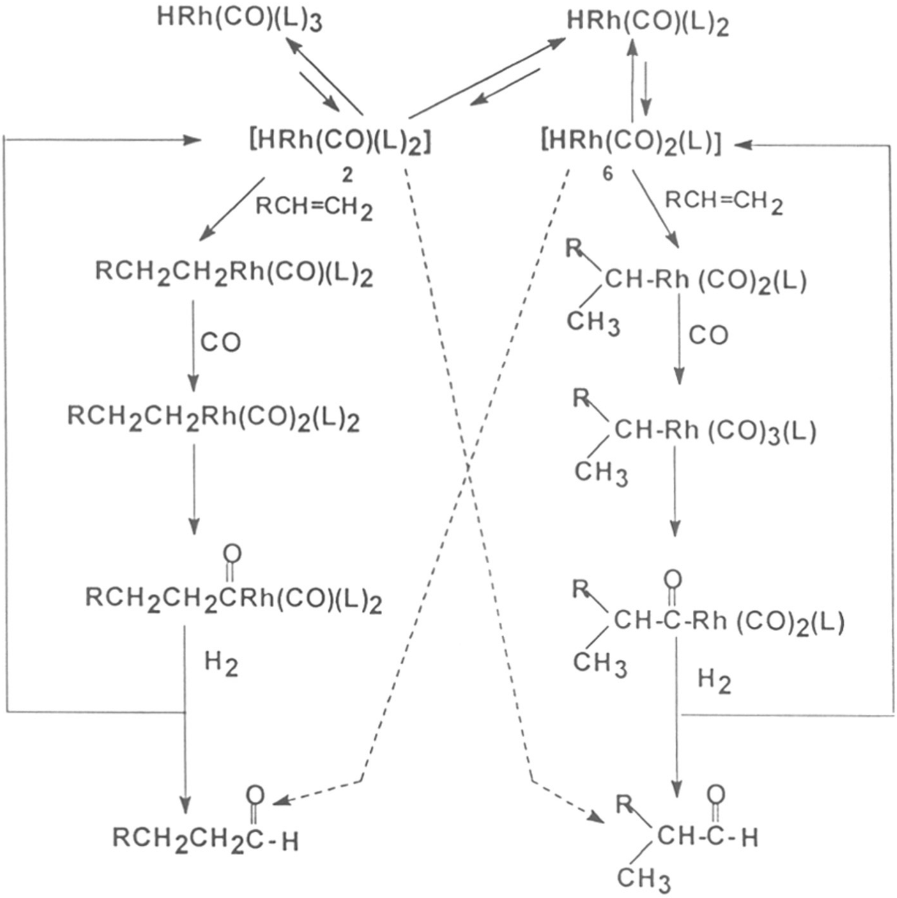


Fig. 1.6 : Modified dissociative mechanism of hydroformylation using $HRh(CO)(PPh_3)_3$ complex catalyst (Bahrmann 1991)

TABLE 1.5

A SUMMARY OF STUDIES ON THE KINETICS OF HYDROFORMYLATION

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

Serial No.	Catalyst	Olefin	Range of condition		Remark	Rate model	Reference
			Temp. K	Press. MPa			
1	$Co_2(CO)_8$	Methyl oleate	383-403	7.1 21.3	R independent of (A+B)	—	Natta and Beati (1945).
2	$Co_2(CO)_8$	Propene	383-393	12-33	R α C, D R independent of (A+B)	$R = \frac{kACD}{B}$	Natta and Ercoli (1952).
3	$Co_2(CO)_8$	Cyclohexene	383-393	12-38	R α C, D R independent of (A+B)	$R = \frac{kACD}{B}$	Natta et. al. (1954), (1955)
4	$Co_2(CO)_8$	Propylene	383-423	3.5 -10	empirical rate model	$R = \frac{kA^{0.6}BC^{0.8}D}{(1+K_BB)^2}$	Gholap et. al. (1992a).
5	$Co_2(CO)_8$	Propylene	383-423	3.5 -10	R_N, R_{ISO} are the rate of formation of 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 Cyclohexene	348 348	15.2	R independent D R α A, C, D	$R = \frac{kAC}{B}$ $R = kA^{1/2}C^{1/4}D$	Heil and Marko (1968). Csontos et. al.(1974).
7	$Rh_4(CO)_{12}$	Hexene	423	B < 90 B > 90	Rα A, B, $C^{1/4}$, D Rα A, B, $C^{1/4}$, D $\frac{1}{R}$ α B		Gankin et. al. (1967a) (1967b), (1968).

TABLE 1.5 (cont.)

Serial No.	Catalyst	Olefin	Range of condition		Remark	Rate model	Reference
			Temp. K	Press. MPa			
8	Polymer immobilized Rh- complex	Ethylene	373			$R = \frac{kAD}{B^{0.5}}$	Arai et. al. (1975).
9	Rh/ active carbon	Ethylene	393			R = k A B D	Takahashi et. al.(1992).
10	$Rh(CO)Cl(PPh_3)_3$/ SLPC	Propylene	373			$R = kDBAexp(\frac{-E}{RT})$	Hjortkjaer et. al. (1981)
11	$Rh(CO)Cl(PPh_3)_2$	Olefins	343-423	3.5-7	R α D, (A+B) R α 1/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,C, D R α 1/B	$R = \frac{kACD}{B}$	Brown and Wilkinson (1970).
14	$HRh(CO)(PPh_3)_3$	Hexene	363		R α A,C, D R α 1/B	$R = \frac{kACD}{B}$	Strohmeier and Michel (1981).
15	$HRh(CO)(PPh_3)_3$	Hexene	303-323	2.2	Critical conc. of catalyst is needed	$R = \frac{k.AB(C_0 - C_c)D}{(1+K_B B)^{2.5}.(1+K_D D)^2}$	Deshpande and Chaudhari (1988).

TABLE 1.5 (cont.)

Serial No.	Catalyst	Olefin	Range of condition		Remark	Rate model	Reference
			Temperature K	Pressure MPa			
16	$HRh(CO)(PPh_3)_3$	Allyl alcohol	363-383	5.4	R α $A^{1.5}$, C, D R α 1/B	$R = \frac{kA^{1.5}BCD}{(1+K_BB)^3.(1+K_DD)^2}$	Deshpande and Chaudhari (1989).
17	$[Rh(CO)_2Cl]_2$	vinyl acetate	353			$R = \frac{kABCD}{(1+K_CC+K_DD^2)}$	Deshpande and Chaudhari (1989).
18	$HRh(CO)(PPh_3)_3$	polybutadiene	350 -390	2.17		$R = \frac{kAC^{\alpha}D^{\beta}}{B}$	Mills et. al. (1990).
19	$Rh(CO)_{12}(acac)$/ tris(2-tert-Butyl -4 methyl Phenyl) phosphine	octene Cyclohexene	313-373			$R = \frac{kAC}{(K_BB)}$ $R = \frac{K_1kCD}{(K_1+B)}$	van Rooy et. al. (1995).
20	$[RhCl(1,5\text{-}COD)]_2$/ TPPTS	octene	333-343			$R = \frac{kABCD}{(1+K_BB)^2(1+K_AA)}$	Purwanto and Delmas (1994).

The kinetics of hydroformylation of polybutadiene using $HRh(CO)(PPh_3)_3$ complex catalyst has been reported (Mills et. al. 1990) in a temperature range of 350-390, K and a total pressure ($CO+H_2$) of 2.172, MPa ($CO : H_2 = 1 : 1$). A power law type of rate equation is proposed to predict the observed rate dependencies. The activation energy for the above reaction was found to be 51.41, kJ/mol. For similar reaction conditions and considering the effect of CO/H_2 concentrations, the rate equation has been proposed (Tremont et. al. 1990) (see Table (1.5)).

The kinetics of hydroformylation of 1-hexene using $HRh(CO)(PPh_3)_3$ complex catalyst in benzene has been reported in a temperature range of 290-305, K (Brown and Wilkinson 1970). It was observed that the rate varies linearly with catalyst concentration and partial pressure of hydrogen. The rate was inhibited at higher partial pressures of carbon monoxide, due to the formation of catalytically inactive species. With 1-hexene concentration, the rate of the reaction increases linearly at lower concentration of 1-hexene and showed a zero order at higher concentration. In this study, no rate equations have been developed.

The kinetics of hydroformylation of 1-hexene using $HRh(CO)(PPh_3)_3$ complex catalyst in ethanol has been reported in a temperature range of 303-323, K (Deshpande and Chaudhari 1988). The most striking observations made in the study are that (i) the rate is inhibited at higher concentration of 1-hexene and (ii) a critical concentration of the catalyst is required to initiate the reaction. An empirical rate equation has been proposed (see Table (1.5)).

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

The kinetics of hydroformylation of vinyl acetate using $[Rh(CO)_2Cl]_2$ complex catalyst in ethanol has been reported at a temperature of 353, K (Deshpande and Chaudhari 1989b). The effect of various process parameters on the rate of reaction is investigated and a rate equation has been proposed based on these observed trends (see Table (1.5)).

In homogeneous medium, the dependencies of the rate of reaction on various process parameters in general for cobalt as well as rhodium complex catalyst has been reported as follows (Cornils 1980).

Order with respect to	Hydroformylation catalyst	
	Cobalt	Rhodium
Olefin concentration	1	0 to 1
P_{H_2}	1	1
P_{CO}	1 to -1	1 to -1
Catalyst concentration	1 to 0.5	1 to 0.6

For many industrially important hydroformylation reactions, the kinetic data is not available. For example, ethylene hydroformylation is important in a new process for methyl methacrylate (Chauvel et. al. 1994; Schwaar 1991), and hydroformylation of olefins > C_{10} range is important in the fragrance and plasticizer industries. For these systems the kinetic data is not available.

Also, in almost all the earlier kinetic reports, mainly empirical rate equations have been developed. The information on correlation between the kinetic data and the reaction mechanism is very limited. It is more appropriate to develop rate equations based on a mechanism. These models are mechanistically more meaningful compared to the empirical rate equations.

Also, the hydroformylation involves simultaneous absorption of two or more gases followed by a chemical reaction in the liquid phase, and hence, it is important to ensure that the data is in the kinetic regime and that mass transfer is not rate controlling.

1.7 BIPHASIC CATALYSIS WITH WATER SOLUBLE COMPLEXES

It is well known that separation of catalyst and products has been a major problem in application of homogeneous catalysis inspite of their several advantages. Many attempts were made to heterogenize the metal complex catalysts using polymer anchoring, supported liquid phase catalysis and more recently the water soluble catalysis in biphasic media. While extensive research has been done on polymer anchored and supported liquid phase catalysis, these systems were not found to be useful for industrial applications. The biphasic catalysis using two immiscible liquid phases is very attractive from practical point of view and has opened up new opportunities for applications of metal complex catalysis in industry (Herrmann and Kohlpaintner 1993 ; Chaudhari et. al. (1995b)).

Biphasic catalysis involves two distinct phases such that the catalyst is soluble in one phase whereas, the products separate out into the other phase. It is essential that the solubility of the catalyst in the other phase is almost negligible. The reaction takes place either in the catalytic phase or at the liquid-liquid interface. This approach is applicable for a variety of gas-liquid-liquid reactions for easy catalyst/product separation (Chaudhari et. al. (1995a)).

The overall performance of these multiphase reactions would depend on both the catalysis and reaction engineering aspects. However, the effectiveness of the gas-liquid and liquid-liquid contacting is also very important. The catalysis part includes the proper choice of catalysts, ligands, solvents and surface active agents etc. The engineering aspects like the hydrodynamics of gas-liquid-liquid dispersion, interface mass transfer, solubility, phase equillibria and intrinsic kinetics of the reaction are equally important in understanding the performance of biphasic catalysts (Chaudhari et. al. (1995a)).

Advantages of biphasic catalysis

1 Easy separation of catalysts and products by simple phase separation which has direct impact on the recovery/recycle of the catalysts and their economic usage.

2 Contamination of the products with the catalyst is minimized or completely eliminated.

3 Higher activity is achievable in the case of substrate inhibited kinetics as the concentration of reactants in the catalyst phase can be controlled by taking the advantage of the solubility limitations. In certain cases, a desired selectivity can also be obtained.

4 This approach is applicable where conventional separation methods are uneconomical due to the problems associated with the non-volatility of products, e.g. hydroformylation of higher alpha olefins (C_6-C_{20}) to aldehydes and alcohols using water soluble rhodium complex catalyst.

5 New catalyst systems with improved activity and selectivity at milder operating conditions can be developed. e.g. Co complex - PTC combined catalyst for carbonylation of organic halides in a two phase system. This combination is practical only in biphasic media.

In recent years, the biphasic catalytic systems ,using water soluble catalysts have been extensively investigated to develop new routes and efficient processes for a variety of products. This class of reactions are important in the context of the present thesis. Therefore, it was thought worthwhile to present a detailed literature survey on the synthesis of different water soluble ligands and catalysts which are used particularly for the hydrogenation and hydroformylation reactions.

In 1958, Ahrland et. al.(1958) first reported the synthesis of water soluble triphenyl phosphine monosulfonate (TPPMS) ligand by direct sulfonation of triphenylphosphine. Later on, the complexes of Rh and Ru with water soluble TPPMS ligand were used for the hydrogenation of pyruvic and lactic acid in a homogeneous medium (Joo and Beck, 1975).

The major breakthrough in this area was the synthesis of triphenyl phosphine trisulphonate (TPPTS) by sulfonation of triphenyl phosphine (Kuntz 1987). The complex of this ligand with rhodium chloro cyclooctadine dimer ($[RhCl(COD)]_2$) forms a completely water soluble catalyst which was shown to be very effective for the hydroformylation of propylene in biphasic media (Kuntz 1976). Based on this work, a commercial plant of n-butyraldehyde was setup by Ruhrchemie in 1984. This led to extensive research work in this area on the synthesis of new water soluble ligands and catalysts and their applications to various reactions. The synthesis of water soluble phosphines and their use in biphasic catalysis has been reviewed recently by Kalck and Monteil (1992) and Herrmann and Kohlpaintner (1993).

1.7.1 Water soluble ligands

The ligands which are commonly used in catalysis e.g. phosphines, amines are modified by introduction of polar hydrophilic groups such as $-SO_3H$, $-COOH$, $-OH$ and $-NH_2$ in the ligand structure to make them water soluble. These ligands on co-ordination with the metal form complexes which are highly soluble in water. The complexes prepared from these ligands are then used as catalysts in biphasic media. The solubility of modified ligands in water is dependent on the nature (alkyl or aryl) and the number of hydrophilic group(s) on the ligand (Joo and Toth 1980).

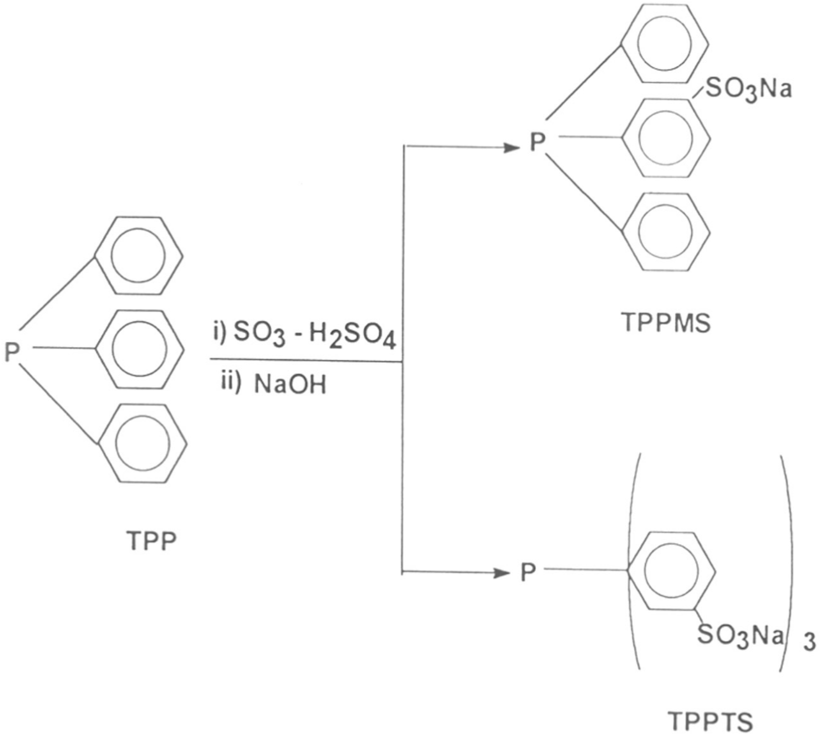
1.7.1.1 Sulfonated phosphines

The water soluble triphenylphosphine monosulfonate (TPPMS) or diphenylphosphino monosulfonate (dpm) and triphenylphosphine trisulfonate (TPPTS) ligands can be used either in the aqueous phase (homogeneous) or in the aqueous-organic (biphasic) system.

The TPPMS (also called dpm) was first synthesised by Chatt and coworkers (Ahrland et. al. 1958) by sulfonation of triphenylphosphine using oleum / sulfuric acid mixture.

For the synthesis of TPPTS, precise concentration of oleum combined with controlled operating conditions (micromixing, temperature and reaction time) are necessary (Kuntz 1976).

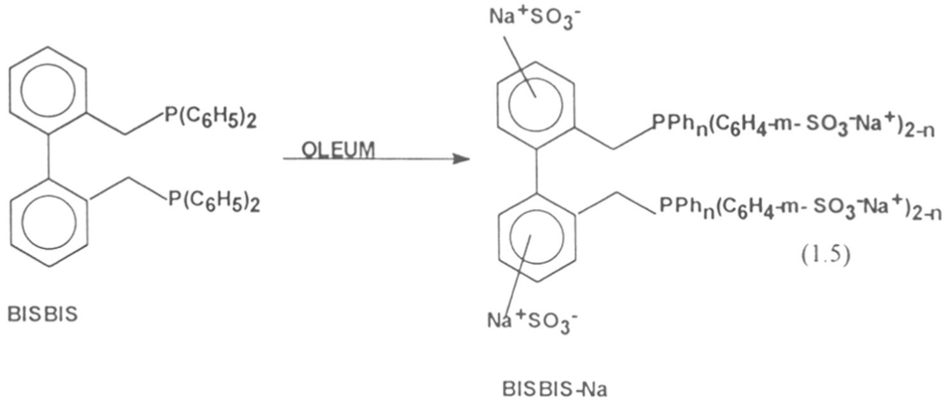
While synthesizing TPPTS by sulfonation of TPP, 9 as shown in scheme 4) the by-products like mono and disulfonates along with TPPTS oxide are also formed (Morel and Jenck 1983; Varre et. al. 1984).



Scheme 4 : Synthesis of TPPMS and TPPTS by direct sulfonation of TPP

The TPPTS is a versatile ligand and it has the properties similar to triphenylphosphine. The solubility of TPPTS in water is of the order of 1100, kg/m^3 whereas for TPPMS, it is ≈ 80, kg/m^3.

Like TPPTS, another water soluble ligand BISBIS-Na has been synthesized by sulfonation of BISBI [2-2'-bis (diphenylphosphinomethyl)-1, 1-biphenyl] as shown below (Herrmann et. al. 1992). This ligand has the solubility in water to the extent of 1500, kg/m^3.



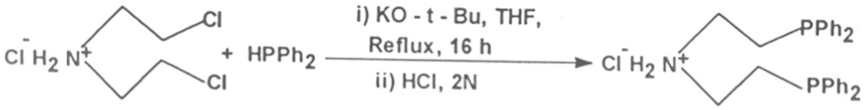
(1.5)

The sulfonation of alkyl phosphines can be carried out to yield water soluble ligands. Thus the sulfonation of tris(w-phenylalkyl phosphanes $P[(CH_2)x(C_6H_5)]_3$ (x = 1,2,3 and 6) is carried out as shown below (Bartik et. al. 1993).

$$P[(CH_2)_x(C_6H_5)]_3 \xrightarrow[\text{iii) 20\% NaOH}_{aq}\text{ - 0 }^{o}\text{C}]{\text{i) H}_2\text{SO}_4\text{ - 25 }^{o}\text{C} \quad \text{ii) 20\% SO}_3\text{- H}_2\text{SO}_4} P[(CH_2)_xC_6H_4\text{-p-}SO_3Na]_3 \qquad (1.6)$$

x = 0, 1, 2, 3 & 6

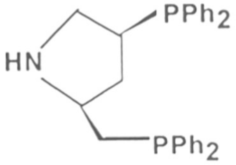
Wilson and co-workers (1978) developed a new method in which a diphosphine intermediate is prepared (yield ~ 90%) insitu as given below :



(1.7)

This diphosphine is then acylated with acid chlorides such as trimellitic anhydride acid chloride or tricarballytic anhydride acid chloride or ethyl oxalyl chloride. Further reaction with sodium taurinate gave the derivatives which are diphosphine ligands having a sulfonate group on the side chain.

By using similar methodologies, the synthesis of chiral phosphine ligand is reported (Benhamza et. al. 1985) starting from 2-(diphenylphosphino methyl)-4-(diphenyl phosphino) pyrolidine.



(1.8)

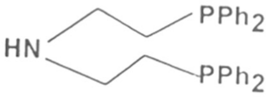
The PPM 2-(diphenylphosphino methyl)-4-(diphenyl phosphino) pyrolidine can be functionalized by acylation of the N-H bond with trimellitic anhydride acid chloride. This is then reacted with NaOH or sodium taurinate to yield sulfonated asymmetric water soluble ligand.

The ligands (S,S)-chiraphos and skewphos can be successfully sulfonated with oleum containing 20% SO_3 by a procedure similar to that described for triphenylphosphine. Depending on the oleum /phosphine ratio, disulfonates or tetrasulfonates are formed (Sinou 1987; Alario et. al. 1986).

(1.9)

1.7.1.2 Other ligands

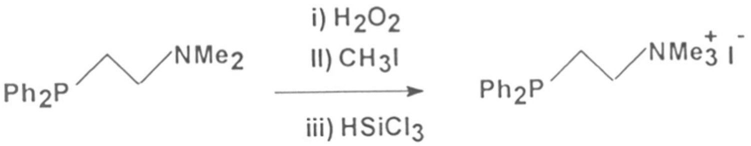
The synthesis of carboxylic phosphine is reported by many workers (Kalck and Monteil 1992). The condensation of a phosphido salt with an ω-haloester or ω-halocarboxylate leads to corresponding ω-phosphinoesters or acids (Issleib and Thomas 1960, Issleib et. al. 1965). Similarly, ω-phosphinoesters (Issleib and Thomas 1961; Empsall et. al. 1977). It was also shown that bis(2-diphenylphosphino ethyl) amine (I) appears to be a very useful starting material for the preparation of carboxylic diphosphines by using trimellitic anhydride acid chloride and camphoric as well as succinic anhydrides (Nuzzo et. al. 1979; Nuzzo et. al. 1981; Wilson et. al. 1978).



(1.10)

(I)

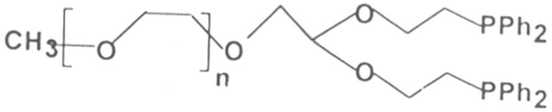
These are generally obtained through the synthesis of nitrogen containing phosphine ligands followed by quaternization. However, before the nitrogen atom can be alkylated, the (more active) phosphorus center has to be protected, either by oxidation or by coordination to a metal. Subsequent reduction or decomplexation, respectively, yields the desired phosphine ligands. The important class of these ligands is the 'amphos' reported by Smith et. al. (1982).



(1.11)

This synthetic procedure is extended to prepare many other mixed water soluble ligands.

By varying the length of the polyether chain of substituted phosphines, the solubility of the resulting ligands can be deliberately adjusted. Bisphosphines of the type (II) (n=5) are insoluble in water. For n > 16 (e.g. n = 42) however, they are highly soluble (Amrani and Sinou 1984).


(II)

(1.12)

1.7.2 Hydroformylation reactions

The water soluble complexes of TPPMS (dpm) are employed for the hydrogenation of unsaturated acids in aqueous medium and the kinetics of reduction of unsaturated substrates has been investigated using $RuCl_2(TPPMS)_2$, $HRuCl(TPPMS)_3$, $HRu(OOCCH_3)(TPPMS)_3$, $RuCl(TPPMS)_3$ (Joo and Beck 1975; Joo and Toth 1980). These ruthenium catalysts are used in hydrogenation of maleic, fumaric, crotonic and cinnamic acids. It was found that when only two phosphines are present in the coordination sphere of the metal, the keto acid coordinates strongly enough to produce a catalytically inactive species. The species like $[HRuCl(TPPMS)_3]$ or $[HRu(OAC)(TPPMS)_3]$ was found to be active catalytic species in the hydrogenation of pyruvic acid.

Dror and Manassen (1977) have investigated the hydrogenation of cyclohexene in a two phase system with $RhCl(TPPMS)_3$ complex/ excess TPPMS as a catalyst, generated insitu from $RhCl_3.3H_2O$ / TPPMS. The various cosolvents were used and it was observed that a cosolvent has a profound effect on the activity of the catalyst. Among ethanol, methanol, dimethylacetamide and dimethoxyethane, highest activity of the catalyst was obtained when methanol was used as a cosolvent.

The hydrogenation of 1-hexene, cis- trans 2-hexene and cyclohexene has been studied using $[RuCl(TPPMS)_3]$ and $[HRuCl(TPPMS)_3]$ in two phase system without a co-solvent (Borowski et. al. 1978, 54). $[RuCl(TPPMS)_3]$ was found to be the most active and selective catalyst. Significant amount of isomerisation product were observed in the case of hexene as a substrate. This was thought to be due to competing isomerisation reaction due to the limitation of hydrogen transfer to the aqueous catalytic phase. The reaction was conducted at 25-80°C and 0.3, MPa pressure. It is further reported that with $RuCl_3$/TPPMS as a catalyst precursor, 30 catalytic recycles were possible whereas with $[HRuCl(TPPMS)_3]$ complex catalyst, 1400 cycles

The hydroformylation of allyl alcohol and 1-hexene using water soluble Ru(EDTA)-complex catalyst has been reported at 5, MPa and in a temperature range of 90-130°C (Taqui Khan et. al. 1988a; Taqui Khan et. al. 1988b). In the hydroformylation of allyl alcohol 35% hydroxybutyraldehyde, 25% γ-butyrolactone, 25% dihydrofuran and remaining polymerised products were observed. For 1-hexene, excellent selectivity to linear C_7-aldehyde was reported (98-100%). The catalyst recycle without its degradation has also been demonstrated.

The solubilisation of the metal complexes in aqueous phase has led to its use in aqueous-organic (biphasic) media. These systems can be applied to the reactions like hydroformylation, hydrogenation, telomerization and oligomerization (Southern 1989; Kalck and Monteil 1992).

n-Butyraldehyde is an important intermediate to produce n-butanol and 2-ethylhexanol which are commonly used solvents. If $[RhCl(COD)]_2$/TPPTS complex catalyst system is used for the hydroformylation of propylene, selectivity greater than 90% towards linear aldehyde with minimum hydrogenation of alkene was observed (Kuntz 1975). Most of the work on this industrially important reaction is patented (Jenck (1980) ; Kuntz (1976) ; Hibbel et. al. (1982) ; Cornils et. al. (1983) ; Cornils et. al., (1984)).

The process for the hydroformylation of propylene was first operated industrially by Ruhrchemie in 1984 and a 10,0000, tpa plant was set up at Oberhausen. A schematic of this process is shown in Fig. (1.7).

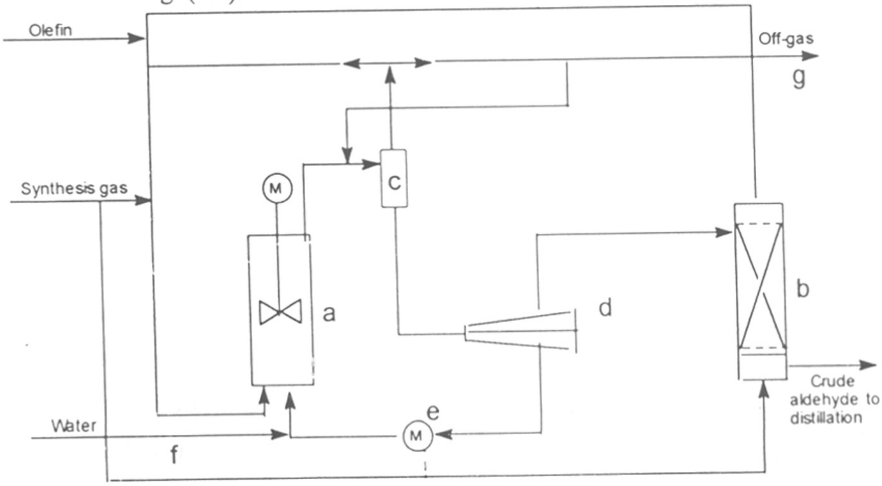


Fig. 1.7 : **A schematic diagram of continuous process for the hydroformylation of olefins (Bahrmann 1991)**

In this process the reaction takes place in a stirred tank reactor (a), which contains the catalyst solution, the reactants are introduced from below. Before entering the reactor, the synthesis gas is first passed through a stripping column (b), in counter current to the crude aldehyde stream, in order to recover the unreacted propylene. Furthermore purification of the reactants can be avoided by this procedure (Cornils et.al. (1983)). The crude aldehyde product leaves the top of the reactor and passes through the trap (c), into the phase separator (d), where it is separated from the entrained catalyst solution. The catalyst solution is returned to the reactor via the heat exchanger (e), (Barhmann et. al (1991)). The active catalytic species was found to be HRh(CO)(TPPTS)$_2$ (Kalck et.al. 1988) which is formed insitu by the reaction of [RhCl(COD)]$_2$ and TPPTS under CO/H$_2$ atmosphere.

Continuous hydroformylation of propylene using water soluble Rh-BISBIS complex catalyst has also been reported. The P/Rh ratio used was 6.7:1. The activity of Rh-BISBIS catalyst is compared with Rh-TPPTS as a catalyst under hydroformylation conditions. It was found that the catalytic activity of Rh-BISBIS complex was higher (three times) than Rh-TPPTS complex as a catalyst, even at P/Rh ratio twelve times lower than in the former case. Selectivity to linear aldehyde was found to be 97% and the other products include 6-7% alcohol and 1.5% condensation products (Herrmann et. al. (1992)).

The success of the use of water soluble ligands to prepare water soluble catalysts for the hydroformylation of gaseous reactants led its way for the researcher to use this approach for liquid reactants as well. Many studies have been reported with 1-hexene and 1-octene as substrates for hydrogenation and hydroformylation reactions. Several water soluble ligands and catalysts have been employed and their catalytic activity, selectivity and stability of these complexes have been established (Monteil (1993) ; Hablot (1991) ; Kalck et. al. (1988) ; Herrmann et. al. (1992)).

Borowski et. al. (1978) have reported the use of HRh(CO) (TPPMS)$_3$ complex catalyst for the hydroformylation of 1-hexene at 90°C and 6, MPa pressure. This catalyst is not stable at high temperatures in solution. The addition of excess ligand (TPPMS) not only stabilized the catalyst but also led to improved selectivity. Isomerisation is also a competing reaction and therefore only 30% conversion to aldehydes was obtained in 24, hrs. The n/iso ratio was observed to be 3/1. The complex PtHCl(TPPMS)$_3$ showed poor activity towards hydroformylation below 90°C and at higher temperatures the decomposition of the complex to platinum metal was observed (ibid.).

Hydroformylation of 1-hexene with [Rh(m-Cl)$_2$(NBD)$_2$]/amphos catalytic system is reported by Smith et. al. (1983) at 90°C and 4, MPa total pressure (CO/H$_2$=1). A yield of 90% heptanal and n/iso ratio of about 4 was obtained. The selectivity was found to be dependent on solvent as well as pH of the reaction medium. The addition of excess ligand (amphos / Rh = 10), was found to lower the selectivity towards linear aldehyde (3.4 instead of 4). It was noted that acidic media favor hydrogenation of 1-hexene to hexane (16% at pH 5). The leaching of rhodium to the organic phase was found to be about 0.5, ppm which is less than 0.1% of the total rhodium charged.

The hydroformylation of 1-hexene with [HRh(CO)(TPPTS)$_3$] complex catalyst has been investigated at 80°C and 0.5, MPa pressure. The selectivity to linear aldehyde was found to be about 93% (Thorez (1985)).

Horvath et. al. (1989) have obtained [HRh(CO)(TPPTS)$_3$] complex catalyst from two precursors viz. [Rh(CO)$_2$(acac)] and [Rh(C$_2$H$_4$) (acac)]. The catalyst was found to be undissociated even under high pressures (20, MPa) of syngas. This phenomenon is contradictory to the Wilkinson's complex [HRh(CO)(PPh$_3$)$_3$], wherein a dicarbonyl species is formed under hydroformylation conditions. As a result excellent selectivity to n-aldehyde was observed.

The dinuclear Rhodium complex [Rh$_2$(m-SR)$_2$(CO)$_2$(TPPTS)$_2$] provided good performance in the hydroformylation of 1-hexene at a slight excess of ligand (Kalck et.al 1988). Total conversion of hexene to heptanal was observed at 0.5, MPa pressure and a temperature of 80°C with P/Rh of 3 and selectivity to linear aldehyde was found to be 94%. It was further reported that at a P/Rh of 6 and pressure of 1, MPa, the selectivity can be increased upto 97%.

Ligand variation has a considerable effect on the performance of the water soluble catalysts. The use of BISBIS as a ligand instead of TPPTS for the hydroformylation of 1-hexene has been investigated (Herrmann et. al. 1992). The increase in catalytic activity [mol(n+iso)aldehyde /g Rh min] from 0.73 to 10.7 was obtained in a temperature range of 123-155°C and pressure of 5, MPa (CO/H$_2$=1). The selectivity to linear aldehyde decreased from 97.3 to 94.6 % with increase in temperature. The catalyst was found to remain stable for 16, hrs for continuous hydroformylation at P/Rh ratio of 6.7:1 at pH of 5.2.

The hydroformylation of 1-octene with dinuclear [Rh$_2$(m-SR)$_2$(CO)$_2$(TPPTS)$_2$] and [HRh(CO)(TPPTS)$_3$] complex catalyst has been investigated by Monteil (1993). The rate of reaction is controlled by the solubility of 1-octene in the aqueous catalytic phase. To increase the solubility, the use of co-solvents such as methanol, ethanol, acetone and acetonitrile has been suggested and ethanol was found to be the best cosolvent. The selectivity to linear aldehyde was found to be proportional to the amount of ethanol in the aqueous phase. Here, an interesting solvophobicity parameter Sp is considered rather than the polarity of the medium (Abraham et al. 1988). The Sp values are established from the difference between free energies for the transfer of a given solute from water to another solvent. They have been expressed at 25°C relative to two fixed solvents and the range between 1 for water and 0 for the most hydrophobic solvent, hexadecane. In the case of octene hydroformylation the linear correlationship between log (n/i) vs Sp was observed (Monteil et. al. 1994)

Previous work in biphasic catalytic system is mainly carried out with rhodium containing water soluble catalyst but the metals other than rhodium are also reported to be active for these reactions.

The hydroformylation of 1-hexene with cobalt catalyst at 140°C and 13, MPa pressure in $CO:H_2$ ratio of 1:2 yielded 89% heptanals in 3, hrs and selectivity to linear aldehyde was 62%. In the case of 2-hexene hydroformylation, 68% aldehydes were produced with 59% linear aldehyde. The leaching of cobalt to the organic phase was found to be of the order of 1% of the total initial metal charged (Jenck and Kuntz 1979). Thus, cobalt appears to be less attractive than rhodium for the selective hydroformylation of alkenes, except the internal ones. This is because i) the operating conditions for olefin hydroformylation using cobalt are generally more severe ii) loss of catalyst/metal to organic solution is higher and iii) selectivities are poor with respect to rhodium.

Similar results are obtained in the hydroformylation of 1-hexene with $[Co(CO)_3(amphos)_2][PF_6]_2$ complex catalyst in biphasic media (Markiewicz and Baird 1986). The products contained 35% heptanal, 33% isoheptanal and 32% n-heptanol. Hydrogenation of aldehydes can be avoided by the addition of benzene as a cosolvent.

In the hydroformylation of 1-tetradecene, a catalyst system consisting of $[Rh_4(CO)_{12}]$ and tris(2-pyridyl)phosphine sulphoalkylated by octane-1,2-sultone, at 125°C and 7.5, MPa pressure for 3, hrs, gave a yield of 79%. The surface active phosphine ligand improved the contact between the catalyst and the organic layer and also allowed quantitative recovery of the active catalytic species by simple decantation (Fell and Papadogianakis 1991).

All the studies so far on biphasic hydroformylation reactions have dealt mainly with the synthesis and screening aspects of various water soluble ligands and catalysts, their activity and selectivity for various reactions. There are very few reports on the kinetics of hydroformylation and hydrogenation using the water soluble complex catalysts. As these reactions involve mainly gas-liquid-liquid systems, the study of mass transfer and intrinsic kinetics of these reactions become important.

The kinetics of hydrogenation of 1-octene using Rh-TPPTS complex catalyst in biphasic media has been investigated (Hablot 1991). The rate of reaction is dictated by the solubility of octene in the aqueous catalytic phase. Thermodynamic analysis and the solubility studies involved in the hydrogenation reaction have also been reported. The effect of various co-solvents was studied and ethanol was found to be the best cosolvent. Monteil (1993) has studied the hydroformylation of 1-octene with $[Rh_2(m\text{-}SR)_2(CO)_2(TPPTS)_2]$ as a catalyst. The author compared the effect of different cosolvents viz. ethanol, acetonitrile, acetone and methanol. The highest reaction rate was obtained with ethanol as a co-solvent.

In one of the recent reports, kinetics of hydroformylation 1-octene using $[RhCl(COD)]_2$ /TPPTS as a catalyst system in octane as a solvent and ethanol as a cosolvent has been reported (Purwanto and Delmas 1994) (.see Table (1.5)). The effect of various reaction conditions on the rate of reaction were found to be complex in nature. The rate was found to first order with respect to catalyst concentration and shows zero order with octene concentration. Inhibition in rate was observed at higher partial pressures of CO whereas rate varied linearly at lower partial pressure of hydrogen and showed zero order at higher pressure. An empirical rate equation has been developed based on the general trends observed in the study. The activation energy was found to be 14.9, kcal/mol.

The approach of immobilized catalyst has been developed to overcome the difficulties associated with poor rate of reactions due solubility limitations of organic substrates in the aqueous phase containing the catalyst. In this new methodology, also called supported aqueous phase catalysis (SAPC), a water soluble organometallic complex [e.g. $HRh(CO)(TPPTS)_3$] is dissolved in a thin film of water which is then supported onto a high surface area hydrophilic silica (e.g. CPG 240) (Arhancet et. al. (1989) ; Arhancet et. al. (1990)). This solid impregnated catalyst is used in an immiscible organic phase. The reactants, diffuse from the bulk phase into the porous solid.

The main advantage of employing this approach is that the reaction occurs at liquid-liquid interface eliminating the problems associated with the marginal solubility of organic substrates into the aqueous catalytic phase (Davis 1992). Similar activities and selectivities are obtained when 1-hexene, 1-octene and 1-decene were hydroformylated with the catalyst prepared from [HRh(CO)(TPPTS)$_3$] /TPPTS supported on a silica (e.g. CPG 240). It is also shown that these catalysts are more active compared to their biphasic counterparts. The results with cobalt-complex catalysts supported on hydrophilic support indicated that they were twice as active as in the biphasic systems. The higher activity was attributed to the increased mass transfer rate of the reactants to the active catalytic site and also the stabilisation of complex onto the support. The loss of metals (Co, Rh) due to leaching is significantly avoided. However, large variation in the selectivity to desired product have been realised due to the changes in the active catalytic species on immobilisation. Even though, the commercial applications of these type of catalysts are yet to be proven, the results are promising.

Horvath and Rabai (1994) have developed a novel approach of fluorous biphase system (FBS) for performing stoichiometric as well as catalytic chemical transformations. This concept is based on the limited solubility of the fluorinated solvents into non-fluorinated solvents. The fluorous (similar to aqueous) phase is the fluorocarbon (mostly perfluorinated alkanes, ethers and tertiary amines) rich phase and an FBS compatible reagent or catalyst containing enough fluorous moeities such that it will be soluble only or preferentially in the fluorous phase. The reaction takes place either in fluorous phase or at the interface. The application of FBS has been demonstrated for the hydroformylation of 1-decene and also for the extraction of metals like rhodium from toluene. This approach has many advantages (i) water sensitive reagents can be used (ii) at higher temperatures, the system becomes homogeneous and can be employed where mass transfer from non-fluorous phase to the fluorous phase is rate limiting (iii) heavy metal recovery is possible, which is one of the extremely important areas of environmental chemistry.

This concept has many challenges in near future which include extraction of toxic metals, selective functionalisation of variety of organic molecules and chiral fluorous reagents for asymmetric transformations.

1.7.3 Interfacial catalytic approach

One of the major achievements in the area of water soluble catalysis is the significant improvement in rate of reaction by promotion of an interfacial catalytic reaction (Chaudhari et al. 1995). In this approach the catalyst concentration is enriched at the liquid-liquid (aqueous-organic) interface using a catalyst binding ligand present in organic phase. The access of catalyst to very high reactant concentrations in the organic phase leads to a dramatic increase in the rates. This catalyst system offers following advantages over the conventional biphasic systems.

* Significant enhancement in the rate of reaction
* No leaching of the catalyst to the organic phase
* Can be applied to the hydroformylation of water insoluble substrates

This approach can be applied in the reverse way to the substrates which are completely soluble in water. In this case, the catalyst is dissolved in the organic phase whereas the catalyst binding ligand (water soluble) e.g. triphenylphosphine trisulphonate sodium salt is added to the aqueous phase. e.g. hydroformylation of allyl alcohol using $HRh(CO)(PPh_3)_3$ complex as a catalyst.

This catalytic system can be used on a broader scale in various industrial processes like hydroformylation, hydrogenation oxidation, polymerisation, etc., in principle, for any homogeneous catalytic reaction.

1.8 SCOPE AND OBJECTIVE OF THE PRESENT WORK :

Hydroformylation of olefins is a subject of considerable interest in the last three to four decades as it offers direct commercial route for the manufacture of aldehydes and alcohols (oxo alcohols) from various olefin feedstocks. These products find major applications as solvents, intermediates for variety of bulk and speciality chemicals.

As seen in the previous sections, the literature on this industrially important reaction mainly deals with activity and selectivity of various catalyst-ligand systems. There are very few studies directed to investigate the detailed kinetics and mechanism of the reaction. The oxo process is important from both industrial and academic point of view. This is because this technology is in operation in many industrial plants. The reaction involves simultaneous absorption of two or more gases in the liquid followed by a complex catalytic reaction. Thus, the study of reaction engineering aspects like rate behaviour, intrinsic kinetics and the mechanism of such a complex multiphase reaction becomes important. These studies are not only useful for optimisation of the process and improvement of catalytic system but are also required as the basic information for the design and scale up of suitable reactors.

Keeping these viewpoints, it was thought necessary to investigate and understand in detail the rate behaviour, mass transfer phenomenon, intrinsic kinetics and mechanism in hydroformylation reaction using various olefins as a feedstocks using a homogeneous and biphasic Rh complex catalyst. The following specific problems were chosen for the present thesis

1 Solvent effects and deactivation studies in the hydroformylation of 1-hexene using homogeneous $HRh(CO)(PPh_3)_3$ complex catalyst

2 Kinetics and selectivity behaviour in the hydroformylation of 1-decene using a homogeneous $HRh(CO)(PPh_3)_3$ complex catalyst

3 Kinetics of hydroformylation of ethylene using homogeneous $HRh(CO)(PPh_3)_3$ complex catalyst

4 Catalysis and kinetics of ethylene hydroformylation using water soluble Rh-TPPTS catalyst in homogeneous and biphasic media.

REFERENCES

Abraham M. H., Grellier P.L. and Mcgill R. A., J. Chem. Soc. Perkin Trans II, 339, (1988).

Adkins H. and Krsek G., J. Am. Chem. Soc., **71**, 3051, (1949).

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

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

Alario F., Amrani Y., Colleuille Y., Dang T.P., Jenck J., Morel D. and Sinou D., J. Chem. Soc. Chem. Commun. 202 (1986).

Amrani Y. and Sinou D., J. Mol. Catal., **24**, 231, (1984).

Arai H., Kaneko T. and Kunugi T., Chem. Lett 265, (1975).

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

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

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

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

Bannerjee T.K., Saha C.R. and Sen D., J. Chem. Technol. Biotechnol., **31**, 737, (1981).

Bartik T., Bartik B., Hanson B.E., Guo I.and Toth I., Organometallics, **12,** 164, (1993).

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

Benhamza R., Amarani Y. and Sinou D., J. Organomet. Chem. **288**, C37, (1985).

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

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

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

Carrick W.L., Macromol. Syn., **2**, 133, (1966).

Cavalieri d'Oro P., Raimondi L., Pagani G., Montrasi G., Gregorio G., and Andreetta A., Chem. Ind. (Milan), 62, 572, (1980).

Cavalieri d'Oro P., Raimonde L., Pagani G., Montrasi G., Gregorio G., Oliveri del Castillo G.F.

and Andreetta A., Symp. Rh Homogenous Catal [Proc] 121, (1978).

Chatt J., Leigh G. J. and Slade R. M., J. Chem. Soc. Dalton Trans., 2021, (1973)

Chaudhari R. V., Bhattacharya A. and Bhanage B. M., Catal. Today, **24,** 123, (1995)

Chaudhari R. V., Bhanage B. M., Deshpande R. M. and Delmas H., Nature, **373,** 501, (1995)

Chauvel A., Delmon B. and Holderich W., Appl. Catal A : General, **11,** 173, (1994).

Chem. Week., Nov. 20, 71, (1974).

Chalk A.J., Chem. Ind. (Dekker), **33**, 43, (1988).

Chin Y., Oxo alcohols, Standford Research Institute Report No. 21C, SRI International, Menlo Park, California, (1986).

Claridge J.B., Douthwaite R.E., Green M.L.H., Lago R.M., Tsang S.C. and York A.P.E., J. Mol. Catal., **89**(1-2), 113, (1994).

Coover H.W. and Hart R.C., Chem. Engg. Prog., 72, (1992).

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

Cornils B., Hibbel J., Konkol W., Lieder B., Much J., Schmidt V. and Wiebus E., Eur. Pat. 0103810, (1983).

Cornils B., Konkol W., Bach H., Dambkes G., Gick W., Greb W. and Wiebus E., Eur. Pat. 0158246, (1984).

Csontos G., Heil B. and Marko L. Ann. N. Y. Acad. Sci. **239**, 47, (1974).

Davis M.E., CHEMTECH, 498, (1992).

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

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

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

Dror Y. and Manassen J. J. Mol. Catal., **2,** 219, (1977).

Dubois R.A., Garrou P.E., Lavin K.D. and Allcock H.R., Organometallics, **3**(4), 649, (1984).

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

Empsall H. D., Hyde E. M., Pawson D. and Shaw B. L., J. Chem. Soc. Dalton Trans., 1292, (1977).

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

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

Fell B., Chem. - Ztg. **101**, 343, (1977).

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

Gankin Y.V. and Rudkowski D.M., Kinet. Katal. **8**(4), 908, (1967a).

Gankin Y. V., Genender L. S. and Rudkowski D. M., Zh. Prikl. Khim. **40**(9), 2029, (1967b).

Gankin Y. V., Genender L. S. and Rudkowski D. M., Zh. Prikl. Khim. **41**(7), 1577, (1968).

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

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

Gregorio G., Montrasi G., Tampieri M., Cavalieri d'Oro P., Pagani G. and Andreetta A., Chem. Ind. (Milan), **62**, 389 (1980);

Grimbolt J., Bonnelle J.P., Vaccher C., Mortreux A., Petit F. and Peiffer G., J. Mol. Catal., **9**(4), 357, (1980).

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

Hablot I., Ph. D. Thesis INP Toulouse (1991).

Haggin J., Chem. and Engg. News, **65**(44), 27, (1987).

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

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

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

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

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

Heil B. and Marko L., Chem. Ber., **104**, 3418, (1971).

Hennico A., Leonard J., Forestiere A. and Glaize Y., Hydrocarb. Process **69**(3), 73, (1990).

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

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

Hibbel J., Kessen G., Konkol W., Lieder B., Wiebus E., Kalbfeu H. and Bach H., Eur. Pat. 0111257, (1982).

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

Hjortkjaer J., Scurrell M. S., Simonsen P. and Svendsen H., J. Mol. Catal., **12**, 179, (1981).

Hjortkjaer J. and Toromanova - Petrova P., J. Mol. Catal. **50,** 203, (1989).

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

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

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

Issleib K. and Thomas G., Chem. Ber. **93,** 803, (1960).

Issleib K. and Mobius H. M., Chem. Ber. **94,** 102, (1961).

Issleib K., Kummel R. and Zimmermann H., Angew. Chem. Int. Ed. Engl. **4,** 155, (1965).

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

Jap. Pat. 8155323, (1981).

Jenck J. and Kuntz E., Fr. Patent 2,473,504 (1979).

Jenck J. Fr. Patent 2,478,078 (1980).

Jenck J.F. and Kuntz E., 187 ACS National Meeting, April 8-12, St. Louis, MO INDE, paper 72, (1984).

Jira R., Ethylene and its industrial derivaties edited by Miller S.A. (Ernet Benn Ltd), 650, (1969).

Joo F. and Beck M. T., React. Kinet. Catal. Lett., **2,** 257, (1975).

Joo F. and Toth Z., J. Mol. Catal. **8,** 369, (1980).

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

Kalck P., Escaffre P. Serein-Spriau F., Thorez A., Besson B., Colleuille Y. and Perron R., New J. Chem., **12,** 687, (1988).

Kirschenbaum I. and Inchalik E.J., Encyclopedia of Chemical Technology edited by Krik Othmer,

3^{rd}Edition (John Wiley & Sons, New York), **16,** 637, (1982).

King R.B., King A.D.Jr. and Iqbal M.Z., J. Am. Chem. Soc., **110**(17), 4893, (1979).

Kuntz E., Fr. Patent 2,314,910, (1975)

Kuntz E., Fr. Patent 2,349,562, (1976)

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

Larpent C., Patin H., Thilmont N. and Valdor J.F., Syn. Comm., **21,** 495, (1991).

Ludecke V.D., Encyclopediea of Chemical Processing and Design edited by Mcketta J.J. and Cunnigham W.A. (Marcel Dekker, New York and Basel), **1**, 146, (1976).

Markiewicz M. K. and Baird M. C. Inog. Chim. Acta **113,** 95, (1986).

Marko L., Aspects of Homogeneous catalysis edited be Ugo R. (Riedel Publishing Co. Dordrecht Holland) **2,** 3, (1974).

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

Mills P. L., Tremont S. J. and Remsen E. E., Ind. Engg. Chem. Res., **29,** 1443, (1990).

