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[A], $C_A$ = concentration of $H_2$ in liquid, (in M)

$A_i$, $C_{Ai}$ = concentration of $H_2$ in the interphase

B = carbon monoxide (CO)

[B], $C_B$ = concentration of CO, (in M)

$C_{Bi}$ = concentration of CO in the interphase

C = catalyst concentration, (in M)

D = 1-hexene concentration, (in M)

$H_A$ = Henry law constant for $H_2$ï benzene system, (in $barM^{-1}$)

$H_B$ = Henry law constant for COï benzene system, (in $barM^{-1}$)

$r_i$ = rate of reaction with the respective species, (in M.sec.)

k = reaction rate constant

$k_{la}$ = gas-liquid mass transfer coefficient, (in $sec^{-1}$)

Ki = equilibrium constants with the respective species

$pH_2$ = partial pressure of hydrogen, (in bar)

pCO = partial pressure of carbon monoxide, (in bar)

E = activation energy

$E_0$ = pre-exponential factor

R = gas constant

T = reaction temperature

N = agitation speed, rpm

$D_t$ = diameter of tank, (in meter)

$D_i$ = diameter of impeller, (in meter)

$\phi$ = enhancement factor

$\phi_{min}$ = minimized sum of square of errors between calculated and experimental rates

cal. = predicted values by kinetic models

exp. = observed values by kinetic experiments

e = experimental error

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ylation reaction has been applied commercially for almost five decades yet, its reaction mechanism and the kinetics have not been elucidated with much detail. Many aspects of the proposed reaction pathways are still under investigation. Extensive studies have appeared in the hydroformylation literature dealing with catalyst, ligands, substrate, product distributions, *in-situ* spectroscopic analysis of catalytic cycles on a molecular level. On the other hand, the kinetic and modeling aspects and their consequences in the reaction engineering, for the development of the rate laws, which are obviously crucial factors for controlling various steps of this industrially important reaction, drew rather less attention [1-6] of research community. For ethylene and propylene hydroformylation reactions, some knowledge has been gathered about macro-kinetic influences of temperature, pressure, composition of syn-gas and the catalyst concentration. However, rather little information is available on micro-kinetics influences like rate laws and the conclusions about the rate determining steps (r. d. s.). The knowledge of intrinsic reaction kinetics and development of rate equations are the most essential part of reaction engineering studies, which aim to evolve strategy for reactor designs. For that, kinetic modeling of catalytic reactions is one of the key investigations in order to understand the rate behavior of catalytic reactions as well as reaction mechanism.

As a first step in kinetic modeling, it is important to consider the reaction mechanism for any given system. The mechanism of homogeneous catalytic reactions is highly complex, even if, only a single reaction is involved, since the catalytic cycle consists of several stoichiometric reactions. The homogeneous catalytic reactions can be categorized as follows:

(i) single or multi-step reactions with only one catalytic component, the examples of this class are found in hydroformylation of olefins, oligomerization of ethylene using Ni complex catalyst, etc.

(ii) single or multi-step reactions with multi-component catalyst systems, for example Wacker process for oxidation of ethylene to acetaldehyde using $PdCl_2/CuCl_2$.

(iii) reactions involving two or more gas phase reactants with catalyst in solution, for examples hydroformylation, oxidative carbonylation and copolymerization, etc.

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without gas phase reactants and catalyst being soluble in nples hydroformylation, carbonylation, hydrogenation etc. using water soluble metal complex catalysts.

Due to the various complexities involved as mentioned in the above examples, the kinetics of such reactions are often represented by non-linear rate equations, some are purely empirical and some are derived based on reaction mechanisms. In some cases, a close analogy to the rate equations used in heterogeneous catalysis (e.g. based on Langmuir-Hinshelwood mechanism) is observed except that in homogeneous catalysis the mechanisms considered involve molecular level description of the catalytic intermediate species. For some cases like hydroformylation reactions, even though the catalytic cycle is reasonably well established, the rate equations used are empirical due to complexities such as substrate inhibition with carbon monoxide. However, it would be more appropriate to develop rate equations using a molecular level basis and correlate the observed trends with the established mechanism of the hydroformylation reactions.

The triphenylphosphine ligand and its derivatives are most cited ligands in the metal complex catalysts and is most investigated ligand for the kinetic and mass-transfer studies of the hydroformylation of olefins. The use of the other ligands of Group (V) elements (like $AsPh_3$), in the kinetic and mass-transfer studies of the hydroformylation of olefins, is not available in the literature. The lower basicity of $AsPh_3$ compared to $PPh_3$ is expected [7-8] to result into faster rates for the hydroformylation reaction with $AsPh_3$ based catalysts. In fact, few recent interesting studies [9-10] in the hydroformylation of olefins showed higher catalytic activity of metal complexes with arsine ligands. In addition to that during our comparative studies [11-12] on hydroformylation of 1-hexene and ethylene with Rh, Co, Ru and Pd complexes with ligands of Group (V) elements, $PPh_3$, $AsPh_3$ and $SbPh_3$, an identical activities for Rh/$PPh_3$ and Rh/$AsPh_3$ catalyst systems was observed, with former showing higher n/iso ratio of aldehydes.

The present chapter concerns with the first report on the kinetic and mass transfer analysis of the hydroformylation of 1-hexene using $RhCl(AsPh_3)_3$ as a catalyst. The synthesis of complex $RhCl(AsPh_3)_3$, an analogue of $RhCl(PPh_3)_3$ has been reported by Wilkinson et al. [13] but they have not studied the kinetics and mass-transfer studies of the hydroformylation reaction with this complex.

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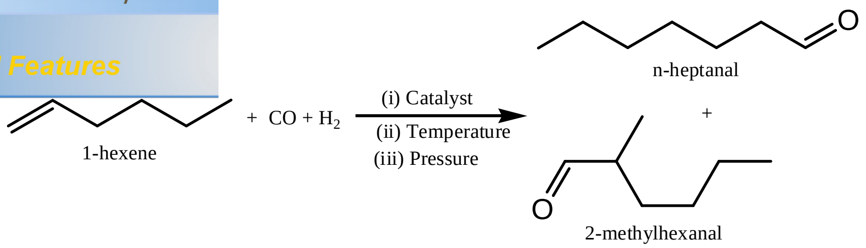

The effect of variations of, concentration of 1-hexene and catalyst, partial pressure of CO and $H_2$, reaction temperature and agitation speed on the rate of hydroformylation as well as their effects on the n/iso ratio of heptanal formed has been studied. Finally, a rate equation has been anticipated based on the rate data. It was observed that on increasing the temperature the conversion of 1-hexene and selectivity towards the aldehydes decreased significantly. This could be due to the deactivation of catalyst on increasing temperature. The deactivation studies for the hydroformylation catalyst $HRh(CO)(PPh_3)_3$, [14-18] have shown the decomposition of the complex which resulted into the formation of by-products. Therefore, deactivation of $RhCl(AsPh_3)_3$ catalyst due to thermal pretreatment was also studied.

## 4.2. Experimental

### 4.2.1. Materials

1-Hexene (99.9%), benzene (99.8%) and n-decane (99.9%) were purchased from Sigma-Aldrich, U.S.A. Rhodium trichloride ($RhCl_3.3H_2O$) and tripheneylarsine ($AsPh_3$), were procured from E. Merck, U.S.A. CO (99.8%) and $H_2$ (99.8%) were purchased from Alchemie Gases and Chemicals Pvt. Ltd., India.

### 4.2.2. Synthesis and characterization of $RhCl(AsPh_3)_3$

The detail about the synthesis and characterization of the $RhCl(AsPh_3)_3$ complex is given in Chapter 3, section 3.2.2.

### 4.2.3. Hydroformylation reaction

The particulars of the autoclave reactor are given in Table 4.1. The detail experimental, operational and safety procedures for conducting hydroformylation reactions in autoclave reactor has already been described in Chapter 2, Section 2.2.7.1.

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ave reactor

| lars | Dimensions |
|---|---|
| Tank capacity | $1 \times 10^{-4}$ $m^3$ |
| Tank diameter (inside) | 46 mm |
| Tank depth | 84 mm |
| Impeller height | 67 mm |
| Blade diameter | 35 mm |
| Impeller diameter | 20.5 mm |