Mirbach M.F., J. Organomet. Chem. **265**, 205, (1984)

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

Monteil F., Ph. D. Thesis, INP Toulouse, (1993).

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

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

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

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

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

Nuzzo R. G., Feitler D. and Whitesides G. M., J. Am. Chem. Soc., **101,** 3683, (1979).

Nuzzo R. G., Haynie S. L., Wilson M. E. and Whitesides G. M., J. Org. Chem., **46,** 2861, (1981).

Okano T., Tobayashi T., Konishi H. and Kiji J., Tetrahedron Lett., **23**(47), 4967, (1982)

Onoda T., Catalytic Sci. and Technol. **1**, 47, (1991) Orchin M. and Rupilius W., Catal. Rev. **6**(1), 85, (1972).

Osborn J. A., Young J. F. and Wilkinson G. W. J. Chem. Soc. Chem. Commun., 17, (1965)

Oswald A. A., Jermansen T. G., Westner A. A. and I-Der Huang, DE 3034352, (1980)

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

Parshall G.W. and Nugent W.A., CHEMTECH, 184, (1988).

Piacenti F., Bianchi M., Frediani P., Matteoli U. and Moro A.L., J. Chem. Soc. Chem. Commun. 789 (1976); Chim. Ind. (Milano) **58**(11), 759, (1976)

Pittman C.U. and Hirao A., J. Org. Chem., **43**, 640, (1978).

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

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

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

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

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

Serio M.D., Garaffa R. and Santacesaria J.J., J. Mol. Catal., **69**, 1, (1991).

Schwaar R. H., SRI-PEP Report 11D, (1991).

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

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

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

Slaugh L. H. and Mullineaux R. D., Ger. Patent. Appl. 1,186,455, (1961).

Slaugh L. H. and Mullineaux R. D., US Patent. 3,239,566, (1966).

Smith R.T., Ungar R.K. and Baird M.C., Trans. Metal. Chem., **7**, 288, (1982).

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

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

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

Southern T.G., Polyhedron **8**, 407, (1989).

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

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

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

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

Thorez A., Ph. D. Thesis, INP Toulouse, (1985).

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

Tremont S. J., Remsen E. E. and Mills P. L., Chem. Eng. Sci., **45**(8), 2801, (1990).

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

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

van Rooy A., Orij E. N., Kamer P. C. J. and van Leeuwen P. W. N. M., Organometallics **14,** 34, (1995).

van Leeuwen P.(Shell Int. Res.), Eur. Pat. EP 33554, (1981).

Varre C., Desbois M. and Nouvel J., Fr. Pat. 2,561,650, (1984).

Weissermal K. and Arpe H.J., Industrial Organic Chemistry, Verlag Chemie , Weinheim, (1978).

Wender I., Orchin M. and Storch H. H., J. Am. Chem. Soc. **72**, 4842, (1950).

Wender I., Sternberg H. W. and Orchin M., J. Am. Chem. Soc. **75**, 3041, (1953).

Wilson M. E., Nuzzo R. G. and Whitesides G. M., J. Am. Chem. Soc., **100,** 2269, (1978).

CHAPTER 2

* * *

KINETIC MODELLING, SOLVENT EFFECTS AND CATALYST DEACTIVATION IN HYDROFORMYLATION OF OLEFINS USING A HOMOGENEOUS $HRh(CO)(PPh_3)_3$ COMPLEX CATALYST

* * *

2.1 INTRODUCTION :

The hydroformylation of olefins to aldehydes is an example of one of the largest scale applications of homogeneous catalysis. The relevant literature on catalysis, chemistry and kinetics is summarised in Chapter 1. It is evident that the entire range of α-olefins are hydroformylated to obtain products of commercial interest. The best catalytic systems consist of Rh-complexes in a homogeneous phase, though their applications are limited to lower olefin substrates for which the volatile products are conveniently separated from catalysts by simple distillation. Considering the practical relevance of hydroformylation of alpha-olefins, it is important to improve the catalysts to achieve commercially viable activity and selectivity. For this purpose, it is necessary to understand the role of different types of catalyst precursors, ligands, solvents, nature of catalyst deactivation and kinetics and mechanism. While, extensive work on some of these aspects has already been published (Chapter 1), specific data on higher olefin substrates is lacking. Therefore, this work was undertaken to investigate kinetic modelling, solvent effects and catalyst deactivation in Rh catalysed hydroformylation of olefins.

In the previous reports, the kinetics of hydroformylation of olefins using both Co and Rh catalysts has been discussed (see Table (1.5)). Detailed investigations on kinetic modelling were also made by Deshpande and Chaudhari (1988, 1989a, 1991) for 1-hexene, allyl alcohol and vinyl acetate as substrates respectively. Some important observations include the inhibition of rate with increase in partial pressure of CO and olefin and a linear dependence with partial pressure of hydrogen with the exception of 1.5th order for the hydroformylation of allyl alcohol. In most of these reports, empirical rate equations have been proposed and attempts have been made to correlate the observed trends with reaction mechanism.

The kinetics of hydroformylation of polybutadiene using $HRh(CO)(PPh_3)_3$ complex catalyst has been reported (Mills et. al. 1990) in a temperature range of 350 - 390, K and a total pressure ($CO / H_2 = 1$) of 2.172, MPa. A power law type of rate equation was proposed to predict the observed rate dependencies. The activation energy was found to be 51.41, kJ/mol.

In a recent report, a molecular level approach to kinetic modeling has been reported for the hydroformylation of 1-octene, cyclohexene and styrene using $Rh_4(CO)_{12}$(acac) as a catalyst precursor and tris (2-tert-butyl-4-methyl phenyl) phosphine as a ligand in toluene solvent, in a temperature range of 313 - 373, K (van Rooy et. al 1995). For 1-octene and styrene hydroformylation, the rate determining step is reported to be the reaction of H_2 with the acylrhodium complex, whereas for cyclohexene hydroformylation, the addition of cyclohexene to the starting rhodium hydride complex is reported as the rate determining step. A negative order in CO concentration was observed. Rate equations based on mechanistic approach have been proposed for all these systems.

Hydroformylation of 1-decene has been studied previously using $Co_2(CO)_8$ (Wender et. al 1956), $Rh_4(CO)_{12}$ (Heil and Marko 1971), $Co_2(CO)_8$ with ethylene bis(3-2-pyridyl)propionate as a ligand (Matsuda et. al. (1978)) and $Rh(CO)_2(acac)$ (acac, acetylacetonate) with $P[CH_2CH_2(CF_2)_5CF_3]_3$ (Horvath and Rabai (1994)) catalyst system. In all these cases, undecanal and 2-methyl,decanal were found to be the main products with selectivity depending on the catalyst used. The kinetics of this reaction has not been studied in detail in any of the previous work. Undecanal is a product of commercial interest as it is used in perfumery industry (Jpn. Kokai Tokkyo Koho JP 58,117, 296 1982). Therefore, it was thought worthwhile to investigate in detail the kinetics and selectivity aspects of this reaction

Since,the mechanism of hydroformylation is reasonably well understood, it would be more appropriate to develop a molecular level approach to kinetic modeling. Therefore, it was the goal of this work to not only obtain the experimental data on a specific reaction system (the hydroformylation of 1-decene using $HRh(CO)(PPh_3)_3$ complex catalyst), but also to attempt a molecular level approach to kinetic modeling.

It is also well known that solvent and ligand can have an important role to play in the rate and selectivity of hydroformylation as well as the inhibition, deactivation of the catalyst systems. The experiments were also carried out to understand the role of solvents in the rate behavior and deactivation of the catalyst. Such a study would be particularly useful to develop a practically relevant catalyst system.

2.2 EXPERIMENTAL

2.2.1 Materials

Rhodium trichloride ($RhCl_3.3H_2O$), was obtained from Arora Mathey Ltd. 1-decene (> 99% purity) was procured from Aldrich Chemicals, USA. Triphenylphosphine (PPh_3) was procured from Fluka A. G., Switzerland. Solvents like benzene and ethanol were freshly distilled prior to their use. Hydrogen gas was supplied by Indian Oxygen Ltd., Bombay and Carbon Monoxide with > 99.9% pure was used directly from cylinders. The syngas with 1:1 ratio of H_2: CO was prepared by mixing H_2 and CO in one cylinder. This mixture was analyzed quantitatively by using ORSAT apparatus and gas chromatography to confirm the H_2 /CO ratio equal to unity.

2.2.2 Preparation of $Rh(CO)Cl(PPh_3)_2$

The complex $Rh(CO)Cl(PPh_3)_2$ was prepared by a procedure described by Evans et al.

(1968a). To a refluxing solution of PPh_3 (7.2 x 10^{-3}, kg) in 3 x 10^{-4}, m^3 ethanol, $RhCl_3.3H_2O$ (2 x 10^{-3}, kg in 7 x 10^{-5}, m^3 ethanol), was added under constant stirring. $RhCl(PPh_3)_3$ was formed after some time, indicated by brown crystals. Formaldehyde (1 - 2 x 10^{-5}, m^3) was added slowly to the mixture, under constant stirring. After 30 minutes, $RhCl(PPh_3)_3$ was converted to $Rh(CO)Cl(PPh_3)_2$ as indicated by a color change from red brown to yellow crystals. The complex was filtered from hot solution and repeatedly washed with hot and finally with cold ethanol and dried. The product trans-$Rh(CO)Cl(PPh_3)_2$ is highly crystalline, bright yellow complex. The infra red spectrum of the complex (nujol mull) showed a carbonyl absorption at 1960, cm^{-1}, which is typical of this complex. The elemental analysis confirmed the formation of the above complex.

	Theoretical %	**Experimental %**
C	64.3	64.36
H	2.46	2.44
Cl	5.14	5.1

2.2.3 Preparation of $HRh(CO)(PPh_3)_3$

A procedure for the synthesis of $HRh(CO)(PPh_3)_3$ was followed from the work of Evans et al. (1968a). $Rh(CO)Cl(PPh_3)_2$ (1.0 x 10^{-3} kg) and PPh_3 (1.5 x 10^{-3} , kg) were added to ethanol(1.0 x 10^{-4}, m^3) and refluxed under constant stirring. To this solution $NaBH_4$ (0.5 x 10^{-3} , kg in 6 0 x 10^{-5} , m^3 ethanol) was added very slowly. After complete addition, the mixture was refluxed till the suspended complex sample (washed and dried) showed no absorption at 1960, cm^{-1} corresponding to $Rh(CO)Cl(PPh_3)_2$. A small absorption at 2024, cm^{-1} ($=\nu_{Rh\text{-}H}$) and a carbonyl stretch at 1920, cm^{-1}, are typical of $HRh(CO)(PPh_3)_3$ complex. The product complex was filtered from hot solution and washed several times with hot and finally with cold ethanol and dried. The infra red spectrum of the complex (nujol mull) showed a characteristic absorption at 1920, cm^{-1} and 2024, cm^{-1}, as expected. The elemental analysis obtained was

	Theoretical %	**Experimental %**
C	71.9	71.92
H	5.01	5.16

2.2.4 Apparatus

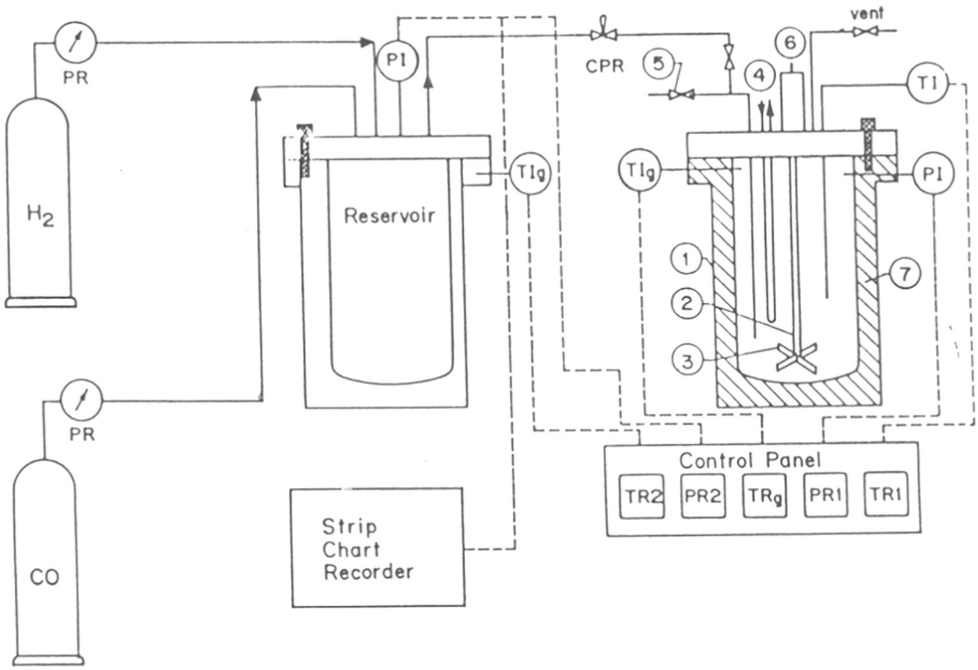
The hydroformylation experiments were carried out in a dead end type autoclave reactor of 3.0 x 10^{-4}, m^3 capacity made of stainless steel T316 (Parr Instruments Co., USA). This reactor was equipped with automatic temperature control and variable agitation speed. For withdrawal of liquid samples, a dip tube was fitted to the autoclave. This tube was also used for the introduction of the gas in to the reactor. An outlet valve was provided for taking gaseous samples as well as for releasing the pressure when necessary. A safety rupture disc was also fitted to the reactor. The reactor was designed for a working pressure of 13.78, MPa. In order to maintain the pressure in the reactor constant, CO and H_2 were supplied to the reactor through a constant pressure regulator from a gas reservoir. Fig. 2.1 shows a schematic diagram of the experimental set-up used for this study. Other details regarding the reactor are given in Table (2.1). A pitched blade type agitator was used in this work.

2.2.5 Experimental Procedure

In a typical experiment, known quantities of the catalyst, olefin and solvent were charged into the reactor. After flushing with N_2 and then with CO/ H_2 mixture, the contents were heated to a desired temperature. The mixture of CO and H_2 in a required ratio was then introduced into the autoclave to a desired pressure. The initial sample of the liquid was 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 a reservoir vessel, through a constant pressure regulator. Since, in this study the major products were expected to be isomeric aldehydes, supply of (CO + H_2) in a ratio of 1:1 (as per the stoichiometry) was adequate to maintain a constant composition of H_2 and CO in the autoclave. This was confirmed in a few cases by analysis of CO content at the end of the reaction. Liquid samples were analyzed for reactants and products by gas chromatography. In a few cases, liquid samples were also withdrawn at different time intervals and analyzed to obtain a concentration - time profile of reactants and products. Also, in every experiment, the amount of CO or H_2 consumed as a function of time, was observed by following the pressure drop vs. time profile in the reservoir vessel.

2.2.6 Procedure for kinetic experiments

For kinetic studies, the procedure followed was similar to that described above, except that the reactions were carried out for short durations such that the conversion of liquid phase reactant (1-decene) was less than 10-15%, to ensure differential conditions. In each of the kinetic runs, initial and final samples were analyzed for reactants and products in order to check the material balance. It was generally observed that in this low conversion range



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

TI : Thermocouple
PI : Pressure transducer
TI$_g$: Thermocouple for gas
H$_2$: Hydrogen cylinder
CO : Carbon monoxide cylinder
PR : Pressure regulator
CPR : Constant pressure regulator

<u>Control Panel</u>

TR1 : Reactor temperature indicator
PR1 : Reactor pressure indicator
TR2 : Reservior temperature indicator

TRg : Gas temperature indicator
PR2 : Reservior pressure indicator

Fig. 2.1 : A schematic of the high pressure set up used for kinetic studies.

TABLE 2. 1

DETAILS OF THE AUTOCLAVE USED

Tank Diameter, m	6.30×10^{-2}
Effective volume of the reactor, m^3 (in the presence of internals)	3.08×10^{-4}
Impeller diameter, m	3.9×10^{-2}
Impeller height from the bottom, m	1.2×10^{-2}
Height of the liquid, m	3.2×10^{-2}
Agitation speed, rps	15
Volume of the liquid, m^3	1.0×10^{-4}

(<10-15%), the rate of hydroformylation was constant. The reproducibility of the experiments was found to be in a range of 5-7%. Following this procedure, the effect of catalyst and olefin concentrations, partial pressures of H_2 and CO, and temperature on the rate of hydroformylation was studied in a temperature range of 323 - 343, K.

2.2.7 Analytical methods

The analysis of reactants (1-hexene and 1-decene) and products (heptaldehyde, 2-methyl hexaldehyde, undecanal and 2-methyl decanal) was carried out using gas chromatography (GC). For this purpose, Varian 3600 Gas Chromatograph with Flame Ionization Detector was used. Other conditions of analysis are given below :

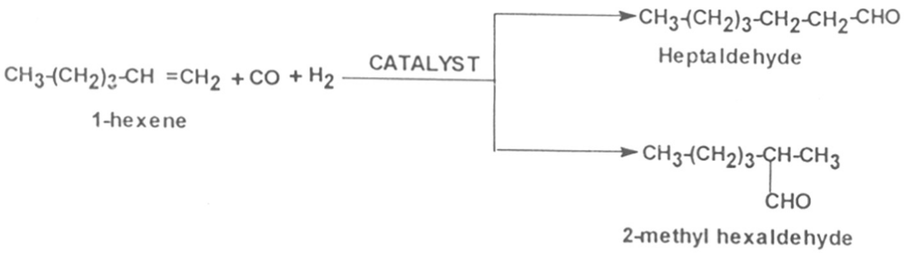
Column	5%PEG 20M on Chromosorb W-AW, 6' x 1/4"
Injection temperature (K)	523
Flame Ionization Detector temperature (K)	573
Oven temperature programmed between (K)	333 - 393 (rate 20, K /min)
Carrier gas (nitrogen) flow rate (m^3/hr.)	3.33×10^{-7}

A typical gas chromatogram is shown in Fig. 2.2. In order to identify the products, authentic standards were used for comparison. For quantitative analysis, synthetic standards of olefins and aldehyde products were used.

2.3 RESULTS AND DISCUSSION

2.3.1 Solvent effects

In this study, we report some interesting results on the solvent effects on the hydroformylation of 1-hexene. The stoichiometric reaction for 1-hexene hydroformylation can be represented as :



$$CH_3\text{-}(CH_2)_3\text{-}CH=CH_2 + CO + H_2 \xrightarrow{\text{CATALYST}} \begin{cases} CH_3\text{-}(CH_2)_3\text{-}CH_2\text{-}CH_2\text{-}CHO \\ CH_3\text{-}(CH_2)_3\text{-}\underset{\displaystyle CHO}{\underset{|}{CH}}\text{-}CH_3 \end{cases} \qquad (2.1)$$

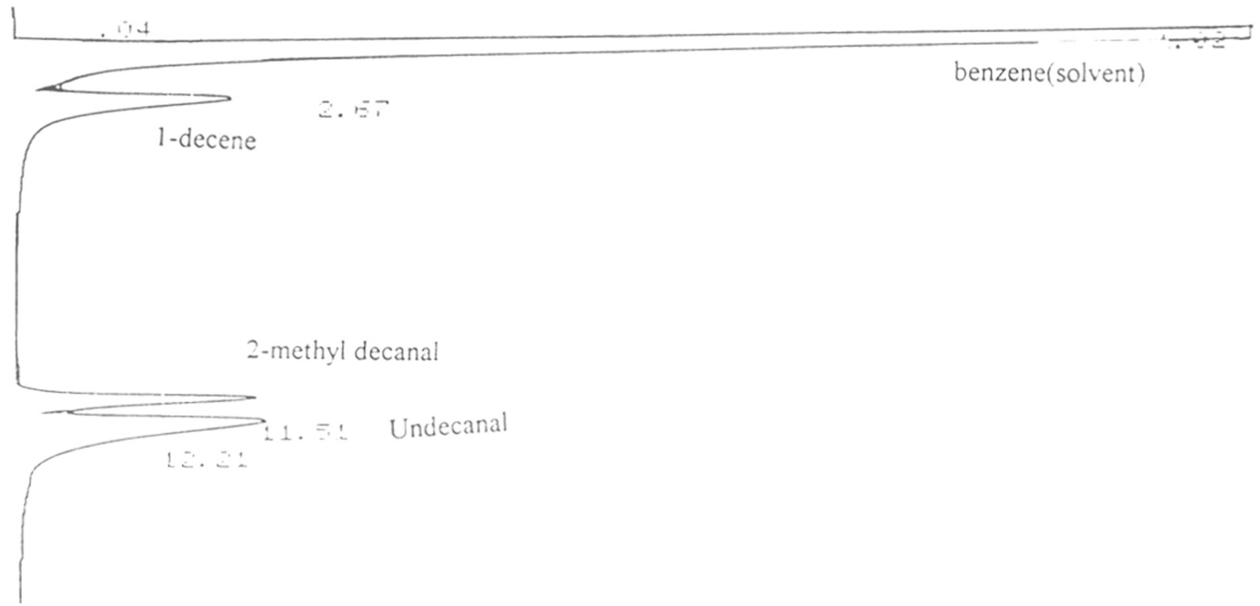


Fig. 2.2. A typical gas chromatogram in hydroformylation of 1-decene

The hydroformylation reactions were carried out at a catalyst [$HRh(CO)(PPh_3)_3$] concentration of 1.0×10^{-3} , kmol m^{-3} and $P_{CO} = P_{H2} = 1.034$, MPa, with the objective of understanding the effect of solvents for different olefin concentrations. The results are presented in Fig. 2.3. It was observed that the rate is inhibited at higher concentrations of 1-hexene in all the solvents. However, the maximum rate was found to be strongly dependent on the type of solvent used. Interestingly, the position of the maximum in the rate with respect to olefin concentration was found to shift, depending on the solvent.

In ethanol as a solvent, the maximum rate was observed at an olefin concentration of 0.35, kmol m^{-3} [olefin to catalyst ratio = 350]. In case of benzene as a solvent, the maximum occurred at an olefin concentration of 5.0, kmol m^{-3} [olefin to catalyst ratio = 5000]. The maxima in case of n-heptanol and toluene were found to lie within these two extremes, viz. at olefin concentrations of 1.35, kmol m^{-3} [olefin to catalyst ratio = 1350] and 3.3, kmol m^{-3} [olefin to catalyst ratio = 3300] respectively. Thus, the maximum in the rates was found to be strongly solvent dependent. The n/iso ratio was however, not significantly affected by a change in 1-hexene concentration for each solvent. Formation of solvent co-ordinated catalytic species was observed earlier by Evans et. al. (1968b) for ethanol, and benzene as solvents. Since, the inhibition of rate is observed mainly as a function of olefin to catalyst ratio, it is unlikely that the co-ordination by solvent should play an active role in the inhibition of the rate at higher olefin concentrations. In the absence of the solvent, when pure 1-hexene was used as the medium, the rate was strongly inhibited indicating that the olefin interaction with catalyst is a likely reason for inhibition.

Wilkinson and coworkers (Evans et. al., (1968b)) have proposed a catalytic cycle for the hydroformylation reaction as shown in Fig. 2.4. This mechanism consists of two routes, viz. the associative and the dissociative mechanisms. In either of these routes, the oxidative addition of hydrogen to acyl complex (step 6) is rate controlling.

It is reported (King et. al. (1980), Tolman (1972)) that formation of alkyl olefinic Rh species occurs in the hydroformylation of ethylene using $Rh_4(CO)_{12}$ catalyst, as shown in scheme 1.

$$\underset{S1}{C_2H_5Rh(CO)_3 + C_2H_4} \longrightarrow \underset{S2}{C_2H_5Rh(CO)_3(C_2H_4)}$$

$$C_2H_5Rh(CO)_3(C_2H_4) \longrightarrow \underset{S3}{C_2H_5CORh(CO)_2(C_2H_4)}$$

Scheme 1

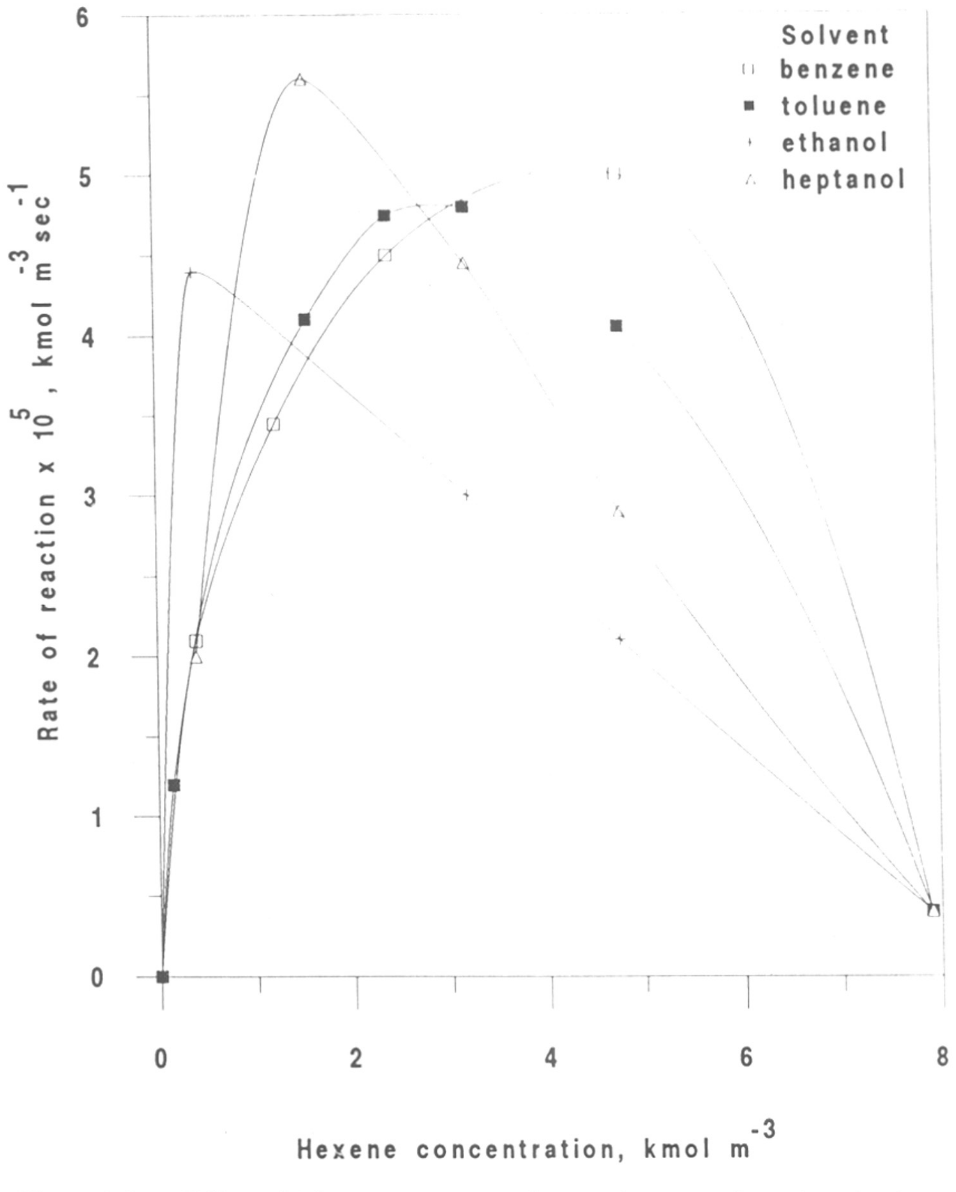


Fig : 2.3 Effect of 1-hexene concentration on the rate of catalyst in the hydroformylation of 1-hexene

* Pure hexene

Reaction Conditions :

Concentration of Catalyst = 1.00 x 10^{-3}, kmol m^{-3};

Tempertaure = 323, K

Total pressure ($CO/H_2 = 1$) = 2.068, MPa

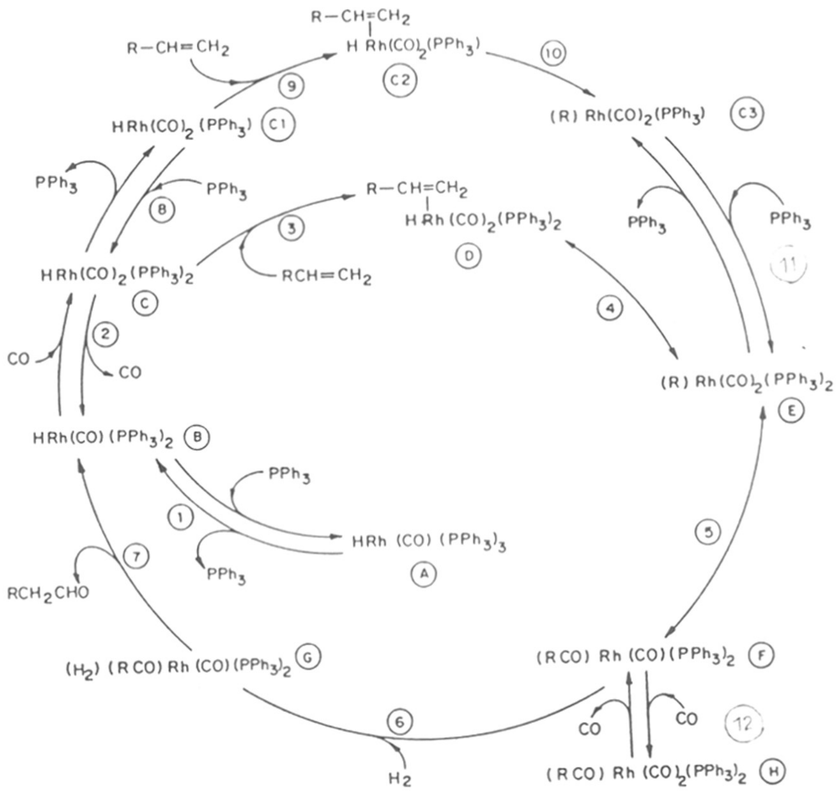


Fig : 2.4 Mechanism of HRh(CO)(PPh$_3$)$_3$ catalysed hydroformylation reactions. (Evans et. al. (1968 b).

This type of mechanism has been proposed for the formation of dialkyl ketones. It is likely that similar species may form in the hydroformylation of 1-hexene using $HRh(CO)(PPh_3)_3$ as a catalyst. Such a species can be formed by attack of 1-hexene on species E and F as shown in Fig. 2.4. This will lead to a reduction in the concentration of active catalyst available for the reaction, causing a reduction in rates. Depending on the properties of solvents the formation of such inhibited species will occur to a different extent. This will result in a shift in the maximum in rate with variation of solvent.

King et. al. (1980) have also reported that these species (S2) and (S3) are formed at lower partial pressures of CO. To observe the exact nature of the inhibition in the rate, in hydroformylation of 1-hexene, few reactions were taken to check indirectly the formation of inhibited species. Reactions were taken in ethanol solvent under different conditions and the results are shown in Fig. 2.5. The increase in rate with total pressure at low olefin concentrations was also marginal. It was observed that at low partial pressures of CO and H_2, the inhibition in rate was severe at higher olefin concentration. At high pressure of CO and H_2, however, the inhibition in rates was negligible at corresponding olefin concentrations. These observations show that higher partial pressures of CO can prevent formation of inhibited species as suggested by King (1980).

2.3.2 Deactivation of catalyst

The aim of this work was to experimentally demonstrate the deactivation of $HRh(CO)(PPh_3)_3$ catalyst in the hydroformylation of 1-hexene. Particularly, the effect of temperature, ligand (PPh_3) concentration and solvents on the deactivation has been studied.

It was observed that with increase in temperature, the maximum conversion of 1-hexene decreased significantly but, the initial rate of hydroformylation was enhanced. At 373, K, 82% conversion was obtained, whereas at 398, K, the maximum conversion achieved was 31% (see Fig. 2.6). At 423, K the maximum conversion obtained was even lower (17 %). This clearly shows the deactivation of the catalyst at higher temperatures. A similar observation has been reported previously by Russell (1988) and Matsumoto and Tamura (1983). With increase in temperature, the n/iso ratio was found to decrease, though, the overall aldehyde selectivity was not affected.

As discussed earlier, two types of inactive Rh- species are likely to be formed. Abatjoglou and Bryant (1984), reported formation of dimeric phosphido bridged clusters, which are inactive for hydroformylation as well as hydrogenation.

Wilkinson has observed formation of a brown complex (II) containing Rh bound to the phenyl ring of triphenylphosphine (PPh_3). An inactive Rh dimer is also reported to be formed

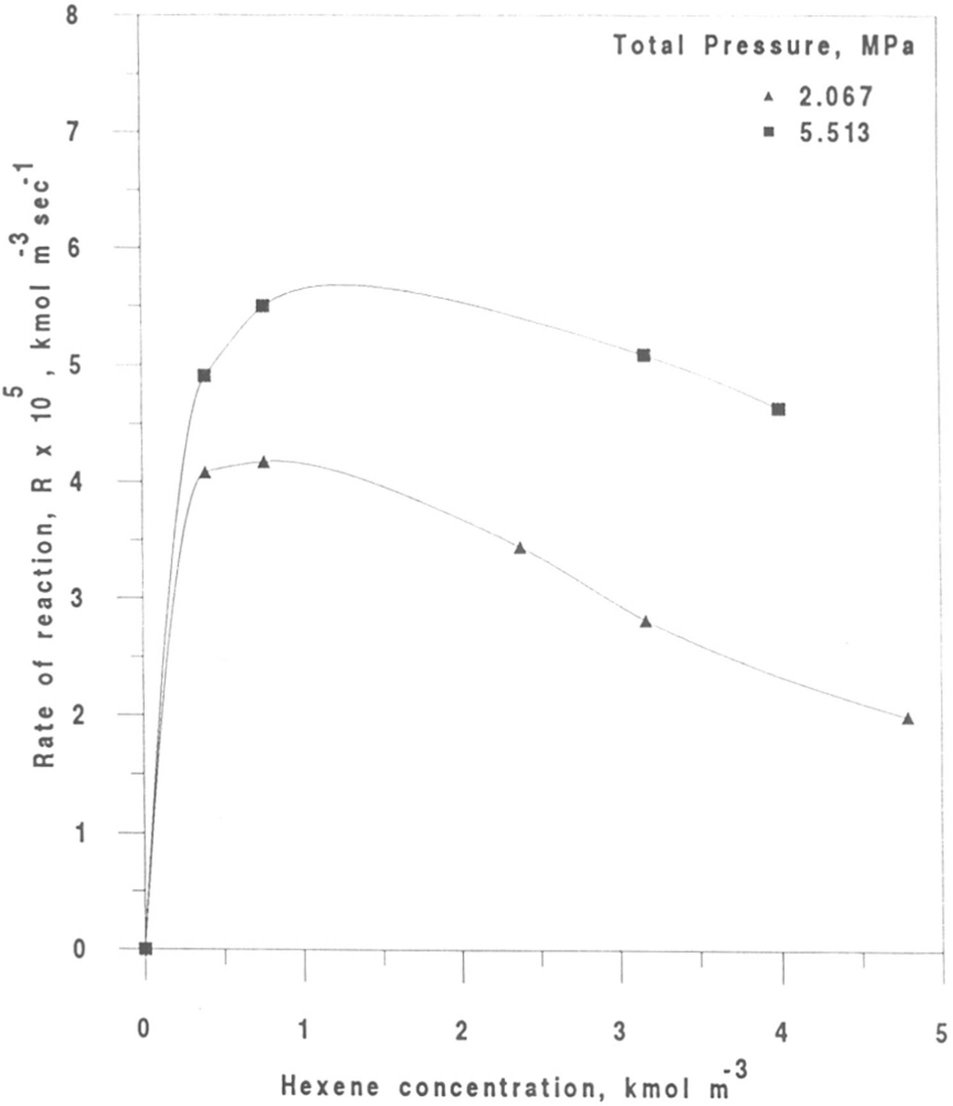


Fig : 2.5 Effect of total pressure on the rate of hydroformylation of 1-hexene at 398 K

Reaction Conditions :
Concentration of 1-hexene = 0.797, kmol m^{-3};
Concentration of Catalyst = 5.45 x 10^{-4}, kmol m^{-3};
$CO/H_2 = 1$

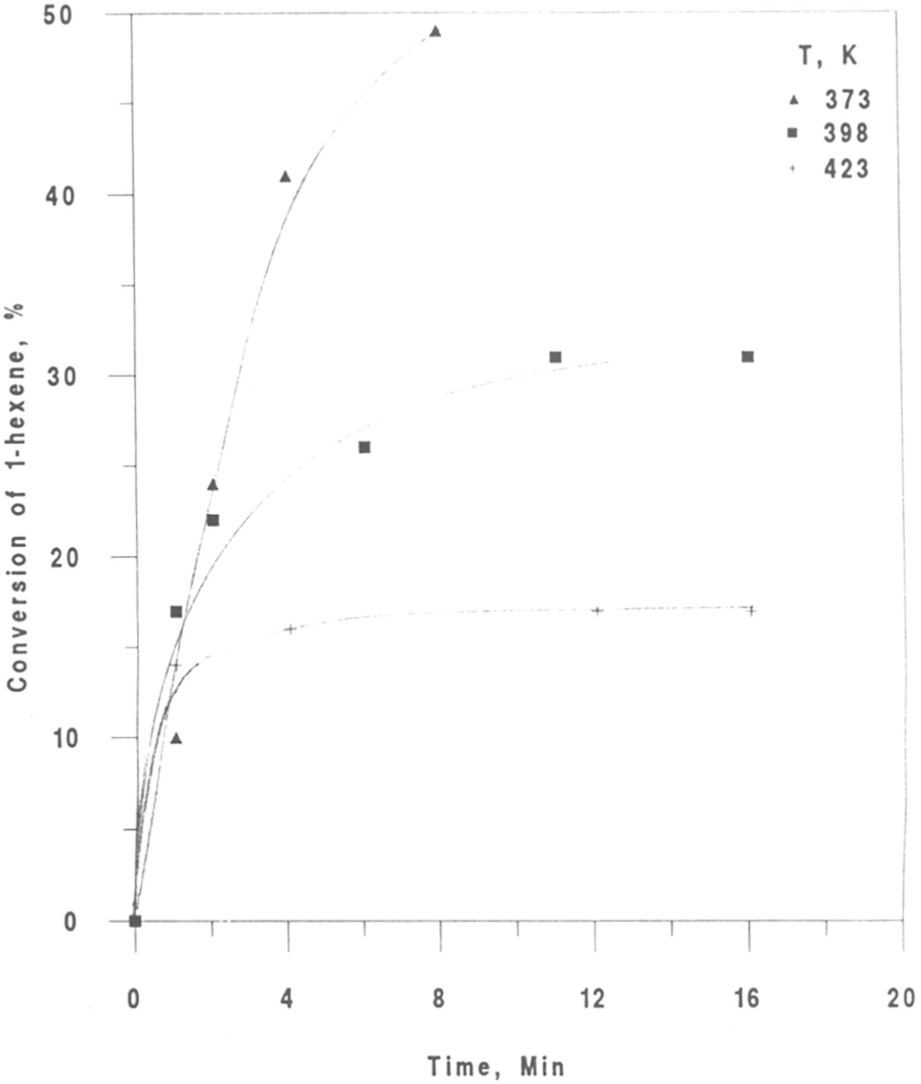
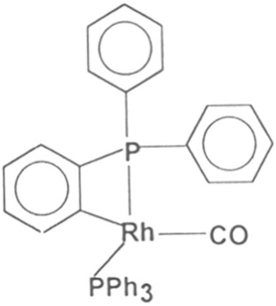


Fig : 2.6 Effect of temperature on the activity of catalyst in the hydroformylation of 1-hexene

Reaction Conditions :
Concentration of 1-hexene = 0.797, kmol m^{-3};
Concentration of Catalyst = 5.45 x 10^{-4}, kmol m^{-3};
Total pressure (CO/H_2 = 1) = 2.756, MPa

under hydroformylation conditions (Wilkinson et. al. 1970).



(II)

In several experiments, it was observed that the reaction stopped before achieving complete conversion of the olefin, indicating deactivation of the catalyst. The results at different conditions are discussed below.

The main products observed in the hydroformylation of 1-hexene were n-heptaldehyde and 2-methyl hexaldehyde, as also reported previously (Deshpande and Chaudhari 1988). Although, hydrogenation of 1-hexene at higher temperatures is expected, no hexane was observed in the products, in the range of conditions studied in this work. The amount of aldehyde products formed, was found to be proportional to CO, H_2 and 1-hexene consumed, indicating a high selectivity of aldehydes. In order to understand the deactivation behavior of the catalyst, in each experiment, CO + H_2 consumed versus time data were obtained. At the end of each experiment, concentrations of the liquid phase reactants and products were also observed. The effect of temperature on the maximum conversion and selectivity in the hydroformylation of 1-hexene was studied at temperatures of 373, 398 and 423, K, CO + H_2 pressure of 2.76, MPa. CO to H_2 ratio of 1:1 and initial catalyst and olefin concentrations of 5.45 x 10^{-4} , and 0.797, kmol m^{-3}, respectively. The results are presented in Table (2.2). At higher temperatures, the formation of phosphido bridged Rh complexes is likely to occur, leading to a drop in the activity of the catalyst (Table (2.2)). This effect is expected to be more pronounced at higher temperatures. It was noted that the catalyst was active in the beginning of the reaction but later on, after going through a few cycles, a decrease in the activity was observed indicating deactivation. In order to understand the nature of catalyst deactivation, the catalyst $HRh(CO)(PPh_3)_3$ was heated to 423, K, under P_{co} and P_{H2} = 1.39, MPa, in the absence of olefin for 15, min. This catalyst was then tested for its hydroformylation activity at 353, K. No conversion of CO/H_2 and 1-hexene was observed in this experiment, clearly indicating deactivation of the catalyst due to heating at 423,

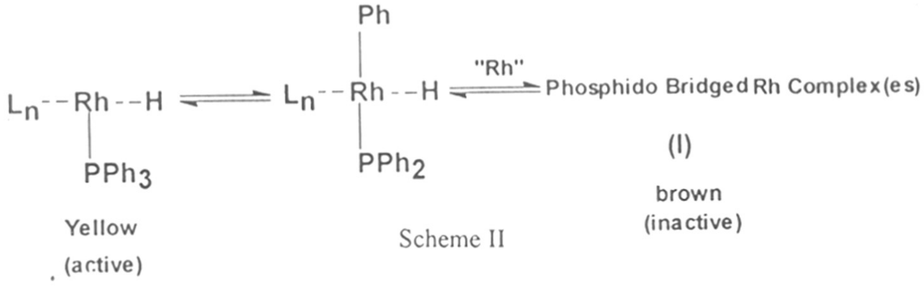
TABLE 2.2

EFFECT OF TEMPERATURE ON ACTIVITY AND SELECTIVITY IN HYDROFORMYLATION OF 1-HEXENE

Temperature K	Reaction time (Min.)	Maximum conversion %	Selectivity to aldehyde, %	n/iso
373	71	82	99	1.09
398	11	31*	98	0.94
423	12	17*	98	0.72

* The conversion remained constant even after 60 minute reaction time

K. A possible mechanism of formation of species (I) leading to catalyst deactivation is shown below in shceme II (Abatjoglou and Bryant 1984).



Scheme II

The formation of species II and the dimer (Wilkinson et. al. 1970), is unlikely under conditions investigated in this work (Hanson and Davis 1987). As per the mechanism in scheme 1, the coordinatively unsaturated Rh species (A) will undergo cleavage of the P-C bond of phosphine and form phosphido complex (I). At higher temperatures, the predominance of the dissociative mechanism of hydroformylation over the associative mechanism is known (Russell 1988). Since, the active catalytic species is coordinatively less saturated, it is even more likely to undergo reaction according to scheme I, at higher temperatures, causing rapid deactivation.

The effect of triphenylphosphine concentration was investigated at 373 and 398, K at $P_{CO}=P_{H2} = 1.38$, MPa and catalyst and olefin concentration, of 5.45×10^{-4} , and 0.797, kmol m^{-3} respectively. The results are presented in Table (2.3). The maximum conversion achieved at 373, K was found to be about 80 - 85%. It was observed that increase in triphenylphosphine concentration increases the rate of reaction at 373, K as shown in Fig. 2.7. At higher temperature (398, K, Fig. 2.8), although the initial rate of reaction increases, the catalyst was found to be deactivated in a short time. Addition of triphenylphosphine is found to prolong the hydroformylation activity of the catalyst upto a ratio of 1:4 and further addition of triphenyl phosphine does not increase the activity significantly (with respect to the activity obtained at a ratio of 1:4). Higher triphenylphosphine concentration is likely to inhibit further dissociation of $HRh(CO)(PPh_3)_2$, thus preventing formation of the phosphido complexes, and retarding deactivation.

Since, severe deactivation was observed in the hydroformylation of 1-hexene at higher temperatures in benzene as a solvent, the effect of other solvents on the deactivation pattern was also studied at 398, K. The results in Fig. 2.9 indicate that while in benzene as a solvent, the maximum conversion achieved was ~ 31 % (at 11, min.), in butyraldehyde and n-heptanol, it increased to 52 and 64% respectively (at 11, min.). Besides enhancement in the activity, the life

TABLE 2.3

EFFECT OF EXCESS PHOSPHINE ON ACTIVITY AND SELECTIVITY : HYDROFORMYLATION OF 1-HEXENE

Temperature 373 K

catalyst : phosphine ratio	Reaction time (Min.)	Maximum conversion %	n/iso
1 : 0	71	82	1.09
1 : 2	41	80	1.24
1 : 5	30	86	2.73

Temperature 398 K

catalyst : phosphine ratio	Reaction time (Min.)	Maximum conversion %	n/iso
1 : 0	11	31	0.94
1 : 2	10	50	1.04
1 : 4	7	60	0.96
1 : 10	10	58	1.06

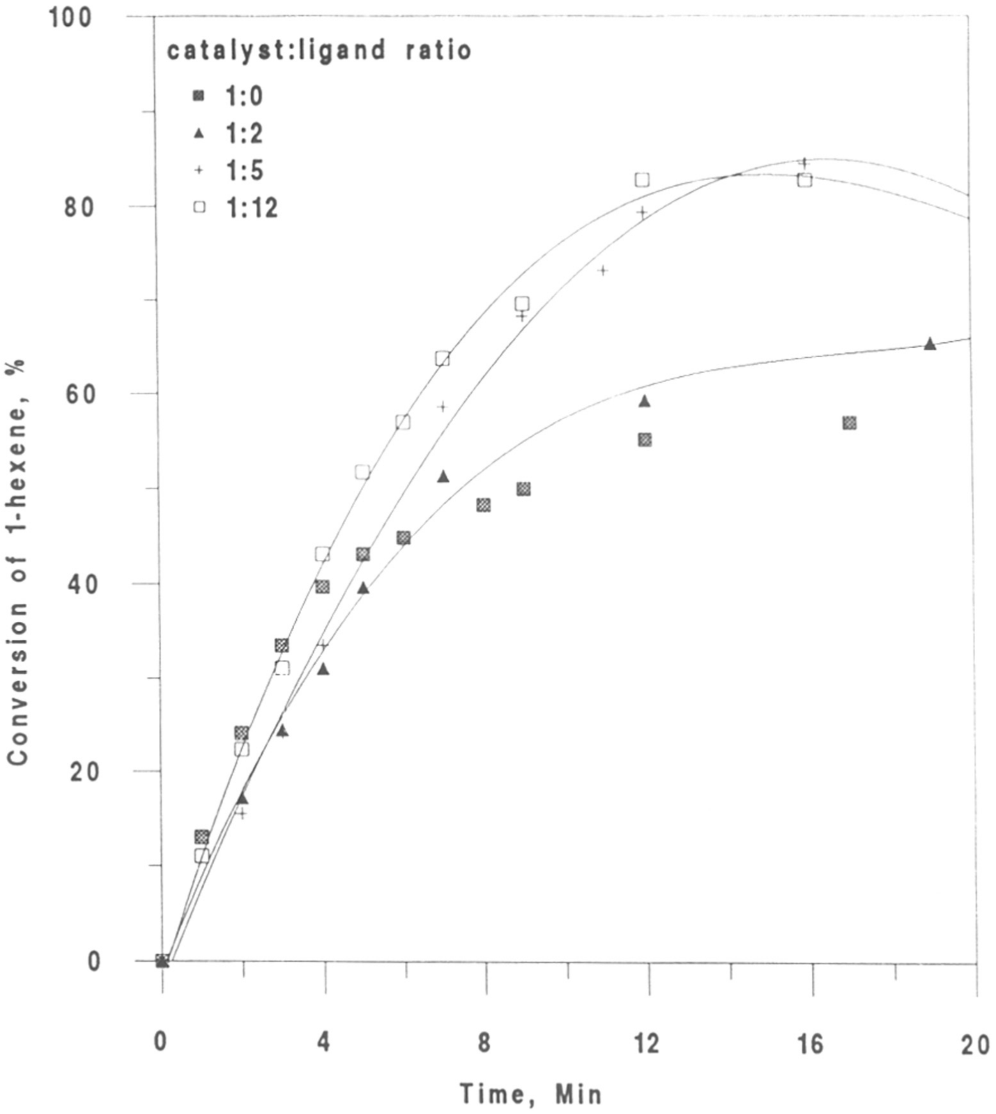


Fig : 2.7 Effect of excess phosphine on the activity of catalyst at 373 K in the hydroformylation of 1-hexene

Reaction Conditions :

Concentration of 1-hexene = 0.797, kmol m^{-3};

Concentration of Catalyst = 1.00×10^{-3}, kmol m^{-3};

Total pressure ($CO/H_2 = 1$) = 2.756, MPa

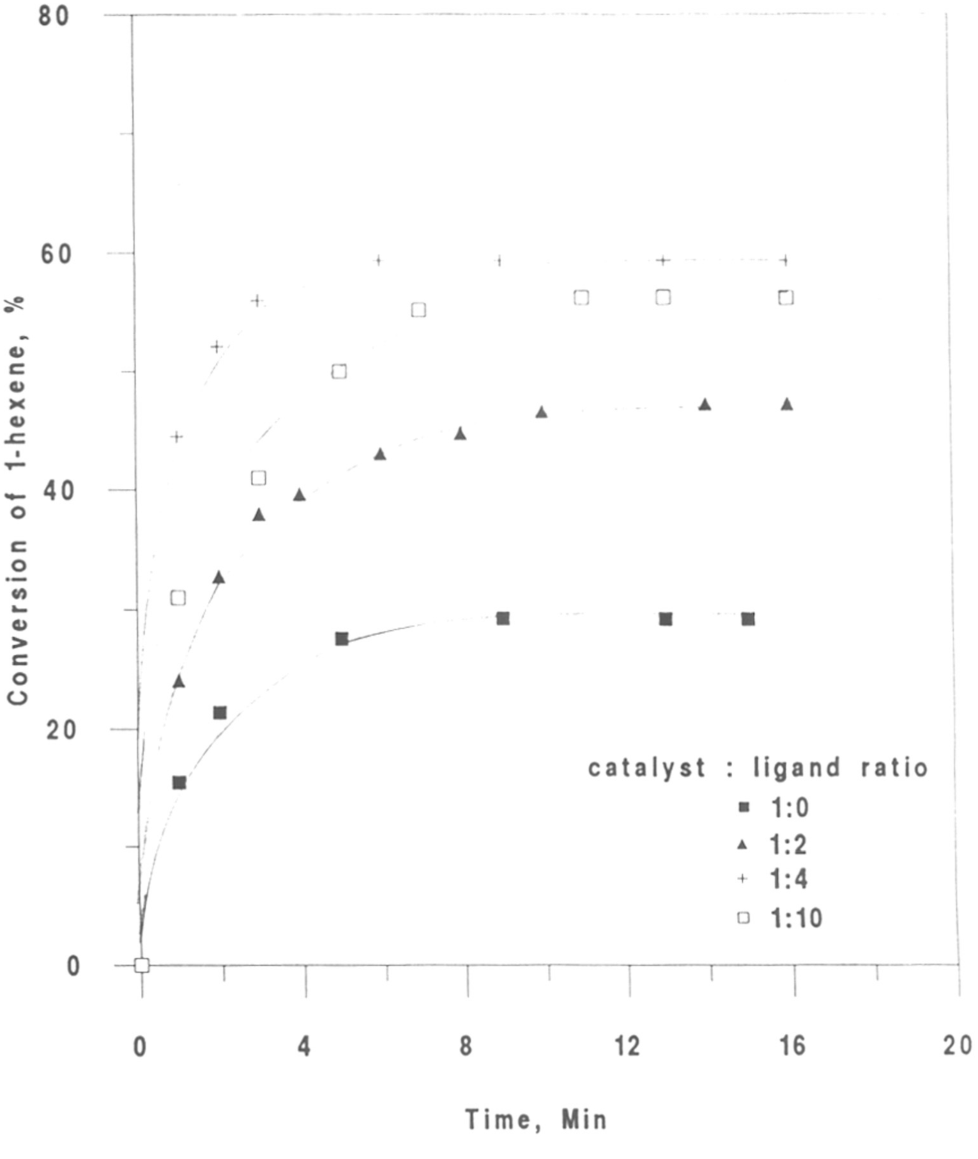


Fig : 2.8 Effect of excess phosphine on the activity of catalyst at 398 K in the hydroformylation of 1-hexene

Reaction Conditions :

Concentration of 1-hexene = 0.797, kmol $m^{-3;}$

Concentration of Catalyst = 5.45×10^{-4}, kmol $m^{-3;}$

Total pressure ($CO/H_2 = 1$) = 2.756, MPa

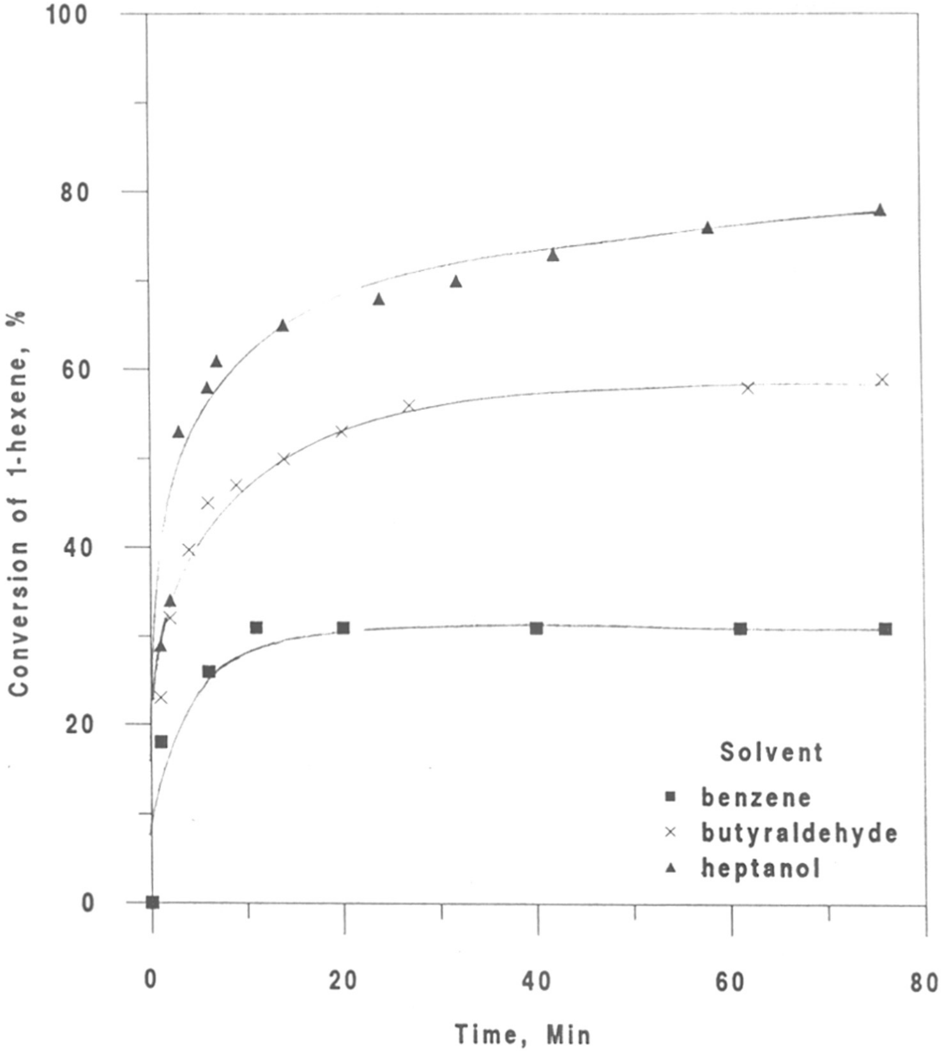


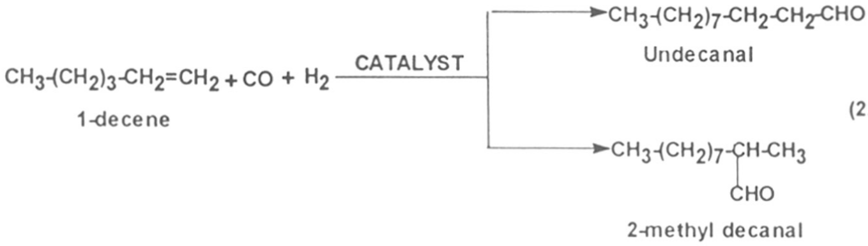
Fig : 2.9 Effect of solvent on the activity of catalyst at 398 K in the hydroformylation of 1-hexene

Reaction Conditions :
Concentration of 1-hexene = 0.797, kmol m^{-3};
Concentration of Catalyst = 5.45×10^{-4}, kmol m^{-3};
Total pressure ($CO/H_2 = 1$) = 2.756, MPa

of the catalyst was also increased. The maximum conversion obtained in butyraldehyde solvent was 52% whereas with n-heptanol it was 77%. No side products were observed in any of the reactions studied.

2.3.3 Kinetics of hydroformylation of 1-decene

The hydroformylation of 1-decene is represented as follows:



$$\underset{\text{1-decene}}{\mathrm{CH_3\text{-}(CH_2)_3\text{-}CH_2{=}CH_2 + CO + H_2}} \xrightarrow{\text{CATALYST}} \begin{cases} \underset{\text{Undecanal}}{\mathrm{CH_3\text{-}(CH_2)_7\text{-}CH_2\text{-}CH_2\text{-}CHO}} \\ \underset{\text{2-methyl decanal}}{\mathrm{CH_3\text{-}(CH_2)_7\text{-}\underset{\displaystyle CHO}{CH}\text{-}CH_3}} \end{cases} \qquad (2.\ 2)$$

Though, there are some kinetic studies reported for the hydroformylation of higher olefins, they are limited only to the development of empirical rate models. These rate equations are based on the observed trends with respect to various process parameters. There are very few literature reports on a mechanistic model development for $HRh(CO)(PPh_3)_3$ catalyzed hydroformylation of higher olefins. Therefore, the objective of the present work was to investigate the kinetics and selectivity behavior of hydroformylation of 1-decene.

For kinetic study, a few experiments were carried out in which the amount of 1-decene consumed, products formed, and syngas consumed were compared. A typical concentration profile is shown in Fig. 2.10. It was observed that the quantities of CO or H_2 and 1-decene consumed were consistent with the amount of total aldehyde products formed as per the stoichiometry. The material balance in all these reactions was found to be > 95 %. The results are presented in Table (2.4). Also, in the range of conditions covered in this work (for details see Table (2.5)), the only products formed were undecanal and 2-methyldecanal. No hydrogenation or isomerisation products were observed. Thus, the overall hydroformylation kinetics could be followed by observing the consumption of syngas, in a 1:1 ratio of CO and H_2. For the purpose of detailed kinetic modeling, several experiments were carried out to understand the influence of catalyst and olefin concentrations, hydrogen and carbon monoxide partial pressures and temperature on the rate of reaction. The results are discussed below. Here the initial rate data evaluated from H_2 or CO consumed versus time plots were used.

2.3.3.1 Effect of agitation speed

The effect of agitation speed on the rate of hydroformylation was studied at 323 - 343,

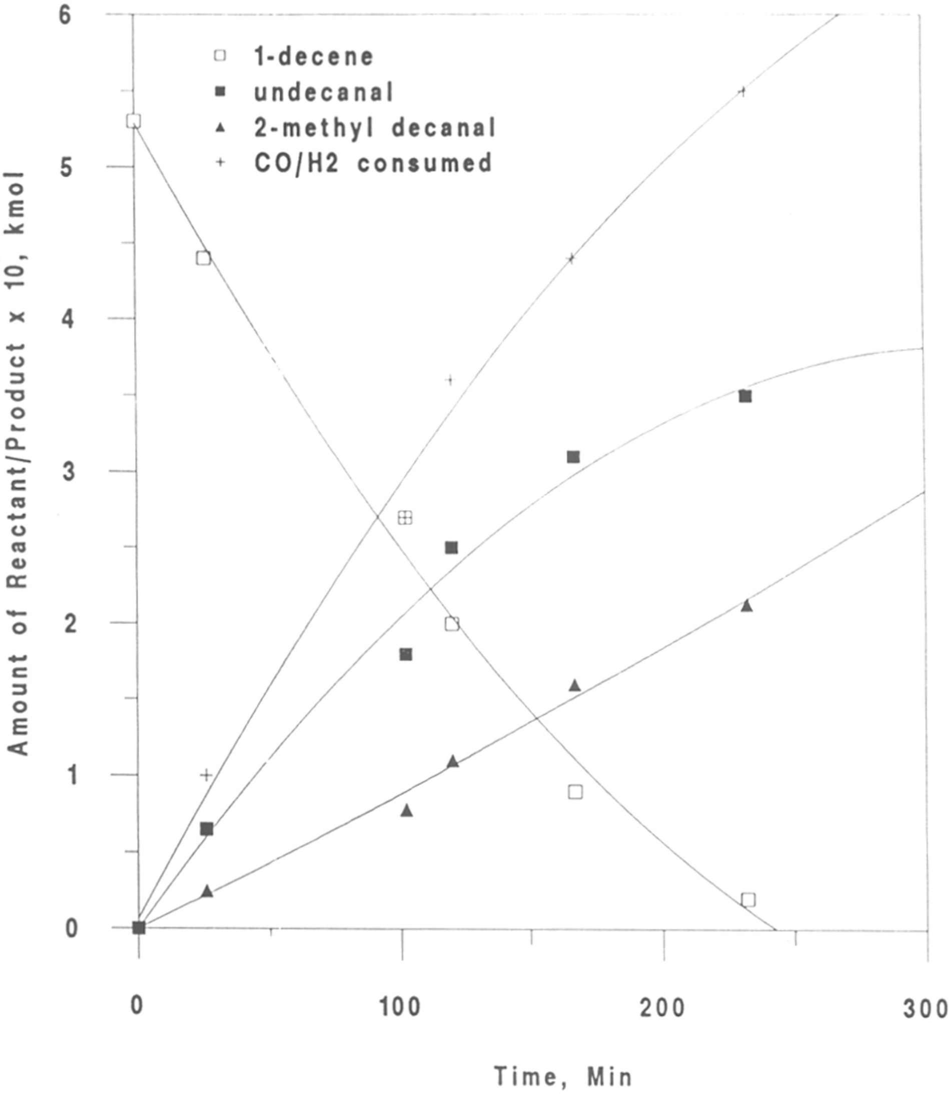


Fig : 2.10 A concentration time profile for the hydroformylation 1-decene at 323, K

Reaction Conditions :
Concentration of 1-decene = 52.80, kmol m^{-3};
Concentration of Catalyst = 1.00×10^{-3}, kmol m^{-3};
Concentration of PPh_3 = 4.00×10^{-3}, kmol m^{-3};
Total pressure ($CO/H_2 = 1$) = 2.756, MPa

TABLE 2.4

RESULTS SHOWING MASS BALANCE

Serial Number	1-decene x 10^5 (kmol)		1/2 $(CO+H_2)$ absorbed x 10^5, kmol	Mass balance with respect to CO and H_2 absorption (%)
	Initial	Final		
1	5.60	0.84	4.42	92.86
2	5.50	0.10	5.31	98.30
3	5.80	0.40	5.30	98.12
4	5.50	0.54	5.22	105.5

Reaction Conditions :

Concentration of 1-decene	0.528 kmol m^{-3}
Concentration of catalyst	1.0×10^{-3} kmol m^{-3}
Partial pressure of CO	1.38 MPa
Partial Pressure of H_2	1.38 MPa
Solvent	Benzene
Temperature	323 K

TABLE 2.5

RANGE OF CONDITIONS INVESTIGATED FOR THE KINETIC STUDY

Concentration of Catalyst (kmol m^{-3})	0.5 to 4.0×10^{-3}
Concentration 1-decene (kmol m^{-3})	0.264 to 2.64
Partial pressure of Hydrogen (MPa)	6.8 to 27.2
Partial pressure of CO (MPa)	1.32 to 27.2
Temperature (K)	323 to 343
Solvent	Benzene
Reaction Volume (m^3)	1.0×10^{-4}

K to check the significance of mass transfer. It was observed that beyond 6.67, rps the rate was independent of the agitation speed. All the experiments were carried out at 15, rps to ensure kinetic regime.

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

The effect of P_{CO} on the rate of hydroformylation of 1-decene was studied at a constant partial pressure of H_2 = 1.38, MPa, 1-decene concentration of 0.528, kmol m^{-3}, and catalyst concentration of 1.0×10^{-3}, kmol m^{-3} The results are shown in Fig. 2.11 for all the temperatures studied. The rate was found to decrease with increase in P_{CO}. It is a general observation that the hydroformylation rates are inversely proportional to the partial pressure of CO (Deshpande and Chaudhari (1988), (1989a), (1989b); Pino (1980)), however, an important observation made here is that the rate of hydroformylation is very sensitive to slight changes in the partial pressures of CO. The sensitivity was found to be more pronounced with increase in temperature. This observation can be explained on the basis of a mechanism proposed earlier (Evans et. al. 1968b, Brown and Wilkinson 1970) (see Fig. 2.4).

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 species $(RCO)Rh(CO)_2(PPh_3)_2$ and further $(RCO)Rh(CO)_3(PPh_3)$ (Fig. 2.4). The formation of these species reduces the effective concentration of the active catalytic species and hence the rate of the reaction is reduced. The equilibrium reaction leading to the formation of $(RCO)Rh(CO)_3(PPh_3)$ will be more pronounced at higher partial pressures of CO causing a sharp decrease in the rate of reaction, as observed in this work.

2.3.3.3 Effect of partial pressure of H_2 (P_{H2})

A typical plot of absorption of CO or H_2 with time showing the effect of partial pressure of H_2 at 333, K is shown in Fig. 2.12. The effect of partial pressure of H_2 on the rate of hydroformylation of 1-decene was investigated at a constant partial pressure of CO = 1.38, MPa, 1-decene concentration of 0.528, kmol m^{-3}, and a catalyst concentration of 1.0×10^{-3}, kmol m^{-3}. The results are shown in Fig. 2.13. The rate of reaction was found to vary with 1.5th order with P_{H2}. No hydrogenation products were observed in the range of conditions studied. At lower P_{H2} formation of a dimeric species (T) is possible (Brown and Wilkinson 1970) as shown below :

$$2\ HRh(CO)\ (PPh_3)_3 \rightarrow \underset{T)}{[Rh(CO)\ (PPh_3)_3]_2} + H_2 \qquad (2.3)$$

This will lead to a reduction in the concentration of the active catalytic species. With

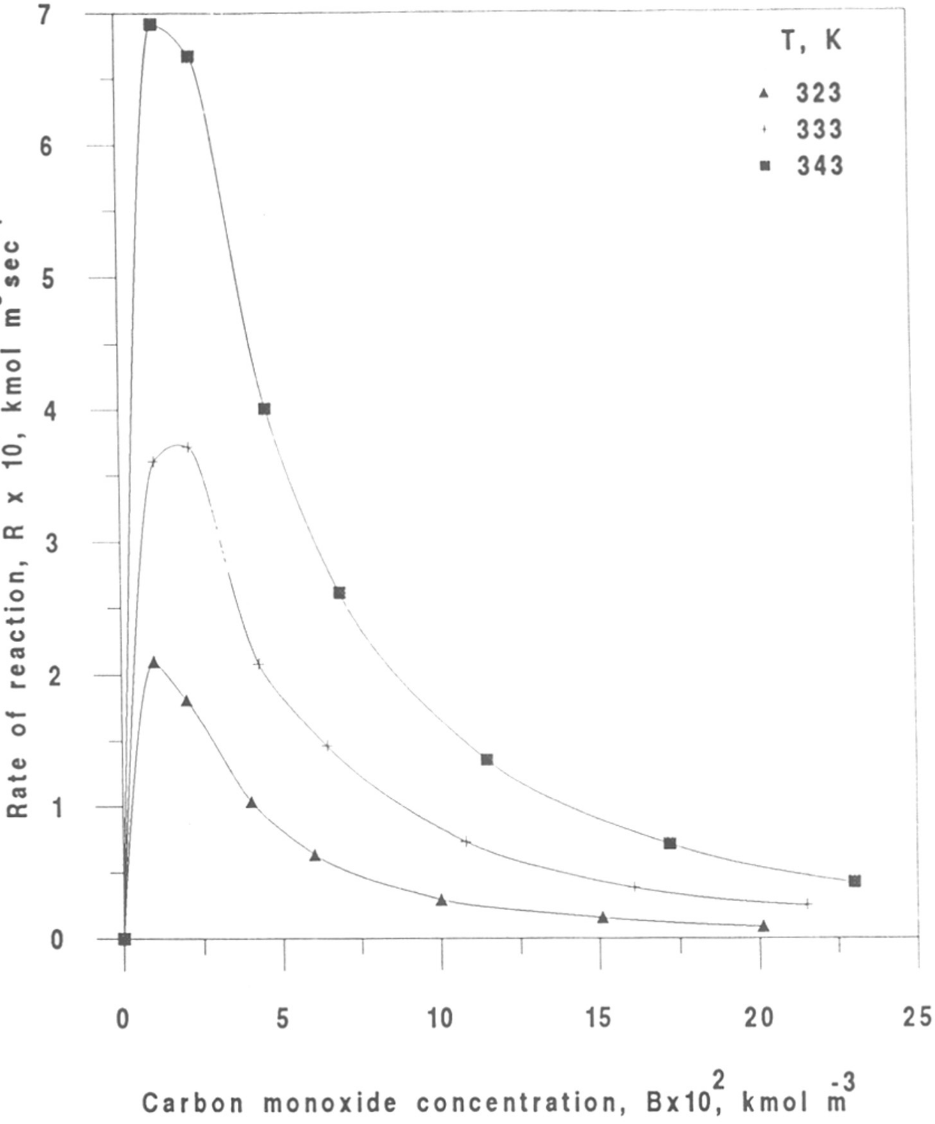


Fig : 2.11 Effect of liquid phase carbon monoxide concentration on the rate of reaction in the hydroformylation of 1-decene

Reaction Conditions :
Concentration of 1-decene = 52.80, kmol m^{-3};
Concentration of Catalyst = 1.00 x 10^{-3}, kmol m^{-3};
Partial pressure of H_2 = 1.38, MPa

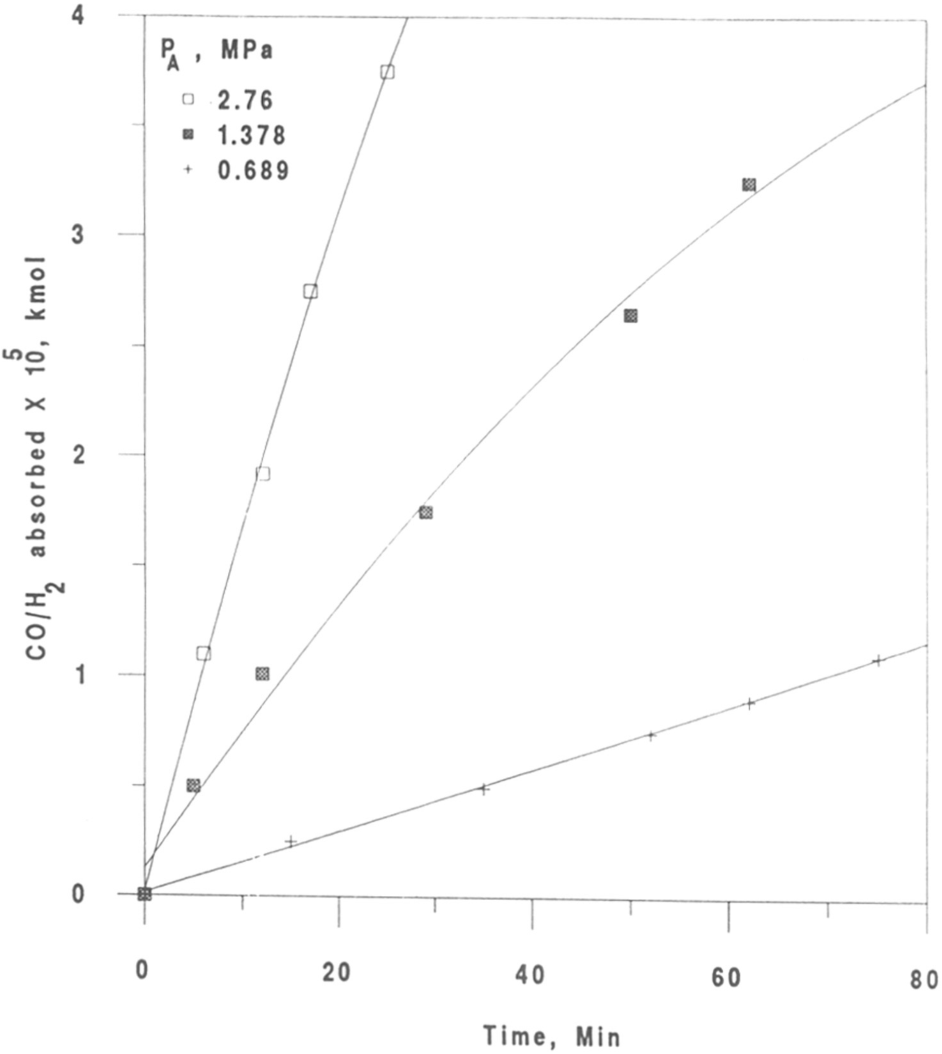


Fig : 2.12 A plot of CO/H_2 absorbed vs time for effect of hydrogen partial pressure at 333, K in the hydroformylation of 1-decene

Reaction Conditions :
Concentration of 1-decene = 52.8, kmol m^{-3};
Concentration of Catalyst = 1.00 x 10^{-3}, kmol m^{-3};
Partial pressure of CO = 1.38, MPa

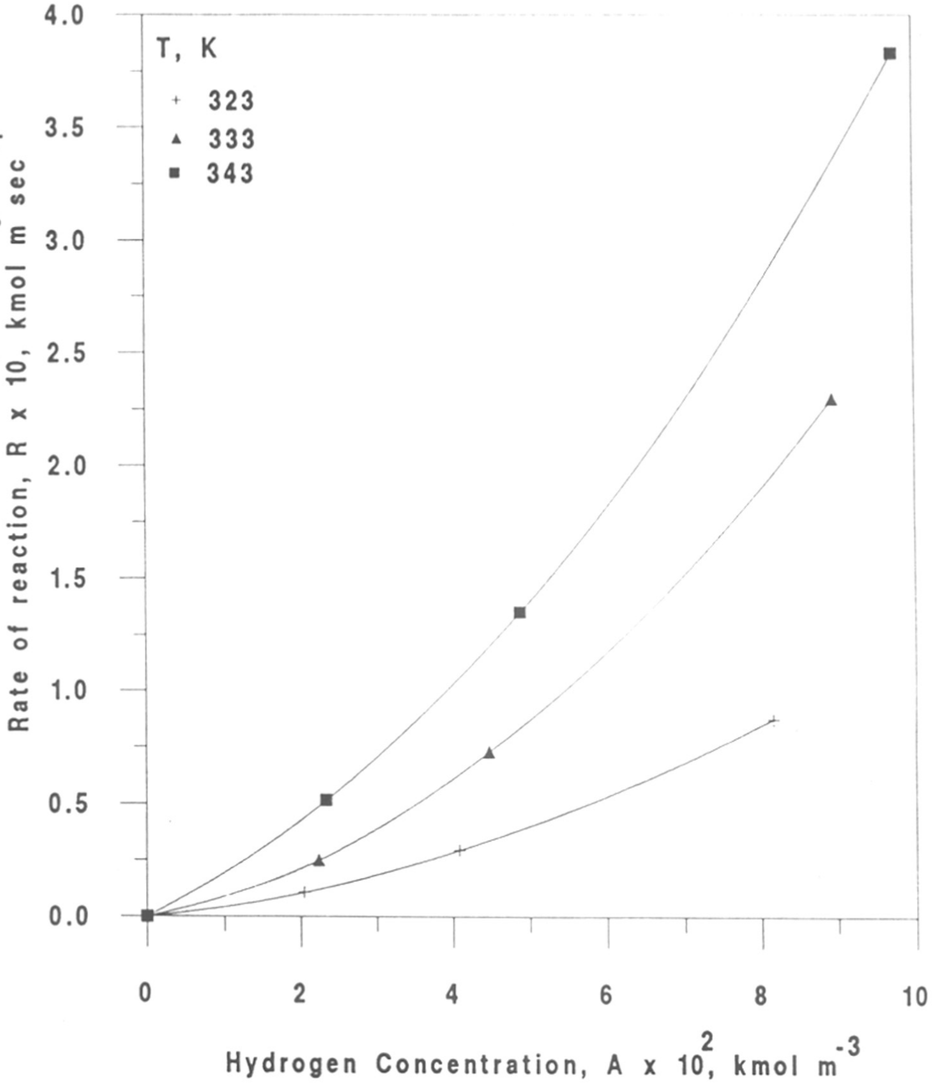


Fig : 2.13 Effect of liquid phase hydrogen concentration on the rate of reaction in the hydroformylation of 1-decene

Reaction Conditions :
Concentration of 1-decene = 52.8, kmol m^{-3};
Concentration of Catalyst = 1.00 x 10^{-3}, kmol m^{-3};
Partial pressure of CO = 1.38, MPa

increase in P_{H2}, the formation of the dimer (T) will be inhibited, thereby increasing the rate of hydroformylation. Besides this, the oxidative addition of H_2 to acyl complex (step 6 in Fig. 2.4) is also dependent on H_2 concentration. An overall order of reaction higher than unity can arise from a combined effect of these two steps.

2.3.3.4 Effect of 1-decene concentration

Fig. 2.14 shows the effect of 1-decene concentration on the rate of hydroformylation, at a total pressure of 2.76, MPa ($CO/H_2 = 1$), a catalyst concentration of 1.0×10^{-3}, kmol m^{-3}, in a temperature range of 323 - 343, K. The rate was found to be directly proportional to the concentration of 1-decene showing a first order dependence but for higher concentrations, the effect was marginal. These observations are also consistent with the mechanism shown in Fig. 2.4. The near zero dependence observed at higher olefin concentrations is probably due to the equilibrium in the steps (4) and (10) in Fig. 2.4. At higher olefin concentrations, the reverse equilibrium in steps (4) and (10) may become significant. These observations are however in contrast to the inhibition observed at higher olefin concentrations for other substrates (Deshpande and Chaudhari (1988), Deshpande and Chaudhari (1989)).

2.3.3.5 Effect of catalyst concentration

The effect of catalyst ($HRh(CO)(PPh_3)_3$) concentration was studied in a temperature range of 323 to 343, K, 1-decene concentration of 0.528, kmol m^{-3}, and a total pressure of $CO + H_2 = 2.76$, MPa ($CO/H_2 = 1$). The results are shown in Fig. 2.15. The rate was found to vary with 1.2th order with respect to the catalyst concentration at all the temperatures studied.

2.3.4 Rate equation

The kinetic modeling of hydroformylation of olefins has been studied previously for many substrates (Chaudhari and Deshpande 1988, Deshpande and Chaudhari 1989, Tremont et. al. 1990, van Rooy et. al. 1995). Considering the complexities that have been observed, regarding the variation of the rates with different parameters, it is important to develop suitable empirical as well as mechanistic rate models to describe the intrinsic kinetics of the hydroformylation reaction. Since, the hydroformylation reaction is the typical case involving the reaction of two dissolved gases in a liquid medium, a careful consideration must be given to ensure that the rate data are in the kinetic regime. The aim of this work, was, therefore to analyse carefully all these aspects and propose a suitable rate model for the hydroformylation of 1-decene using $HRhCO(PPh_3)_3$ catalyst.

As discussed in the experimental section, the initial rates of hydroformylation were

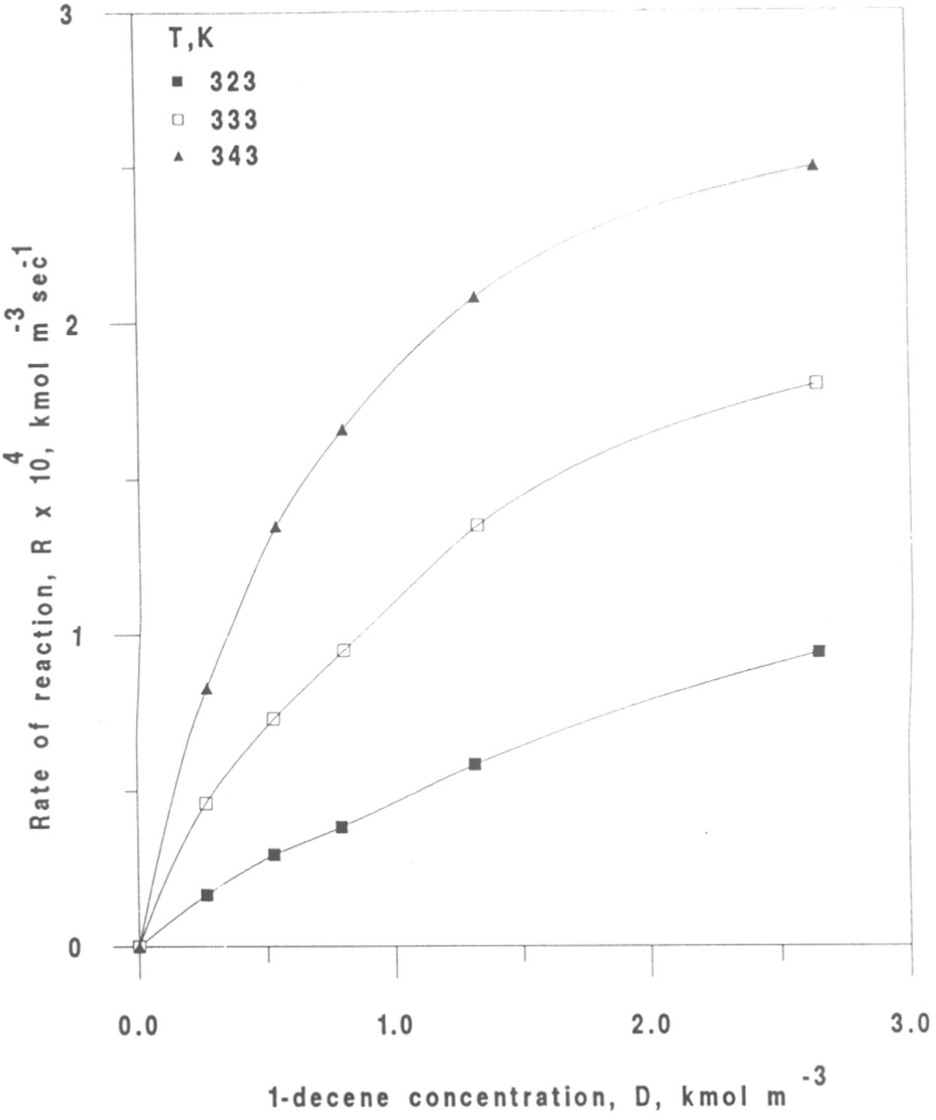


Fig : 2.14 Effect of 1-decene concentration on the rate of reaction in the hydroformylation of 1-decene

Reaction Conditions :
Concentration of Catalyst = 1.00 x 10^{-3}, kmol m^{-3};
Partial pressure of H_2 = 1.38, MPa
Partial pressure of CO = 1.38, MPa

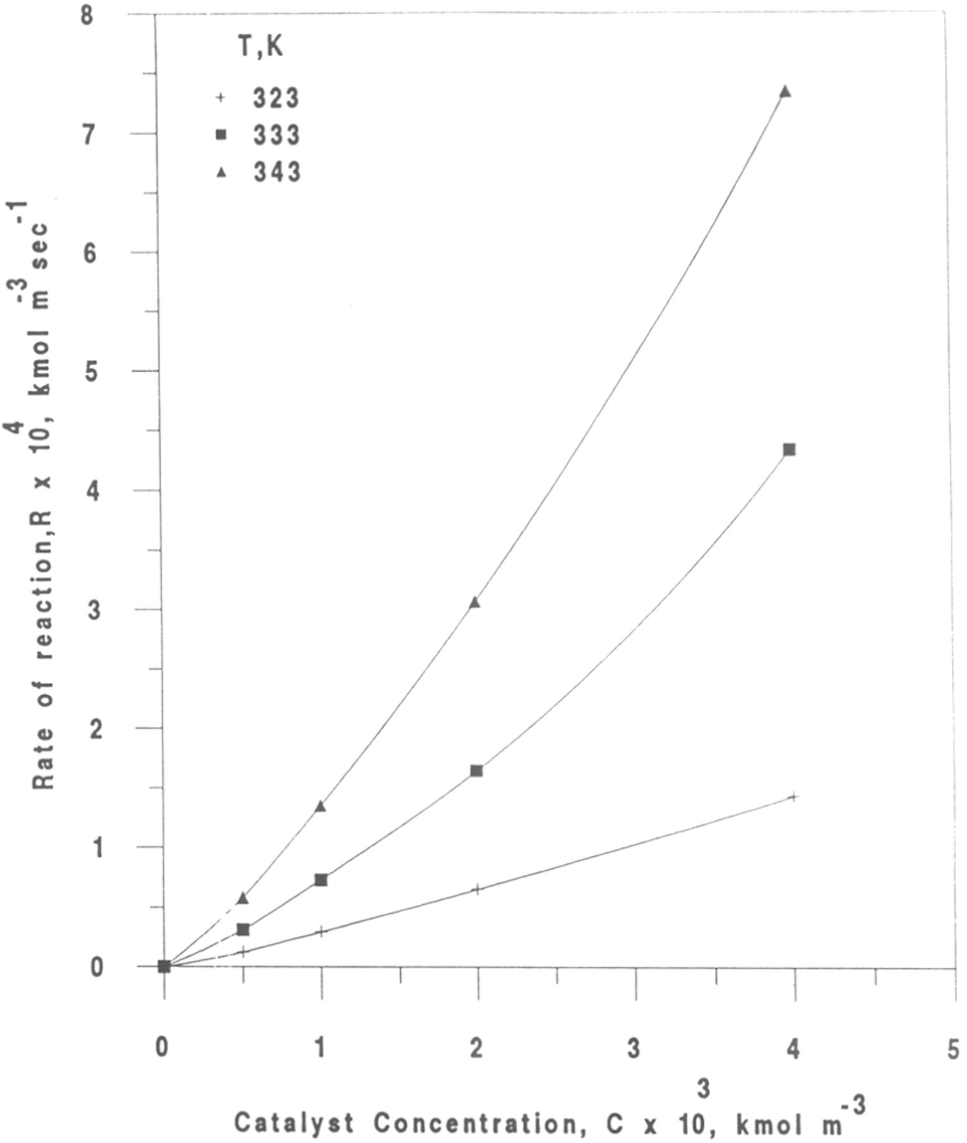


Fig : 2.15 Effect of catalyst concentration on the rate of reaction in the hydroformylation of 1-decene

Reaction Conditions :
Concentration of 1-decene = 52.8, kmol m^{-3};
Partial pressure of CO = 1.38, MPa
Partial pressure of H_2 = 1.38, MPa

observed under a variety of conditions. First, these data were analysed for the significance of mass transfer resistance. Since, the rate of stirring had no effect on the rate of reaction the absence of mass transfer resistance and hence, kinetic regime is indicated. This conclusion is further supported upon comparing the rates with the maximum rates of mass transfer of CO and H_2 at the respective conditions. For these purpose, the factors α_1 and α_2, defined as follows, were calculated (Chaudhari and Doraiswamy 1974)

$$\alpha_1 = \frac{R}{k_L a A^*} \tag{2.4}$$

$$\alpha_2 = \frac{R}{k_L a B^*} \tag{2.5}$$

where R represents the rate of hydroformylation, kmol m^{-3} sec^{-1}; $k_L a$ is the volumetric mass transfer coefficient, sec^{-1}, and A^* and B^* are the concentrations of H_2 and CO at the gas liquid interface in kmol m^{-3}, respectively. The evaluation of α_1 and α_2 requires a knowledge of $k_L a$ and solubilities of H_2 and CO in addition to the rate data. For the purpose of kinetic studies, a knowledge of solubility of gaseous reactants in the reaction medium is essential to evaluate the dissolved concentrations. For CO-Benzene and H_2-Benzene systems, the solubility data were not available in the literature in the range of conditions used. Therefore, these data were obtained following the procedure described in the literature with an accuracy of 2-3% (Choudhary et. al. 1982). These results are presented in Table (2.6). These data were used in the calculation of the concentrations of dissolved CO and H_2 in the liquid medium. While the Henry's law constants, presented in Table (2.6) were used to calculate A^* and B^*, respectively, $k_L a$ values were obtained from the correlation proposed by Chaudhari et. al. (1987). For the present case $k_L a$ was found to be 0.238, sec^{-1} at 15, rps. The correlation of Chaudhari et. al. (1987) for $k_L a$ was proposed based on the data obtained in the same type of reactor (Parr Autoclave) as used in this work and hence was thought to be more appropriate. The values for α_1 and α_2 were calculated for all the data and were found to be less than 0.12. This clearly shows that the rates observed in the entire range of conditions studied are much smaller than the mass transfer rates that would prevail under these conditions, and hence the rate data are in the kinetic regime.

Several empirical rate forms were evaluated for fitting the initial rate data. These were

TABLE 2.6

SOLUBILITY OF H_2 AND CO IN BENZENE

Serial Number	Temperature K	Solubility m^3 MPa $kmol^{-1}$	
		H_2	CO
1	323	33.32	13.73
2	333	30.79	12.81
3	343	28.63	12.00

selected based on the trends observed on the dependence of the rates on different parameters. The concentrations of dissolved H_2 and CO, required in kinetic modeling were evaluated from the solubility data obtained experimentally (see Table (2.6)). In order to fit the rate data, an optimization routine based on Marquardt (1963) method was used. The rate equations and the corresponding parameters evaluated are presented in Table (2.7). The following rate equation was found to represet the data best:

$$R = \frac{k\,A^{1.5}\,B^{*}\,C^{1.2}\,D}{(! + K_B B^{*})^3\,(1 + K_D D)} \qquad (2.6)$$

where, R is the rate of reaction, kmol m^{-3} sec^{-1}, k is the intrinsic reaction rate constant ($m^{11.1}$ $kmol^{-3.7} sec^{-1}$), $A^* = P_{H2} / H_A$ and $B^* = P_{CO} / H_B$ are the concentrations of H_2 and CO in benzene at the gas liquid interface (kmol m^{-3}), respectively, and C and D represent the concentrations of the catalyst and 1-decene (kmol m^{-3}) respectively.

The rates predicted using eq. (2.6) were found to agree within 6-8% error with the experimental data. The rate parameters for eq. 2.6 at 323 - 343, K are presented in Table (2.8). The Arrhenius plot showing the effect of temperature on the rate constants is shown in Fig. 2.16 from which the activation energy was evaluated as 49.16, kJ/mol. The dependence of the rate parameters K_B and K_D on temperature (Fig. 2.17) shows opposite trends, however, it is important to note that these parameters may not be representative of a single equilibrium step and are infact lumped parameters describing the observed overall trends.

For hydroformylation of olefins, a catalytic cycle has been proposed (Evans et. al. 1968b, Brown and Wilkinson 1970) based on well defined catalytic species. Hence, it is only appropriate to consider a mechanistic approach to kinetic modeling. Based on the mechanism shown in Fig. 2.3, rate equations were derived assuming different steps as rate controlling. The rate data on hydroformylation of 1-decene was also fitted using these equations. For step 6 as rate controlling the following rate equation was derived.

The first step is the generation of active catalytic species in the presence of CO from the catalyst precursor ($HRh(CO)(PPh_3)_3$) (eq. (2.7) to eq (2.8)).

$$HRh(CO)L_3 \rightleftharpoons HRh(CO)L_2 \qquad (2.7)$$

$$HRh(CO)L_2 + CO \rightleftharpoons HRh(CO)_2L_2 \qquad (2.8)$$

TABLE 2.7

MODELS EXAMINED TO FIT THE DATA ON 1-DECENE HYDROFORMYLATION

Serial number	Rate Model	Temperature K	K_B	K_D	K	m	n	σ_{min}
1	2	3	4	5	6	7	8	9
1	$\frac{(A^\bullet)^{1.5}\ B^\bullet\ C^{1.2}\ D}{(1 + K_B\ B)^3(1 + K_Da\ D)}$	323	55.25	0.3064	1.081×10^{13}	1.5	1.2	2.939×10^{-13}
		333	38.10	0.8882	1.441×10^{13}	1.5	1.2	2.111×10^{-12}
		343	37.67	1.472	2.840×10^{13}	1.5	1.2	1.352×10^{-12}
2	$\frac{(A^\bullet)^1\ B^\bullet\ C\ D}{(1 + K_B\ B)^3(1 + K_D\ D)}$	323	51.89	370.9	1.081×10^{13}	1	1.2	7.000×10^{-12}
		333	36.10	442.9	1.441×10^{13}	1	1.2	2.035×10^{-11}
		343	36.77	1.637	2.023×10^{13}	1	1.2	1.226×10^{-11}
3	$\frac{(A^\bullet)^{1.5}\ B^\bullet\ C^{1.2}\ D}{(1 + \sqrt{K_B\ B})^4(1 + K_D\ D)}$	323	55.03	1.257	1.081×10^{13}	1.5	1.2	2.234×10^{-12}
		333	40.24	1.814	1.441×10^{13}	1.5	1.2	6.893×10^{-11}
		343	38.91	2.406	2.911×10^{13}	1.5	1.2	1.079×10^{-11}
4	$\frac{(A^\bullet)^{1.5}\ B^\bullet\ C^{1.2}\ D}{(1 + K_B\ B)^2(1 + K_D\ D)}$	323	141.8	0.3019	1.081×10^{13}	1.5	1.2	1.4400×10^{-11}
		333	99.27	0.5851	1.441×10^{13}	1.5	1.2	3.301×10^{-11}
		343	106.2	0.7630	2.840×10^{13}	1.5	1.2	1.106×10^{-10}
5	$\frac{(A^\bullet)^m\ B^\bullet\ C^n\ D}{(1 + K_B\ (B)^2)(1 + K_D\ D)}$	323	55.46	1.257	1.081×10^{13}	1.5	1.2	4.559×10^{-6}
		333	39.19	0.8337	1.441×10^{13}	1.5	1.2	7.064×10^{-6}
		343	376.6	1.471	2.840×10^{13}	1.5	1.2	2.541×10^{-5}

TABLE 2.8

RATE PARAMETERS

Temperature K	$k \times 10^{13}$ ($m^{11.1}$ $kmol^{-3.7}$ s^{-1})	K_B (m^3 $kmol^{-1}$)	K_D (m^3 $kmol^{-1}$)
323	1.08	55.30	0.306
333	1.44	38.10	0.834
343	2.08	37.67	1.470

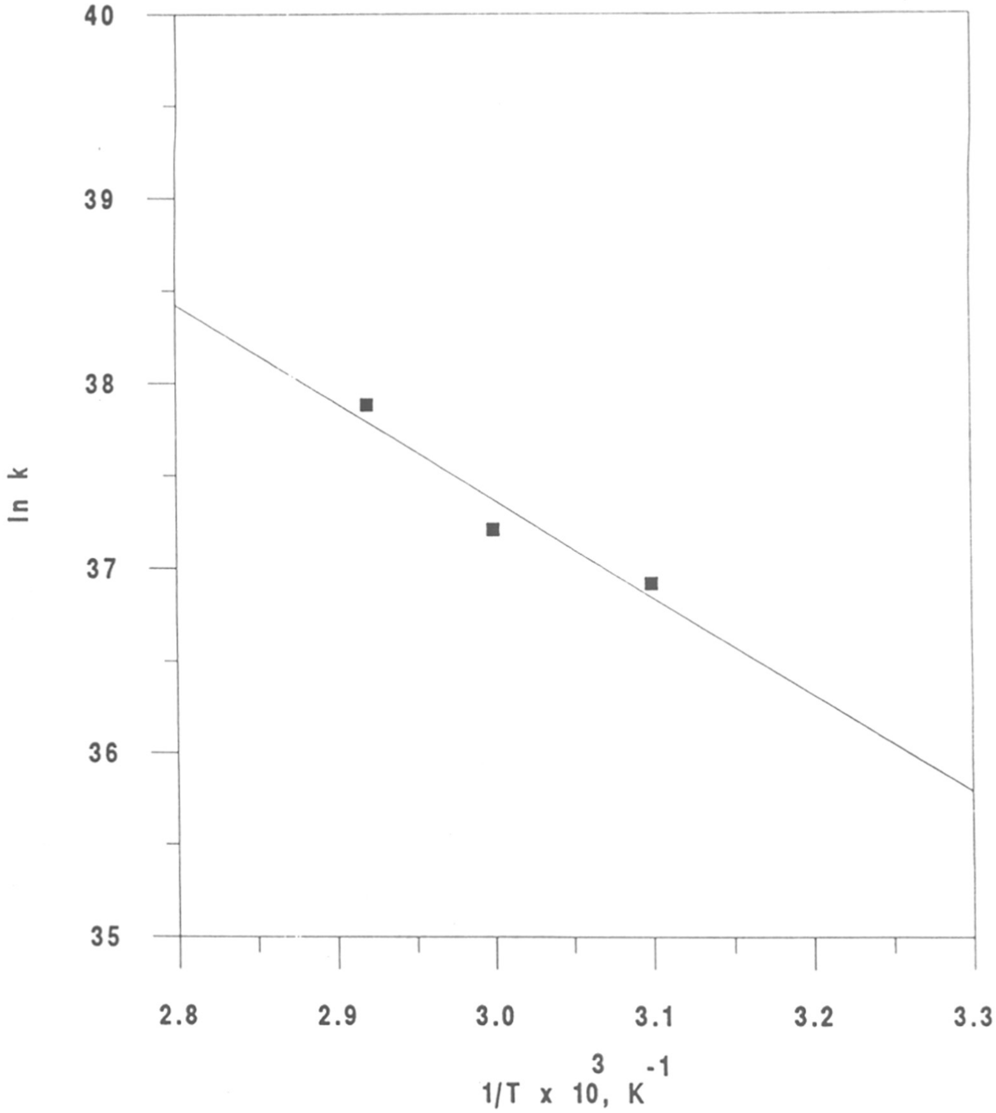


Fig : 2.16 A plot of ln k vs 1/T (Arrhenius plot)

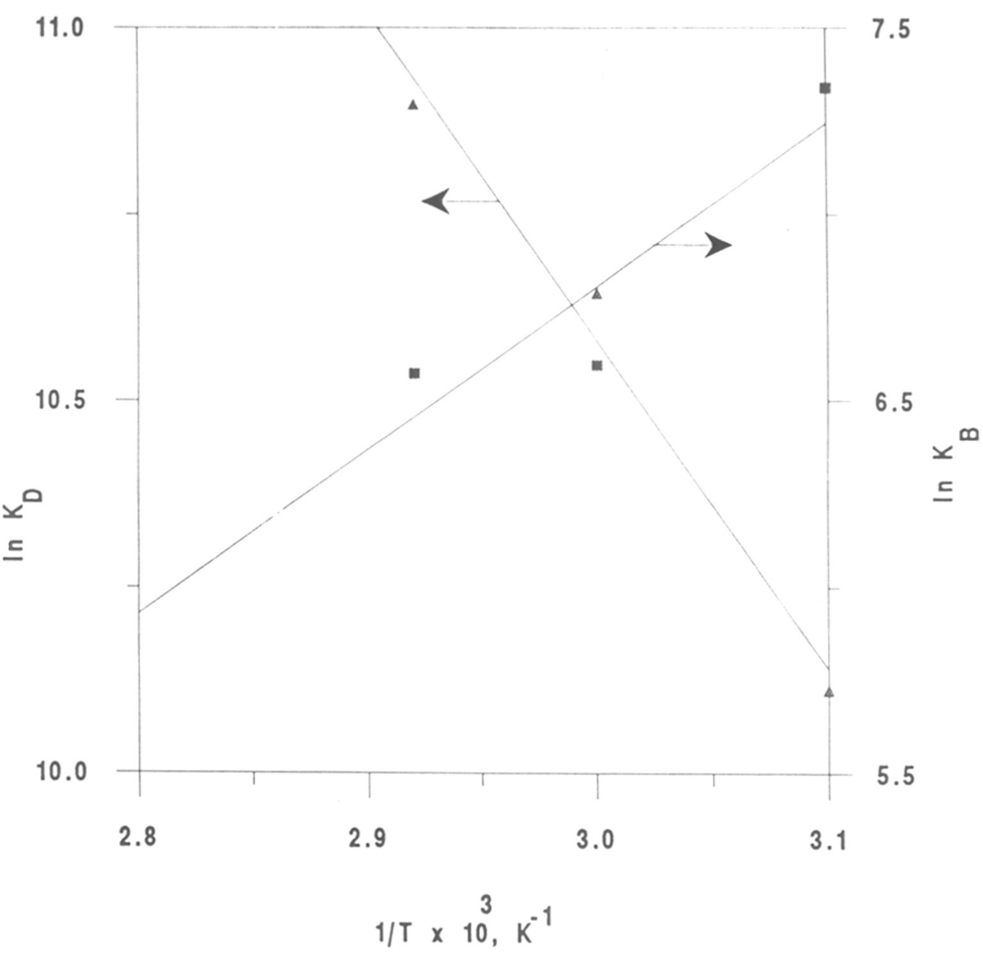


Fig : 2.17 A plot of ln $K_{B,}$ K_D vs 1/T

The addition of olefin to the active catalytic species (C_1) occurs via an intermediate to pi olefin-Rh complex, which reaaranges itself to a σ alkyl complex (eq. (2.9))

$$\underset{C_1}{HRh(CO)_2L_2} + \underset{D}{Olefin} \overset{K_1}{\rightleftharpoons} \underset{C_2}{R'Rh(CO)_2L_2} \qquad (2.9)$$

This alkyl complex rearranges by alkyl migration or CO insertion to the acyl complex (eq. (2.10))

$$R'Rh(CO)_2L_2 \rightleftharpoons (R'CO)Rh(CO)L_2 \qquad (2.10)$$

Oxidative addition of hydrogen to the acyl complex yields product aldehyde and the active catalytic species is regenerated in the presence of CO (eq. (2.11) and eq. (2.12))

$$\underset{C_2}{R'Rh(CO)_2L_2} + \underset{A}{H_2} \xrightarrow{k} \underset{P}{R'CHO} + \underset{C_3}{HRh(CO)L_2} \qquad (2.11)$$

$$\underset{C_3}{HRh(CO)L_2} + \underset{B}{CO} \overset{K_2}{\rightleftharpoons} \underset{C_1}{HRh(CO)_2L_2} \qquad (2.12)$$

At higher partial pressures of CO, side reactions as shown below may take place

$$\underset{C_2}{(R'CO)Rh(CO)L_2} + \underset{B}{CO} \overset{K_3}{\rightleftharpoons} \underset{C_4}{(R'CO)Rh(CO)_2L_2} \qquad (2.13)$$

$$\underset{C_4}{(R'CO)Rh(CO)_2L_2} + \underset{B}{CO} \overset{K_4}{\rightleftharpoons} \underset{C_5}{(R'CO)Rh(CO)_3L_2} \qquad (2.14)$$

For step (2.11) as rate determining, the reaction rate is given as

$$\text{Rate} = k\, C_2\, A \qquad (2.15)$$

For the determination of the rate, all the intermediate catalytic species have to expressed in terms of C_2 the total concentration of catalyst charged (eq. (2.15)). These rearrangements can be shown as follows (eq. (2.16) to eq. (2.19)).

$$C_1 = C_2 / K_1 D \qquad (2.16)$$

$$C_3 = C_2 / K_1 K_2 BD \qquad (2.17)$$

$$C_4 = K_3 C_2 B \qquad (2.18)$$

$$C_5 = K_3 K_4 C_2 B^2 \qquad (2.19)$$

The total catalyst concentration is the sum of the concentrations of all these species (eq. (2.20))

$$C = C_1 + C_2 + C_3 + C_4 + C_5 \qquad (2.20)$$

By substituting the values of C_1 to C_5 in eq. (2.20) we get the following equation in terms of C_2:

$$= C_2 / K_1 D + C_2 + C_2 / K_1 K_2 BD + K_3 C_2 B + K_3 K_4 C_2 B^2 \qquad (2.21)$$

Rearranging eq. (2.21), we get

$$C_2 = \frac{K_1 K_2 BCD}{1 + K_2 B + K_1 K_2 BD + K_1 K_2 K_3 B^2 D + K_1 K_2 K_3 K_4 B^3 D} \qquad (2.22)$$

substituting for value of C_2 (eq. (2.22)) in eqn. (2.15) we get the following form of equation for the rate of hydroformylation in terms of A, B, C, D.

$$R = \frac{k\,K_1K_2ABCD}{1 + K_2B + K_1K_2BD + K_1K_2K_3B^2D + K_1K_2K_3K_4B^3D} \qquad (2.23)$$

where, the K_1, K_2, K_3, K_4 are the equilibrium constants for the elementary reactions. Eq. (2.23) was found to be consistent with the general trends of dependence of the rates on P_{H2}, P_{CO} and 1-decene concentration and particularly with the negative order dependence on P_{CO}. The results comparing the rates predicted by eq. (2.23) and the experimental data are shown in Fig. 2.18, which indicate that eq. (2.23) also fits the data reasonably well. Though the predictions are not in precise agreement, there is a close analogy between the empirical rate equation (eq. (2.6)) and eq. (2.23) with respect to the general trends. However, eq. (2.23) is mechanistically more meaningful. There are obvious difficulties in fitting the rate data with these mechanistic models due to its complex form, and rigorous optimization procedure is necessary to evaluate these. The values of the rate parameters evaluated for eq. (2.23) at 333, K are $k = 1.236 \times 10^3$, $m^3\ kmol^{-1}\ sec^{-1}$; $K_1 = 1.28 \times 10^{-2}$, $m^3\ kmol^{-1}$; $K_2 = 5.7 \times 10^6$, $m^3\ kmol^{-1}$; $K_3 = 1.302 \times 10^2$, $m^3\ kmol^{-1}$ and $K_4 = 2.425 \times 10^2$, $m^3\ kmol^{-1}$.