In a typical kinetic experiment, the desired quantity of 1-hexene, catalyst, *n*-decane (as an internal Gas Chromatography standard) dissolved in benzene solvent (50 ml) were charged in the autoclave. The reactor was then brought to desired reaction temperature. The autoclave was flushed twice with $N_2$ prior to successively introducing CO and $H_2$ at a desired pressure. At that time, a sample of the reaction mixture was withdrawn, which was considered as zero time reading. The hydroformylation reaction was then initiated by starting the magnetic stirrer. The reaction was then continued at constant pressure, by supplying carbon monoxide and hydrogen (1:1) from the reservoir vessel. When the supply of carbon monoxide and hydrogen was done from the separate cylinders instead of the reservoir, the carbon monoxide was introduced into the reactor before the supply of $H_2$ to avoid hydrogenation and isomerization as side reactions. For kinetic studies, liquid samples were withdrawn at a regular time interval during the course of the experiment from the sampling valve of the autoclave reactor. A total number of six samples were taken during a typical five-hour experimental run. The sampling during the course of the reaction resulted a pressure loss of 2-3 psi each time; thus, the total pressure loss in the reactor was normally in the range of approximately 1-1.5 bar during the course of the reaction corresponding to maximum of 1-4% change in the total reaction pressure. After the set reaction time, the reaction was quenched by disconnecting the gas supply to the reactor. The autoclave was then brought to room temperature, the pressure drops were noted.

#### 4.2.3.1. Reaction mixture analysis

The reaction mixtures withdrawn during the course of the reaction were analyzed using Gas Chromatography (GC) (Shimadzu 17A, Japan); equipped with a 5% diphenyl

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niversal capillary column (60 m length and 0.32 mm

detector (FID). The column temperature was increased from 40 to 200$^0$C at the rate of 10$^0$C/min. $N_2$ gas (3.4 ml/min) was used as a carrier gas. The temperature of injection port and FID were kept constant at 200$^0$C during product analysis. The retention times for different compounds were determined by injecting pure compounds under identical conditions of Gas Chromatography.

### 4.2.4. Thermal deactivation study of $RhCl(AsPh_3)_3$ catalyst

The thermal deactivation studies were carried out with the partial pressure of carbon monoxide and hydrogen at 19.73 bar for each, 1-hexene concentration 0.5 M and catalyst concentration $20x10^{-5}$ M. The thermal heat treatment of catalyst $RhCl(AsPh_3)_3$ was done, for 60 minutes at 80$^0$C, 100$^0$C, 150$^0$C and 200$^0$C and also for 30 minutes at 150$^0$C and 200$^0$C. Except the temperatures, all other parameters were kept same during these experimental runs.

In a typical deactivation experiment, the desired quantity of the catalyst dissolved in benzene (50 ml) was charged in the autoclave. The autoclave was twice flushed with nitrogen prior to successively introducing CO and $H_2$ at desired pressure. The reactor was then brought to pre-decided temperatures of heat-treatment and the reaction was initiated by starting the stirrer. The starting time of magnetic stirrer was considered as zero time. After a set reaction time, the reaction mixture was cooled to room temperature within five minutes (through internal cooling system of reactor) to avoid any side reaction during long run cooling period. Then 0.5 M of 1-hexene along with known amounts of *n*-decane as an internal standard was charged in the reactor and the conventional hydroformylation reaction as described in section 4.2.3 was started.

### 4.2.5. Reproducibility and material balance

In order to ensure the reproducibility of hydroformylation of 1-hexene with $RhCl(AsPh_3)_3$ catalyst, four experiments of hydroformylation of 1-hexene under identical conditions were done. The results obtained, including conversions, selectivities and n/iso ratio of formation of aldehydes, were found to be within less than 10% variation, confirming the reproducibility of results. In order to see the material balance of the reaction, the amounts of products formed and amount of 1-hexene and $CO+H_2$ consumed were compared. The material balance of $CO+H_2$ consumed was consistent with heptanal

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owards the aldehyde was 92ï 98% during all the kinetic consumption of reactants and formation products, shown in Figure 4.1. The Table 4.2. represents the material balance with respect to 1-hexene consumption.