2.3.5 Selectivity in hydroformylation of 1-decene

The hydroformylation of 1-decene was studied at 323, K using $HRh(CO)(PPh_3)_3$ as a catalyst to understand the selectivity behavior as a function of reaction conditions. The effect of various solvents on the conversion as well as the product distribution has been investigated and the results are presented in Fig. 2.19. The hydroformylation of 1-decene in aromatic solvents like benzene and toluene gave higher conversions with a n/iso ratio of 1.56 and 1.22 respectively with a total selectivity to aldehyde products. In these solvents, a higher n/iso ratio at higher olefin concentrations (low conversion levels) was observed and this ratio decreased with increase in the conversion as shown in Fig. 2.19.

Under identical conditions, with alcoholic solvents, such as ethanol, n-butanol and n-heptanol, the n/iso ratio observed was 1.13, 2.92 and 4.54 respectively. In comparison with this, with benzene and toluene as solvents, a lower n/iso ratio was obtained, although the average rates of hydroformylation were found to differ marginally.

It is well known that solvents consisting of aliphatic alcohols tend to co-ordinate with Rh metal during hydroformylation (Evans et. al 1968b). Such co-ordinated species are likely to affect

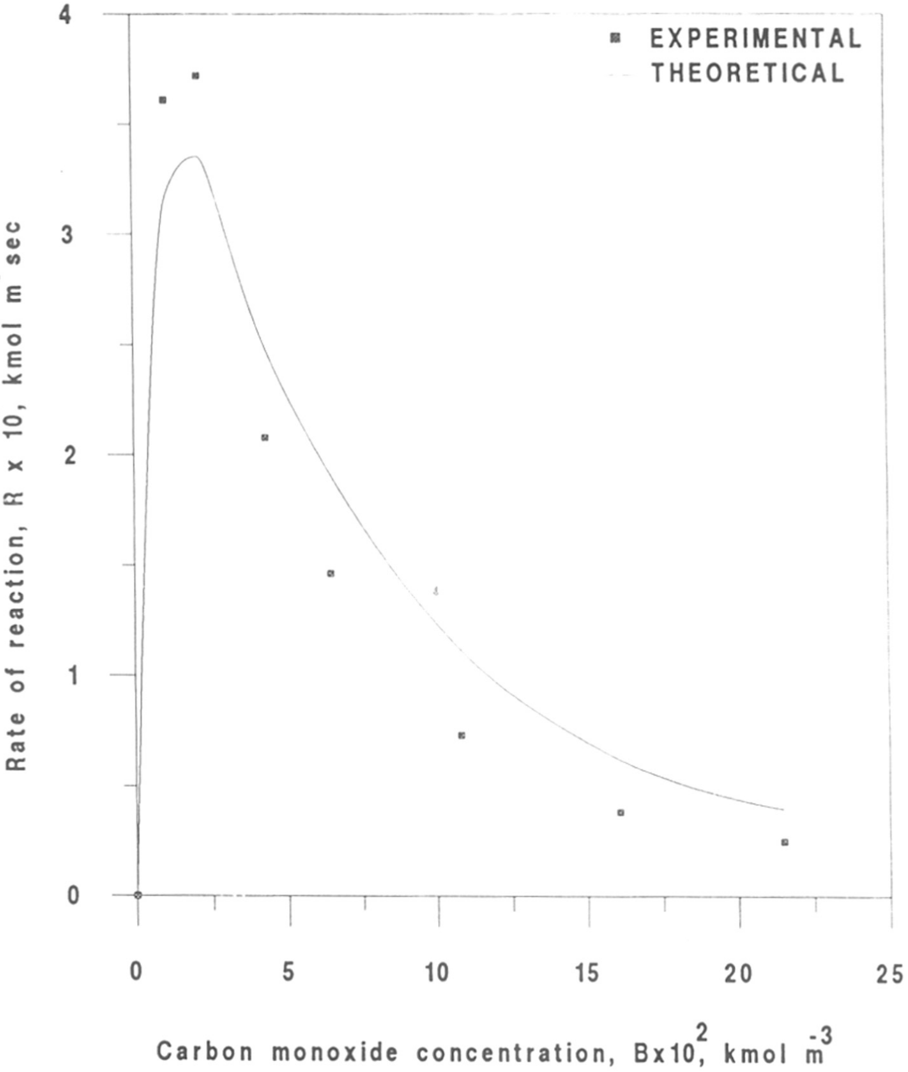


Fig: 2.18 Comparision of experimental and predicted rates using mechanistic model in the hydroformylation of 1-decene

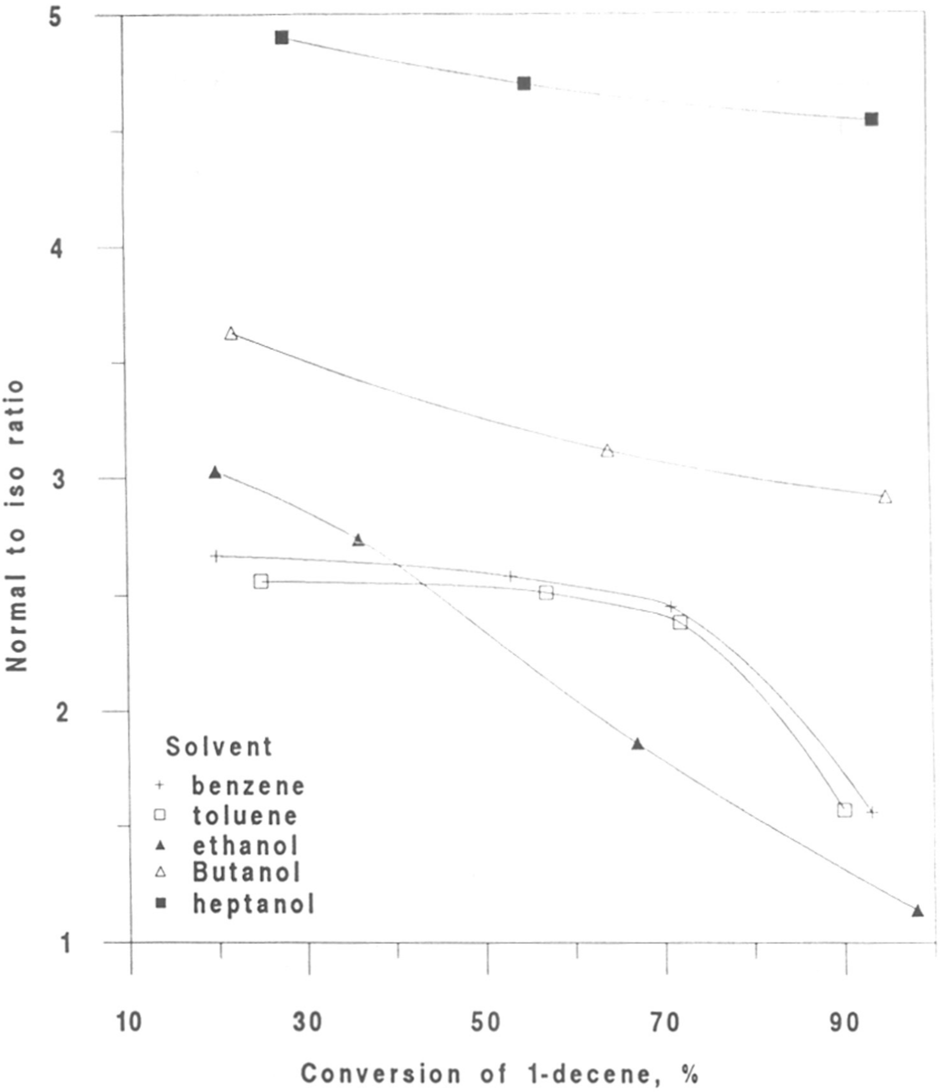


Fig : 2.19 Effect of solvent on n/iso ratio as a function of conversion of 1-decene at 323, K

Reaction Conditions :

Concentration of 1-decene = 52.80, kmol m^{-3};

Concentration of Catalyst = 1.00 x 10^{-3}, kmol m^{-3};

Total pressure ($CO/H_2 = 1$) = 2.756, MPa

the electronic as well as the steric environment of the central metal atom resulting in a change in the selectivity pattern. For example, the factors reducing the electron density on the central metal atom would enhance the n/iso ratio as well as the rate of reaction (Moser et al. 1987). For the present work, the electron density on central Rh atom will be highest with ethanol as a solvent and decrease with increase in chain length of carbon atoms in the alcohol solvents. Also, the increase in chain length of carbon atom in the solvent will favour the formation of a terminal alkyl-Rh species due to steric effect and hence, a higher n/iso ratio is expected for higher alcohols as solvents. This explains the observed jump in selectivity with n-heptanol as a solvent. In solvents like acetone and methyl ethyl ketone, the reaction was extremely slow, giving low conversions. While the conversion of 1-decene was 49 and 34%, the n/iso ratio was 2.12 and 2.24 respectively. For methyl ethyl ketone as a solvent a lower selectivity ($\leq$ 70%) to aldehydes, was observed due to formation of high boiling products.

The concentration-time profile of 1-decene and aldehyde products in the hydroformylation of 1-decene in benzene solution is shown in Fig. 2.10. It was observed that in the initial stages of the reaction,(where conversion of 1-decene is low) the formation of the n-aldehyde predominates. With the progress of the reaction, there is a reduction in the formation of the n-aldehyde, while corresponding formation of the branched aldehyde increases. As a result, a reduction in n/iso with conversion is observed.

Undecanal is a product of commercial interest, and hence a high n/iso ratio is desired in the final product. It was observed that in solvents like benzene and toluene, the n/iso ratio dropped considerably at higher conversions of 1-decene (Fig. 2.19). Hence, it was thought necessary to investigate the effect of excess PPh_3 concentration on the n/iso ratio as a function of conversion. This was studied to see if the n/iso ratio could be maintained at higher level even at high conversions of 1-decene. In order to study the effect of excess phosphine concentration on the hydroformylation of 1-decene, in benzene, reactions were conducted at different P/Rh ratios. The results are presented in Figure 2.20. When no excess PPh_3 was added the n/iso ratio was found to drop considerably with the progress of the reaction. The n/iso ratio at P/Rh = 2 was slightly improved (with respect to P/Rh = 0) and was affected to a lesser extent with 1-decene conversion. At higher P/Rh (= 4) ratio, the n/iso ratio was almost independent of both, conversion of 1-decene as well as P/Rh ratio. It was observed that unlike in the earlier case (Fig. 2.10), there is a consistent increase in the formation of both undecanal and 2-methyl nonanal, with conversion of 1-decene. The n/iso ratio for this system is found to be independent of conversion levels. A concentration time profile is shown in Fig. 2.21.

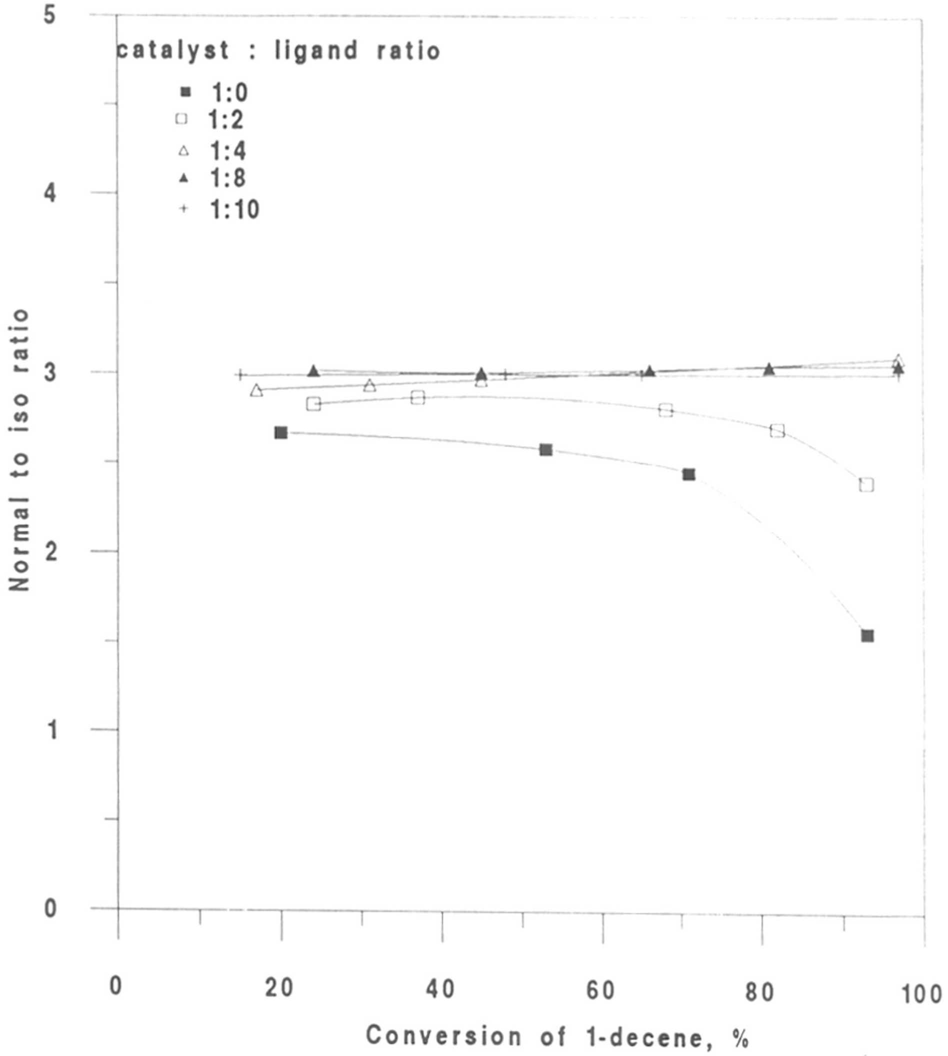


Fig : 2.20 Effect of addition of excess ligand on n/iso ratio as a function of conversion of 1-decene at 323, K

Reaction Conditions :

Concentration of 1-decene = 52.80, kmol m^{-3};
Concentration of Catalyst = 1.00×10^{-3}, kmol m^{-3};
Total pressure ($CO/H_2 = 1$) = 2.756, MPa
Solvent = Benzene

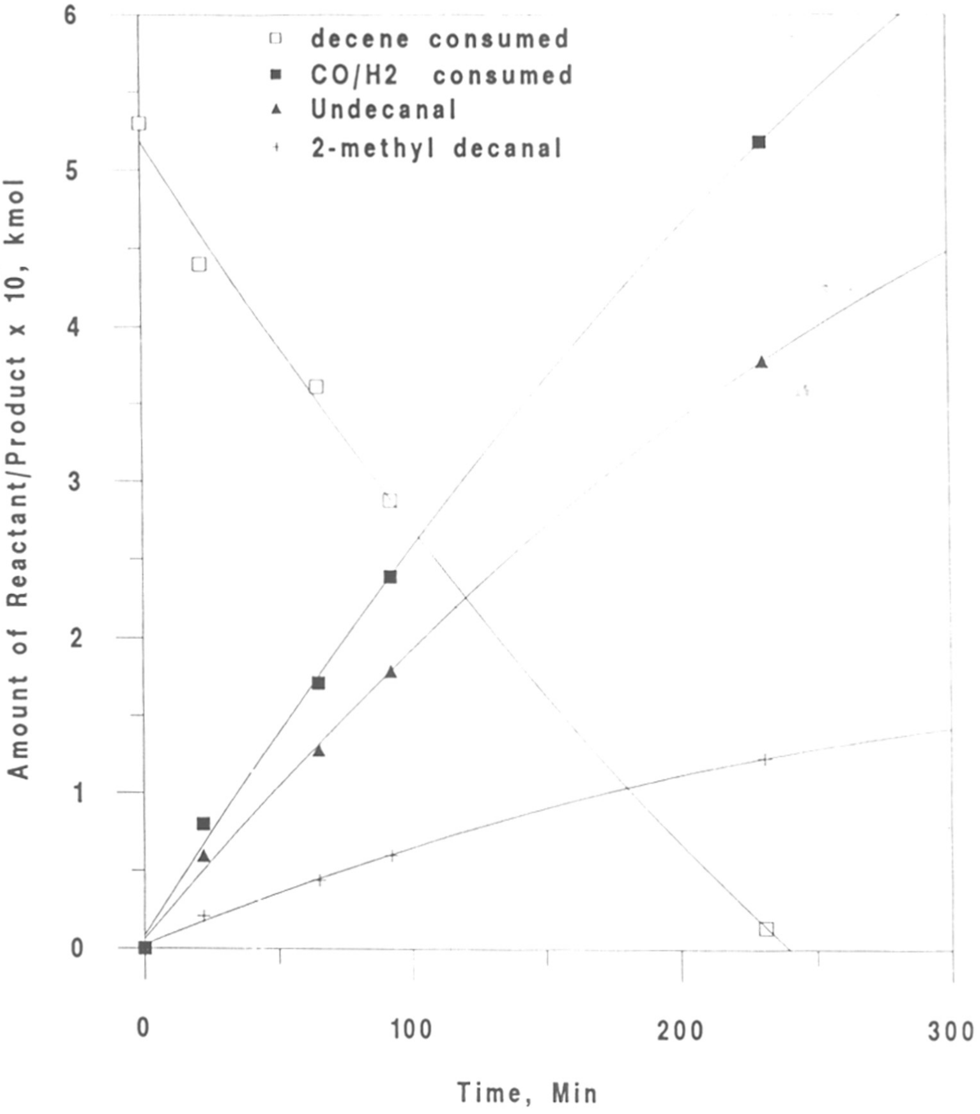


Fig : 2.21 A concentration time profile for the hydroformylation 1-decene at catalyst : ligand ratio of 1 : 4, at 323, K

Reaction Conditions :
Concentration of 1-decene = 52.80, kmol m^{-3};
Concentration of Catalyst = 1.00×10^{-3}, kmol m^{-3};
Concentration of PPh_3 = 4.00×10^{-3}, kmol m^{-3};
Total pressure ($CO/H_2 = 1$) = 2.756, MPa

For P/Rh ≥ 4, no change in n/iso ratio with conversion of 1-decene was observed. These observations are presented in Fig. 2.19 and are consistent with the literature reports (Gregorio et. al. 1980, Cavalieri et. al 1980) on propylene as a substrate. The results can be explained on the basis of a catalytic species involving more number of coordinated PPh_3 ligands. Due to the steric hindrance of these bulky phosphines, the terminal alkyl complex is more favored leading to higher yield of the n-isomer.

The change in the productivity of the normal and branched aldehydes as a function of conversion could be due to several reasons. The solvent properties will be affected by the aldehyde formed in the progress of the reaction, as a result the n/iso ratio may be affected (Carlock 1984).

Fell and Muller (1972) have observed similar trends in hydroformylation of 1-octene using $HRh(CO)(NBz)_3$ catalyst (NBz = tribenzylamine). The n/iso ratio drops from 13.3 at 24% conversion to 4.9 at 62% conversion at 293 and 303, K, respectively. Similar results are also reported in hydroformylation of 1-hexene using $HRh(CO)(PPh_3)_3$ catalyst at 398, K along with excess phosphine (Hanson and Davies 1987). The major side reaction, which causes a decrease in n/iso ratio in both the above cases, is believed to be the isomerisation. In this study the temperature was much lower and therefore the isomerisation could be suppressed. Also, the change in the solvent properties due to formation of aldehyde may change the mechanism. The observed results in this work could be a combined effect of these two reasons.

2.4 CONCLUSIONS

The maximum in rate with 1-hexene concentration was found to highly dependent on the solvent used. The shift in the maximum in rate with olefin was probably due to formation of inhibited species and its stabilization in the solvent. Although, some contribution to this phenomena by solvent co-ordination cannot be ruled out, it appears unlikely, that this could be a major factor in causing inhibition in rate with 1-hexene concentration. Further investigations on these systems are necessary for identification of the inhibiting species. The hydroformylation catalyst $HRh(CO)(PPh_3)_3$ was found to be deactivated at higher temperatures in the hydroformylation of 1-hexene. Excess of phosphine was found to prolong deactivation, which, however could not be prevented. Solvents were also found to play an important role in the deactivation of the catalyst.

The kinetics of hydroformylation of 1-decene using a homogeneous $HRh(CO)(PPh_3)_3$ catalyst has been studied in a temperature range of 323 - 343, K. The reaction was found to be 1.2th order with catalyst concentration and 1.5th order with P_{H2}. The rate of reaction varied linearly at lower concentrations of 1-decene but at higher concentrations the effect was marginal. With respect to P_{CO}, the rate decreased with increase in P_{CO}, indicating a negative order kinetics. Based on these data, a rate equation has been proposed, after examination of several empirical and mechanistic rate models. A molecular level approach to kinetic modeling has also been discussed. A rate equation derived from a reaction mechanism assuming oxidative addition of H_2 to acyl Rh species as rate determining was found to predict the observed trends. The kinetic parameters for this model have been reported and an activation energy of 49.16, kJ/mol was obtained.

Investigations on the effect of excess PPh_3 concentration in different solvents showed that a higher PPh_3 concentration caused enhancement of the n/iso ratio at all conversions in the hydroformylation of decene. In the absence of triphenylphosphine, the n/iso ratio dropped with conversion.

APPENDIX :

Nomenclature

[A] concentration of H_2 in benzene at the gas-liquid interface (kmol m^{-3})

[B] concentration of CO in benzene at the gas-liquid interface (kmol m^{-3})

[C] concentration of catalyst (kmol m^{-3})

[D] concentration of 1-decene (kmol m^{-3})

[H_A] Henry's law constant for the H_2-benzene system (MPa m^3 $kmol^{-1}$)

[H_B] Henry's law constant for the CO-benzene system (MPa m^3 $kmol^{-1}$)

[k] Reaction rate constant ($m^{11.1}$ $kmol^{-3.7}$ sec^{-1})

[K_B] Constant in eq. (2.6) (m^3 $kmol^{-1}$)

[K_D] Constant in eq. (2.6) (m^3 $kmol^{-1}$)

[m] Constant in Table (2.7)

[n] Constant in Table (2.7)

[P_{H2}] Partial pressure of hydrogen (MPa)

[P_{CO}] Partial pressure of carbon monoxide (MPa)

[R] Rate of hydroformylation (kmol $m^{-3}sec^{-1}$)

[T] Reaction temperature (K)

[O_{min}] Minimized sum of the squares of the difference between observed and predicted rates

[K_1] constant in eq. (2.25)

[K_2] constant in eq. (2.25)

[K_3] constant in eq. (2.25)

[K_4] constant in eq. (2.25)

[α_1] as defined in eq. (2.4)

[α_2] as defined in eq. (2.4)

REFERENCES

Abatjoglou A. G. and Bryant D. R.; Organometallics, **3**, 932, (1984).

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

Carlock J. T., Tetrahedron **40**(1), 185, (1984).

Cavalieri d'Oro P., Raimondi L., Pagani G., Montrasi G., Gregorio G., and Andreetta A., Chem. Ind. (Milan), 62, 572, (1980).

Chaudhari R.V., Gholap R.V., Emig E. and Hofmann H.,Can. J. Chem. Engg. **65**(5), 744, (1987)

Chaudhari R.V. and Doraiswamy L.K., Chem. Eng. Sci.**29**, 349, (1974)

Chaudhary V.R., Parande M.G. and Brahme P.H., Ind. Eng. Chem. Fundam. , **21**(4), 472, (1982)

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

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

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

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

Deshpande R. M. and Chaudhari R. V., J.Mol. Catal. **64**, 143, (1991).

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

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

Fell B., Muller E., Monats. Fur Chemie **103**, 1222, (1972).

Gregorio G., Montrasi G., Tampieri M., Cavalieri d'Oro P., Pagani G. and Andreetta A., Chem. Ind. (Milan), **62**, 389, (1980).

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

Heil B., and Marko L., Chem. Ber. **104**, 3418, (1971).

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

Jpn. Kokai Tokkyo Koho, JP 58,117,296 (1982) to Lion Corp.

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

Marquardt D. W., J. Soc. Ind. Appl. Math. **2**, 431, (1963).

Matsuda A., Shin S., Nakayama J., Bando K. and Murata K., Bull. Chem. Soc. Jpn **51**(10), 3016, (1978).

Matsumoto M. and Tamura M.; J. Mol. Catal., **19,** 365, (1983).

Mills P. L., Tremont S. J. and Remsen E. E. Ind. Eng. Chem. Res. **29**, 1443, (1990).

Moser W. R., Papile, C. J., Brannon D. A., Duwell R. A., Weininger S. J., J. Mol. Catal. **41**, 271, (1987).

Pino P., J. Organomet. Chem. **200**, 223, (1980).

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

Pruett R. L.; J. Chem. Edu., **63**, 196, (1986).

Russell M. J. H.; Platinum metals rev. **32** (4), 179, (1988).

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

Tolman C. A. Chem. Soc. Rev. **1,** 337, (1972).

Van Rooy A., Orij E. N., Kamer P. C. J. van Leeuwen P. W. N. M. Organometallics **14**, 34, (1995).

Wender I., Metlin S., Ergun S., Sternberg H. W. and Greenfield H., J. Am. Chem. Soc. **78**, 5401, (1956).

Wilkinson G., Yagupsky M., Brown C. K., Yagupsky G.; J. Chem. Soc (A), 937, (1970).

CHAPTER 3

****

KINETIC MODELING OF HYDROFORMYLATION OF ETHYLENE USING A HOMOGENEOUS RHODIUM COMPLEX CATALYST

****

3.1 INTRODUCTION

Catalytic hydroformylation of olefins has been extensively studied and the relevant literature on this subject has been summarized in Chapter 1. It is clearly implied from the literature reports that hydroformylation technology is primarily based on homogeneous catalysis and is one of the largest scale application of soluble metal complexes in industry (Cornils 1980). Besides, a wide range of olefin feedstocks are processed via hydroformylation to the corresponding aldehydes and alcohols (oxo alcohols). This indicates that hydroformylation catalysis is of great significance from practical point of view and therefore a detailed understanding of such reaction systems is demanded. Hydroformylation of ethylene is one of the examples leading to propionaldehyde and n-propanol as major products. The stoichiometric reaction for ethylene hydroformylation can be represented as follows :

$$\underset{\text{Ethylene}}{CH_2=CH_2} + CO + H_2 \xrightarrow{\text{CATALYST}} \underset{\text{Propionaldehyde}}{CH_3-CH_2-CHO} \qquad 3.1$$

Propionaldehyde and n-propanol have significant markets as solvents as well as intermediates in the manufacture of pharmaceuticals, pesticides and perfumery products. The aim of the present work was to specifically investigate the kinetics and mechanism of hydroformylation of ethylene using a Rh-complex catalyst. This problem is important from both academic and industrial point of view. A commercial process is in practice at BASF, Germany for 70,000, tpa of propionaldehyde (Weissermal and Arpe 1978). At the same time, the reaction involves simultaneous absorption of three gaseous reactants with reaction in a liquid phase to produce a liquid product. It is important to understand the rate behavior, kinetics and mechanism of such a complex multiphase reaction. Such a study is not only useful for optimization of the process and improvement of the catalytic system but also provides the basic information for the design and scale up of suitable reactors.

The hydroformylation of ethylene is catalyzed by variety of metal complexes consisting of Co, Rh, etc. and some important studies are summarized in Table (3.1). The kinetics of hydroformylation of olefins using homogeneous Rh-complex catalysts has been studied earlier by many investigators, however, for ethylene as a substrate, the available information in the literature is scanty. A few reports describe the kinetics of this reaction using supported

TABLE 3.1

A SUMMARY OF CATALYTIC SYSTEMS USED IN THE HYDROFORMYLATION OF ETHYLENE

Serial No.	Catalytic system	Olefin	Range of condition		solvent	Remarks	Reference
			Temp. K	Press. MPa			
1	aq. solution of $Rh(NO_3)_3$	Ethylene	373	24	ethanol	100% conversion	Mitsuo and Takeshi (1969).
2	$Rh_4(CO)_{12}$	Ethylene	573	13	butanol	—	Anthony and Thigpen (1972).
3	$HRh(CO)(PPh_3)_3$	Ethylene, methane, H_2S, air			dibutyl pthalate	lean gas from oil cracking is used	Kummer and Platz (1975).
4	$RhCl(CO)(PPh_3)_2$ + excess $PPhO_3$	Ethylene	411	0.81	dioctyl pthalate		Iwamoto et. al. (1977)
5	RhH_2(allyl)(CO)-$(PPh_3)_2$	Ethylene				kinetics of the reaction, studied	Tjan and Scholten (1977)
6	Rh complexes	Ethylene	308	5-10	n-tetradecane	mechanistic studies with IR spectroscopy	King et. al. (1979).
7	$Rh_4(CO)_{12}$	Ethylene				intermediates involved in the reaction studied	King et. al. (1980).

TABLE 3.1 (contd.)

Serial No.	Catalytic system	Olefin	Range of condition		solvent	Remarks	Reference
			Temp. K	Press. MPa			
8	$Rh(CO)Cl(PPh_3)_2$	Ethylene	303-403	5	toluene	reaction first order in ethylene and rate passed through maxima	Polievka et. al. (1980).
9	Co_2CO_8	Ethylene	408-448	15-30	non polar solvent	95% propionaldehyde	Neth Appl. 6,412,249 (1965).
10	Co carbonyl hydride	Ethylene	433	25		90% propionaldehyde	Hans and Werner (1961).

Rh-complex catalysts. Since, the homogeneous Rh-complex is used on an industrial scale, it is more important to investigate the kinetics using a soluble Rh-complex catalyst. Therefore, the present work was undertaken with this specific objective of studying the intrinsic kinetics of homogeneous catalytic hydroformylation of ethylene. None of the previous studies so far have addressed the problem of kinetic modeling

In this work, the rate data were obtained at different conditions to understand the dependence of the rate on the concentrations of reactants. For this purpose, the effect of CO, H_2 and ethylene partial pressures and catalyst concentration was studied over a temperature range of 333-373, K in a stirred high pressure gas-liquid reactor. The rate data were interpreted to test different forms of rate equations including both empirical as well as mechanistic rate models. Finally, a rate equation has been proposed and the kinetic parameters evaluated.

3.2 EXPERIMENTAL :

The hydroformylation experiments were carried out in a stirred batch reactor of 3.00 x 10^{-4}, m^3 capacity (for details see Chapter 2). The autoclave was charged with $HRh(CO)(PPh_3)_3$ complex catalyst in toluene (1.0 x 10^{-4}, m^3). The contents were first flushed with nitrogen and then with CO/H_2. The reactor was heated to a desired temperature and after the required temperature is attained, CO + H_2 mixture (1:1) was first introduced. Then, ethylene was charged upto a desired pressure, and the reaction was started by switching the stirrer on. The pressure drop in the reactor was observed with a pressure tranducer-recorder system. The experiments were carried out until no further pressure drop was observed in the reactor. The reactor was cooled to room temperature. The gas phase was analyzed by gas chromatography (see section 3.2.2). The contents were chilled to ~ 278, K (to avoid the evaporation of low boiling propionaldehyde product) and the liquid sample was also analyzed for propionaldehyde by gas chromatography. Thus, the CO, H_2 and ethylene consumed and propionaldehyde formed were determined.

3.2.1 Experimental procedure for kinetic studies

The experimental procedure for kinetic study was the same as that followed in the previous section except that the kinetic runs were carried out for shorter durations. such that approximately 10 - 15% ethylene is converted and the product propionaldehyde concentration does not increase to the extent that it affects the physical properties of the gas - liquid system. Several experiments were carried out to check the material balance of ethylene, carbon monoxide and hydrogen consumed and propionaldehyde formed and the results are presented in Table (3.2) and Table (3.3) for 333 and 353, K, respectively. The initial rates were calculated on the basis

TABLE 3.2

RESULTS SHOWING MASS BALANCE IN THE HYDROFORMYLATION OF ETHYLENE AT 333 K

Sr. No.	Initial reactants × 10^3,kmol			Final reactants × 10^3,kmol			reactants consumed, ×10^3,kmol			Product formed, × 10^3,kmol	% Material Balance With Respect To		
	H_2	CO	ethylene	H_2	CO	ethylene	H_2	CO	ethylene		H_2	CO	ethylene
1	0.115	0.122	0.069	0.051	0.037	0.001	0.071	0.078	0.068	0.072	101	93	106
2	0.125	0.132	0.155	0.027	0.0306	0.0558	0.098	0.103	0.099	0.101	103	98	102
3	0.126	0.134	0.229	0.074	0.078	0.176	0.052	0.056	0.053	0.055	105	98	104
4	0.0576	0.122	0.115	0.0016	0.061	0.060	0.056	0.061	0.055	0.057	102	93	104
5	0.248	0.122	0.115	0.132	0.0018	-	0.116	0.12	0.115	0.118	102	98	103
6	0.115	0.061	0.115	0.05	-	0.053	0.065	0.061	0.062	0.065	100	106	105
7	0.121	0.23	0.115	0.051	0.167	0.048	0.071	0.069	0.067	0.071	101	102	106

TABLE 3.3

RESULTS SHOWING MASS BALANCE IN THE HYDROFORMYLATION OF ETHYLENE AT 353 K

Sr. No.	Initial reactants × 10^3,kmol			Final reactants × 10^3,kmol			reactants consumed, ×10^3,kmol			Product formed, × 10^3,kmol	% Material Balance With Respect To		
	H_2	CO	ethylene	H_2	CO	ethylene	H_2	CO	ethylene		H_2	CO	ethylene
1	0.121	0.122	0.115	0.0052	0.012	0.01	0.11	0.11	0.105	0.108	98	98	103
2	0.121	0.122	0.229	0.033	0.035	0.141	0.088	0.87	0.87	0.87	99	100	100
3	0.231	0.122	0.115	0.108	0.028	0.026	0.123	0.12	0.112	0.118	96	98	97
4	0.115	0.245	0.115	0.231	0.151	0.0183	0.092	0.095	0.097	0.093	102	99	97

of consumption of CO or H_2 or ethylene, from the pressure drop vs time data.

3.2.2 Analytical method

The quantitative analysis of the gaseous reactants like ethylene, carbon monoxide and the liquid product propionaldehyde was done using HP 5840 gas chromatograph. A thermal conductivity detector (TCD) was used for the analysis of gases as well as liquid components. The analytical conditions used for gas phase and liquid components are presented in Table (3.4) and Table (3.5) respectively. A typical gas chromatogram showing gas and liquid phase analysis is shown in Fig. 3.1.

3.3 RESULTS AND DISCUSSION

The aim of this work was to investigate the kinetics of hydroformylation of ethylene using $HRh(CO)(PPh_3)_3$ complex catalyst. It was therefore thought necessary to first ensure the material balance and reproducibility of the experiments. For this purpose, a few experiments were carried out in which the amount of propionaldehyde formed, and the gaseous reactants consumed were compared. It was observed that the quantities of CO, H_2 and ethylene consumed were consistent with the amount of total aldehyde product formed as per the stoichiometry (see Table (3.4) and (3.5)). The material balance in all these experiments was found to be $\geq$ 95 %. Also, in the range of conditions covered in this work, the only product formed was propionaldehyde. No hydrogenation products were observed. Thus, the overall hydroformylation kinetics could be followed by observing the consumption of CO, H_2 and ethylene in a 1:1:1 ratio. For the purpose of detailed kinetic modeling, several experiments were carried out to understand the influence of catalyst concentration, carbon monoxide, hydrogen and ethylene partial pressures and temperatures on the rate of reaction. The range of conditions investigated for kinetic studies are presented in Table (3.6). The results are discussed below

3.3.1 Solubility data

For the purpose of kinetic studies, a knowledge of solubility of the gaseous reactants in the reaction medium is often essential. For CO, H_2 and ethylene - toluene systems, the solubility data were not available in the literature for the range of conditions used. Therefore, these data were obtained experimentally following the procedure described in Chapter 2. These results are presented in Table (3.7). These data were used in the calculation of the concentrations of dissolved CO, H_2 and ethylene in the liquid medium.

3.3.2 Calculation of initial rates

Initial rates of CO or H_2 or ethylene consumption in the liquid phase were calculated from

TABLE 3.4

ANALYTICAL CONDITIONS FOR THE GAS PHASE ANALYSIS

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

TABLE 3.5

ANALYTICAL CONDITIONS FOR THE LIQUID PHASE ANALYSIS

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

Fig. 3.1 A TYPICAL GAS CHROMATOGRAM FOR ETHYLENE, CO AND PROPIONALDEHYDE ANALYSIS

TABLE 3.6

RANGE OF CONDITIONS INVESTIGATED FOR THE KINETIC STUDY

Concentration of Catalyst (kmol m $^{-3}$)	0.5 to 4.0 $\times$ 10 $^{-3}$
Partial pressure of Ethylene (MPa)	0.414 to 2.756
Partial pressure of Hydrogen (MPa)	0.414 to 2.756
Partial pressure of CO (MPa)	0.414 to 2.756
Temperature (K)	333 to 373
Reaction Volume (m^3)	1.0 x 10^{-4}

TABLE 3.7

SOLUBILITY OF ETHYLENE, H_2 AND CO IN TOLUENE

Serial Number	Temperature K	Solubility MPa m^3 $kmol^{-1}$		
		Ethylene	H_2	CO
1	333	1.904	61.693	18.51
2	353	2.791	90.689	23.023
3	373	9.209	153.02	29.62

the experimentally observed pressure drop vs time data. For this purpose, the amount of CO + H_2 + ethylene consumed was calculated from the observed decrease in total pressure in the reactor as follows :

$$n = \frac{[(1 - P/P_0)\ P_0]\ V_G}{3\ Z\ R\ T} \tag{3.2}$$

where,

n = CO or H_2 or ethylene consumed, kmol

V_G = void space in the reactor, m^3

V_L = liquid volume in the reactor, m^3

Z = compressibility factor

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

T = temperature of the gas in the reactor, K

P = total pressure in the reactor at any time less vapor pressure t, MPa

P_0 = initial pressure in the reactor less vapor pressure, MPa

The rates (R) were calculated (kmol/m^3/s) as follows:

$$R = \frac{n}{t\ V_L} \tag{3.3}$$

where, t = time in seconds ; V_L = liquid volume in the reactor.

3.3.3 Effect of agitation speed

The effect of agitation speed on the rate of hydroformylation was studied at 333 - 373, K to check the significance of mass transfer. The results are shown in Fig. 3.2 which indicate that beyond 6.67, rps, the rate was independent of the agitation speed. All the experiments were carried out at 15, rps agitation speed to ensure kinetic regime.

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

The effect of partial pressure of CO was studied keeping H_2 and ethylene partial pressure constant. The results are presented in Fig. 3.3 - 3.5 for 333 to 373, K as change in P/P_0 as a function of time. The effect of P_{CO} on the rate of hydroformylation is shown in Fig. 3.6. The rate decreased with increase in P_{CO} at all temperatures. A negative order dependence with CO is

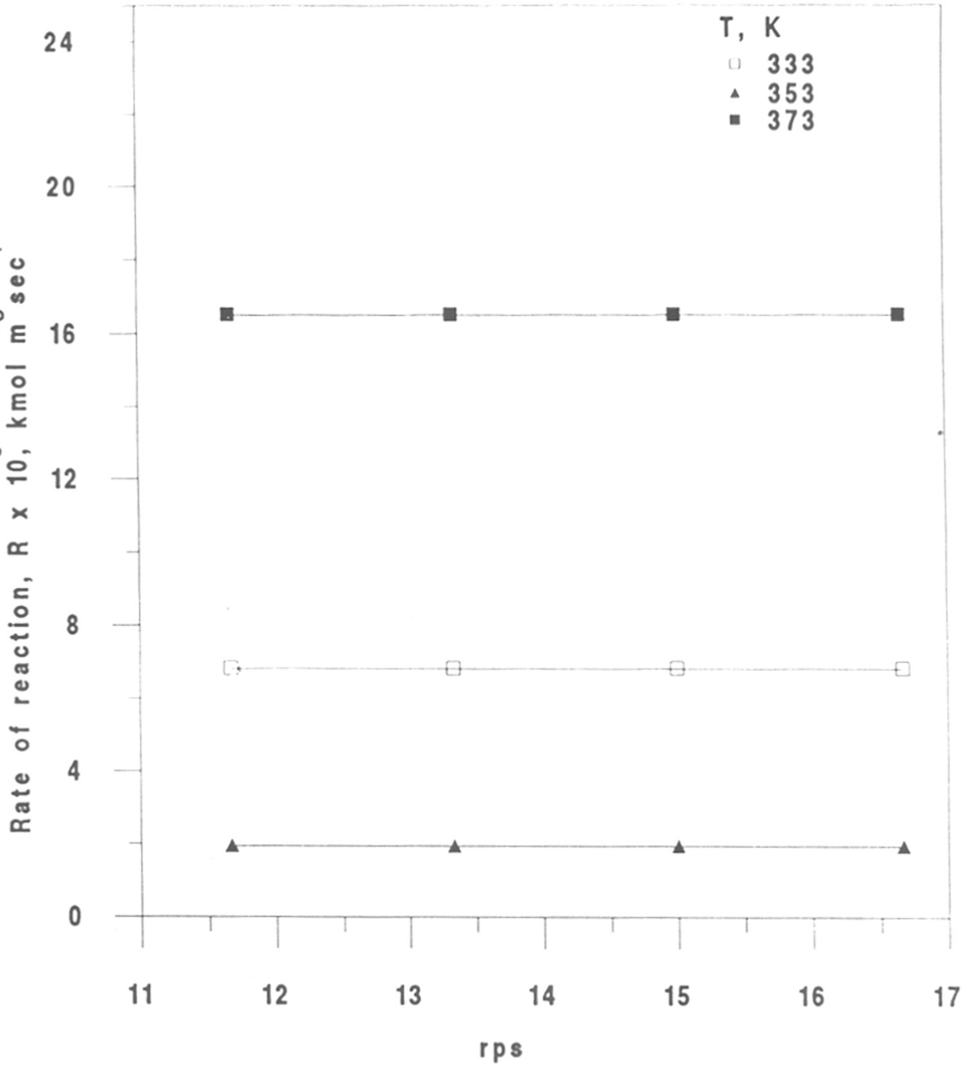


Fig. 3.2 A PLOT OF RATE OF REACTION vs AGITATION SPEED IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :
Concentration of catalyst : 1.0×10^{-3}, kmol m^{-3}
Partial pressure of ethylene : 0.689, MPa,
Partial pressure of CO : 1.378, MPa,
Partial pressure of H_2 : 1.378, MPa

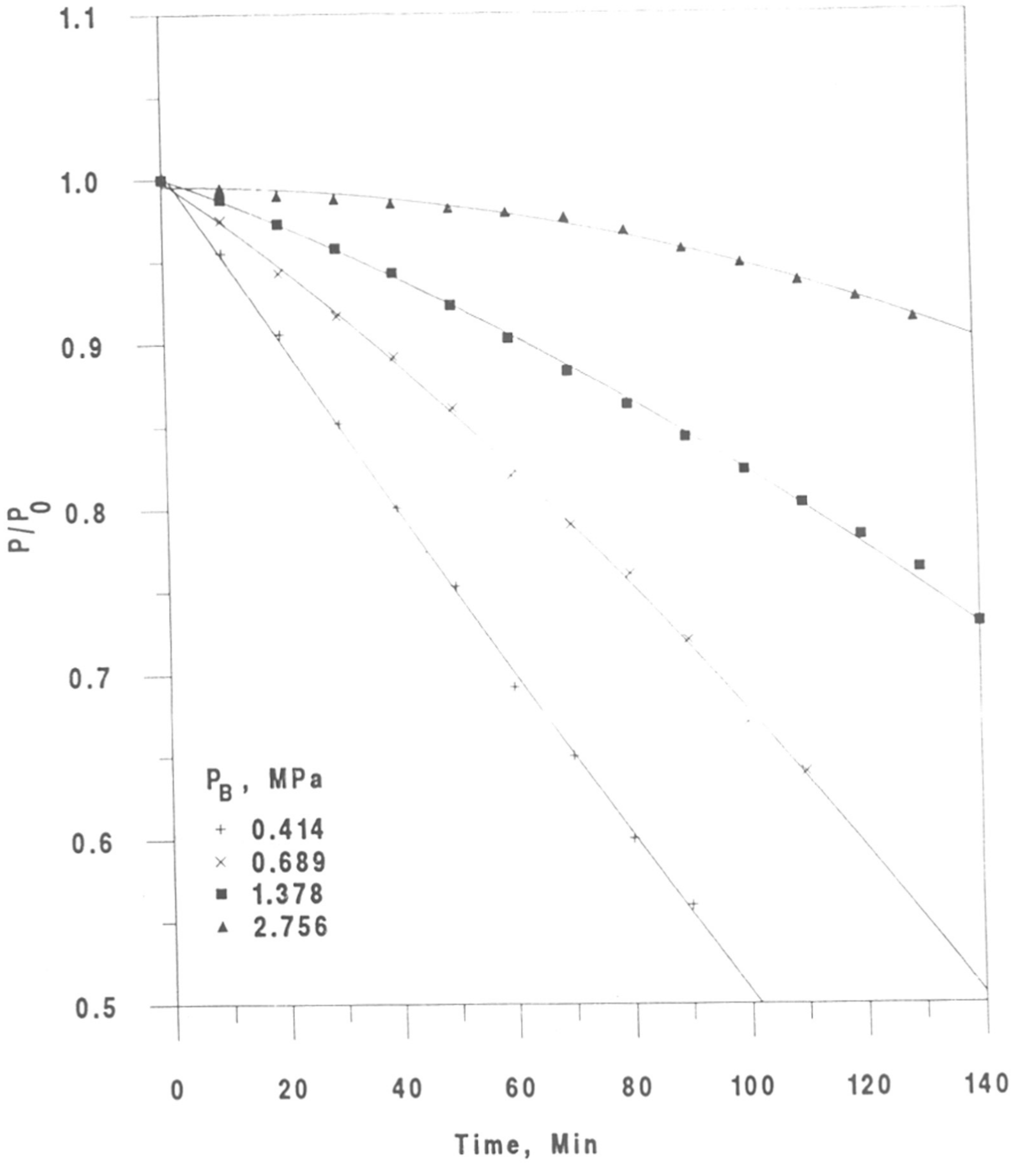


Fig. 3.3. A PLOT OF CO + H_2 + ETHYLENE (P/P_o) CONSUMED vs TIME : EFFECT OF CO PARTIAL PRESSURE AT 333, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Concentration of catalyst	: 1.0×10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of H_2	: 1.378, MPa
Agitation speed	: 15, rps

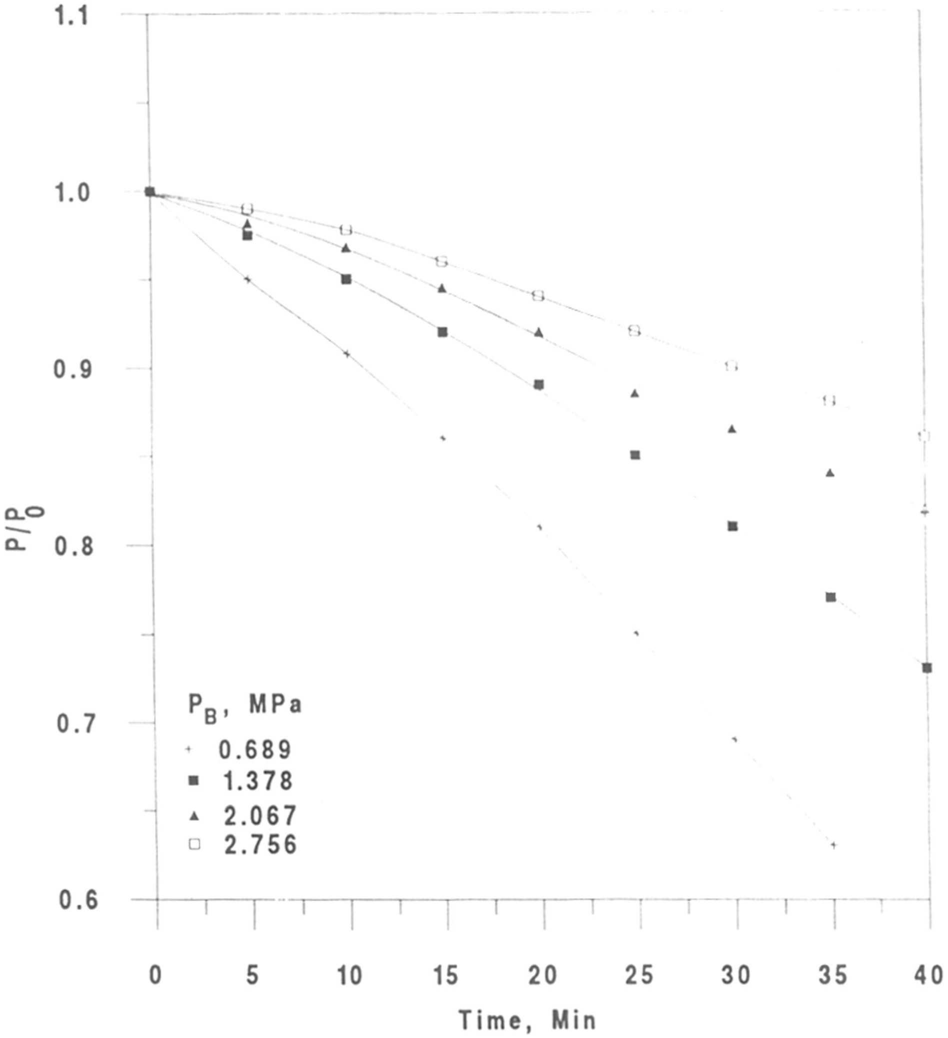


Fig. 3.4. A PLOT OF CO + H_2 + ETHYLENE (P/P_0) CONSUMED vs TIME : EFFECT OF CO PARTIAL PRESSURE AT 353, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Concentration of catalyst	: 1.0 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of H_2	: 1.378, MPa
Agitation speed	: 15, rps

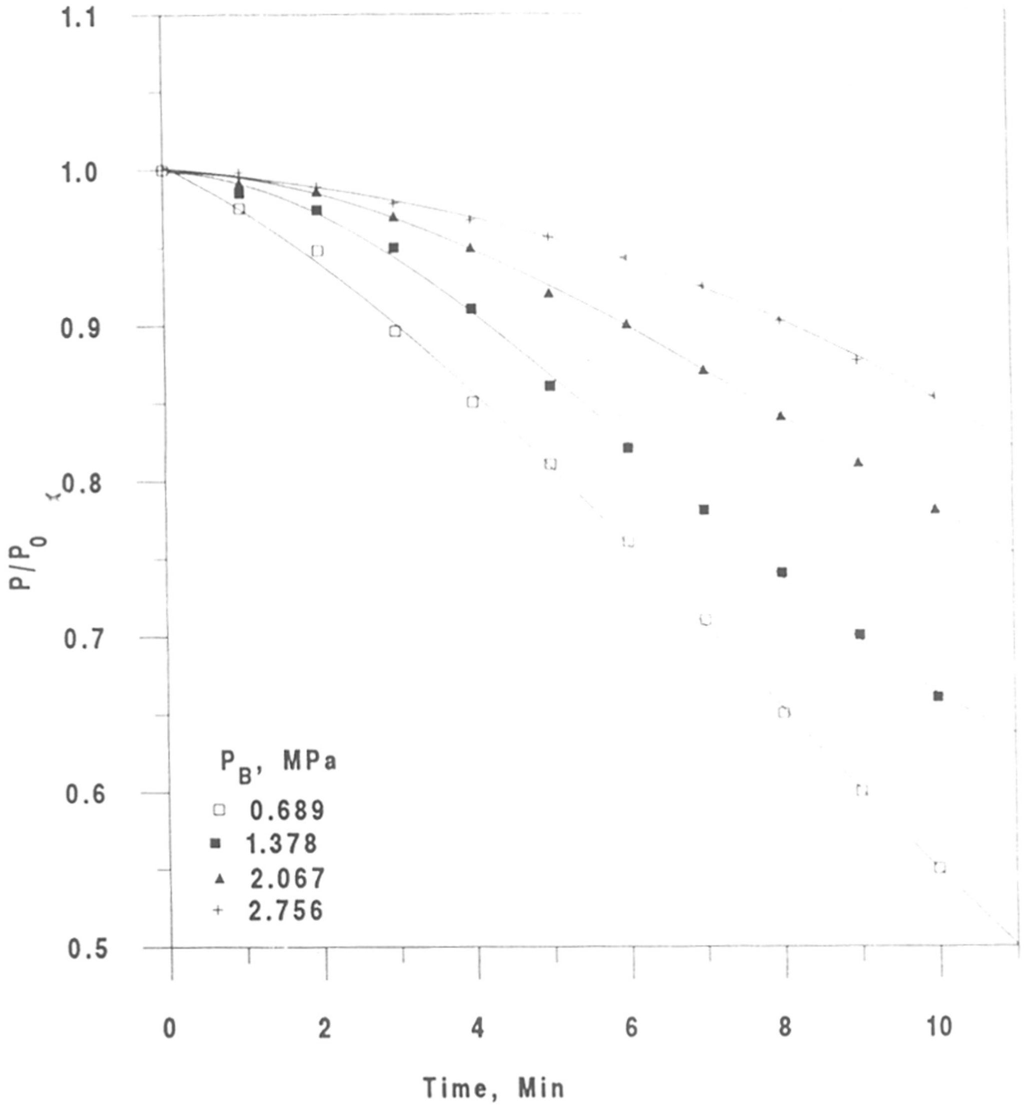


Fig. 3.5 A PLOT OF CO + H_2 + ETHYLENE (P/P_0) CONSUMED vs TIME : EFFECT OF CO PARTIAL PRESSURE AT 373, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Concentration of catalyst : 1.0×10^{-3}, kmol m^{-3}

Partial pressure of ethylene : 0.689, MPa

Partial pressure of H_2 : 1.378, MPa

Agitation speed : 15, rps

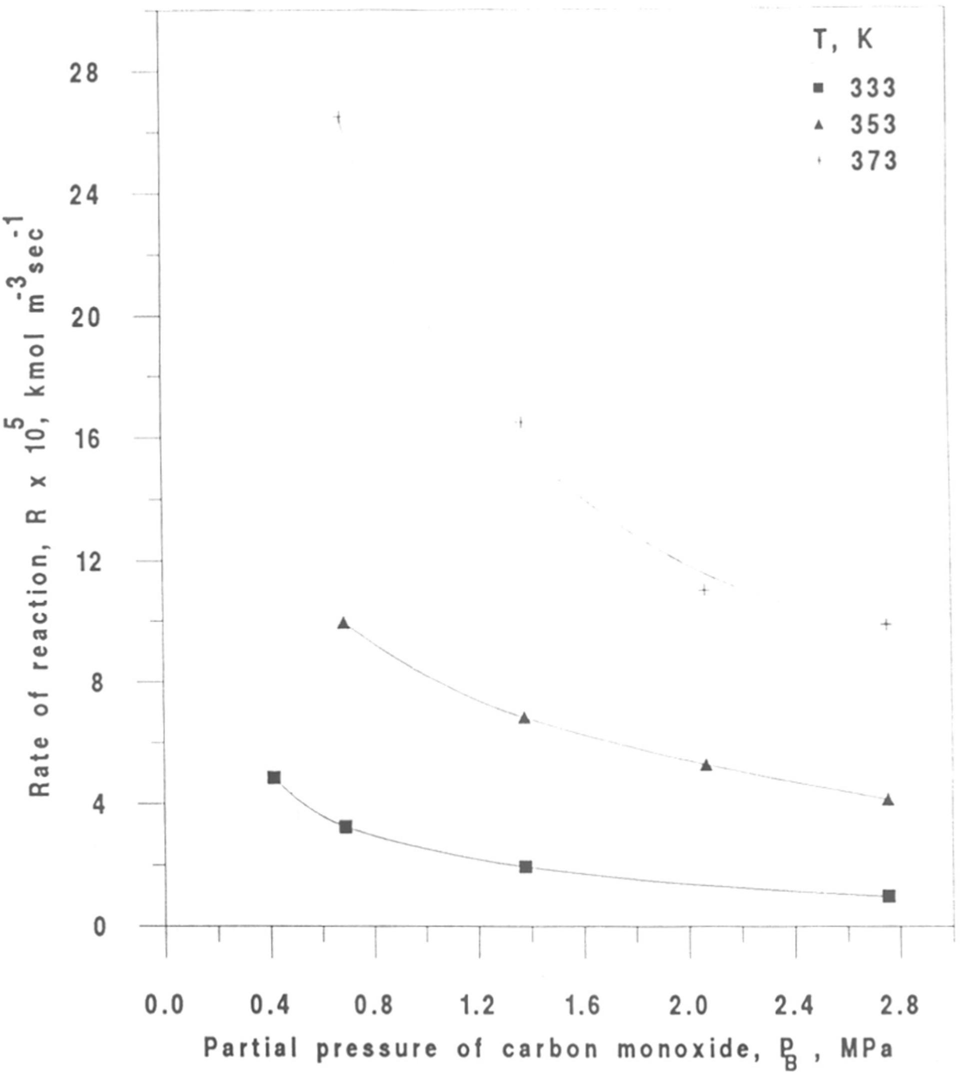


Fig. 3.6. EFFECT OF PARTIAL PRESSURE OF CO ON THE RATE OF REACTION IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :	
Concentration of catalyst	: 1.0 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of H_2	: 1.378, MPa
Agitation speed	: 15, rps

also reported earlier by several investigators for hydroformylation of other olefins (Deshpande and Chaudhari 1988, Deshpande and Chaudhari 1989). This observation is consistent with the mechanism proposed earlier (Evans et. al. 1968b, Brown and Wilkinson 1970) (see Fig. 3.7), wherein, the inhibition in the rate of hydroformylation with increase in partial pressure of CO is a result of formation of an inactive di- and tricarbonyl species $(RCO)Rh(CO)_2(PPh_3)_2$ and $(RCO)Rh(CO)_3(PPh_3)$ (steps 12 and 13 in Fig. 3.7). The formation of these species reduces the effective concentration of the active catalytic species and hence the rate of the reaction is reduced. The equilibrium reaction (step 13) leading to the formation of $(RCO)Rh(CO)_2(PPh_3)_2$ will be more pronounced at higher partial pressures of CO causing a sharp decrease in the rate of reaction, as observed in this work.

3.3.5 Effect of partial pressure of H_2 (P_{H2})

The effect of partial pressure of H_2 on the rate of hydroformylation of ethylene was investigated at a constant partial pressure of CO = 1.378, MPa, partial pressure of ethylene = 0.689, MPa, and a catalyst concentration of 1.0×10^{-3}, kmol m^{-3}, in a temperature range of 333-373, K. The results are shown in Fig. 3.8 - 3.10 as P/P_0 vs time plots. The rate of reaction (see Fig. 3.11) was found to vary with 1.5th order with P_{H2}. At lower P_{H2} formation of a dimeric species (T) is possible (Brown and Wilkinson 1970) as shown below :

$$2\ HRh\,(CO)\,(PPh_3)_3 \rightleftharpoons \underset{T)}{[Rh\,(CO)\,(PPh_3)_2]_2} + H_2 \qquad (3.4)$$

Reaction 3.4 will lead to a reduction in the concentration of the active catalytic species, particularly as lower P_{H2}. With increase in P_{H2}, the formation of the dimer (T) will be reduced, thereby increasing the rate of hydroformylation. Besides this, the oxidative addition of H_2 to the acyl complex (which generally is assumed to be a rate controlling, (step 6 in Fig. 3.7) is also dependent on H_2 concentration. An overall order of reaction higher than unity can arise from a combined effect of these two steps.

3.3.6 Effect of partial pressure of ethylene

Fig. 3.12 to 3.14 show the effect of ethylene partial pressure on P/P_0 vs time and the initial rate data are presented in Fig. 3.15, in a temperature range of 333 - 373, K. The rate was found to be inhibited at higher ethylene concentrations. The formation of an alkyl olefinic complex like $C_2H_5Rh(CO)_3C_2H_4$ in ethylene hydroformylation using $Rh_4(CO)_{12}$ as a catalyst has been reported (King et. al. 1980). Similar species is likely to form in the present work at higher partial pressure

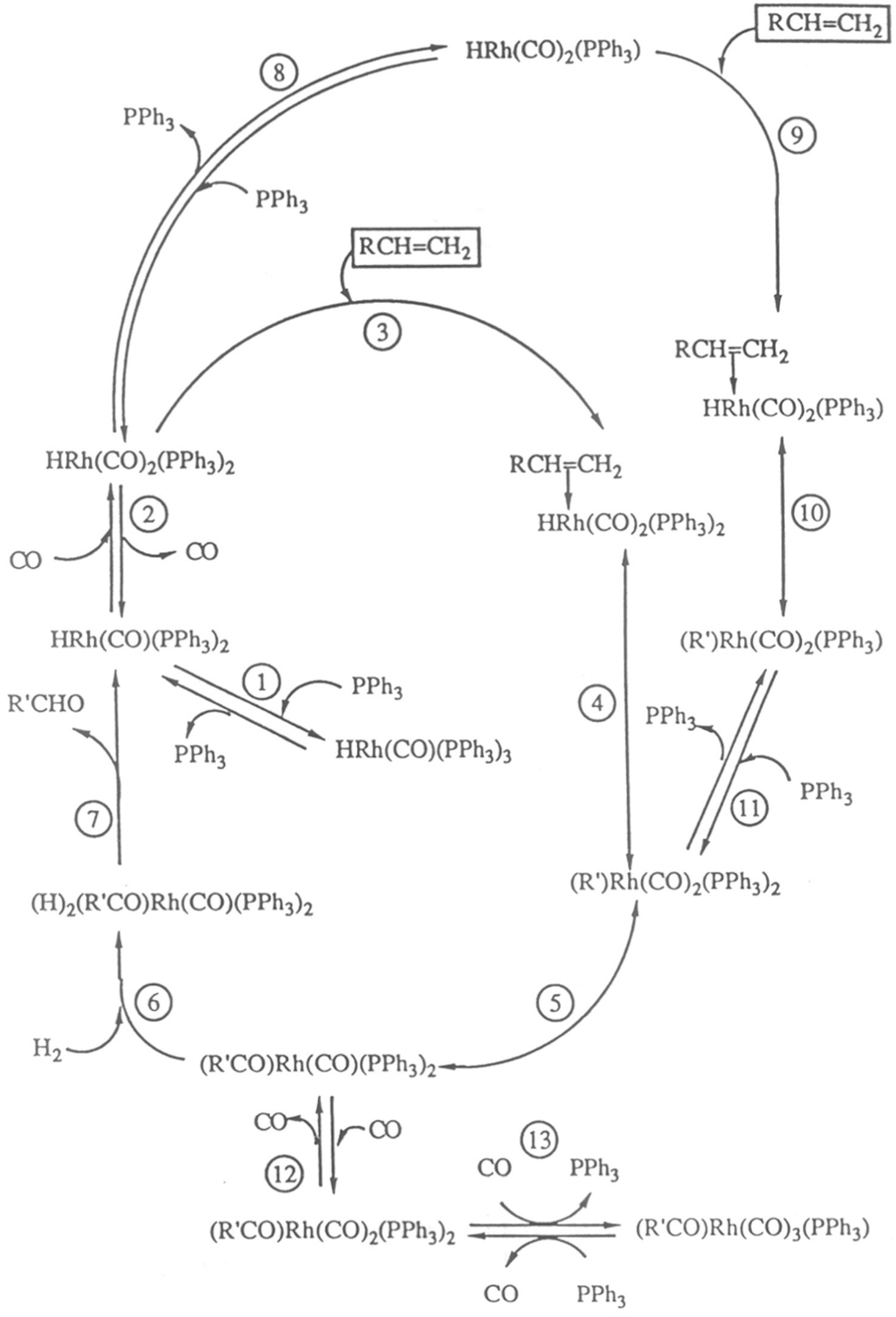


Fig. 3.7. A PROPOSED MECHANISM FOR THE HYDROFORMYLATION OF OLEFINS

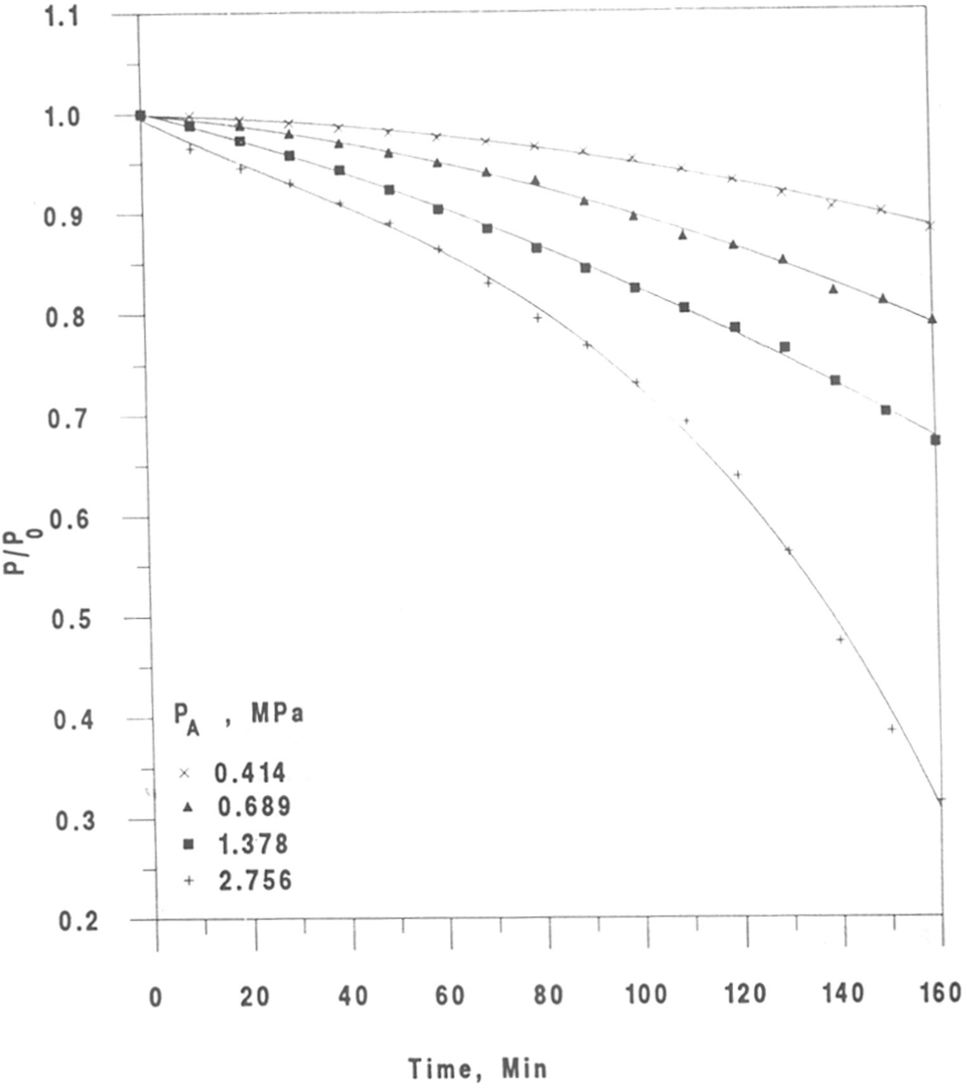


Fig. 3.8. A PLOT OF CO + H_2 + ETHYLENE (P/P_0) CONSUMED vs TIME : EFFECT OF H_2 PARTIAL PRESSURE AT 333, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Concentration of catalyst	: 1.0 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of CO	: 1.378, MPa
Agitation speed	: 15, rps

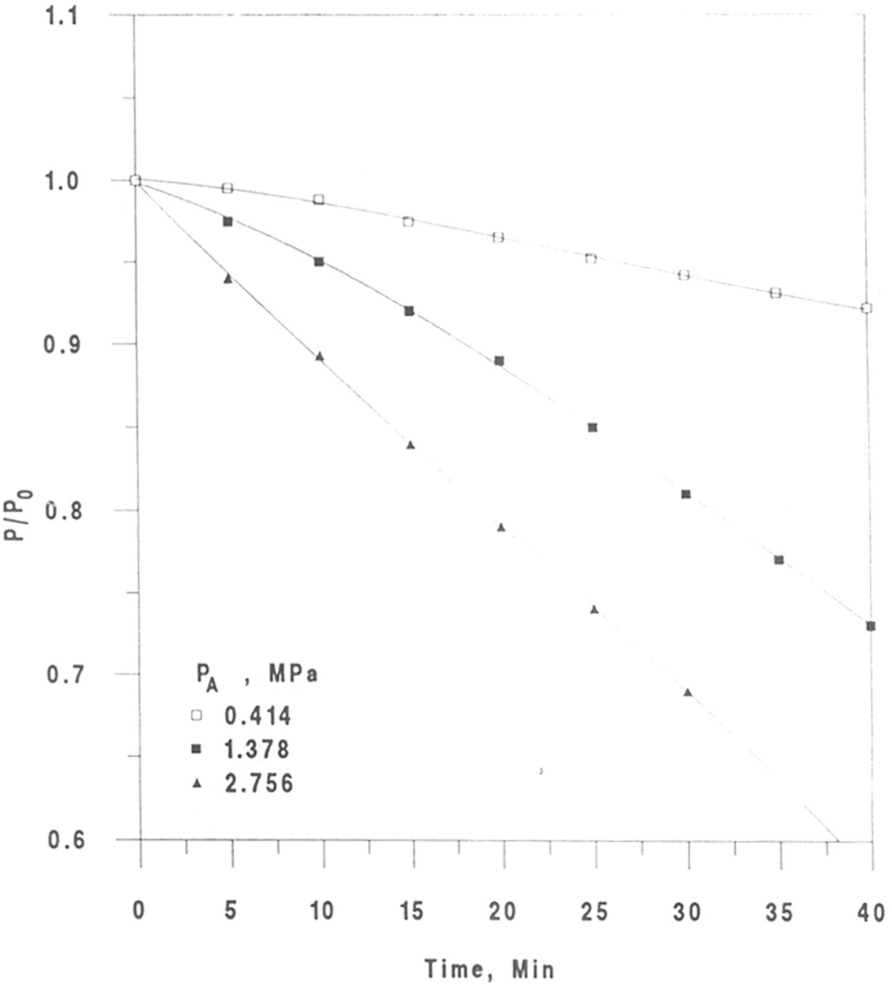


Fig. 3.9. A PLOT OF CO + H_2 + ETHYLENE (P/P_0) CONSUMED vs TIME : EFFECT OF H_2 PARTIAL PRESSURE AT 353, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :
Concentration of catalyst : 1.0×10^{-3}, kmol m^{-3}
Partial pressure of ethylene : 0.689, MPa
Partial pressure of CO : 1.378, MPa
Agitation speed : 15, rps

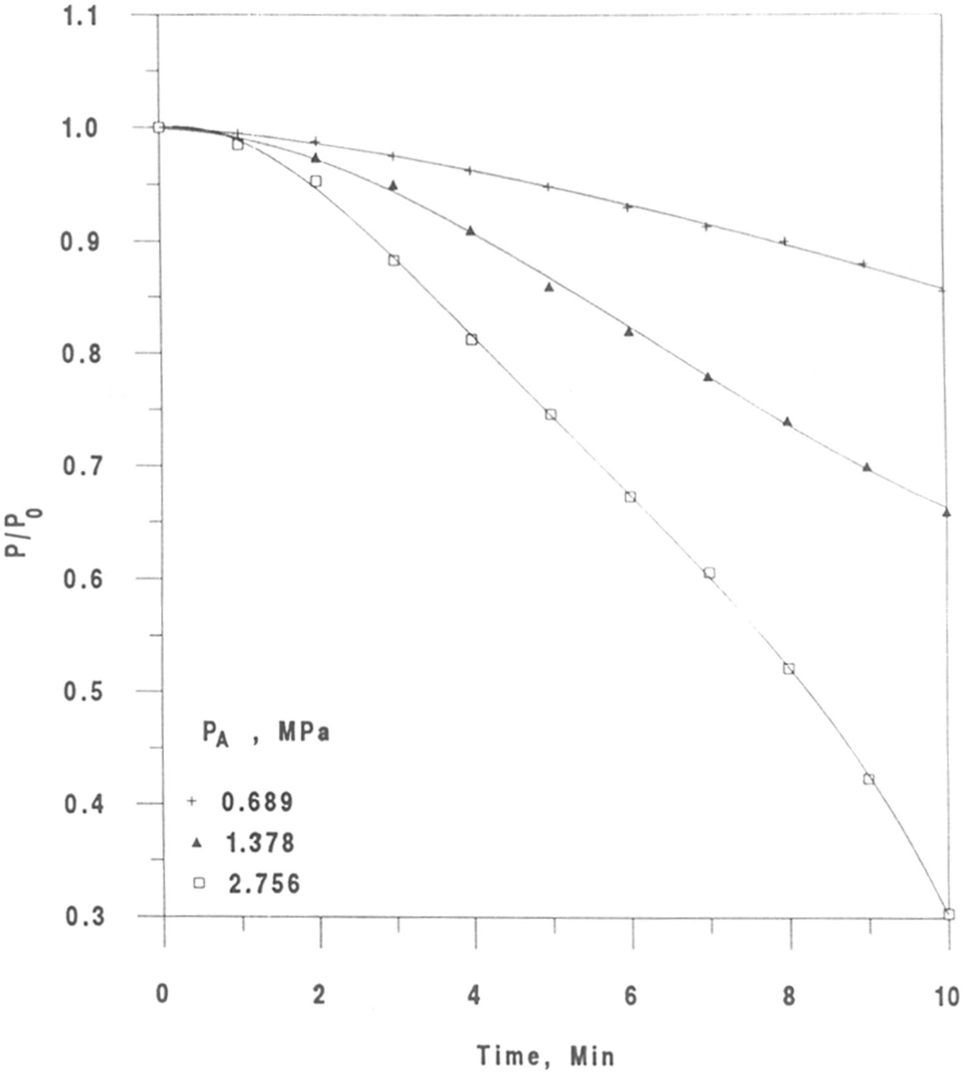


Fig. 3.10. A PLOT OF CO + H_2 + ETHYLENE (P/P_0) CONSUMED vs TIME : EFFECT OF H_2 PARTIAL PRESSURE AT 373, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Concentration of catalyst	: 1.0×10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of CO	: 1.378, MPa
Agitation speed	: 15, rps

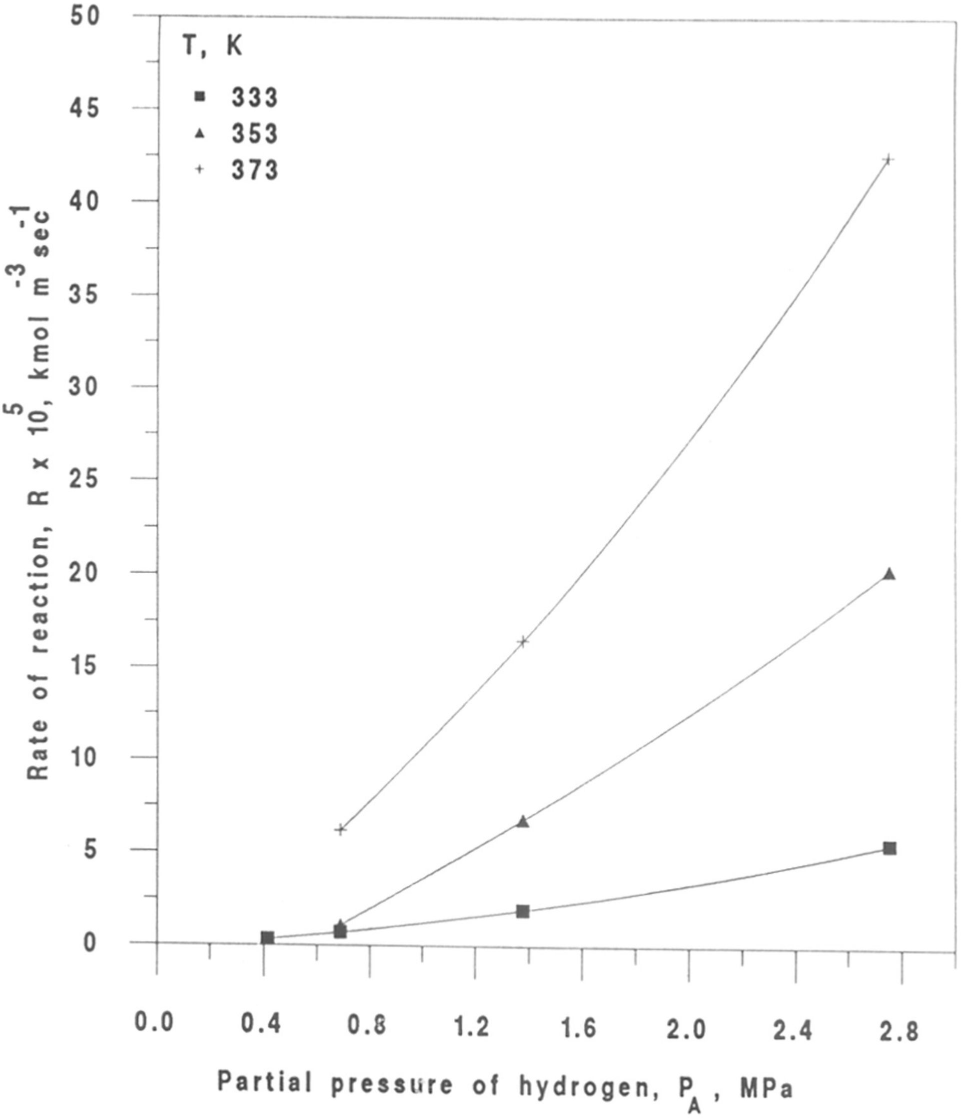


Fig. 3.11. EFFECT OF PARTIAL PRESSURE OF H_2 ON THE RATE OF REACTION IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :
Concentration of catalyst : 1.0×10^{-3}, kmol m^{-3}
Partial pressure of ethylene : 0.689, MPa
Partial pressure of CO : 1.378, MPa
Agitation speed : 15, rps

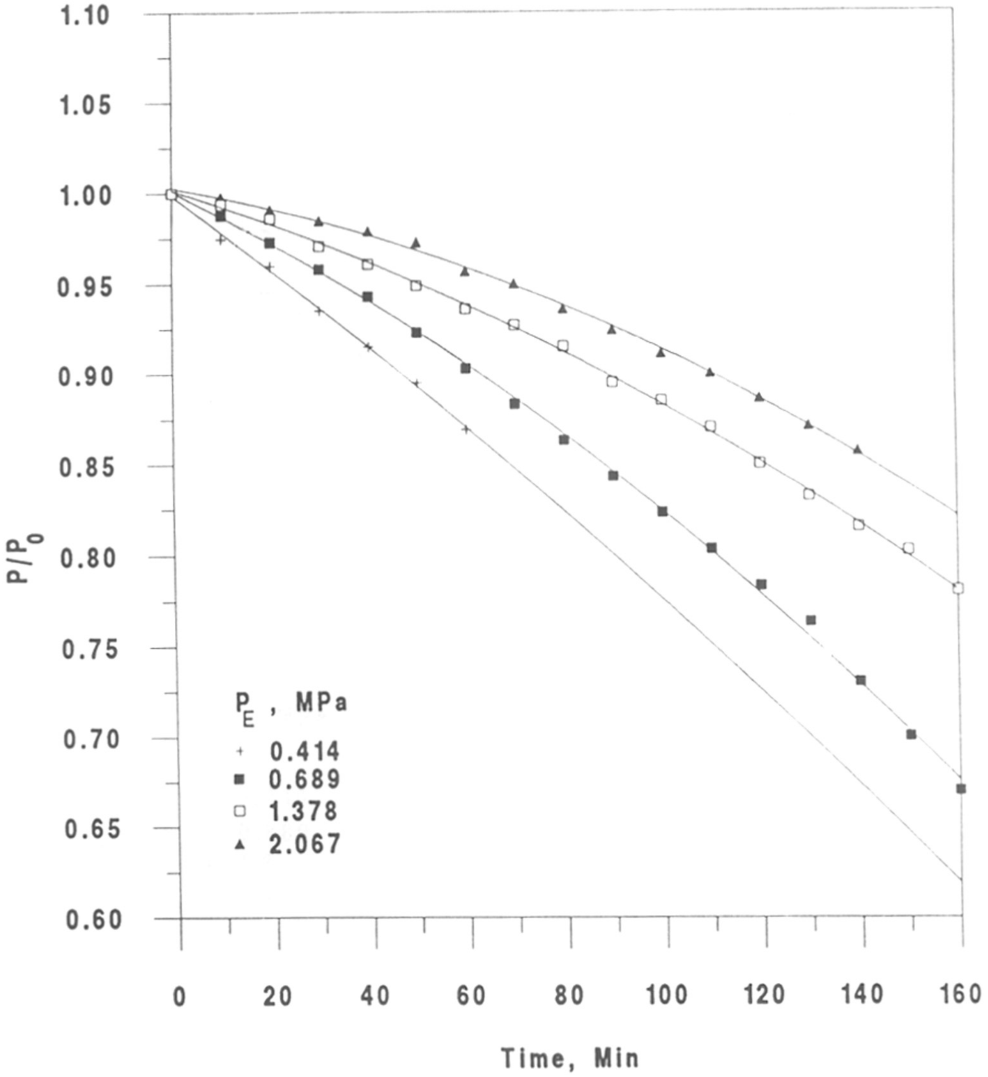


Fig. 3.12. A PLOT OF CO + H_2 + ETHYLENE (P/P_0) CONSUMED vs TIME : EFFECT OF ETHYLENE PARTIAL PRESSURE AT 333, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Concentration of catalyst	: 1.0 x 10^{-3}, kmol m^{-3}
Partial pressure of CO	: 1.378, MPa
Partial pressure of H_2	: 1.378, MPa
Agitation speed	: 15, rps

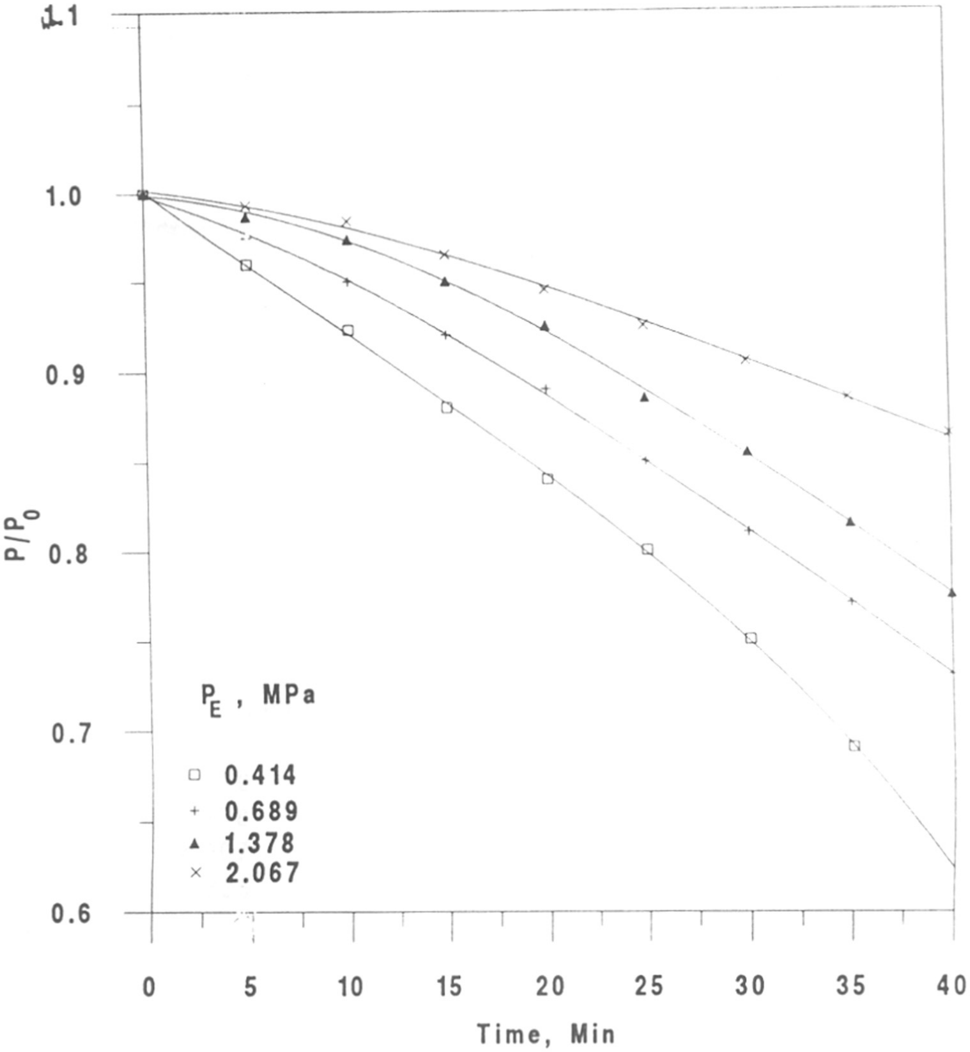


Fig. 3.13. A PLOT OF CO + H_2 + ETHYLENE (P/P_0) CONSUMED vs TIME : EFFECT OF ETHYLENE PARTIAL PRESSURE AT 353, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :
Concentration of catalyst : 1.0×10^{-3}, kmol m^{-3}
Partial pressure of CO : 1.378, MPa
Partial pressure of H_2 : 1.378, MPa
Agitation speed : 15, rps

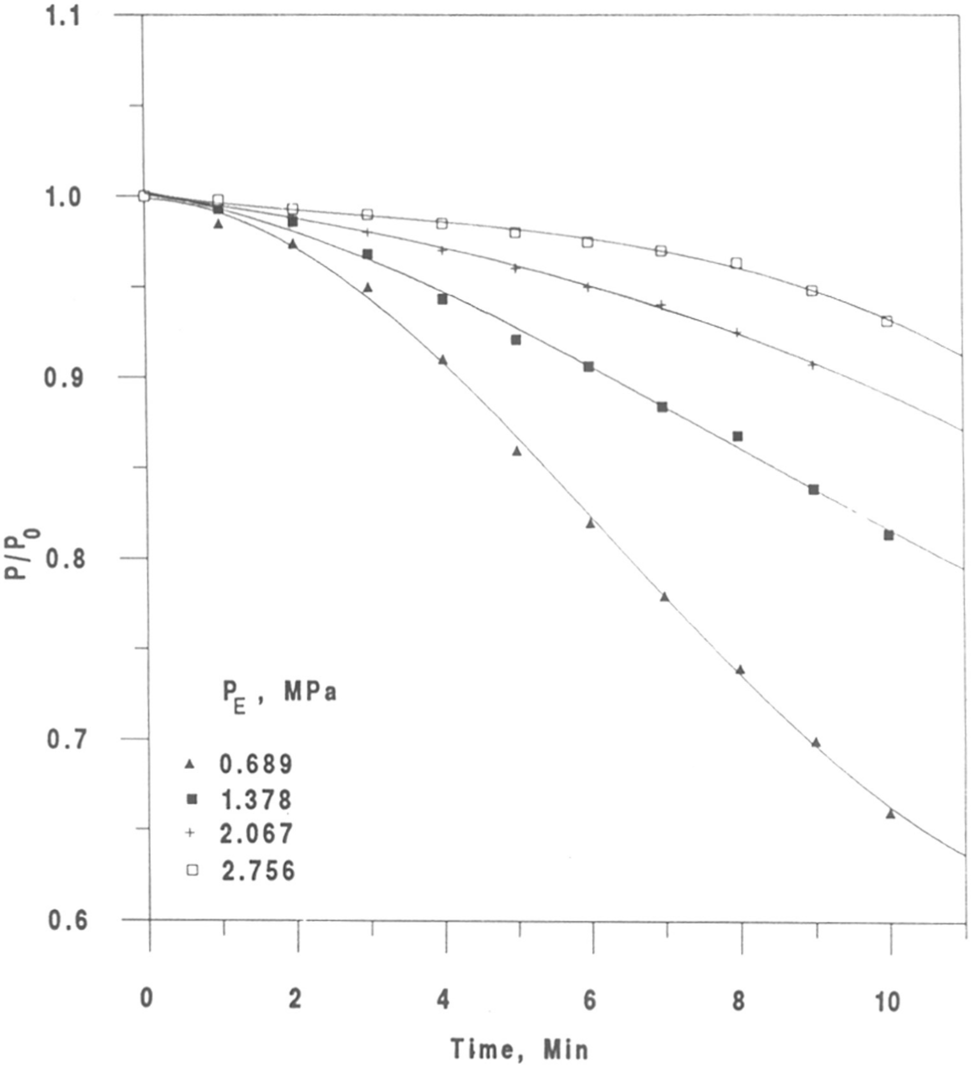


Fig. 3.14. A PLOT OF CO + H_2 + ETHYLENE (P/P_0) CONSUMED vs TIME : EFFECT OF ETHYLENE PARTIAL PRESSURE AT 373, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Concentration of catalyst	: 1.0×10^{-3}, kmol m^{-3}
Partial pressure of CO	: 1.378, MPa
Partial pressure of H_2	: 1.378, MPa
Agitation speed	: 15, rps

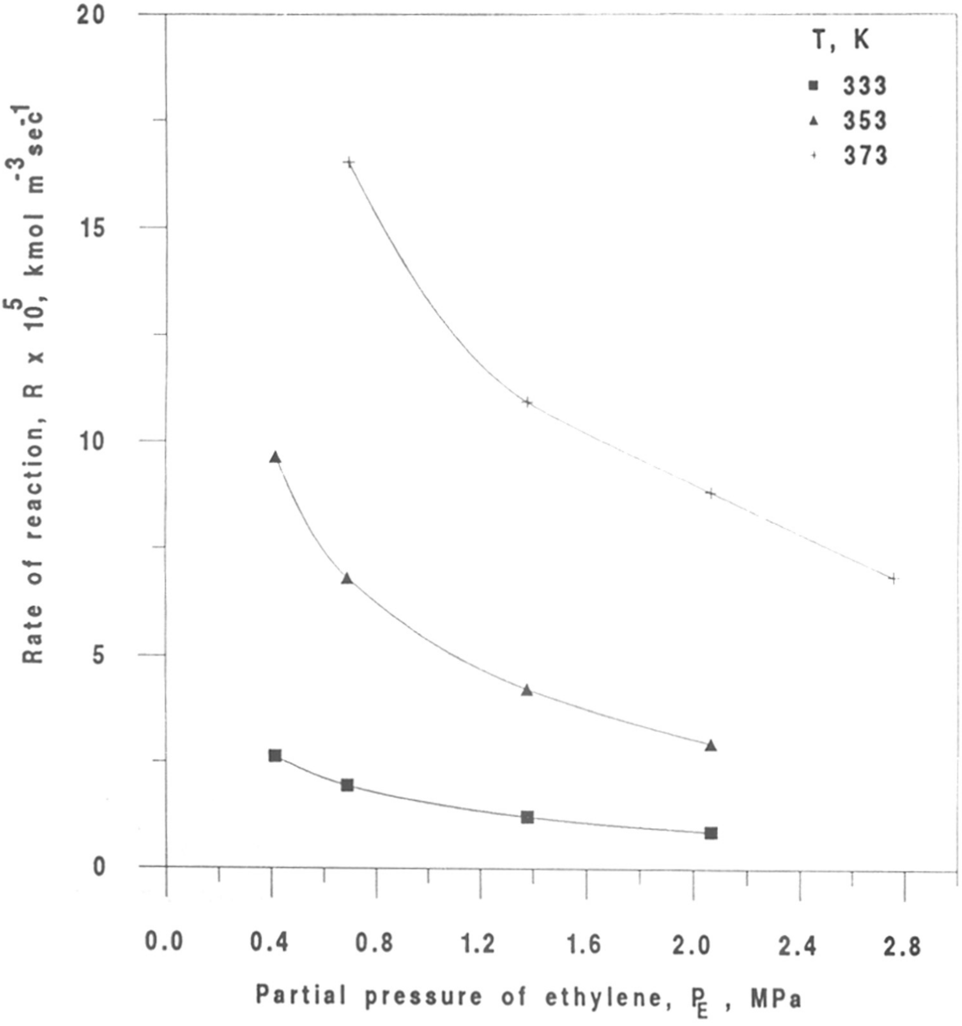


Fig. 3.15. EFFECT OF PARTIAL PRESSURE OF ETHYLENE ON THE RATE OF REACTION IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Concentration of catalyst	: 1.0 x 10^{-3}, kmol m^{-3}
Partial pressure of CO	: 1.378, MPa
Partial pressure of H_2	: 1.378, MPa
Agitation speed	: 15, rps

of ethylene (i. e. higher ethylene to catalyst ratio) leading to the reduction in the active catalytic species and hence the rate of reaction. The formation of inactive dimeric species is also reported in the case of 1-hexene hydroformylation (Deshpande and Chaudhari 1988, Strohmeier and Michel 1981) wherein, in the absence of solvent and excess PPh_3, the rate of hexene hydroformylation was found to be very slow and these observations are explained on the basis of formation of a diolefinic species at higher olefin to catalyst ratio.

3.3.7 Effect of catalyst concentration

The results of absorption of CO, H_2 and ethylene (expressed as P/P_0) vs time at different catalyst concentrations in a temperature range of 333 - 373, K are shown in Fig. 3.16 - 3.18. The rate of reaction (see Fig. 3.19) was found to vary linearly with respect to the catalyst concentration at all the temperatures studied.