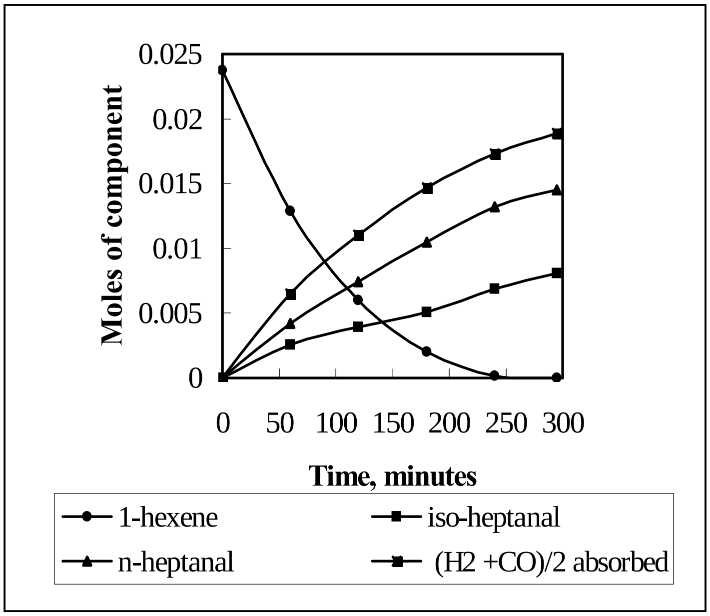

**Figure 4.1.** Concentration profile of 1-hexene hydroformylation at [1-hexene] = 0.5 M; [catalyst] = 20.00 x $10^{-5}$ M; p(CO) = 19.73 bar; p($H_2$) = 19.73 bar; Temperature = $80^0$C and agitation speed = 850 rpm.

**Table 4.2.** Material balance of hydroformylation of 1-hexene using $RhCl(AsPh_3)_3$ catalyst

| Run | 1-Hexene x$10^2$, (mol) | | Partial pressure of CO and $H_2$, (bar) | | Aldehyde x$10^2$, (mol) | Material balance 1-hexene (%) |
|---|---|---|---|---|---|---|
| | Initial | final | CO | $H_2$ | | |
| 1 | 1.18 | 0.0 | 19.74 | 19.74 | 1.16 | 98.30 |
| 2 | 1.78 | 0.0 | 19.74 | 19.74 | 1.70 | 95.50 |
| 3 | 2.14 | 0.0 | 19.74 | 19.74 | 1.97 | 92.05 |
| 4 | 2.38 | 0.0 | 19.74 | 19.74 | 2.25 | 94.53 |
| 5 | 4.75 | 0.0 | 19.74 | 19.74 | 4.50 | 94.74 |
| 6 | 9.50 | 0.0 | 19.74 | 19.74 | 9.10 | 95.78 |

*Reaction Conditions*: [$RhCl(AsPh_3)_3$] = 20.0x$10^{-5}$ M, Temperature = $80^0$C, rpm = 850.

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might have pronounced effects on the rate of 1-hexene hydroformylation reaction, include concentration of 1-hexene and catalyst, partial pressure of carbon monoxide and hydrogen, agitation speed and the reaction temperature. The experiments were carried out by varying these parameters. In each case, amounts of 1-hexene, CO+$H_2$ consumption were measured at a fixed time interval. The change in concentration of 1-hexene was determined by GC analysis while carbon monoxide and hydrogen concentrations were determined using the known initial concentrations combined with the reaction stoichiometry by knowing the moles of aldehydes formation. The rate of reaction was calculated by plotting the concentration of 1-hexene with time, which gave a polynomial fit, and the kinetic analysis was carried out by differential method. By taking the slope at different concentration points with respect to time, these slopes gave the change in concentration of 1-hexene (M) with time ($-dC_A/dt$ = reaction rate). The range of conditions used for kinetic analysis is given in Table 4.3.

**Table 4.3.** Ranges of conditions studied for the kinetics of hydroformylation with $RhCl(AsPh_3)_3$ catalyst

| | |
|---|---|
| Concentration of 1-hexene, M | 0.25 - 1.95 |
| Concentration of catalyst, M | $4.92 \times 10^{-5}$ - $49.20 \times 10^{-5}$ |
| Reaction temperature, ($^0$C) | 60 - 100 |
| pCO, bar | 2.0 ï 24.67 |
| $pH_2$, bar | 4.93 ï 29.61 |
| Solvent | Benzene |
| Reaction volume, ml | 50 |
| Agitation speed, rpm | 50 ï 850 |

### 4.2.7. Selectivity studies

It has been observed [11-12] during comparative studies of the ligands; $PPh_3$, $AsPh_3$ and $SbPh_3$ with the metals; Rh, Co, Ru and Pd for the hydroformylation of 1-hexene that the activity of $PPh_3$ and $AsPh_3$ ligands were similar with respect to conversions and selectivities. The only difference was the n/iso ratio of heptanal, which was higher for $PPh_3$ than those for $AsPh_3$ ligand. One of the interests for undertaking

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roformylation with $RhCl(AsPh_3)_3$ was to understand the n/iso of heptanal. Under present employed reaction conditions, heptanal and 2-methylhexanal were the major products formed upto 98% selectivity in 1-hexene hydroformylation with $RhCl(AsPh_3)_3$ complex catalyst. The formation of these aldehydes was investigated under varied reaction conditions.