3.4 RATE EQUATION

As discussed in the experimental section, the initial rates of hydroformylation (i.e. ethylene or CO or H_2 consumed with respect to time) were observed under a variety of conditions. First, these data were analyzed for the significance of gas to liquid mass transfer. Since, the rate of stirring had no effect on the rate of reaction, the absence of mass transfer resistance and hence kinetic regime is indicated. This conclusion is further supported by comparing the rates with the maximum rates of mass transfer of CO, H_2 and ethylene under the respective conditions. For these purpose, the factors α_1, α_2 and α_3, defined as follows, were calculated (Chaudhari and Doraiswamy 1974).

$$\alpha_1 = \frac{R}{k_L\ a\ A^*} \tag{3.5}$$

$$\alpha_2 = \frac{R}{k_L\ a\ B^*} \tag{3.6}$$

$$\alpha_3 = \frac{R}{k_L\ a\ E^*} \tag{3.7}$$

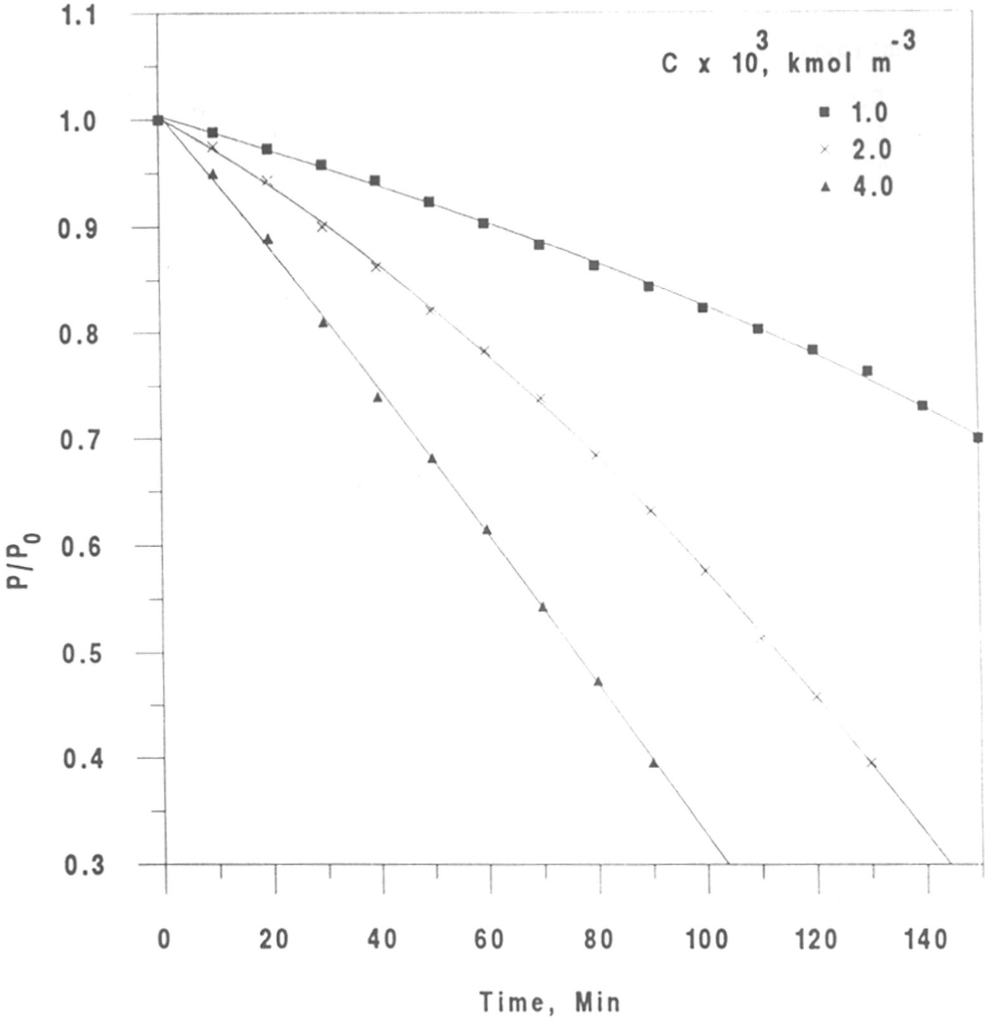


Fig. 3.16. A PLOT OF CO + H_2 + ETHYLENE (P/P_0) CONSUMED vs TIME : EFFECT OF CATALYST CONCENTRATION AT 333, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Partial pressure of CO	: 1.378, MPa
Partial pressure of H_2	: 1.378, MPa
Partial pressure of ethylene	: 0.689, MPa
Agitation speed	: 15, rps

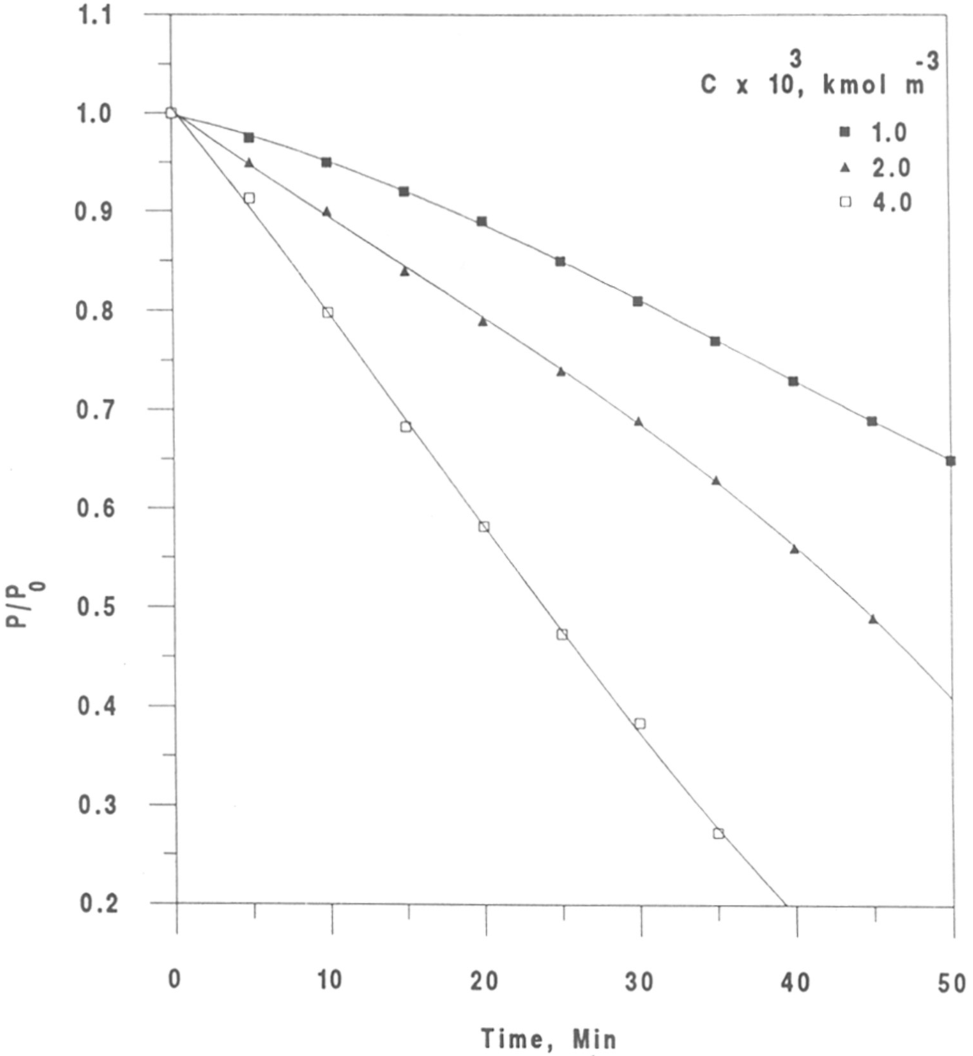


Fig. 3.17. A PLOT OF CO + H_2 + ETHYLENE (P/P_0) CONSUMED vs TIME : EFFECT OF CATALYST CONCENTRATION AT 353, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :
Partial pressure of CO : 1.378, MPa
Partial pressure of H_2 : 1.378, MPa
Partial pressure of ethylene : 0.689, MPa
Agitation speed : 15, rps

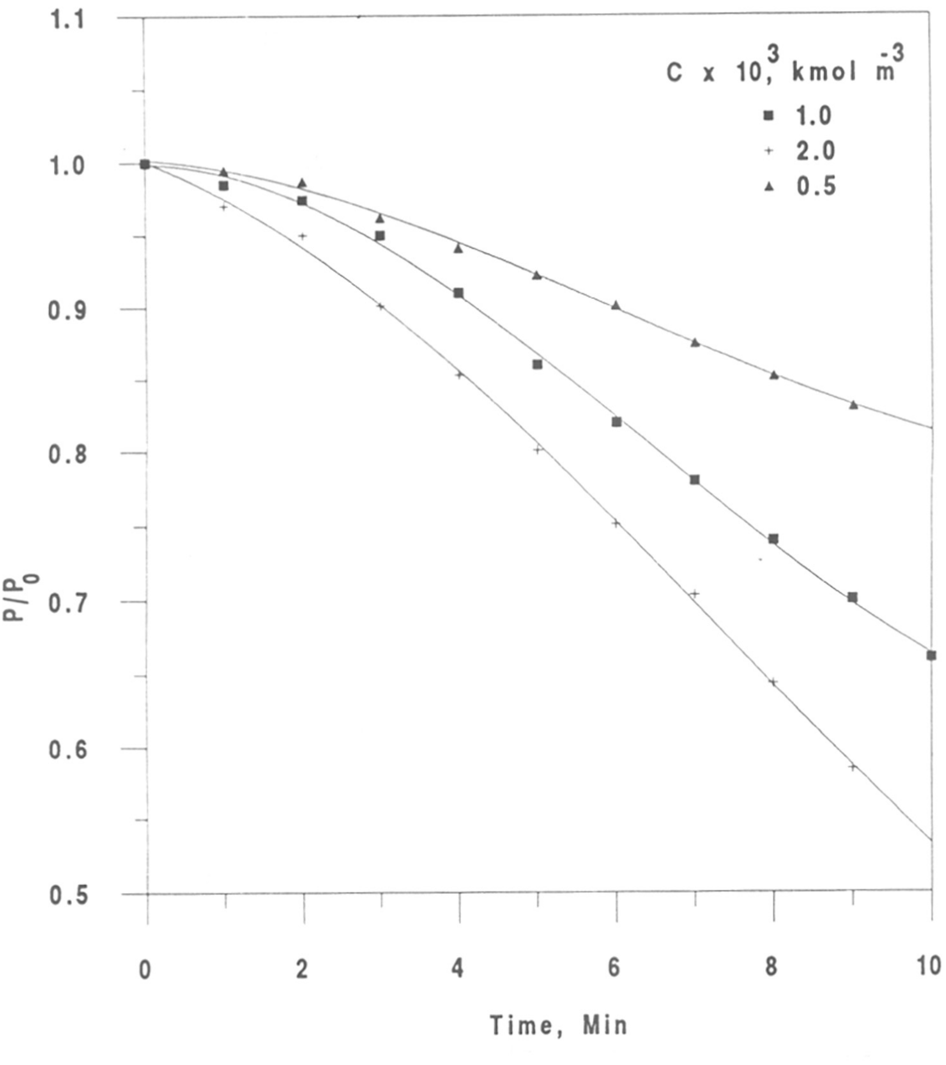


Fig. 3.18. A PLOT OF CO + H_2 + ETHYLENE (P/P_0) CONSUMED vs TIME : EFFECT OF CATALYST CONCENTRATION AT 373, K IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :
Partial pressure of CO : 1.378, MPa
Partial pressure of H_2 : 1.378, MPa
Partial pressure of ethylene : 0.689, MPa
Agitation speed : 15, rps

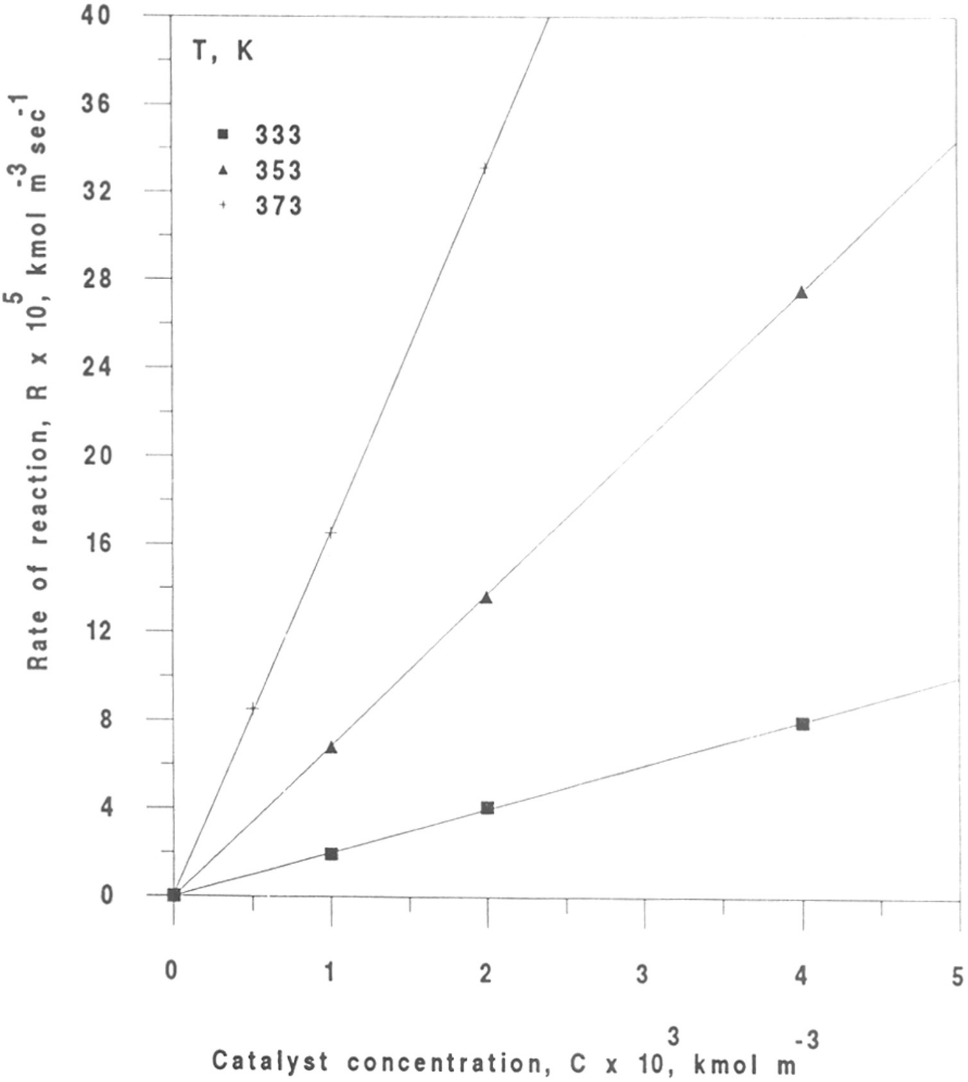


Fig. 3.19. EFFECT OF CATALYST CONCENTRATION ON THE RATE OF REACTION IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Partial pressure of CO	: 1.378, MPa
Partial pressure of H_2	: 1.378, MPa
Partial pressure of ethylene	: 0.689, MPa
Agitation speed	: 15, rps

where R represents the rate of hydroformylation, kmol m^{-3} sec^{-1}; k_La is the volumetric mass transfer coefficient, sec^{-1} and $A^* = P_A/H_A$, $B^* = P_B/H_B$ and $E^* = P_E/H_E$ are the concentrations of H_2, CO and ethylene at the gas liquid interface, kmol m^{-3}, respectively. The evaluation of α_1, α_2 and α_3 requires a knowledge of k_La and solubilities of H_2, CO and ethylene in addition to the rate data. While the Henry's law constants, presented in Table (3.6) were used to calculate A^*, B^* and E^*, respectively, k_La values were obtained from the correlation proposed by Chaudhari et. al. (1987). For the present case k_La was found to be 0.237, s^{-1} at 15, rps. The correlation of Chaudhari et. al. (1987) was proposed based on the data obtained in a reactor (Parr Autoclave) similar to that used in this work and hence was thought to be more appropriate. The values for α_1, α_2 and α_3 were calculated for all the data and were found to be less than 0.12. This clearly shows that the rate data observed in the entire range are in the kinetic regime.

In order to propose a suitable rate equation for the kinetics of hydroformylation of ethylene, the initial rate data presented above were analyzed. For this purpose, various forms of rate equations were considered. The rate equations were selected based on the trends observed on the dependence of the rates on different parameters. In order to discriminate the several rate equations listed in Table (3.8), experimental rate data obtained in a temperature range of 333 - 373, K and at different partial pressures of carbon monoxide, hydrogen and ethylene were used. A non-linear regression analysis was used for each rate equation in Table (3.8) to obtain the best fit values of rate parameters. For this purpose, an optimization program based on Marquardt's method was used. The objective function was chosen as follows

$$\Phi = \Sigma_{j=1}^{N} [R' - R]^2 \tag{3.8}$$

where, ϕ is the objective function to be minimized (ϕ_{min}), representing the sum of the squares of the difference between the observed and predicted rates, N is the number of experimental data points, R' and R represent predicted and experimental rates, respectively. The values of rate parameters alongwith ϕ_{min} are presented in Table (3.8). It is well known that model discrimination is not always easy on the basis of statastical analysis alone (Froment 1975, Froment and Bischoff 1990). Other criteria considered in selecting the best model are :

(a) The estimated kinetic parameters must have physico-chemical meaning. Some of the rules are given below (Boudart, 1972)

Rule 1 Reaction rate constant > 0

TABLE 3.8

MODELS EXAMINED TO FIT THE DATA ON ETHYLENE HYDROFORMYLATION

Sr. No.	Rate Model	Temperature K	K_B	K_E	k	ϕ_{min}
1	$\frac{k(A^*)^{1.5}B^*E^*}{(1+K_BB^*)^2(1+K_EE^*)^2}$	333	1.116×10^2	15.01	8.202×10^2	3.95×10^{-11}
		353	1.268×10^2	23.97	8.873×10^3	2.12×10^{-10}
		373	1.490×10^2	26.74	3.007×10^4	1.00×10^{-9}
2	$\frac{k(A^*)B^*E^*}{(1+K_BB^*)^2(1+K_EE^*)^2}$	333	1.000×10^2	26.47	2.920×10^2	2.350×10^{-10}
		353	1.530×10^2	28.56	2.208×10^3	3.904×10^{-9}
		373	1.820×10^2	58.84	1.520×10^4	7.140×10^{-9}
3	$\frac{k(A^*)^{1.5}B^*E^*}{(1+K_BB^*)^2(1+K_EE^*)}$	333	0.944×10^2	27.69	1.490×10^2	3.830×10^{-10}
		353	1.290×10^2	48.86	2.410×10^3	3.790×10^{-9}
		373	1.780×10^2	43.45	1.704×10^4	2.350×10^{-8}
4	$\frac{k(A^*)^{1.5}B^*E^*}{(1+K_BB^*)(1+K_EE^*)^2}$	333	1.380×10^2	26.50	2.640×10^2	1.430×10^{-9}
		353	1.010×10^2	47.71	2.830×10^3	3.180×10^{-9}
		373	0.153×10^2	27.99	4.718×10^3	8.180×10^{-6}
5	$\frac{k(A^*)^{1.5}B^*E^*}{(1+K_B(B^*)^3)(1+K_EE^*)^2}$	333	0.413×10^2	20.10	9.410×10^2	7.720×10^{-11}
		353	0.375×10^2	-48.61	9.780×10^3	2.020×10^{-9}
		373	9.88	42.20	2.880×10^3	2.210×10^{-8}
6	$\frac{k(A^*)^{1.5}B^*E^*}{(1+K_B(B^*)^3)(1+K_EE^*)}$	333	0.924×10^2	16.98	5.630×10^2	1.260×10^{-9}
		353	1.268×10^2	23.97	8.870×10^3	1.090×10^{-8}
		373	23.3	645.79	2.190×10^4	2.020×10^{-8}

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

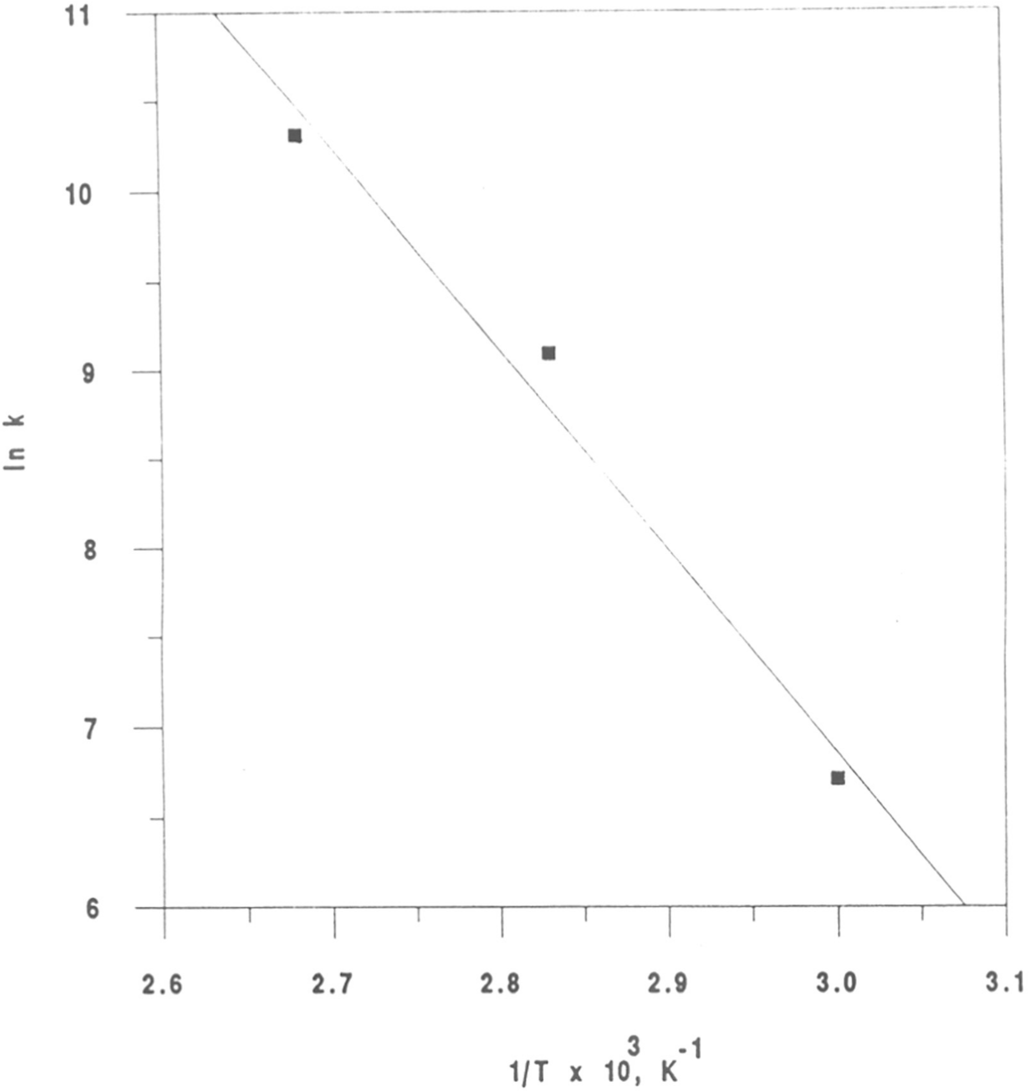


Fig. 3.20 ARRHENIUS PLOT OF ln k vs 1/T

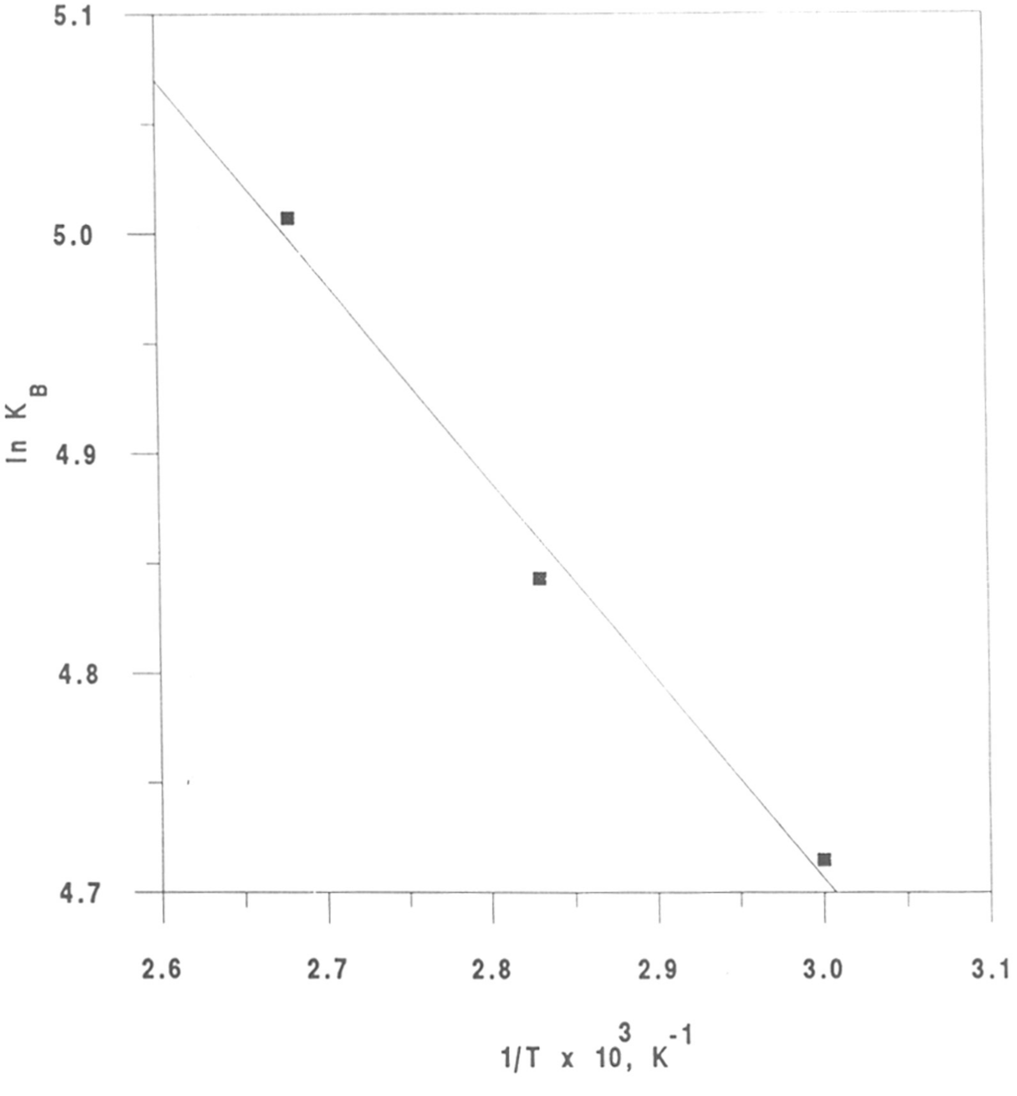


Fig. 3.21 A PLOT OF ln K_B vs 1/T

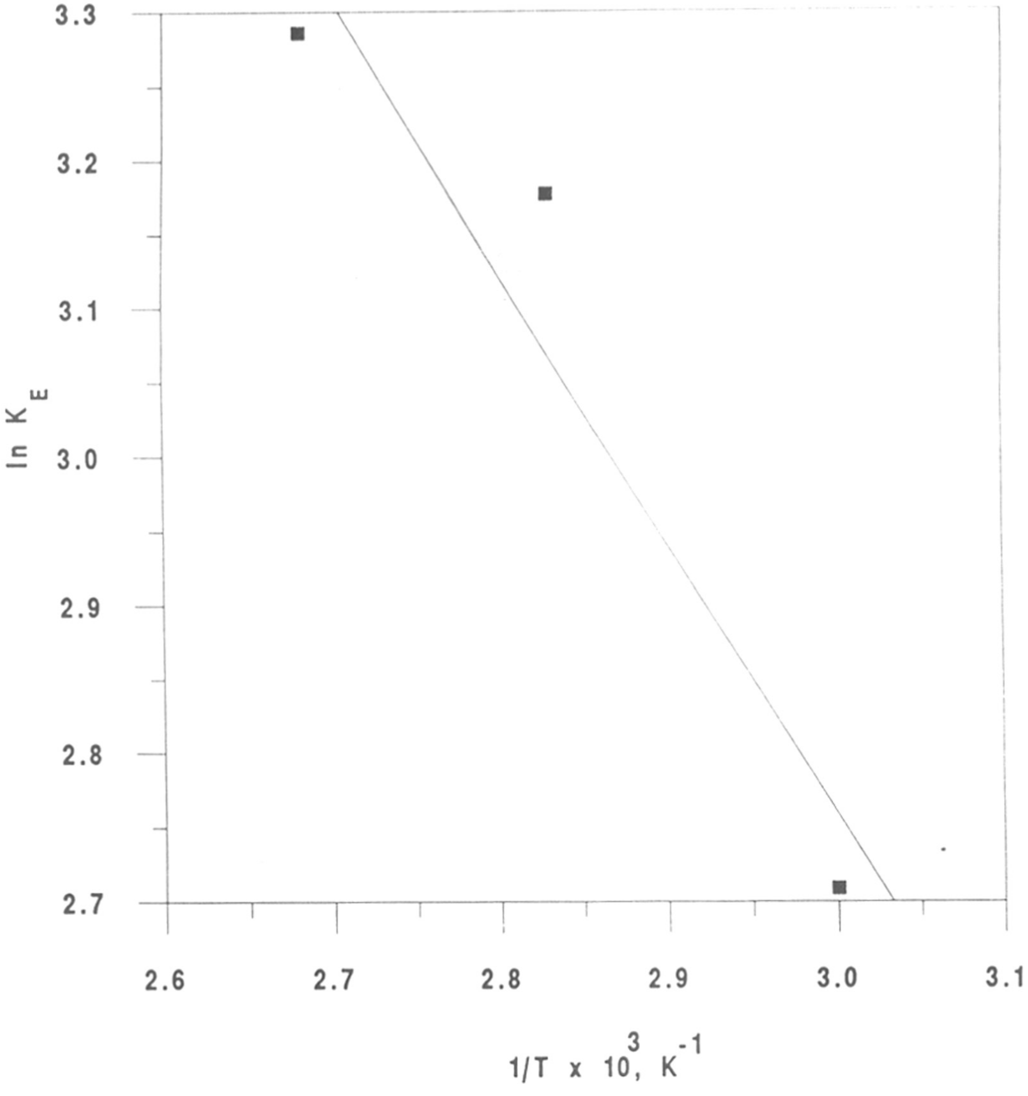


Fig. 3.22 A PLOT OF ln K_E vs 1/T

TABLE 3.9

RATE PARAMETERS

Temperature K	k ($m^{7.5}$ $kmol^{-2.5}$ s^{-1})	K_B (m^3 $kmol^{-1}$)	K_E (m^3 $kmol^{-1}$)
333	821.77	111.64	15.02
353	8873.4	126.81	23.97
373	30072	149.51	26.74

Rule 2 Activation energy > 0

(b) The residuals (R'- R) should be distributed with zero mean and these residuals should have no trend effects, as a function of the independent variables like P_{CO}, P_{H2} and P_E.

The results presented in the Table (3.8) indicate that model (5) has negative rate parameters and hence was rejected. Model (2) overestimates the rate of reaction with respect to the effect of hydrogen partial pressure. Model (3) and (6) show zero order dependence with respect to ethylene partial pressure whereas, model (4) overestimates the initial rates for the effect of partial pressure of CO. Therefore, these models were rejected. Model (1) (as shown below) was found to be superior to all the other models.

$$R = \frac{k\ (A^*)^{1.5}\ (B^*)\ (E^*)}{(1 + K_B(B^*))^2\ (1 + K_E(E^*))^2} \tag{3.9}$$

where, R is the rate of reaction, kmol m^{-3} sec^{-1}, k is the intrinsic reaction rate constant ($m^{7.5}$ $kmol^{-2.5}$ sec^{-1}), $A^* = P_A/H_A$, $B^* = P_B/H_B$ and $E^* = P_E/H_E$ are the concentrations of H_2, CO and ethylene in toluene at the gas liquid interface (kmol m^{-3}), respectively.

The rates predicted using eq. (3.9) were found to agree within 6 - 8% error with the experimental data. The rate parameters for eq. (3.9) at 333-373, K are presented in Table (3.8). The Arrhenius plot showing the effect of temperature on the rate constants is shown in Fig. 3.20 from which the activation energy was evaluated as 9.4×10^4, kJ/kmol. The dependence of the rate parameters K_B and K_E on temperature (Fig. 3.20 and 3.21 respectively) show similar trends. The rate parameters at a constant catalyst concentration for eq. (3.9) are presented in Table 3.9.

3.5 CONCLUSIONS

The kinetics of hydroformylation of ethylene using a homogeneous $HRh(CO)(PPh_3)_3$ catalyst has been studied in a temperature range of 333 - 373, K. The reaction was found to be 1.5th order with P_{H2}. The rate of reaction varied linearly with catalyst concentration. A negative order dependence was observed with respect to partial pressure of ethylene and P_{CO}. Based on these data, a rate equation has been proposed, after examination of several forms of rate models and a rigorous model discrimination procedure. The kinetic parameters for this model have been reported with an activation energy of 9.4×10^4, kJ/kmol.

NOMENCLATURE

[A^*] concentration of H_2 in toluene at the gas-liquid interface (kmol m^{-3})

[B^*] concentration of CO in toluene at the gas-liquid interface kmol m^{-3})

[E^*] concentration of ethylene at the gas liquid interface (kmol m^{-3})

[C] concentration of catalyst (kmol m^{-3})

[H_A] Henry's law constant for the H_2-toluene system (MPa m^3 $kmol^{-1}$)

[H_B] Henry's law constant for the CO-toluene system (MPa m^3 $kmol^{-1}$)

[H_E] Henry's law constant for the ethylene - toluene system (MPa m^3 $kmol^{-1}$)

[k] Reaction rate constant ($m^{7.5}$ $kmol^{-2.5}$ sec^{-1}) in eq (3.7)

[K_B] Constant in eq. (3.9) (m^3 $kmol^{-1}$)

[K_E] Constant in eq.(3.9) (m^3 $kmol^{-1}$)

[P_{H2}] Partial pressure of hydrogen (MPa)

[P_{CO}] Partial pressure of carbon monoxide (MPa)

[P_E] Partial pressure of ethylene (MPa)

[R] Rate of consumption of CO, H_2 or ethylene (kmol m^{-3} sec^{-1})

[T] Reaction temperature (K)

[ϕ_{min}] Minimized sum of the squares of the difference between observed and predicted rates

[α_1] as defined in eq. (3.5)

[α_2] as defined in eq. (3.6)

[α_3] as defined in eq. (3.7)

REFERENCES

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

Boudart M., AIChE J., **18** 465 (1972).

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

Chaudhari R. V. and Doraiswamy L. K., Chem. Eng. Sci. **29**, 349, (1974).

Chaudhari R. V., Gholap R. V., Emig E. and Hoffman H., Can. J. Chem. Eng. **65**(5), 744, (1987).

Choudhary V. R., Parande M. G.and Brahme P.A., Ind. Eng. Chem. Fundam. **21**(4), 472, (1982).

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

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

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

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

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

Froment G. F., AIChE J. **21** (6), 1041, (1975).

Froment G. F., and Bishoff K. B., ` Chemical Reactor Analysis and Design', J. Wiley, New York, 2nd Edn. (1990).

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

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

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

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

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

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

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

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

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

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

CHAPTER 4

***

CATALYSIS AND KINETICS OF HYDROFORMYLATION OF ETHYLENE USING WATER SOLUBLE Rh-TPPTS CATALYST IN HOMOGENEOUS AND BIPHASIC MEDIA

***

4.1 INTRODUCTION

Catalysis by water soluble metal complexes has a major impact in developing new processes due to the advantage of a simple catalyst -product separation. Particularly, for hydroformylation of olefins, such a biphasic catalytic approach has tremendous potential as already proven by the commercialisation of the Ruhrchemie / Rhone Poulenc process (see Chapter 1). The relevant literature on biphasic catalysis, the types of ligands used, their advantages and disadvantages have been summarised in Chapter 1. Considering the wider applicability of water soluble catalysis in industry, it is important to understand the role of different catalysts and reaction conditions on the overall performance of these catalyst systems. For example, the co-solvents, ligands, surfactants, catalyst binding ligands, pH etc. can have a pronounced effect on the activity of these catalysts (Monteil 1993; Dror and Manassen 1977; Fell and Papadogiankis 1991; Ding et. al. 1994; Chaudhari et. al. 1995a; Herrmann et. al. 1992, Herrmann and Kohlpaintner 1993). Similarly, the physico chemical aspects related to solubility of reactants, interphase mass transfer, phase equillibria and interfacial phenomena are also important to understand (Chaudhari et. al. 1995b). These factors are important in the overall rate of biphasic catalytic reactions and hence, detailed investigations on catalysis and kinetics of reactions using water soluble metal complexes are most desirable.

It is evident from the literature (Chapter 1) that in most cases, Rh-TPPTS complexes have been used as precusors. Several reports describing the role of co-solvents (Dror and Manassen 1977; Monteil 1993), pH (Smith et. al. 1992), different types of water soluble ligands (Joo and Toth 1980; Smith et. al 1982; Wilson and Whitesides 1978), surfactants (Ding et. al. 1994; Bartik et. al. 1994; Fell and Papadogiankis 1991) and catalyst binding ligands (Chaudhari et. al. 1995a) have also appeared. A few reports on hydrogenation of carbonyl and olefinic functions have also been published (Joo and Toth 1980; Grosselin et. al. 1991; Dror and Manassen 1977). The overall performance of these gas-liquid-liquid catalytic reactions is also dependent on the hydrodynamics of liquid-liquid dispersion, interface mass transfer and reaction kinetics (Chaudhari et.al. 1995b). Purwanto (1994) has studied the hydroformylation of 1-octene using $[RhCl(COD)]_2$/TPPTS catalyst system with octane as a solvent and ethanol as a co-solvent and a rate equation has been proposed.

In order to understand the role of various catalyst and reaction parameters, it is important to study the intrinsic kinetics of the reaction without any additive. There is also a lack of data on the kinetics of industrially important hydroformylation reactions. This work was undertaken to investigate hydroformylation of ethylene using a water soluble catalyst in both a single as well as a biphasic system. Ethylene being a gaseous substrate, it is convenient to study the hydroformylation in these two modes independently. Hydroformylation of ethylene involves simultaneous absorption of three gases followed by a complex catalytic reaction and hence it provides an interesting system for reaction engineering studies. Particularly, the role of gas-liquid and liquid - liquid mass transfer in biphasic catalytic reactions needs to be understood. Such a study would be useful in understanding the overall performance of these catalysts and in addition the kinetic data can also be useful for design purposes.

4.2 EXPERIMENTAL :

4.2.1 Materials

Rhodium trichloride ($RhCl_3.3H_2O$), was obtained from Arora Mathey Ltd. Triphenylphosphine (PPh_3) was procured from LOBA Chemie, Switzerland. 1,5 cyclooctadiene was procured from Aldrich Chemicals, USA. Solvents like toluene, water and ethanol were freshly distilled prior to their use. Hydrogen gas was supplied by Indian Oxygen Ltd., Bombay and Carbon Monoxide with > 99.9% pure was used directly from cylinders. The syngas with 1:1 ratio of H_2 : CO was prepared by mixing H_2 and CO in one cylinder. This mixture was analyzed quantitatively by using Orsat apparatus and gas chromatography to confirm the H_2/CO ratio equal to unity. Toluene and water which were used as solvents were degassed prior to use.

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

Rhodium trichloride trihydrate (1.0×10^{-3}, kg) in ethanol (3.0×10^{-5}, m^3) containing 1,5 cyclo octadiene (2.0×10^{-6}, m^3) was refluxed for 3, hrs. The solution was cooled and the orange solid filtered off, washed with ethanol, dried, and recrystallised from acetic acid (yield 60%). m.p. 529, K. The elemental analysis of the complex showed the following results

	Theoretical	Observed
C	39.5	39
H	5	4.9
Cl	14.4	14.4

The Infra Red spectrum of the above complex showed following characteristic frequencies

1325 s	993
1301 s	961 s
1227 m	878 w
1210 m	866 s
1172 s	831 w
1153 s	817 s
1076 w	795 m
	771 s

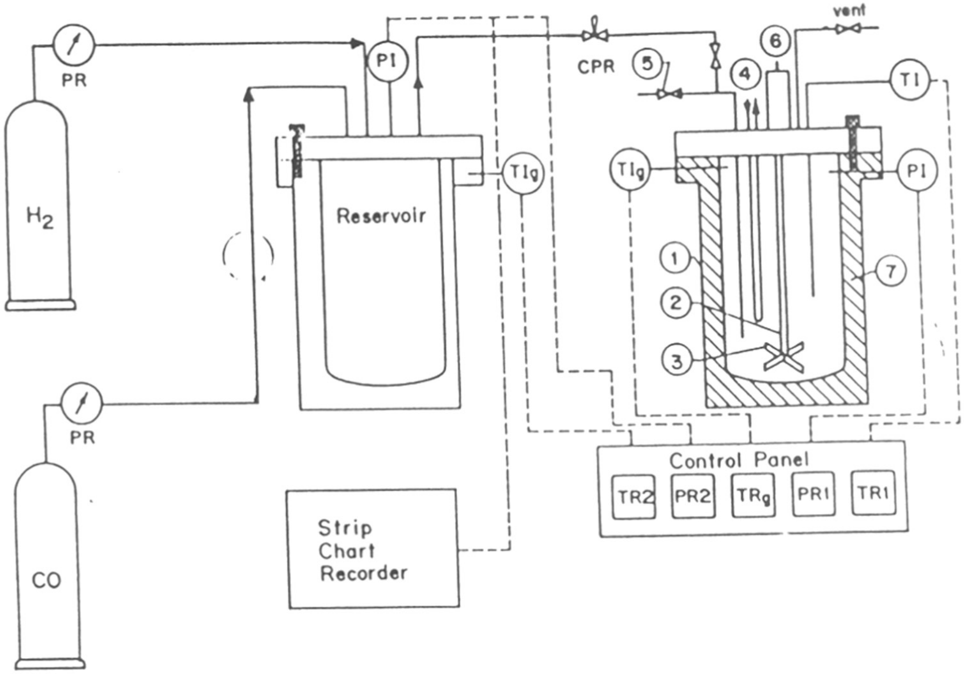
which agree with the earlier reports (Chatt and Venanzi 1957).

4.2.3 Preparation of TPPTS

The procedure for the sythesis of TPPTS was followed from the work of Jenck and Morel (1987). Sulfuric acid (98%) 0.2, kg, was introduced into the sulfonation reactor. The acid was cooled under constant stirring to 285-288, K. 0.05, kg of triphenyl phosphine (1.91×10^{-4}, kmol) was introduced slowly at 288, K. 0.28, kg of 65% oleum (SO_3 content: 2.275×10^{-3}, kmol) was transferred slowly into the sulfonation reactor maintaining a maximum temperature of 288, K with good stirring. The temperature of the reaction mixture was then raised to 295, K and was maintained for 76, hrs.

Thereafter, the temperature of the reaction was lowered to ~ 283, K and 0.05, kg of distilled water was introduced while maintaining the temperature at 283, K. A solution of sulfonated triphenyl phosphine in sulfuric acid was obtained. The reaction mixture was further diluted to approximately 8.0×10^{-4}, m^3 under cooling (283, K). The diluted solution was then transferred into a neutralization reactor under argon atmosphere.

A solution of 50% (w/w) degassed sodium hydroxide solution was added maintaining the temperature constant (283, K). Neutralization was carried out to a point where the solution was slightly acidic. The precipitate of sodium sulfate was obtained along with TPPTS solution. The filtrate was evaporated under reduced pressure at 353-363, K. Methanol was added to the above solution and the mixture refluxed under argon atmosphere for 2 hours. This solution was filtered, the residue comprising of only sodium sulfate. The filtrate was evaporated under reduced pressure and the solid obtained was stored as aqueous solution.



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

TI : Thermocouple
PI : Pressure transducer
TI$_g$: Thermocouple for gas
H$_2$: Hydrogen cylinder
CO : Carbon monoxide cylinder
PR : Pressure regulator
CPR : Constant pressure regulator

Control Panel

TR1 : Reactor temperature indicator
PR1 : Reactor pressure indicator
TR2 : Reservior temperature indicator
TRg : Gas temperature indicator
PR2 : Reservior pressure Indicator

Fig. 4.1 A SCHEMATIC OF HIGH PRESSURE SET UP USED FOR KINETIC STUDIES

^{31}P NMR analysis showed approximately 90% TPPTS and 10% OTPPTS. The TPPTS was further purified by recrystallisation using absolute ethanol.

4.2.4 Preparation of water soluble catalyst

The water soluble catalyst was prepared by exchange method. The metal complex (e. g. $[RhCl(COD)]_2$) is dissolved in a small amount of organic solvent (eg. toluene), which is then extracted with water containing the dissolved ligand (eg. TPPTS). The complete exchange of the organic phase catalyst can be seen from the color change of the aqueous phase (from colorless to yellow orange). This aqueous phase can then be charged as the aqueous phase catalyst.

4.2.5 Apparatus

The hydroformylation experiments were carried out in a batch mode in a stirred pressure reactor (microclave) of 5.0×10^{-5}, m^3 capacity and made of Hastelloy C material (Autoclave Engineers, USA). This reactor was equipped with automatic temperature control, facilities for variable agitation speeds and withdrawal of liquid samples. The agitator used was a gas-induced type, which is efficient for gas-liquid mass transfer. An outlet valve was provided for taking gas samples as well as releasing the pressure when necessary. A safety rupture disc was also fitted to the reactor. The reactor was designed for a working pressure of 27.56, MPa. In order to maintain a constant pressure in the reactor, CO, H_2 and ethylene were supplied (1:1:1 ratio) to the reactor through a constant pressure regulator from a gas reservior (2.5×10^{-5}, m^3 capacity at 298, K) Fig 4.1 shows a schematic diagram of the experimental set-up used in this study.

4.2.6 Experimental procedure for single phase studies

The water soluble complex catalyst was prepared by a procedure described above (see section 4.2.4). The microclave was charged with a required amount of aqueous phase catalyst without any additional solvent. The contents were first flushed with nitrogen and then with CO/H_2. The reactor was heated to a desired temperature under slow stirring. The gaseous mixture of carbon monoxide and hydrogen was first charged to the reactor and then ethylene was charged upto a desired pressure at a very low level of agitation. The reaction was started by switching the stirrer on at a required agitation speed. The pressure drop in the reservior vessel was observed with a very sensitive pressure tranducer-recorder system as a function of time. The experiments were carried out for a fixed duration of 1, hr.

4.2.7 Experimental Procedure for biphasic studies

The microclave was charged with the aqueous phase catalyst alongwith toluene as a second immiscible liquid phase in a required ratio. The contents were first flushed with nitrogen and then with CO/H_2. Other steps were same as those followed in the single phase studies.

In both the cases (single phase and biphasic), after the reaction the reactor was cooled to room temperature and the gas sample was taken. Then it was further cooled to ~ 278, K and the liquid sample was withdrawn.

4.2.8 Analytical Procedure

The gas and liquid samples were analysed by gas chromatography. For this purpose, the method used was the same as described in Chapter 3 .

4.3 RESULTS AND DISCUSSION

4.3.1 Performance of Rh-TPPTS catalyst

In this Chapter, the results on hydroformylation of ethylene using water soluble Rh-TPPTS catalyst are reported. The objective was to understand the overall performance of the catalyst as a function of reaction conditions. This reaction involves a gas-liquid-liquid catalytic reaction and has several complexities : (a) Simultaneous absorption of ethylene, CO and H_2 with reaction. (b) gas-liquid and liquid-liquid mass transfer, (c) homogeneity of the liquid-liquid dispersion and (d) complex reaction kinetics. In order to understand such a complex multiphase system, it is first necessary to study the intrinsic kinetics of the reaction under conditions where mass transfer limitations are not significant. To acheive this in a gas-liquid-liquid system, is not always easy and hence, it was thought appropriate to investigate the intrinsic kinetics of the reaction using a homogeneous Rh-TPPTS catalyst in the water phase alone. Unlike the hydroformylation of liquid olefins (eg. hexene, octene, etc.), wherein such a study is not easy due to immiscibility of the olefin reactant with the aqueous catalyst phase, ethylene being a gaseous reactant, the kinetics in a homogeneous aqueous phase can be conveniently studied. The following sections describe the results on (a) solubility data (b) kinetics using a homogeneous aqueous phase catalyst (c) the influence of the reaction conditions on the average activity of the biphasic catalyst and (d) the rate behaviour in biphasic hydroformylation of ethylene.

4.3.2 Solubility data

In order to interpret the kinetics of any gas-liquid reaction, a knowledge of solubility of gaseous reactants in the liquid medium is essential. The solubility data for H_2, CO and ethylene in toluene and water was required at different pressures and temperatures. The data for toluene as a solvent are presented in Chapter 3 at different temperatures. The solubility of H_2, CO and ethylene in water was determined experimentally in a temperature range of 313-373, K. These experiments were carried out using the apparatus and procedure described in Chapter 2. The results are presented in Table (4.1).

It was thought desirable to develop a correlation for each system to account for changes with temperature. For this purpose, the following form of empirical equation was found to represent the solublity data satisfactorily.

$$ln\ H = k_1 + k_2 / T \tag{4.1}$$

Solubility data were fitted to eq. (4.1) by using a linear least-squares analysis program and the values of the constants evaluated for each system are presented in Table (4.2). The results predicted by eq. (4.1) were found to agree with the experimental data within an average error of about 2%.