Before discussing the results, it is worth noting that for the metal complexes in the hydroformylation reactions, either steric factor or electronic factor or combinations of both play a crucial role for determining the n/iso ratio of aldehydes. The formation of alkyl complex via addition of olefin to the hydrido metal complex may be Markownikov or *anti*-Markownikov and only the latter leads to formation of normal aldehydes [19-20]. The *anti*-Markownikov addition will be favored for highly branched hydridometal complex due to steric requirement. Due to electronic requirement, the mode of addition, however, will depend on the polarity of M-H bond and enhanced polarity favors Markownikov addition, which facilitates the formation of branched aldehydes.

## 4.3. Results and discussion

The experiments were carried out varying parameters namely; the concentrations of 1-hexene and catalyst, partial pressures of the carbon monoxide and hydrogen, temperature and agitation speed, which have pronounced affects on the rate of hydroformylation reaction. In each case the consumption of 1-hexene, carbon monoxide and hydrogen were observed at a fixed time interval.

The rate of reaction was calculated by plotting the typical concentration of 1-hexene with time (Figure 4.2.). This gives the polynomial fit and analysis was carried out by differential method. Then the slopes were calculated at different concentration points with respect to time, these slopes gave the change in concentration of 1-hexene (M) with time ($-dC_A/dt$; rate of reaction). By plotting the logarithm of rate and concentration (Figure 4.3.), data were used to determine the rate constant (k) and the order of reaction (n) as

$$-r_D = k\,(C_D)^n \qquad (4.1)$$

From equation (4.1), by taking log of both sides

$$\mathrm{Log}(-r_D) = \log k + n \log C_D \qquad (4.2)$$

and by comparing equation (4.2) to

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(4.3)

ives the order of reaction and C is the intercept at Y-axis (log k). Taking the antilog of intercept value gives the rate constant of reaction. A comparative look of dependency of the rate of hydroformylation reaction of 1-hexene with different parameters using RhCl(AsPh$_3$)$_3$ as a catalyst is shown in Figure 4.4.

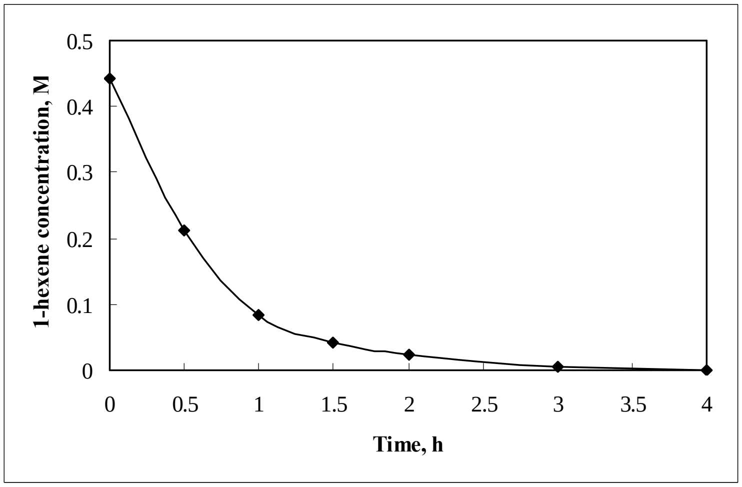

**Figure 4.2.** A typical of the plot of decrease of concentration of 1-hexene v/s time during the kinetic studies for the calculation of the rate of hydroformylation reactions using RhCl(AsPh$_3$)$_3$ as a catalyst.

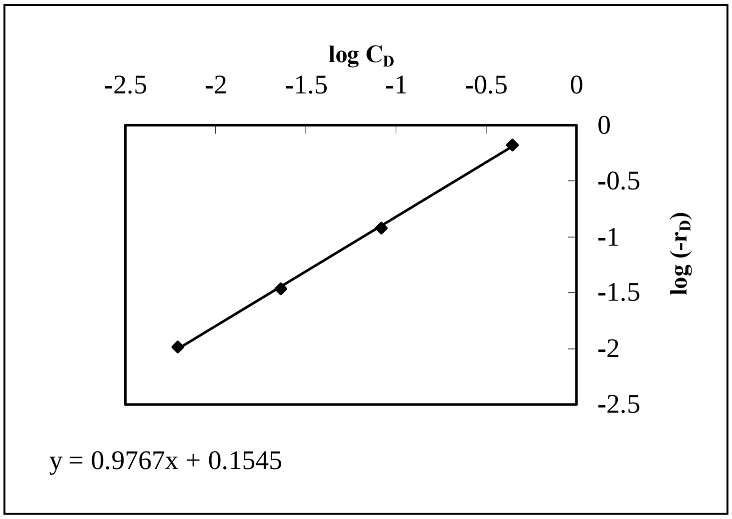

**Figure 4.3.** A typical of the plot of logarithm of concentration of 1-hexene v/s log rate of reaction during the kinetic studies for the calculation of the rate of hydroformylation reactions using RhCl(AsPh$_3$)$_3$ as a catalyst.

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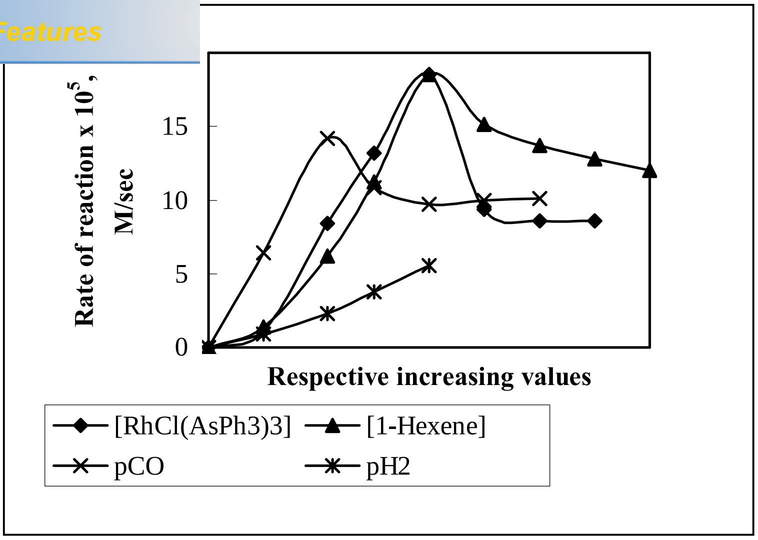

**Figure 4.4.** A comparative look of the hydroformylation rate profile with variation of, concentrations (M) of catalyst (4.92 x $10^{-5}$- 49.20 x $10^{-5}$) and 1-hexene (0.25-1.95), and partial pressure (bar) of hydrogen (4.93-29.61) and carbon monoxide (2.00-24.67) at $80^0$C and 850 rpm in which scales on x-axis are not given for brevity.

### 4.3.1. Effect of stirrer agitation speed on reaction rate

The effect of agitation speed on the rate of hydroformylation reaction using $RhCl(AsPh_3)_3$ catalyst was studied at a concentration of 1-hexene of 0.5 M, partial pressure of carbon monoxide 19.73 bar, partial pressure of hydrogen 19.73 bar, catalyst concentration $20x10^{-5}$ M and $80^0$C temperature. The agitation speed was varied from 50 to 850 rpm. The dependence of rate on agitation speed (Figure 4.5a) shows that rate of hydroformylation increased on increasing the agitation speed from 50 rpm to 100 rpm followed by a decrease with further increasing agitation speed before reaching a steady state. At lower agitation, the initial concentrations of dissolved gases are less, which indicated that the reaction is under diffusion control. On increasing the agitation speed the initial concentrations of dissolved gases get significantly increased [21] and concentration of dissolved CO in reaction mixture becomes higher as solubility of CO > $H_2$ in benzene, which leads to a decreased rate according to kinetic equation where CO concentration term is in denominator. The further increase in agitation speed approaches the kinetic regime, and the rate tends to be independent of agitation speed. Hence, all the other kinetic experiments were carried out at 850 rpm to ensure kinetic regime.