4.3.3 Kinetic study with homogeneous Rh-TPPTS catalyst in aqueous phase

The kinetics of hydroformylation of ethylene using Rh-TPPTS complex catalyst in a homogeneous aqueous phase was studied. It was thought necessary to first ensure the material balance and reproducibility of the experiments. For this purpose, a few experiments were carried out in which the amount of product popionaldehyde formed, and the gases consumed were compared. It was observed that the quantities of CO, H_2 and ethylene consumed were consistent with the amount of total aldehyde product formed as per the stoichiometry. Thus, the overall hydroformylation kinetics could be followed by observing the consumption of CO, H_2 and ethylene, in a 1:1:1 ratio from a reservoir vessel. From the pressure drop (in the reservior) vs time data the initial rate were calculated as

$$R = \frac{(\Delta\ P) V_g}{3\ R\ T\ V_L\ t} \tag{4.2}$$

For the purpose of detailed kinetic modeling, several experiments were carried out to understand the influence of catalyst concentration and carbon monoxide, hydrogen and ethylene partial pressures on the rate of reaction. A few initial experiments were also carried out to understand the importance of gas to liquid mass transfer resistance. The effect of catalyst concentration, agitation speed and temperature was investigated. The results are presented in Figs. 4.2 to 4.3. These data clearly indicate that the results at 333 and 373, K are under conditions of mass transfer limitation (for higher catalyst concentrations (1.0 - 4.0 x 10^{-3}, kmol m^{-3})). Also, the

TABLE 4.1

SOLUBILITY OF GASES IN WATER

Serial Number	Temperature K	Solubility MPa m^3 Kmol^{-1}		
		Ethylene	H_2	CO
1	313	40.33	191.06	211.04
2	333	82.56	348.11	379.4
3	353	119.88	471.16	538.83
4	373	156.3	626.5	700.02

TABLE 4.2

CONSTANTS FOR EQUATION 4.2

No.	System	k_1	$k_2 \times 10^{-3}$	% error
1	CO-water	-12.83	2.32	0.92
2	H_2-water	-12.60	2.28	1.50
3	Ethylene-water	-12.15	2.62	1.98

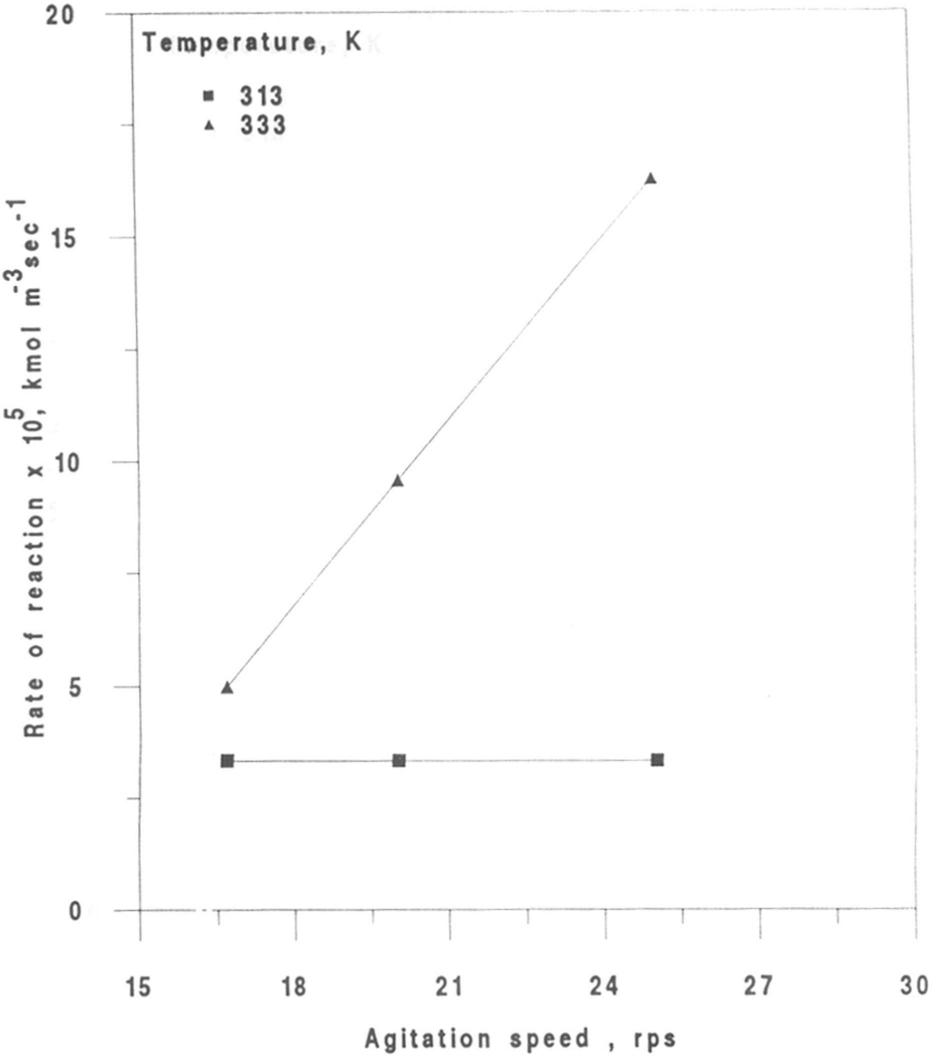


Fig. 4.2 EFFECT OF AGITATION SPEED EFFECT IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :
Concentration of catalyst : 0.5 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene : 0.689, MPa
Partial pressure of CO : 0.689, MPa
Partial pressure of H_2 : 0.689, MPa
Catalyst : TPPTS ratio : 1 : 6

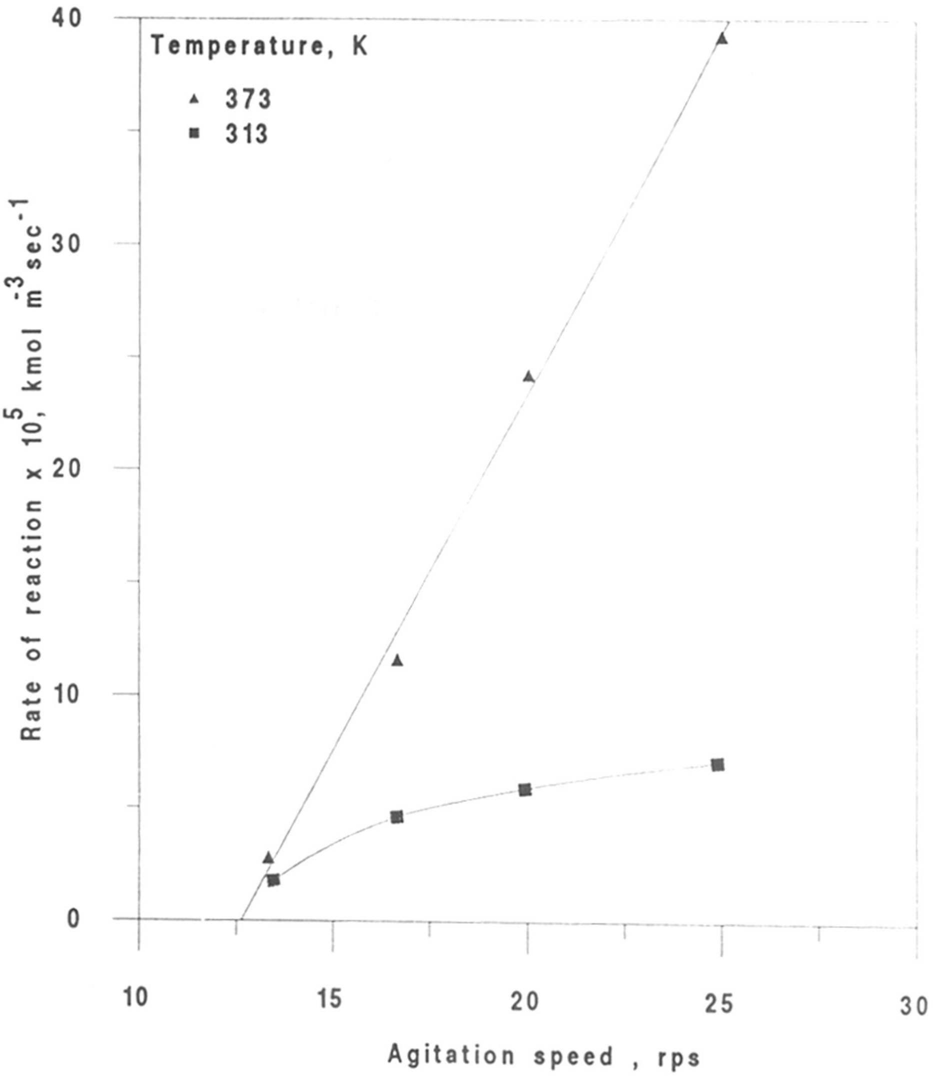


Fig. 4.3 EFFECT OF AGITATION SPEED EFFECT IN HYDROFORMYLATION OF ETHYLENE

Reaction conditions :
Concentration of catalyst : 1.0 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene : 0.689, MPa
Partial pressure of CO : 0.689, MPa
Partial pressure of H_2 : 0.689, MPa
Catalyst : TPPTS ratio : 1 : 6

observation of the rate being independent of catalyst concentration above (5.0×10^{-4}, kmol m^{-3}) is consistent with gas to liquid mass transfer limitations. The data at 313, K and a catalyst concentration below (1.0×10^{-3}, kmol m^{-3}) showed a linear dependence on catalyst concentration and were independent of agitation. Hence, the intrinsic kinetics of the reaction was studied at 313, K. The range of conditions investigated are presented in Table (4.3). The results on initial rate data are discussed below.

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

The effect of P_{CO} on the rate of hydroformylation of ethylene was studied at a constant partial pressure of H_2 and ethylene = 0.689, MPa and a catalyst concentration of 5.0×10^{-4}, kmol m^{-3}. The results as total gas absorbed (CO + H_2 + ethylene) vs time are shown in Fig. 4.4 whereas the rate of reaction vs partial pressure of CO is shown in Fig. 4.5. for 313, K. The rate was found to decrease with increase in P_{CO}. It is a general observation that the hydroformylation rate is inversely proportional to the partial pressure of CO (Deshpande 1994, Purvanto 1994). This observation can be explained on the basis of a mechanism proposed earlier (Herrmann and Kohlpaintner, 1993) (see Fig. 4.6). Inhibition of the rate of hydroformylation with increase in partial pressure of CO is due to the side reactions (steps 7 and 8 in Fig. 4.6) leading to the formation of the inactive species. This trend is similar to that discussed in chapter 2.

4.3.3.2 Effect of partial pressure of H_2 (P_{H2})

The effect of partial pressure of H_2 on the rate of hydroformylation of ethylene was investigated at a partial pressure of CO and ethylene = 0.689, MPa and a catalyst concentration of 5.0×10^{-4}, kmol m^{-3}. The results as total gas absorbed (CO + H_2 + ethylene) vs time are shown in Fig. 4.7 and the rate of reaction vs partial pressure of hydrogen is shown in Fig. 4.8 for 313, K.. The rate of reaction was found to vary linearly with P_{H2}. The first order dependence is consistent with the oxidative addition of H_2 to acyl complex (step 5 in Fig. 4.6) as the rate determining step.

4.3.3.3 Effect of ethylene partial pressure

Fig 4.9 shows the total gas absorbed (CO + H_2 + ethylene) vs time plots for the effect of ethylene partial pressure whereas the rate of reaction vs partial pressure of ethylene is shown in Fig. 4.10 for 313, K. The rate varied with a mild dependence on ethylene partial pressure with inhibition at higher concentrations. At higher olefin concentrations, the reverse equilibrium in step (4) (see Fig. 4.6) may become significant and in addition formation of diolefinic species is also possible, thus leading to the inhibition observed at higher olefin concentration.

TABLE 4.3

RANGE OF CONDITIONS INVESTIGATED FOR THE KINETIC STUDY

Concentration of Catalyst (kmol m $^{-3}$)	0.2 to 1.0 × 10 $^{-3}$
Partial pressure of ethylene (MPa)	0.414 to 2.067
Partial pressure of hydrogen (MPa)	0.414 to 2.067
Partial pressure of CO (MPa)	0.414 to 2.067
Temperature (K)	313
Solvent	water
Reaction volume (m^3)	2.5 x 10^{-5}

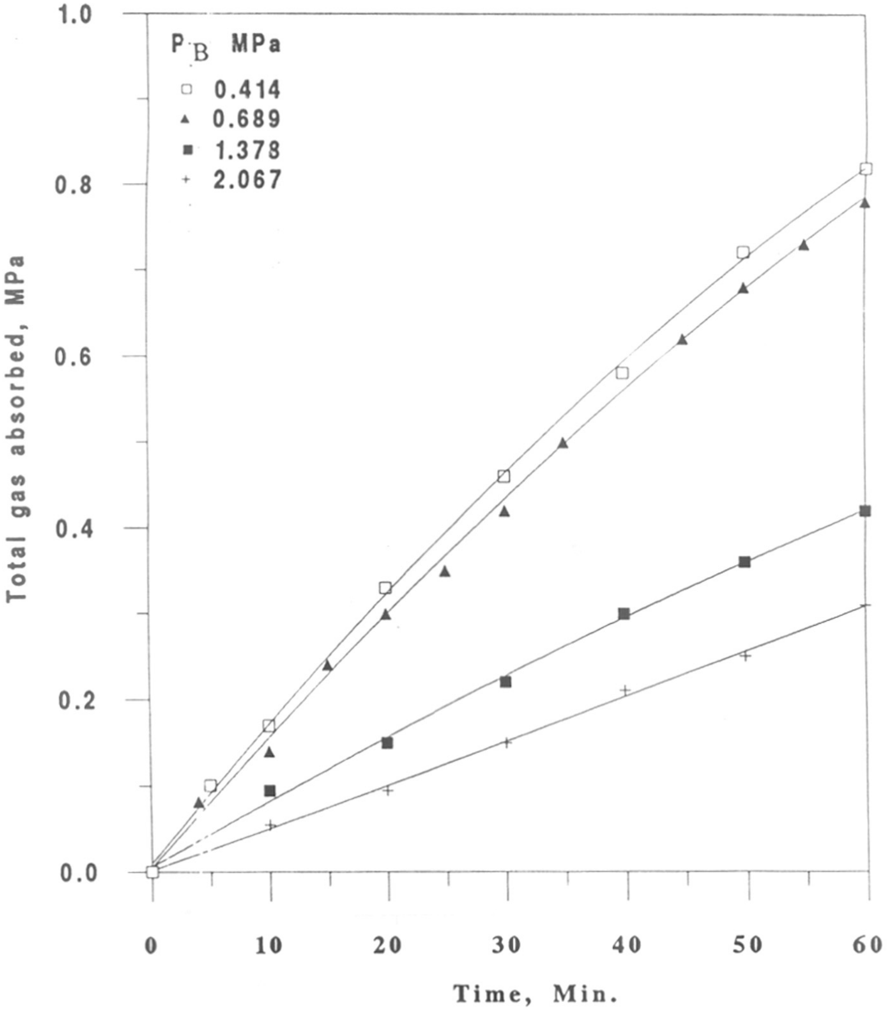


Fig. 4.4 A PLOT OF TOTAL GAS ABSORBED vs TIME FOR EFFECT OF Pco IN HYDROFORMYLATION OF ETHYLENE AT 313,K

Reaction conditions :

Concentration of catalyst : 0.5×10^{-3}, kmol m^{-3}

Partial pressure of ethylene : 0.689, MPa

Partial pressure of H_2 : 0.689, MPa

Catalyst : TPPTS ratio : 1 : 6

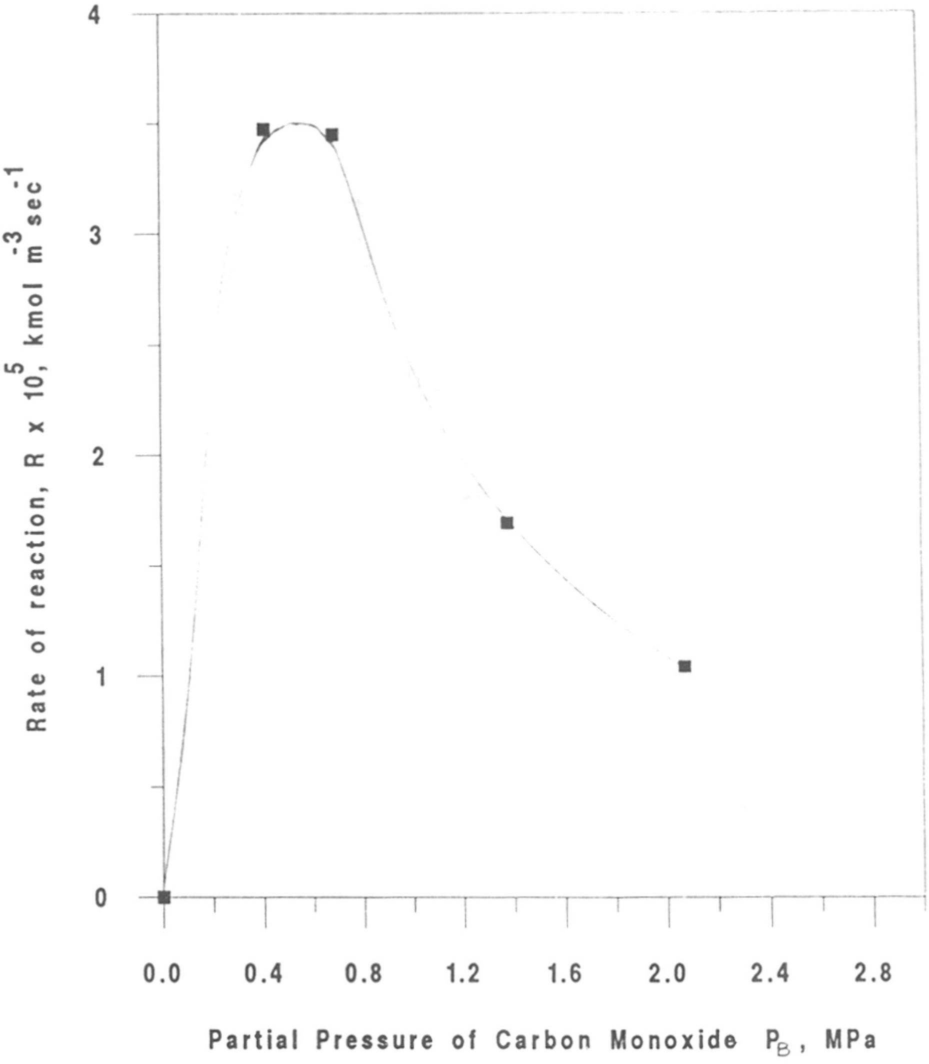


Fig. 4.5 EFFECT OF Pco ON RATE OF HYDROFORMYLATION OF ETHYLENE

Reaction conditions :
Concentration of catalyst : 0.5×10^{-3}, kmol m^{-3}
Partial pressure of ethylene : 0.689, MPa
Partial pressure of H_2 : 0.689, MPa
Catalyst : TPPTS ratio : 1 : 6
Temperature : 313, K

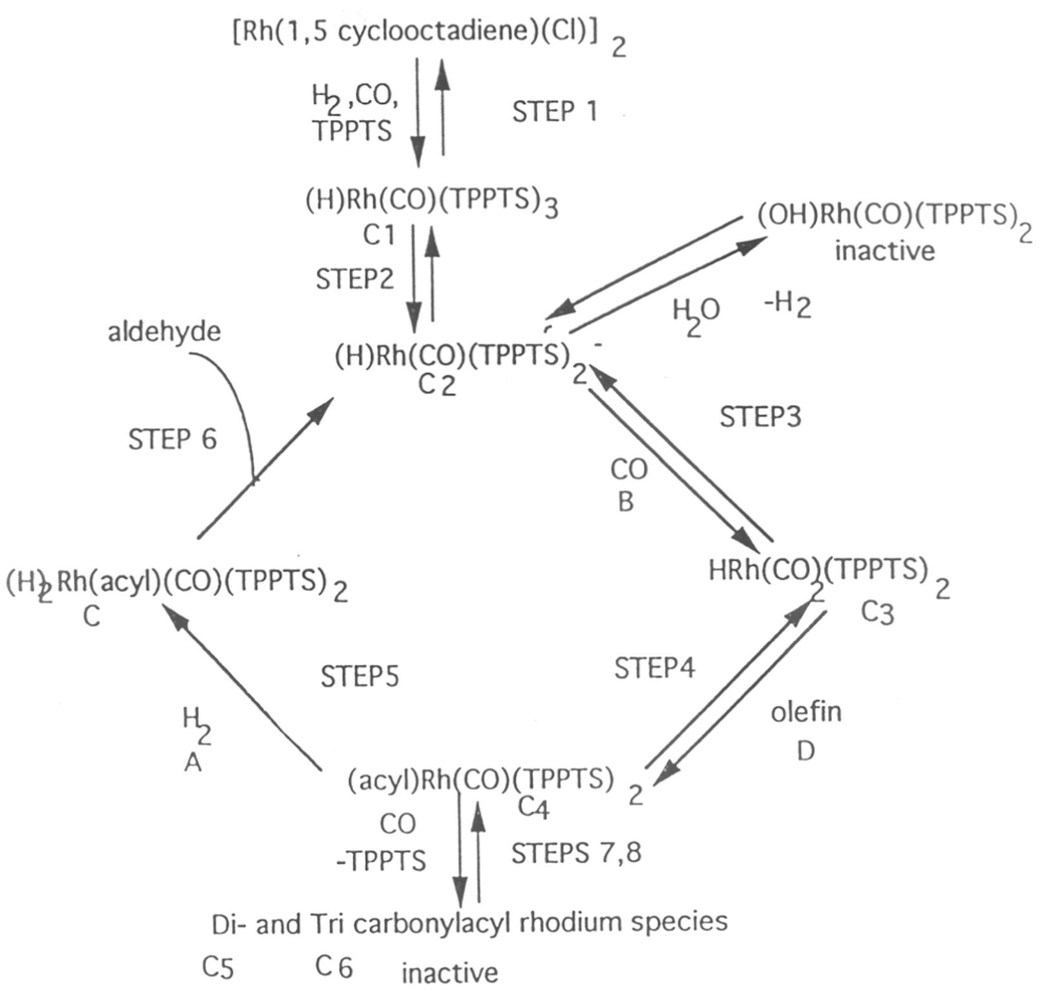


Fig. 4.6 SCHEMATIC REPRESENTATION OF THE MECHANISM OF HYDROFORMYLATION USING WATER SOLUBLE CATALYSTS

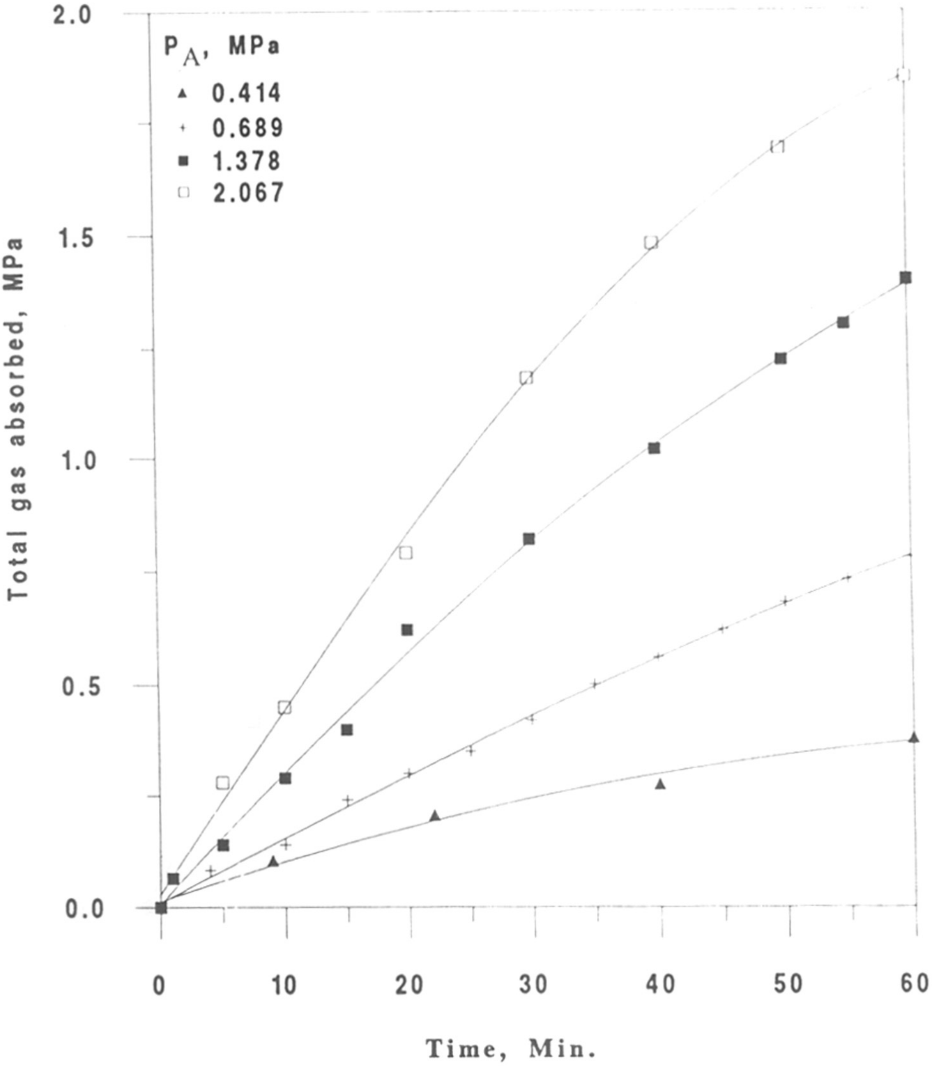


Fig. 4.7 A PLOT OF TOTAL GAS ABSORBED vs TIME FOR EFFECT OF P_{H2} IN HYDROFORMYLATION OF ETHYLENE AT 313,K

Reaction conditions :
Concentration of catalyst : 0.5 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene : 0.689, MPa
Partial pressure of CO : 0.689, MPa
Catalyst : TPPTS ratio : 1 : 6

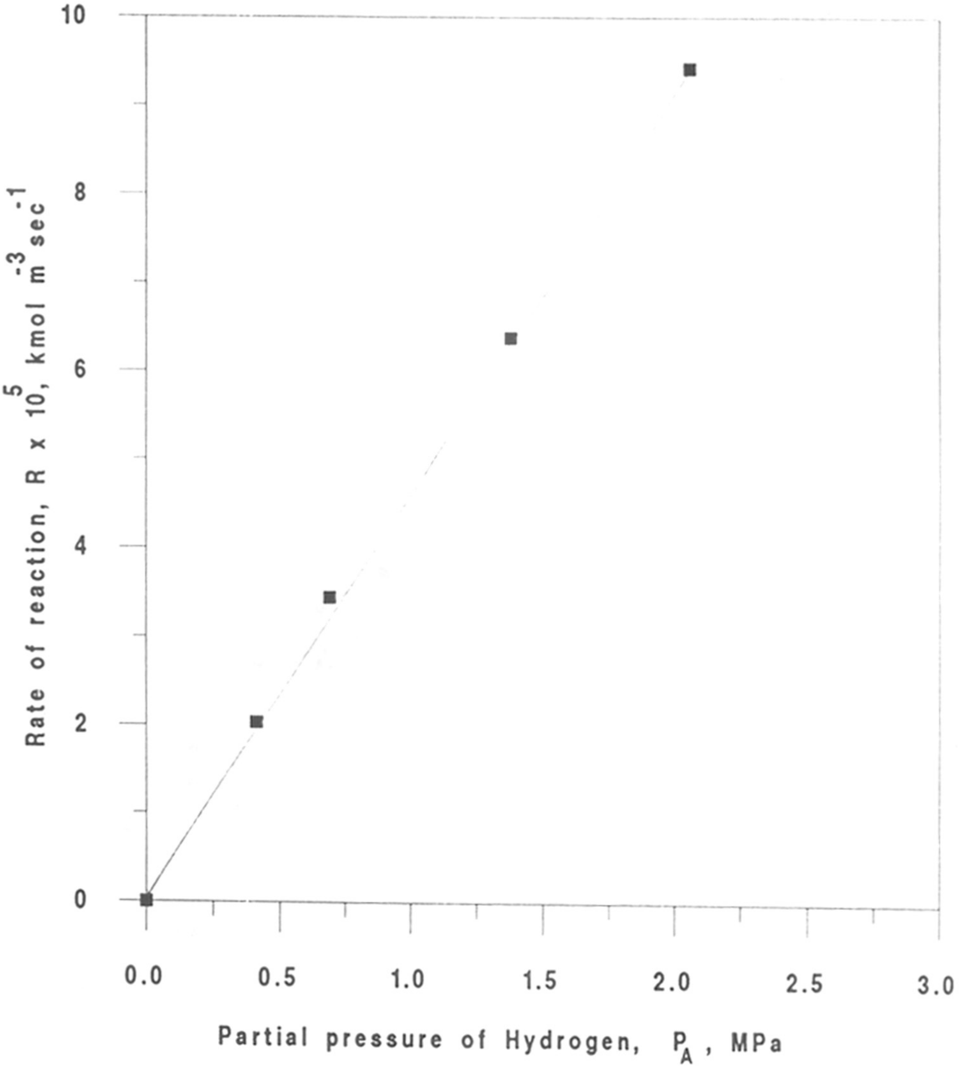


Fig. 4.8 EFFECT OF P_{H2} ON RATE OF HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Concentration of catalyst	: 0.5×10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of CO	: 0.689, MPa
Catalyst : TPPTS ratio	: 1 : 6
Temperature	: 313, K

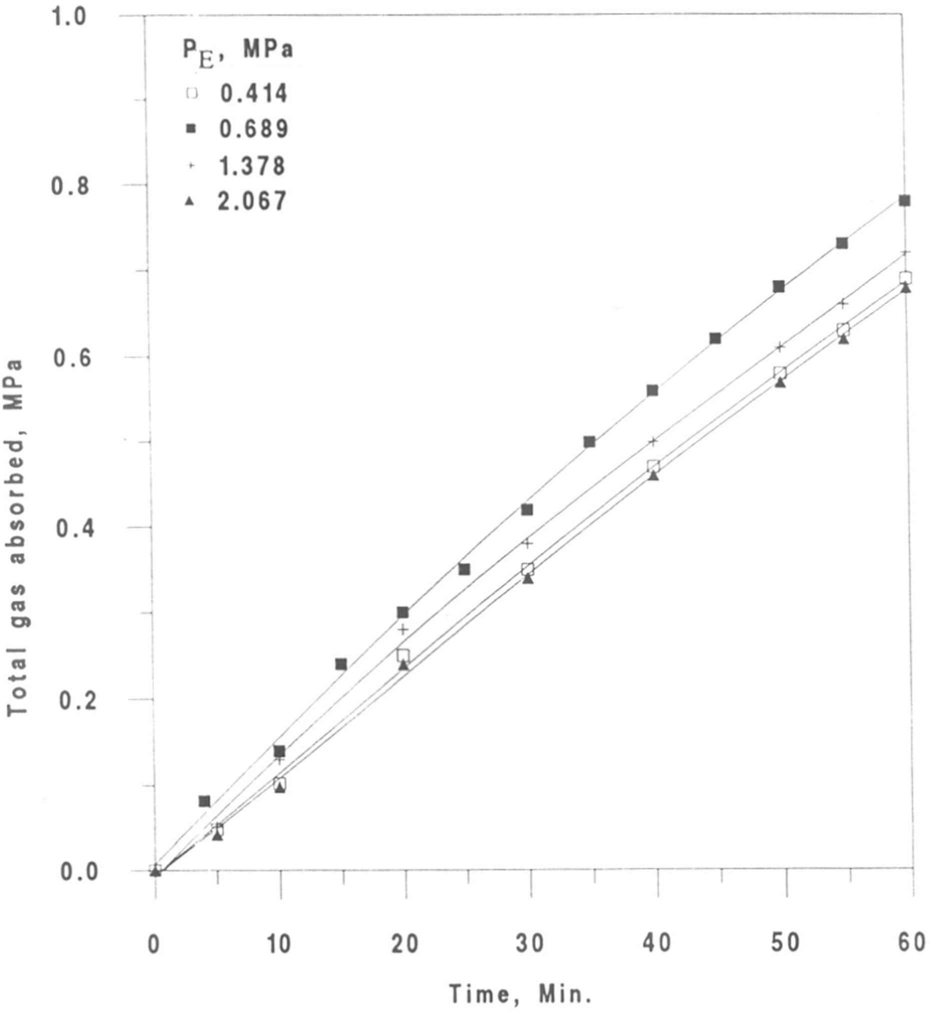


Fig. 4.9 A PLOT OF TOTAL GAS ABSORBED vs TIME FOR EFFECT OF P_E IN HYDROFORMYLATION OF ETHYLENE AT 313,K

Reaction conditions :

Concentration of catalyst	: 0.5×10^{-3}, kmol m^{-3}
Partial pressure of CO	: 0.689, MPa
Partial pressure of H_2	: 0.689, MPa
Catalyst : TPPTS ratio	: 1 : 6

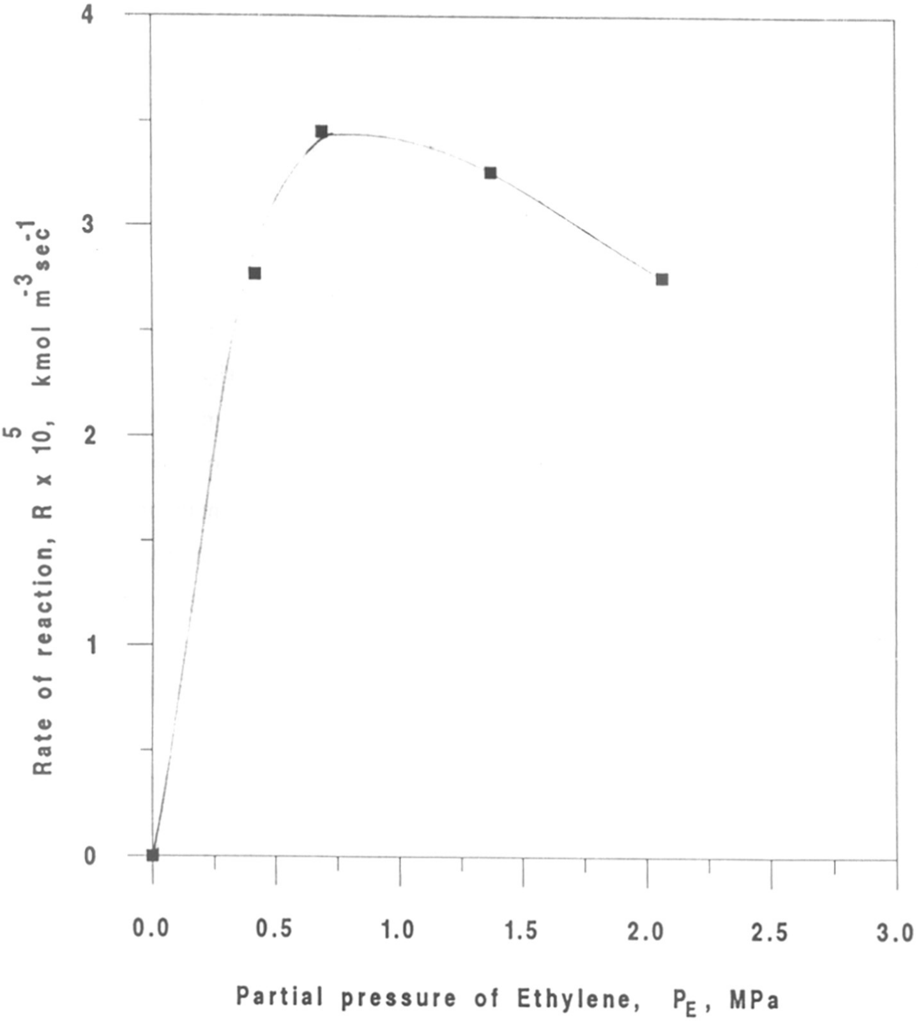


Fig. 4.10 EFFECT OF P_E ON RATE OF HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Concentration of catalyst : 0.5 x 10^{-3}, kmol m^{-3}
Partial pressure of CO : 0.689, MPa
Partial pressure of H_2 : 0.689, MPa
Catalyst : TPPTS ratio : 1 : 6
Temperature : 313, K

4.3.3.4 Effect of catalyst concentration

A typical plot of absorption of CO, H_2 and ethylene with time showing the effect of different catalyst concentrations on the rate of hydroformylation of ethylene at 313, K is shown in Fig. 4.11. The effect of catalyst concentration was studied at a temperature of 313, K, a total pressure of (CO + H_2 + ethylene) 1.376, MPa (CO : H_2 : ethylene =1: 1: 1). The results are shown in Fig. 4.12. The rate was found to vary linearly with respect to the catalyst concentration.

4.3.3.5 Rate equation

The hydroformylation of ethylene is a typical case involving the reaction of three dissolved gases in a liquid medium and hence, a careful consideration must be given to ensure that the rate data are in the kinetic regime. As discussed earlier (section 4.3.3), under certain conditions, the rate of hydroformylation was found to be limited by gas to liquid mass transfer and hence, the data at constant catalyst concentration were used for the purpose of kinetic modelling.

Since, the agitation speed showed no effect on the rate of reaction at 313, K, the absence of mass transfer resistance and hence kinetic regime is indicated. In order to confirm this, quantitative criteria as suggested by Chaudhari and Doraiswamy (1974) and given in eqns. 3.5-3.7 given in chapter 3 were also used. It is important to note here that the absence of mass transfer limitations has to be checked for all the gaseous reactants as all of these are sparingly soluble. The evaluation of α_1, α_2 and α_3 (eqns. 3.5 - 3.7, chapter 3) requires a knowledge of k_La and solubilities of H_2, CO and ethylene in addition to the rate data. While the Henry's law constants, presented in Table (4.1) were used to calculate A^*, B^* and E^*, k_La values were evaluated from the rate data under mass transfer controlled conditions. The values for α_1, α_2 and α_3 were calculated and were found to be less than 0.1 for all the data at 313, K below a catalyst concentration of 1.0×10^{-3}, kmol m^{-3}. This clearly shows that rate data at 313, K are in the kinetic regime. The rate data at 313, K were found to be well represented by the following form of equation

$$R = \frac{k\,(P_A/H_A)\,(P_B/H_B)\,(P_E/H_E)}{(1 + K_B(P_B/H_B))^2\,(1 + K_E(P_E/H_E))^2} \tag{4.3}$$

The concentrations of dissolved H_2, CO and ethylene, required in evaluation of the rate parameter were obtained from the experimental solubility data [see Table (4.1)]. For evaluation of the rate parameters, k, K_B and k_E, an optimization routine based on Marquardt method (1963) was used.

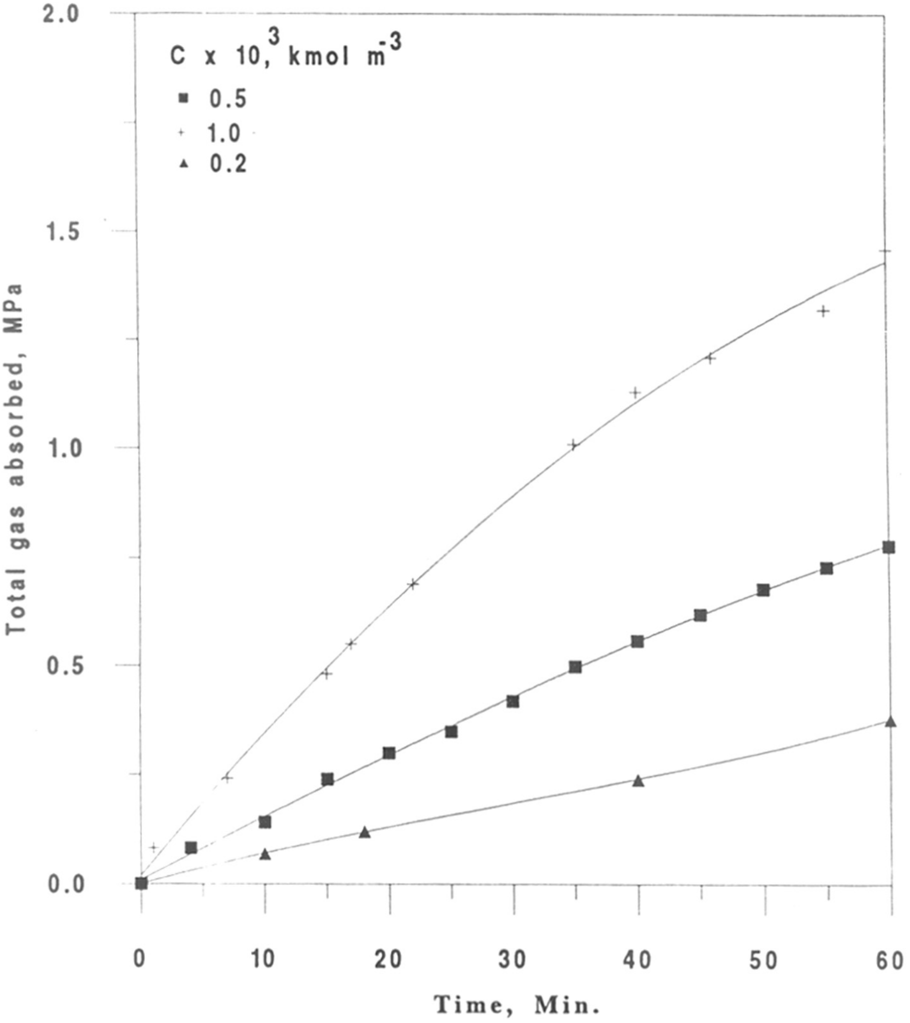


Fig. 4.11 A PLOT OF TOTAL GAS ABSORBED vs TIME FOR EFFECT OF CATALYST CONCENTRATION IN HYDROFORMYLATION OF ETHYLENE AT 313,K

Reaction conditions :
Partial pressure of ethylene : 0.689, MPa
Partial pressure of CO : 0.689, MPa
Partial pressure of H_2 : 0.689, MPa
Catalyst : TPPTS ratio : 1 : 6

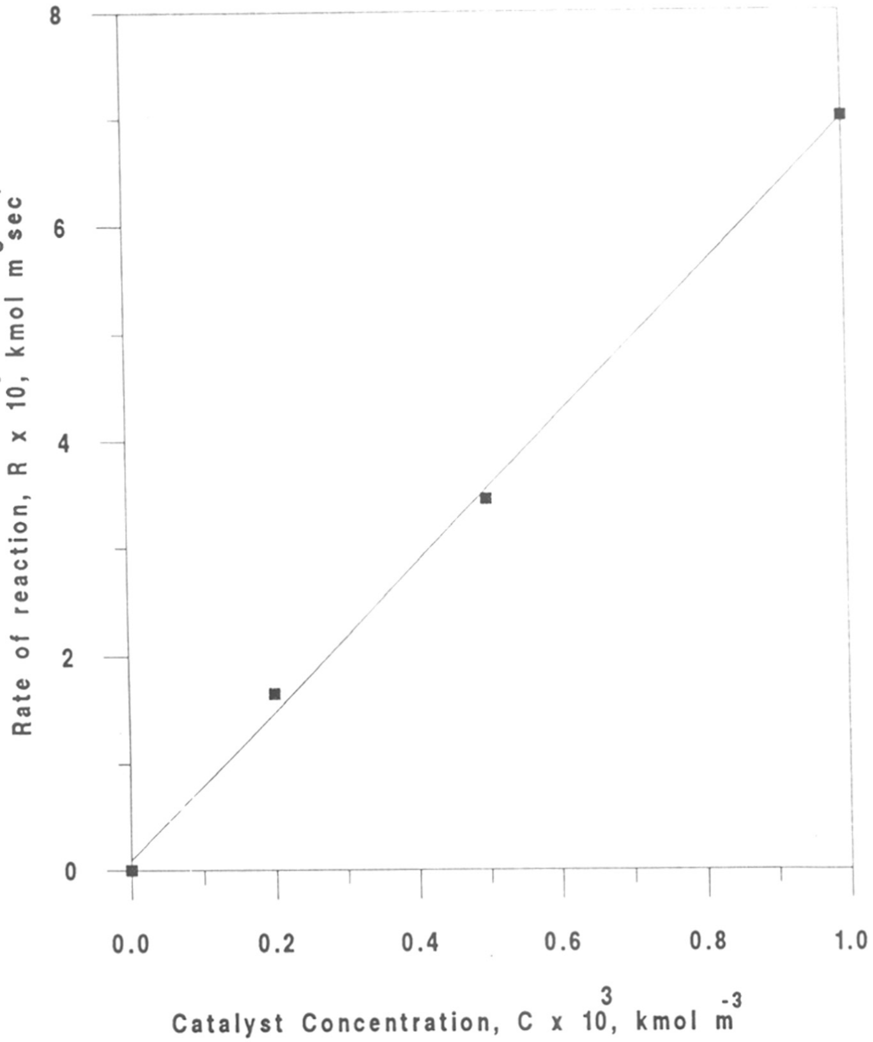


Fig. 4.12 EFFECT OF CATALYST CONCENTRATION ON RATE OF HYDROFORMYLATION OF ETHYLENE

Reaction conditions :
Partial pressure of ethylene : 0.689, MPa
Partial pressure of CO : 0.689, MPa
Partial pressure of H_2 : 0.689, MPa
Catalyst : TPPTS ratio : 1 : 6
Temperature : 313, K

The values obtained for these constants are : k $= 3.455 \times 10^4$, $m^6\,kmol^{-2}\,sec^{-1}$; $K_B = 2.78 \times 10^2$, $m^3\,kmol^{-1}$; $K_E = 38.29 \times 10^2$, $m^3\,kmol^{-1}$

4.3.4 Biphasic catalysis : Activity and rate behavior

Hydroformylation of ethylene using a water soluble catalyst in biphasic medium has an advantage in easy separation of the product propionaldehyde from the catalyst. Also, the use of a second immiscible liquid phase can be useful in enhancing the rate of hydroformylation due to higher solubilities of the gas phase reactants (H_2, CO and ethylene) in the immiscible organic phase. Therefore, a detailed study of the activity of a biphasic Rh-TPPTS catalyst as well as the rate behavior was carried out, using the same apparatus as described in section 4.2.5 except that the reservior volume was 3.5×10^{-5}, m^3. The effect of solvents, TPPTS concentration, catalyst concentration, agitation speed and ratio of organic to aqueous phase holdup on the average activity and initial rates was studied. The results are discussed in the following sections.

4.3.4.1 Effect of solvent

In a biphasic mode of operation, the second immiscible liquid phase (non catalyst phase) also plays an important role in deciding the performance of the catalyst system. In order to understand the behaviour of catalyst, the experiments were carried out at 333, K using three different solvents (aqueous phase hold up = 0.4). The results are presented in Fig. 4.13. The TOF values as well as the rate are significantly increased in the presence of toluene as a second phase. Since, the solubilities of CO, H_2 and C_2H_4 are several times higher in toluene, the rate of reaction at liquid-liquid interface is likely to be enhanced, leading to increase in the overall rate of reaction. For MEK-water and butanol- water, the rates were higher than in the homogeneous aqueous phase but lower than in the toluene-water system.

4.3.4.2 Effect of co-solvent

The effect of co-solvent (ethanol) on the rate of hydroformylation of ethylene was studied at 353, K. The results in Fig. 4.15 show a significant increase in the rate of reaction in the presence of cosolvent ethanol but an inhibition in rate is observed at higher concentration. In the presence of ethanol as cosolvent in the aqueous phase the solubility of ethylene , CO and H_2 in he aqueous phase increases several fold and hence enhancement in the rate is expected. At higher oncentration of ethylene as well as CO, a substrate inhibited kinetics has been observed (see ection 4.3.3.3). Therefore, a decrease in the rate for higher cosolvent concentration can be ttributed to an increase in the concentration of CO and ethylene, at higher cosolvent oncentration.

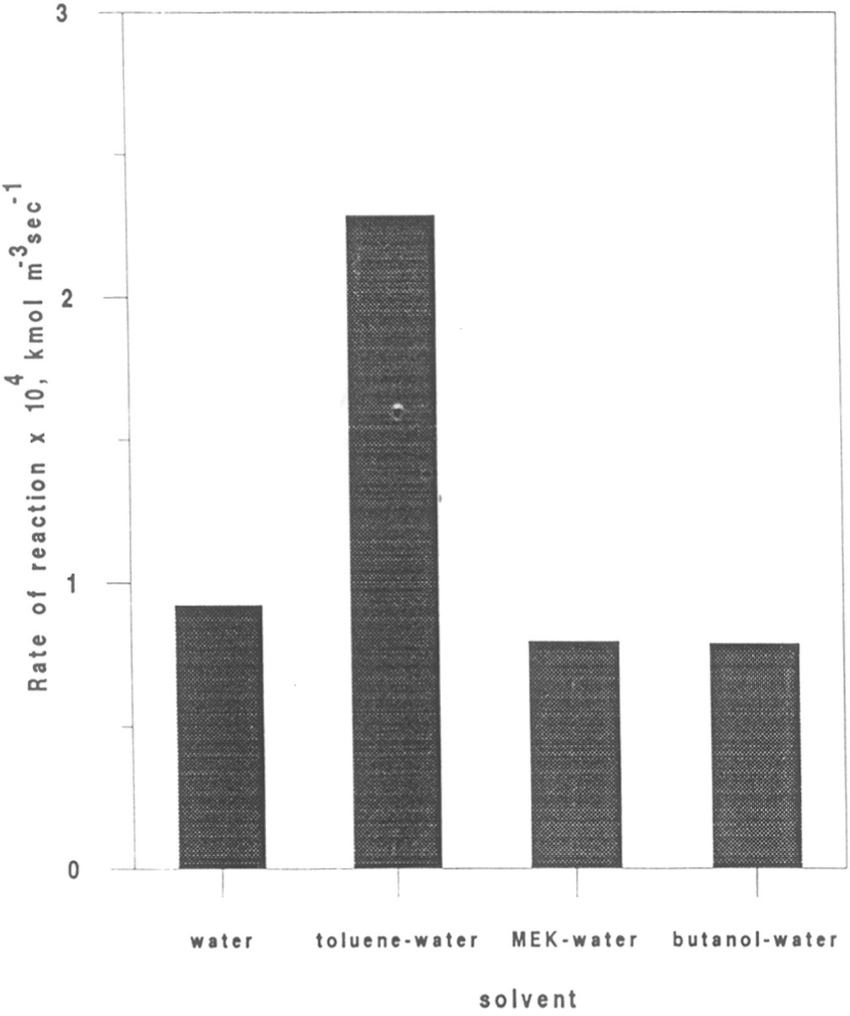


Fig. 4.13 A PLOT OF TOF AS A FUNCTION OF SOLVENT AT 333, K

Reaction conditions :

Concentration of catalyst	: 2.03 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of CO	: 0.689, MPa
Partial pressure of H_2	: 0.689, MPa
Catalyst : TPPTS ratio	: 1 : 6
Aqueous phase hold up	: 0.4
Reaction volume	: 1.5 x 10^{-5}, m^3

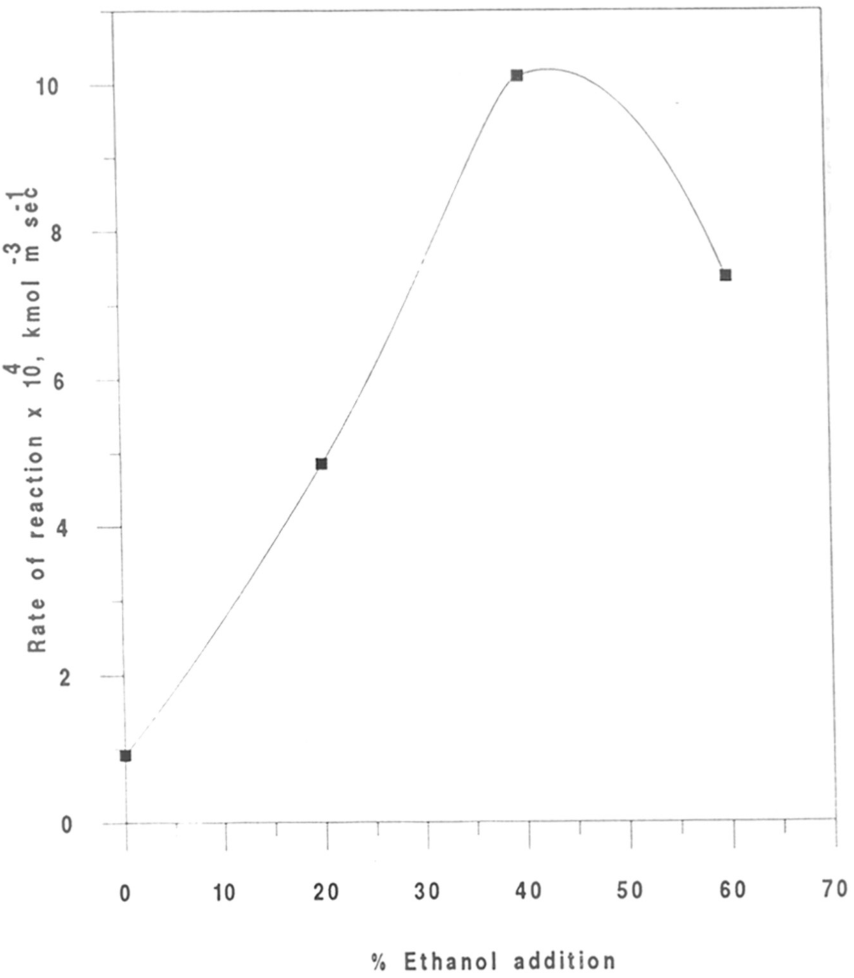


Fig. 4.14 EFFECT OF ETHANOL ADDITION ON RATE OF HYDROFORMYLATION OF ETHYLENE AT 333, K

Reaction conditions :

Concentration of catalyst	: 2.03 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of CO	: 0.689, MPa
Partial pressure of H_2	: 0.689, MPa
Catalyst : TPPTS ratio	: 1 : 6
Reaction volume	: 1.5 x 10^{-5}, m^3
Agitation speed	: 25, rps

4.3.4.3 Effect of TPPTS concentration

The effect of TPPTS concentration on the rate was studied at 353, K and a $[RhCl(COD)]_2$ concentration of 2.03×10^{-3}, kmol m^{-3}. The results are shown in Fig. 4.15, which indicate that the rate vs. TPPTS concentration goes through a maximum. This trend is similar to that observed in homogeneous systems using analogous catalyst based on PPh_3 ligand (Evans et. al. 1970; Sanger et. al. 1988). From the mechanism shown in Fig. 4.6, it is expected that the formation of active species C_2 from C_1 is inhibited at higher concentration of TPPTS leading to lower rates.