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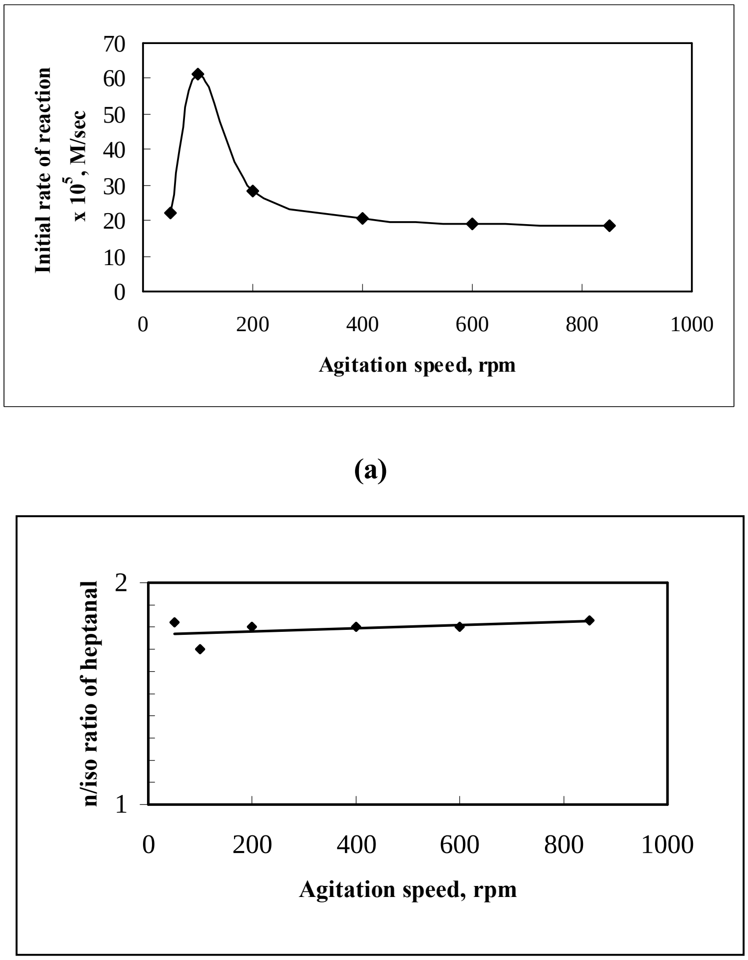
o ratio of formation of aldehyde on agitation speed is so ratio of heptanal was found to be nearly constant by varying the agitation speed from 50 to 850 rpm.



**(a)**

**(b)**

**Figure 4.5.** Effect of stirrer agitation speed on hydroformylation reaction at [1-hexene] = 0.5 M; [catalyst] = 20.00x$10^{-5}$ M; p(CO) = 19.73 bar; p($H_2$) = 19.73 bar; Temperature = $80^0$C and agitation speed = 50 - 850 rpm.

### 4.3.2. Effect of 1-hexene concentration on reaction rate

The effect of 1-hexene concentration on the rate of hydroformylation was studied at catalyst concentration 20.0x$10^{-5}$ M, partial pressure of carbon monoxide 19.73 bar, partial pressure of hydrogen 19.73 bar and $80^0$C temperature. The concentration of 1-hexene was varied from 0.25 to 1.95 M for the kinetic studies. The rates of reaction increased (Figure 4.6a) on increasing the concentration of 1-hexene up to a certain limit,

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with increasing concentration of 1-hexene. In the present howing substrate-inhibited kinetics for 1-hexene, which is an indication of an alteration of rate determining step and consequently a change in reaction pathway. Similar results were also reported for Rh/$PPh_3$ catalytic system [5]. The literature studies [22] reveal a positive dependence on olefin concentration until a critical substrate/catalyst ratio is reached, after which a negative or even independence is reported which is termed as saturation kinetics and is usually attributed to a shift in the rate-determining step.

The dependence of n/iso ratio of formation of heptanal is shown in Figure 4.6b. The n/iso ratio of heptanal was found to increase linearly on increasing 1-hexene concentrations. On increasing 1-hexene concentration 7.8-fold (from 0.25ï 1.95 M), the n/iso ratio was observed to increase 1.8-fold (from 1.4 to 2.6).