4.3.4.4 Effect of $[RhCl(COD)]_2$ concentration

The effect of catalyst precursor $[RhCl(COD)]_2$ concentration on the rate as well as average activity has been investigated at 353, K. The results shown in Fig. 4.16 indicate that the rate of reaction first increases with increase in Rh concentration and then is independent of any further increase. This indicates that gas-liquid mass transfer may be rate limiting under these conditions. In order to confirm this, the effect of agitation speed was studied at a catalyst concentration 2.03×10^{-3}, kmol m^{-3} (see Fig. 4.17). The results show that the rate is strongly dependent on agitation speed. The results in Fig. 4.16 on TOF vs Rh concentration indicate a decrease in TOF values with increase in Rh content. This observation is a result of non-linear dependence of the rate on Rh-concentration.

4.3.4.5 Effect of aqueous phase hold -up

The effect of aqueous phase hold up was studied at 353,K. The results are presented in Figs. 4.18 and 4.19. It was observed that the TOF for the aqueous phase hold up passes through a maximum. The maximum was observed at aqueous phase hold up of 0.4. The rate vs aqueous phase hold up also passes through a maximum. With decrease in the aqueous phase hold up, the fraction of organic phase increases. The solubility of H_2 , CO and ethylene is 6, 20 and 40 times higher in toluene than in water phase, respectively. Hence, a higher flux of reactants to the aqueous phase through the organic phase (toluene) is possible resulting in an increase in the rate with decrease in aqueous phase holdup. At lower aqueous phase hold up the rate decreases as the amount of catalyst in the total dispersion decreases.

4.3.4.6 Effect of partial pressure of carbon monoxide

The effect of P_{CO} on the rate of hydroformylation of ethylene was studied at a constant partial pressure of ethylene and $H_2 = 0.689$, MPa, catalyst concentration of 2.03×10^{-3} , kmol m^{-3} and aqueous phase hold up of 0.8. The result for total gas absorbed (CO + H_2 + ethylene)

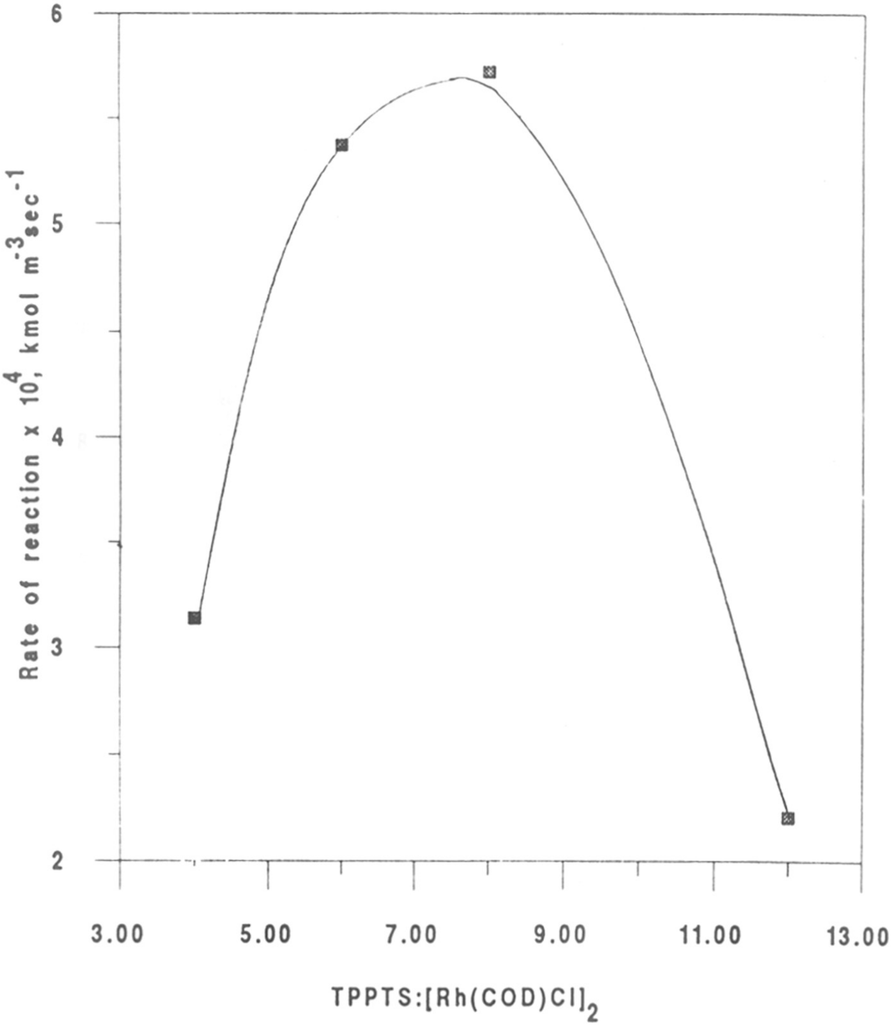


Fig. 4.15 EFFECT OF TPPTS CONCENTRATION ON RATE IN HYDROFORMYLATION OF ETHYLENE AT 353, K

Reaction conditions :

Concentration of catalyst : 2.03×10^{-3}, kmol m^{-3}

Partial pressure of ethylene : 0.689, MPa

Partial pressure of CO : 0.689, MPa

Partial pressure of H_2 : 0.689, MPa

Aqueous phase hold up : 0.8

Reaction volume : 1.5×10^{-5}, m^3

Agitation speed : 25, rps

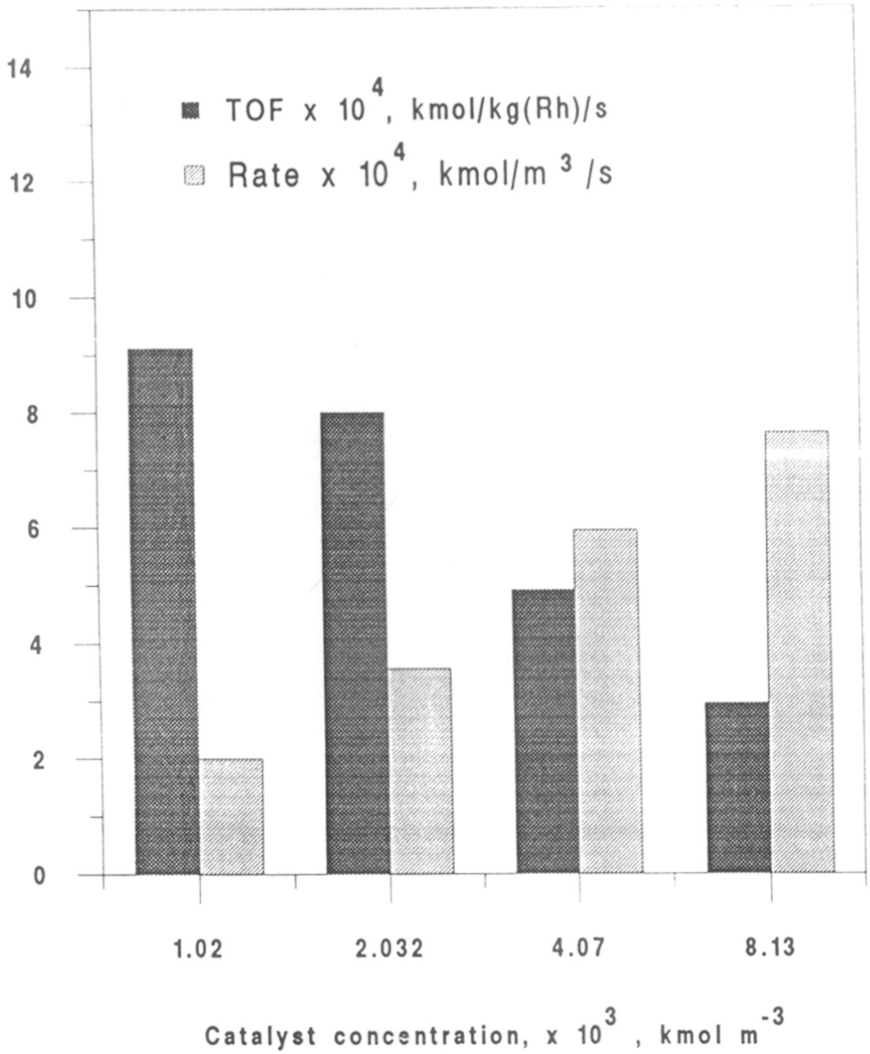


Fig. 4.16 EFFECT OF CATALYST CONCENTRATION ON TOF OF HYDROFORMYLATION OF ETHYLENE AT 353, K

Reaction conditions :

Partial pressure of ethylene : 0.689, MPa
Partial pressure of CO : 0.689, MPa
Partial pressure of H_2 : 0.689, MPa
Aqueous phase hold up : 0.8
Reaction volume : 1.5×10^{-5}, m^3
Agitation speed : 25, rps

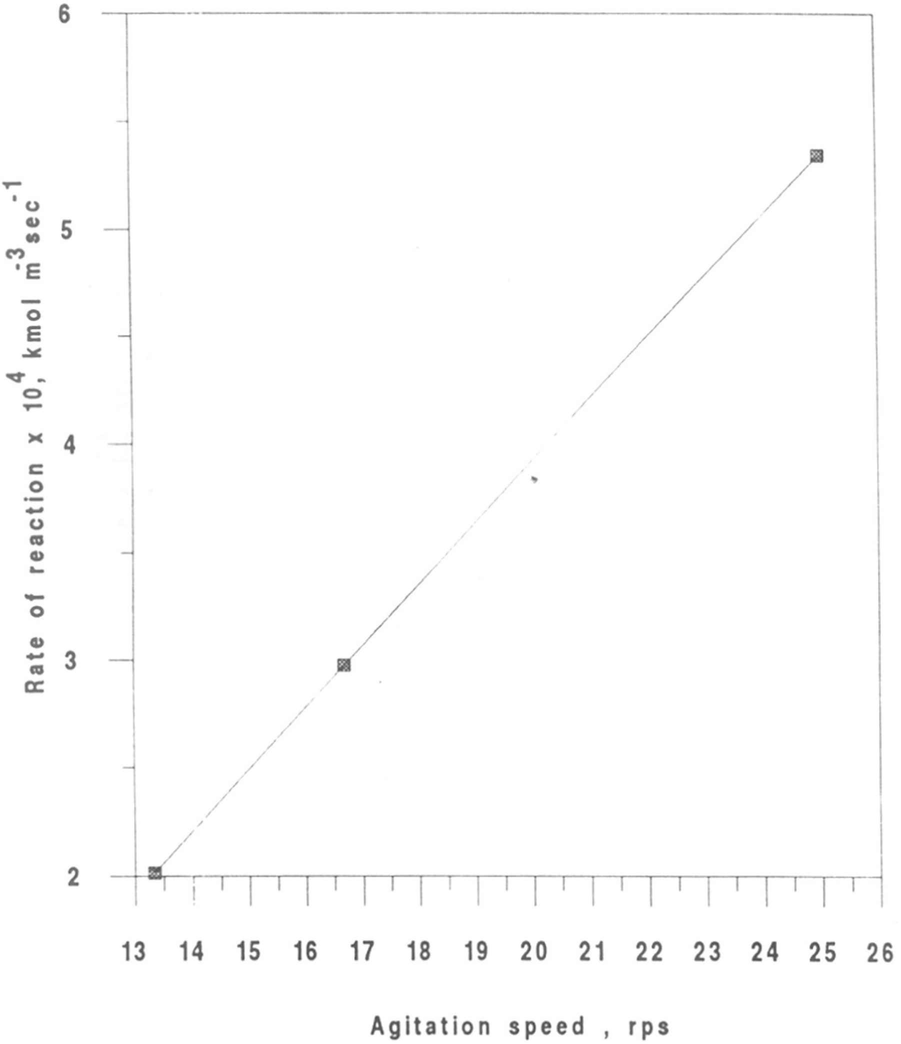


Fig. 4.17 EFFECT OF AGITATION SPEED ON RATE OF HYDROFORMYLATION OF ETHYLENE AT 353, K

Reaction conditions :
Concentration of catalyst : 2.03×10^{-3}, kmol m^{-3}
Partial pressure of ethylene : 0.689, MPa
Partial pressure of CO : 0.689, MPa
Partial pressure of H_2 : 0.689, MPa
Catalyst : TPPTS ratio : 1 : 6
Aqueous phase hold up : 0.8
Reaction volume : 1.5×10^{-5}, m^3

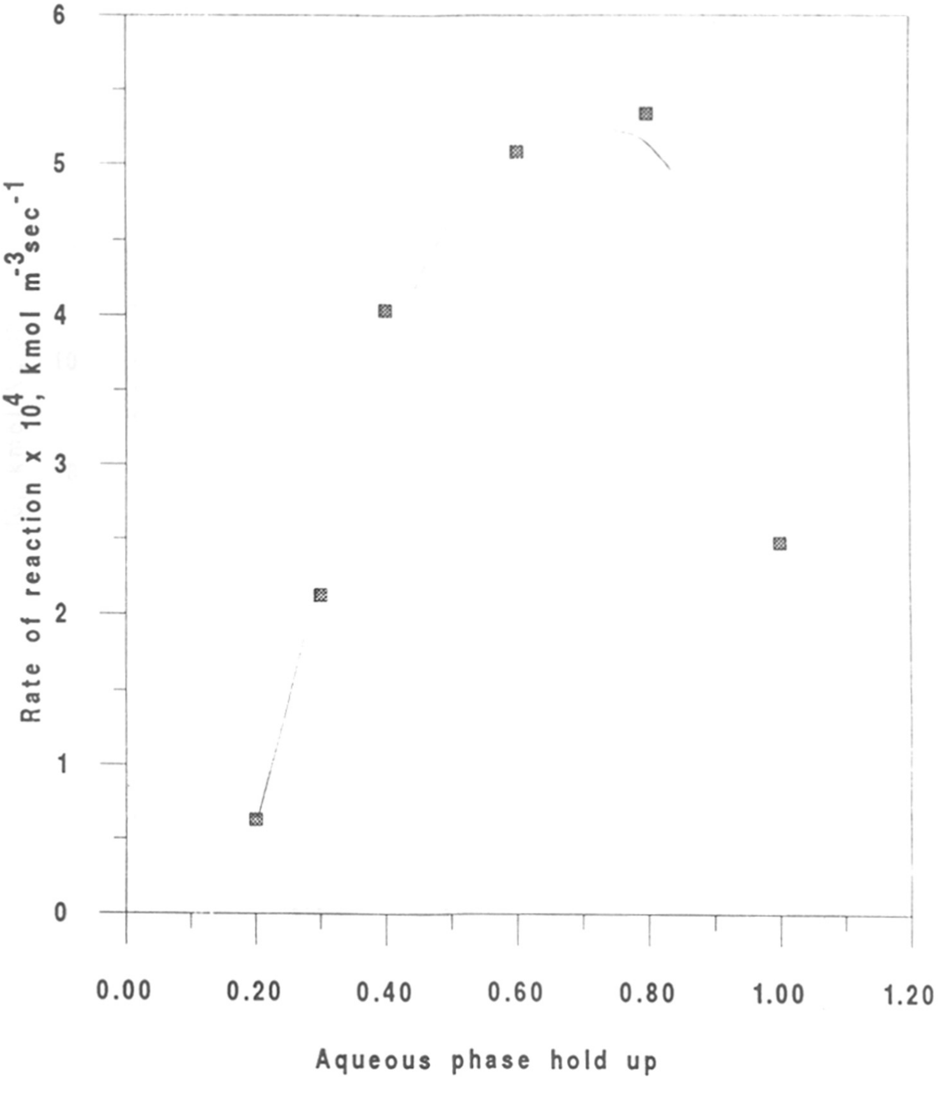


Fig. 4.18 EFFECT OF AQUEOUS PHASE HOLDUP ON RATE OF HYDROFORMYLATION OF ETHYLENE AT 353, K

Reaction conditions :	
Concentration of catalyst	: 2.03 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of CO	: 0.689, MPa
Partial pressure of H_2	: 0.689, MPa
Catalyst : TPPTS ratio	: 1 : 6
Reaction volume	: 1.5 x 10^{-5}, m^3
Agitation speed	: 25, rps

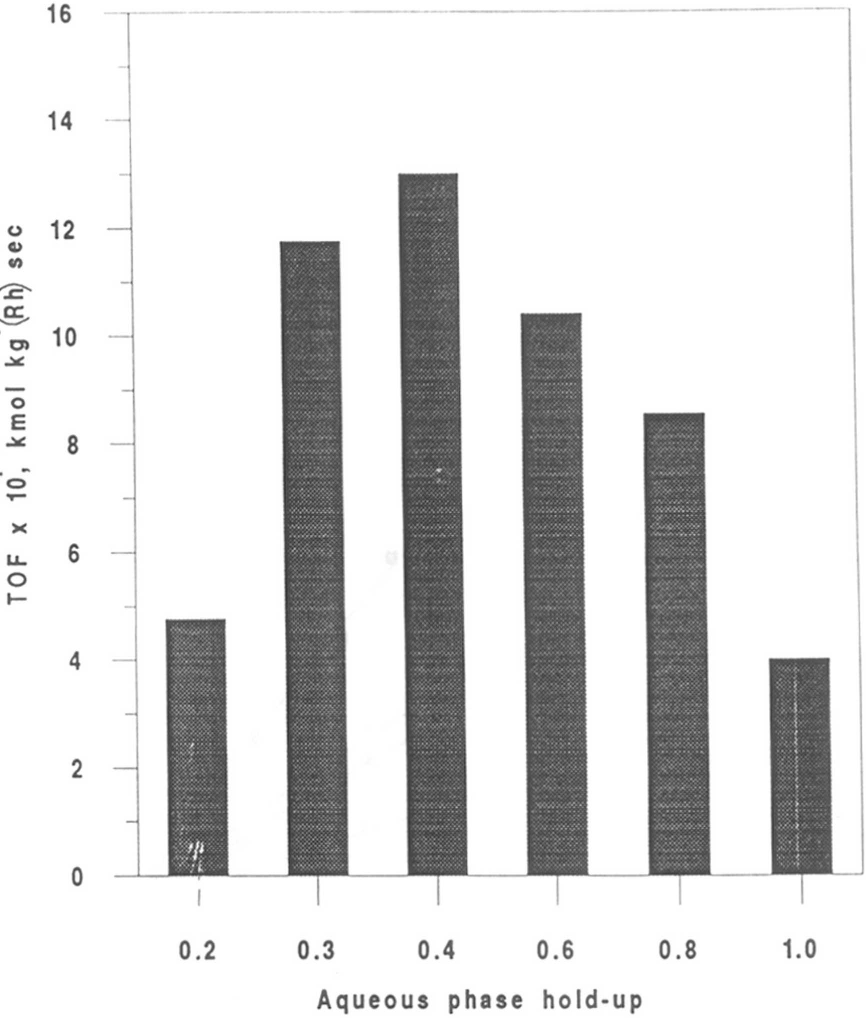


Fig. 4.19 EFFECT OF AQUEOUS PHASE HOLDUP ON TOF OF HYDROFORMYLATION OF ETHYLENE AT 353, K

Reaction conditions :

Concentration of catalyst	: 2.03 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of CO	: 0.689, MPa
Partial pressure of H_2	: 0.689, MPa
Catalyst : TPPTS ratio	: 1 : 6
Reaction volume	: 1.5 x 10^{-5}, m^3
Agitation speed	: 25, rps

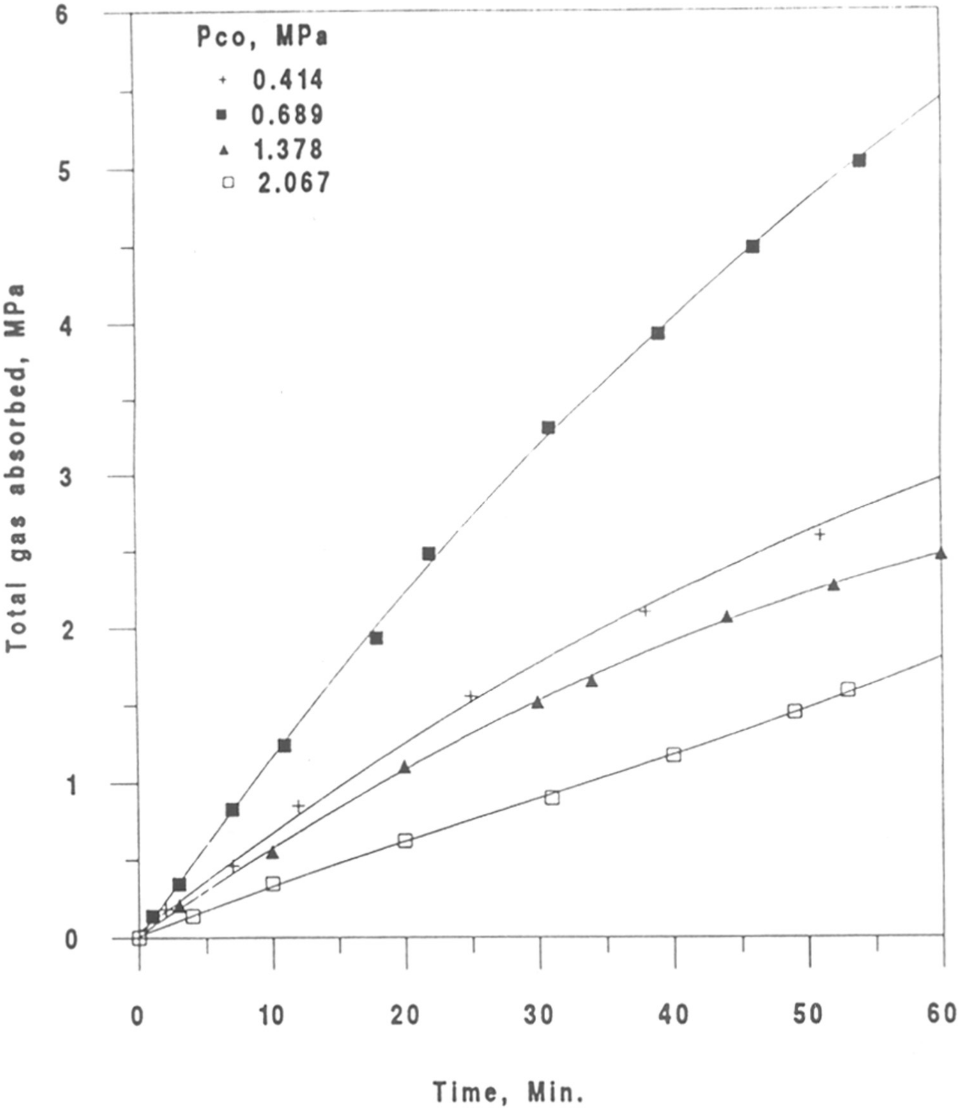


Fig. 4.20 A PLOT OF TOTAL GAS ABSORBED VS TIME EFFECT OF CO PRESSURE IN HYDROFORMYLATION OF ETHYLENE AT 353, K

Reaction conditions :
Concentration of catalyst : 2.03 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene : 0.689, MPa
Partial pressure of H_2 : 0.689, MPa
Catalyst : TPPTS ratio : 1 : 6
Reaction volume : 1.5 x 10^{-5}, m^3
Agitation speed : 25, rps

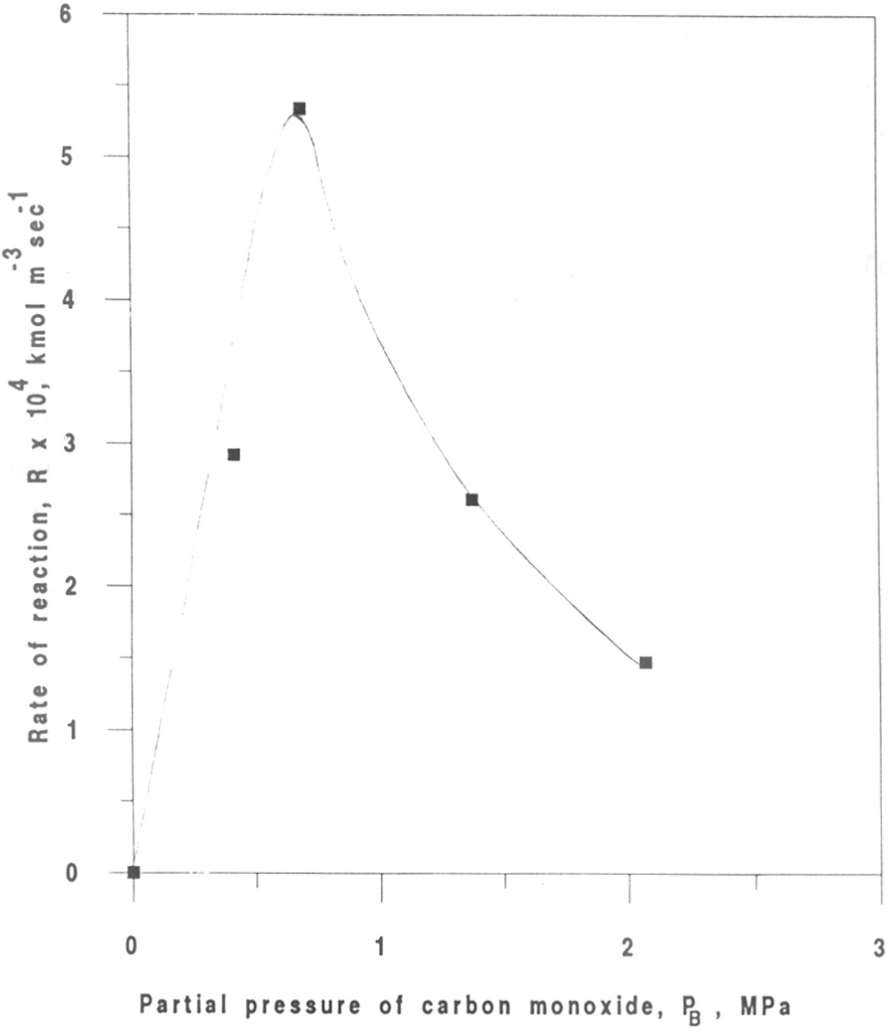


Fig. 4.21 EFFECT OF CO PRESSURE ON RATE OF HYDROFORMYLATION OF ETHYLENE AT 353, K

Reaction conditions :

Concentration of catalyst	: 2.03 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of H_2	: 0.689, MPa
Catalyst : TPPTS ratio	: 1 : 6
Reaction volume	: 1.5 x 10^{-5}, m^3
Agitation speed	: 25, rps

vs time is shown in Fig. 4.20 whereas the rate of reaction vs partial pressure of CO is shown in Fig. 4.21 for 353, K. The rate was found to have a complex dependence with substrate inhibition at higher P_{CO} as is well known in hydroformylation reactions.

4.3.4.7 Effect of partial pressures of H_2 (P_{H2})

The effect of partial pressure of H_2 on the rate of hydroformylation of ethylene was investigated at a constant partial pressure of CO and ethylene = 0.689, MPa, catalyst concentration of 2.03 x 10^{-3}, kmol m^{-3} and aqueous phase hold up of 0.8. The result for total gas absorbed vs time is shown in Fig. 4.22 and the rate of reaction vs partial pressure of hydrogen is shown in Fig. 4.23 for 353, K. The rate of reaction was found to vary linearly with P_{H2}. No hydrogenation products were observed in the range of conditions studied.

4.3.4.8 Effect of ethylene partial pressure

Fig. 4.24 shows the total gas absorbed vs time plots for the effect of ethylene partial pressure whereas the rate of reaction vs partial pressure of ethylene is shown in Fig. 4.25 for 353, K. This effect was studied at a total pressure of 1.378, MPa (CO/H_2 = 1), a catalyst concentration of 2.03 x 10^{-3}, kmol m^{-3} of aqueous phase. The rate was found to be nearly independent of concentration of ethylene.

4.3.4.9 Effect of temperature

The effect of temperature on the TOF was studied in the range of 313 to 393, K. It was observed that the TOF passes through maxima. The results are shown in Fig. 4.26. This study indicated that the catalyst deactivates at higher temperature. A precipitate of Rh metal was observed on the completion of the reaction indicating decomposition of the catalyst.

4.3.4.10 Analysis of mass transfer

The hydroformylation of ethylene using a biphasic catalyst involves gas-liquid, liquid-liquid mass transfer and homogeneous catalytic reaction in the aqueous catalyst phase as the important steps. Due to the multiphase nature of the gas-liquid-liquid catalytic reaction, it is important to understand the significance of mass transfer contribution in the overall rate process. The results presented in Fig. 4.16 on the effect of catalyst concentration and agitation clearly indicate that mass transfer limitations exist under certain conditions.

For the present case, most of the experiments were carried out under the conditions such that the aqueous catalyst phase was continuous with the organic phase and the gas bubbles as dispersed phases. The overall rate would therefore depend on the efficiency of gas to liquid mass transfer (to the aqueous reaction phase) and the liquid-liquid interfacial area through which a higher flux of reactants to the catalyst phase becomes accessible. The strong dependence of the

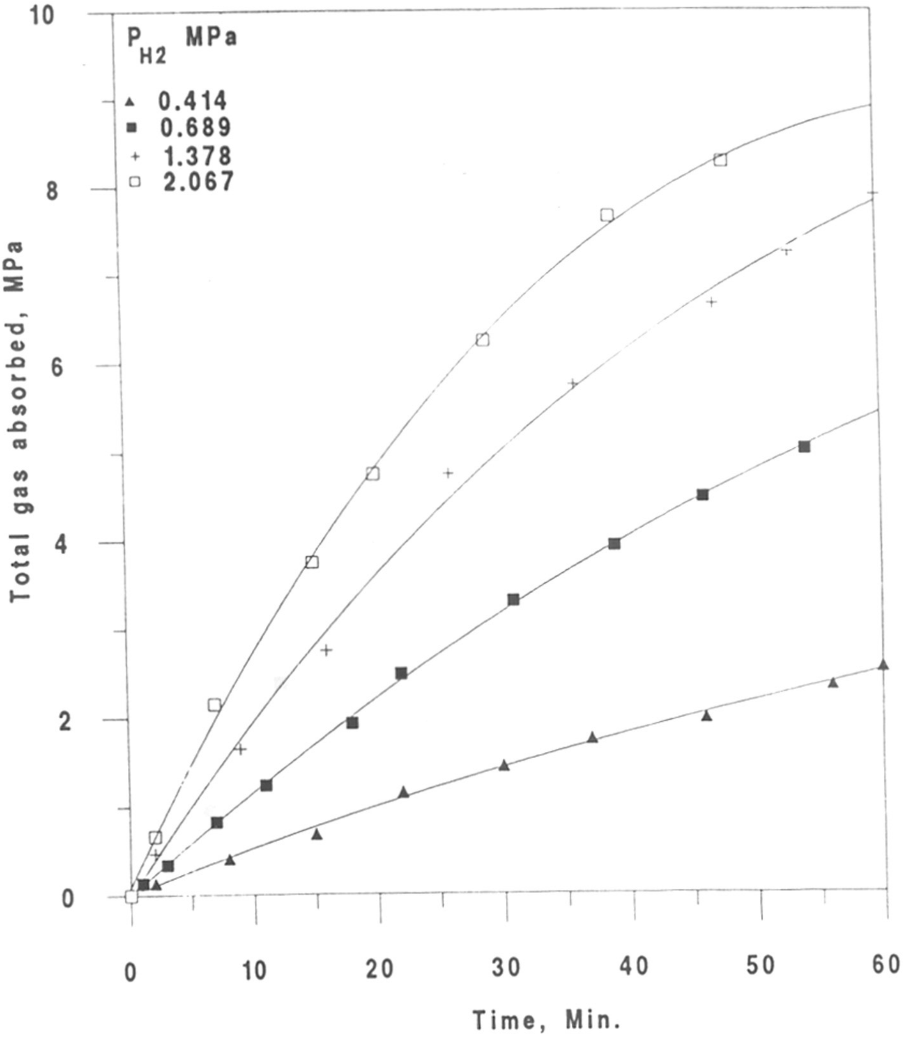


Fig. 4.22 A PLOT OF TOTAL GAS ABSORBED VS TIME EFFECT OF H_2 PRESSURE IN HYDROFORMYLATION OF ETHYLENE AT 353, K

Reaction conditions :
Concentration of catalyst : 2.03 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene : 0.689, MPa
Partial pressure of CO : 0.689, MPa
Catalyst : TPPTS ratio : 1 : 6
Reaction volume : 1.5 x 10^{-5}, m^3
Agitation speed : 25, rps

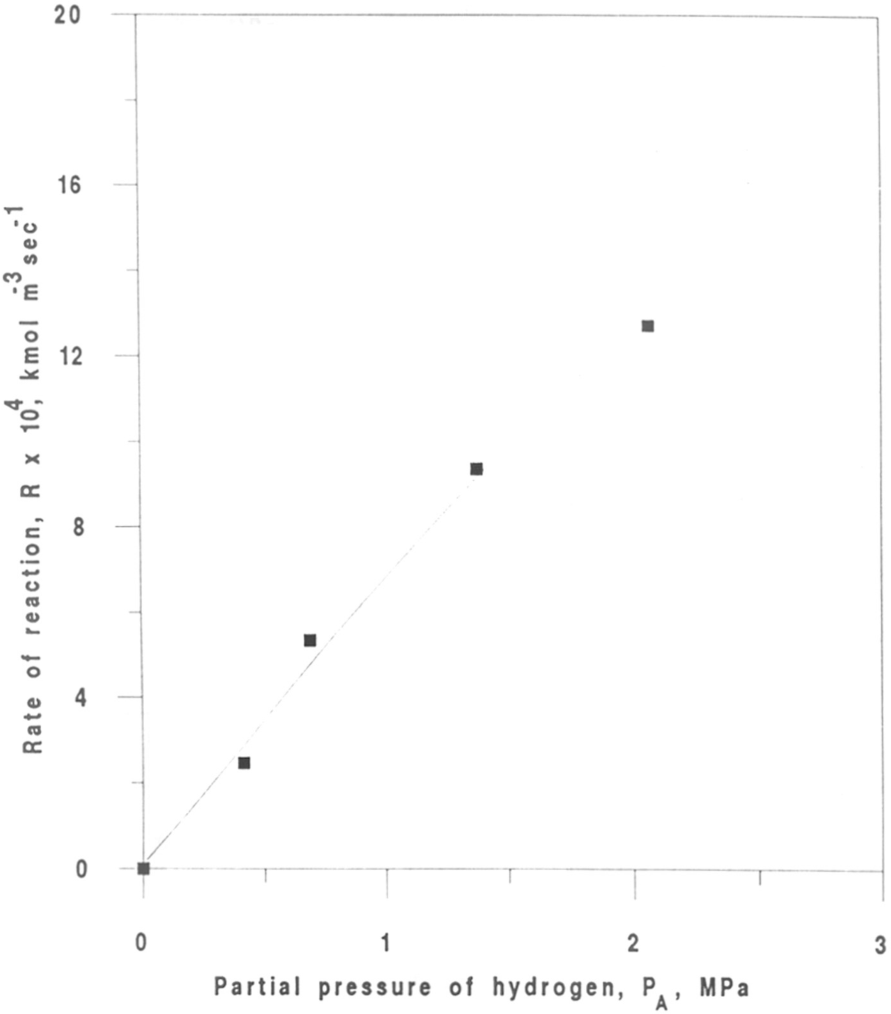


Fig. 4.23 EFFECT OF H_2 PRESSURE ON RATE OF HYDROFORMYLATION OF ETHYLENE AT 353, K

Reaction conditions :

Concentration of catalyst	: 2.03 x 10^{-3}, kmol m^{-3}
Partial pressure of ethylene	: 0.689, MPa
Partial pressure of CO	: 0.689, MPa
Catalyst : TPPTS ratio	: 1 : 6
Reaction volume	: 1.5 x 10^{-5}, m^3
Agitation speed	: 25, rps

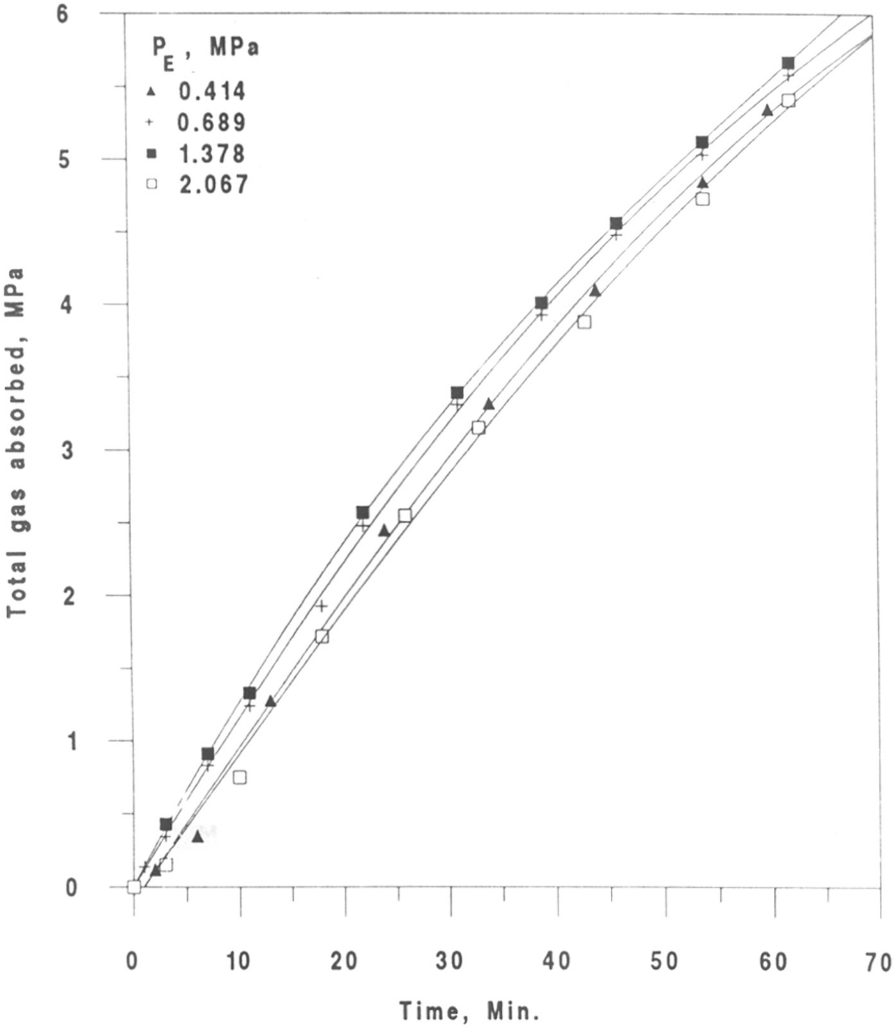


Fig. 4.24 A PLOT OF TOTAL GAS ABSORPTION VS TIME EFFECT OF ETHYLENE PRESSURE IN HYDROFORMYLATION OF ETHYLENE AT 353, K

Reaction conditions :

Concentration of catalyst	: 2.03×10^{-3}, kmol m^{-3}
Partial pressure of CO	: 0.689, MPa
Partial pressure of H_2	: 0.689, MPa
Catalyst : TPPTS ratio	: 1 : 6
Reaction volume	: 1.5×10^{-5}, m^3
Agitation speed	: 25, rps

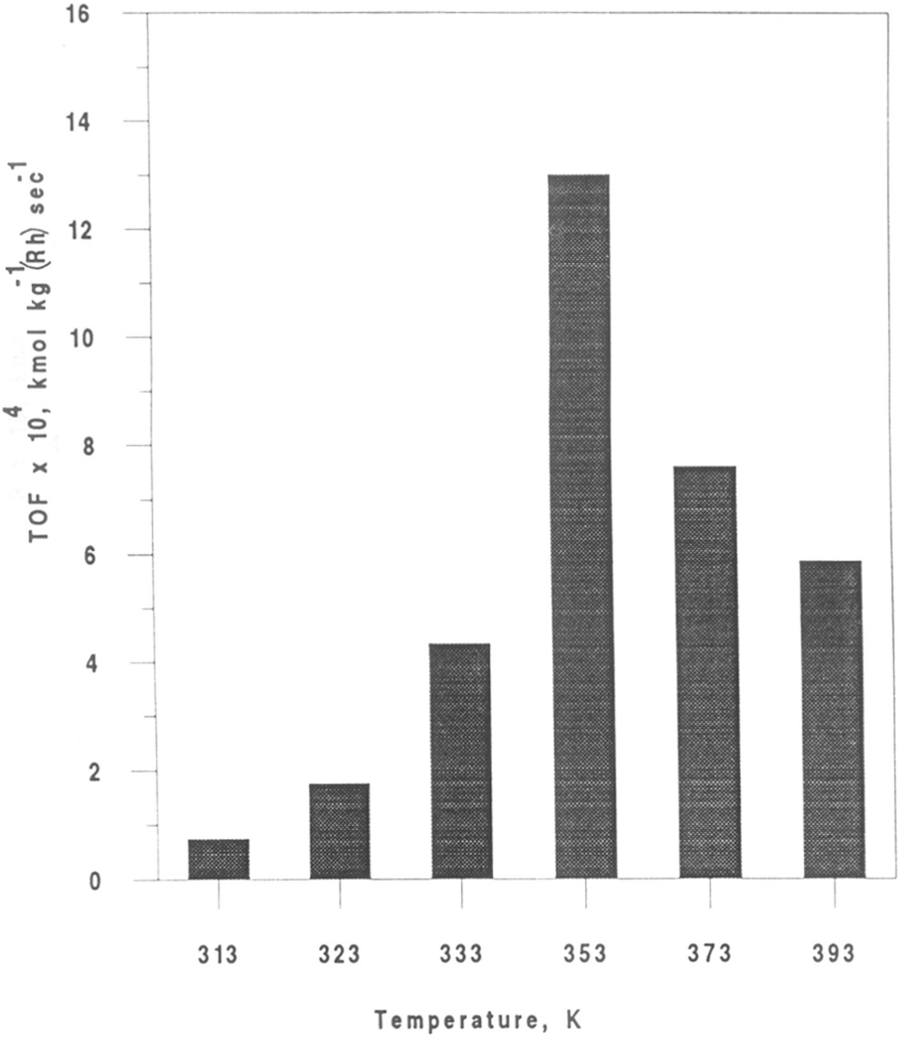


Fig. 4.26 EFFECT OF TEMPERATURE ON RATE OF HYDROFORMYLATION OF ETHYLENE

Reaction conditions :

Concentration of catalyst	: 2.03×10^{-3}, kmol m^{-3}
Partial pressure of Ethylene	: 0.689, MPa
Partial pressure of CO	: 0.689, MPa
Partial pressure of H_2	: 0.689, MPa
Catalyst : TPPTS ratio	: 1 : 6
Reaction volume	: 1.5×10^{-5}, m^3
Agitation speed	: 25, rps
Aqueous phase hold up	: 0.4.

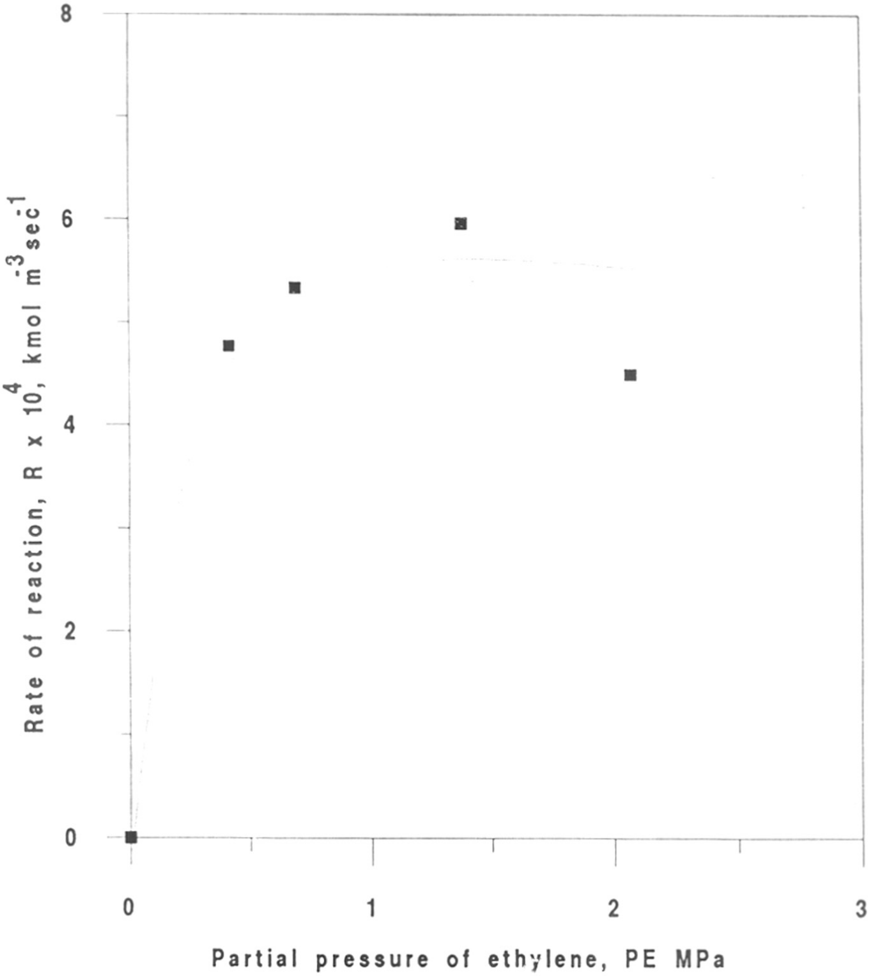


Fig. 4.25 EFFECT OF ETHYLENE PRESSURE ON RATE OF HYDROFORMYLATION OF ETHYLENE AT 353, K

Reaction conditions :

Concentration of catalyst	: 2.03×10^{-3}, kmol m^{-3}
Partial pressure of CO	: 0.689, MPa
Partial pressure of H_2	: 0.689, MPa
Catalyst : TPPTS ratio	: 1 : 6
Reaction volume	: 1.5×10^{-5}, m^3
Agitation speed	: 25, rps

rate on agitation speed at higher catalyst loading indicates that gas to liquid mass transfer is likely to be a rate limiting step rather than liquid-liquid mass transfer. The data at lower catalyst concentration (0.05, kmol/m^3) and above (15, rps) appears to be in the kinetic regime.

CONCLUSIONS:

The hydroformylation of ethylene using $[Rh(COD)Cl]_2$ - TPPTS catalyst system has been investigated in homogeneous (water) and biphasic media. In aqueous medium at 313, K the rate was found to be negative order with respect to CO and ethylene, whereas a linear dependence on hydrogen was observed. At higher catalyst concentration (> 1 x 10^{-3}, kmol/m^3) the rate was found to be strongly dependent on agitation indicating mass transfer limitations, while at a catalyst concentration of 5 x 10^{-4}, kmol/m^3, it was independent of agitation indicating kinetic control. The intrinsic kinetics was found to be represented by the following equation.

$$R = \frac{k\,(P_A/H_A)\,(P_B/H_B)\,(P_E/H_E)}{(1 + K_B(P_B/H_B))^2\,(1 + K_E(P_E/H_E))^2}$$

In the biphasic mode of operation, toluene was found to be the best organic phase. The rate was found to be strongly dependent on the cosolvent added (ethanol) and passed through a maximum with increase in cosolvent concentration. The rate behaviour with aqueous phase hold up also showed a maximum indicating that the reaction at liquid-liquid interface is predominent. The apparent reaction orders with P_{H2} and $P_{ethylene}$ were found to be 1 and zero respectively. A strong inhibition in the rate with increase in P_{CO} and TPPTS concentration was observed. The general trends observed have been explained on the basis of a proposed mechanism.

APPENDIX

$[A^*]$ concentration of H_2 in water at the gas-liquid interface (kmol m^{-3})

$[B^*]$ concentration of CO in water at the gas-liquid interface kmol m^{-3})

$[E^*]$ concentration of ethylene in water at the gas liquid interface (kmol m^{-3})

[C] concentration of catalyst (kmol m^{-3})

$[H_A]$ Henry's law constant for the H_2-water system (MPa m^3 $kmol^{-1}$)

$[H_B]$ Henry's law constant for the CO-water system (MPa m^3 $kmol^{-1}$)

$[H_E]$ Henry's law constant for the ethylene - water system (MPa m^3 $kmol^{-1}$)

[k] Reaction rate constant (m^6 $kmol^{-2}$ sec^{-1})

$[K_B]$ Constant in eq.(4.5) (m^3 $kmol^{-1}$)

$[K_E]$ Constant in Eq.(4.2) (m^3 $kmol^{-1}$)

$[P_{H2}]$ Partial pressure of hydrogen (MPa)

$[P_{CO}]$ Partial pressure of carbon monoxide (MPa)

$[P_E]$ Partial pressure of ethylene (MPa)

[R] Rate of hydroformylation (kmol $m^{-3}sec^{-1}$)

[T] Reaction temperature (K)

[t] Time (sec)

$[V_g]$ Volume of the reservoir, (m^3)

$[V_L]$ Volume of the liquid reactants, (m^3)

$[\Phi_{min}]$ Minimized sum of the squares of the difference between observed and predicted rates

REFERENCES

Bartik T., Bartik K. and Hanson B. E. J. Mol. Catal. **38**, 43, (1994).

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

Chaudhari R.V., Bhanage B.M., Deshpande R.M. and Delmas H., Nature, **373**, 501, (1995a).

Chaudhari R.V., Bhattacharya A. and Bhanage B.M., Catal. Today, **24**, 123, (1995b)

Chaudhari R. V. and Doraiswamy L. K., Chem. Eng. Sci. **29**, 349, (1974).

Chaudhari R. V., Gholap R. V., Emig E. and Hoffman H., Can. J. Chem. Eng. **65**(5), 744, (1987).

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

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

Dror Y. and Manassen J. J.Mol. Catal. **2**, 219 (1977).

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

Fell B. and Papadogiankis G. J. Mol. Catlal. **66**, 143, (1991).

Froment G. F., AIChE J. **21**(6), 1041, (1975).

Froment G. F., and Bishoff K. B., `Chemical Reactor Analysis and Design', J. Wiley, New York, 2nd Edn. (1990).

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

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

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

Jenck J.F. and Morel D., US Patent US 4688824, (1987).

Joo F. and Toth Z., J. Mol. Catal. **8**, 369, (1980).

Monteil F., Ph.D. Thesis, Toulouse, (1993).

Purwanto P. Ph. D. Thesis, INP Toulouse (1994).

Smith R. T., Ungar R. K. and Baird M. C., Trans. Metal. Chem. 7, 288, (1982).

Wilson M. E. amd Whitesides G. M., J. Am. Chem. Soc. **100**, 306, (1978).