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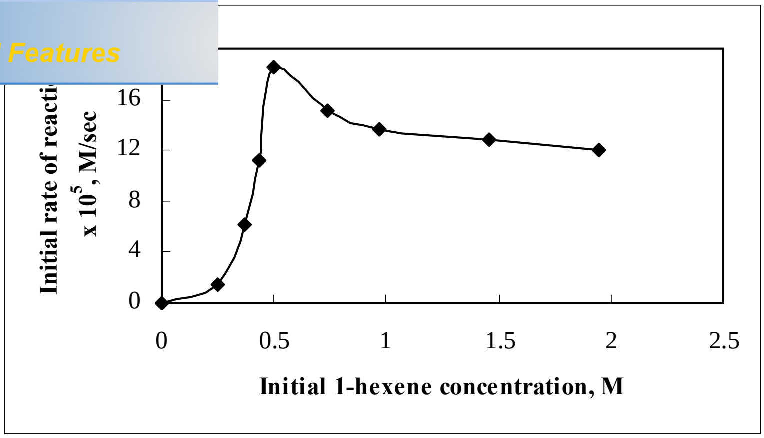
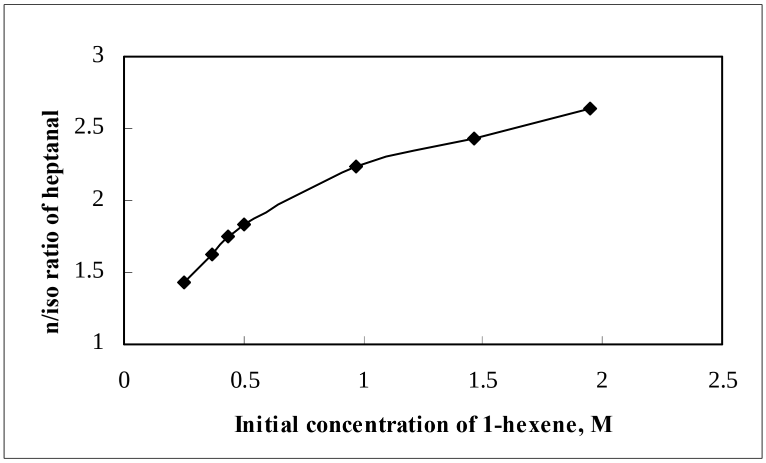


**(a)**



**(b)**

**Figure4.6.** Effect of 1-hexene concentrations on hydroformylation reaction at [1-hexene] = 0.25-1.95 M; [catalyst] = 20.00 x $10^{-5}$ M; p(CO) = 19.73 bar; p($H_2$) = 19.73 bar; Temperature = $80^0$C and agitation speed = 850 rpm.

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### tration on reaction rate

oncentration on the rate of hydroformylation of 1-hexene using $RhCl(AsPh_3)_3$ catalyst was studied at a concentration of 1-hexene of 0.5 M, partial pressure of carbon monoxide 19.73 bar, partial pressure of hydrogen 19.73 bar and $80^0C$ temperature. The concentration of catalyst was varied from $4.92 \times 10^{-5}$ M to $49.2 \times 10^{-5}$ M for the kinetic studies. The observed trend on the effect of catalyst concentration (Figure 4.7a) on the rate of reaction shows that, initially, the rate of hydroformylation increases on increasing catalyst concentration up to $20.0 \times 10^{-5}$ M followed by a decrease and then become independent of catalyst concentration. It is observed that there is a critical catalyst concentration ($4.92 \times 10^{-5}$ M) for the $RhCl(AsPh_3)_3$ catalyst below which reaction does not proceed. Chaudhari et al. [5] report similar observation in their study with $Rh/PPh_3$. However, in the present case it was also observed that above a certain catalyst concentration of $RhCl(AsPh_3)_3$, the rate of hydroformylation of 1-hexene is independent of the catalyst concentration. These observations can be explained in terms of the different Rh-intermediate species present at various catalyst concentrations. According to the equilibrium (shown below) at very low catalyst concentration the concentration of species (I) will be abundant which is less active towards hydroformylation and hence the rate is slow or even zero. On the other hand, at very high catalyst concentration, the concentration of less active species (III) for hydroformylation is dominant. Since, $AsPh_3$ has lower basicity than $PPh_3$, Rh-As bond in $RhH(CO)(AsPh_3)_2$ is easier to break than Rh-P bond in $RhH(CO)(PPh_3)_2$. Therefore, metal-ligand bond will be more sensitive towards catalyst concentrations with $AsPh_3$ as a ligand.

$$\underset{\substack{\textbf{I}\\ \text{Less active}}}{RhH(CO)(AsPh_3)_3} \xrightleftharpoons{-\ AsPh_3} \underset{\substack{\textbf{II}\\ \text{Highly active}}}{RhH(CO)(AsPh_3)_2} \xrightleftharpoons{-\ AsPh_3} \underset{\substack{\textbf{III}\\ \text{Less active}}}{RhH(CO)(AsPh_3)}$$

The trend of n/iso ratio with catalyst concentrations is shown in Figure 4.7b. Unlike, $Rh/PPh_3$ system [19-20] the n/iso ratio with the present $Rh/AsPh_3$ system decreases on increasing catalyst concentrations. The n/iso ratio of heptanal falls from 2.5 to 1.5 by increasing catalyst concentration from $4.92 \times 10^{-5}$ to $49.20 \times 10^{-5}$ M. Since, on increasing the catalyst concentration, the concentration of the ligand $AsPh_3$ having higher

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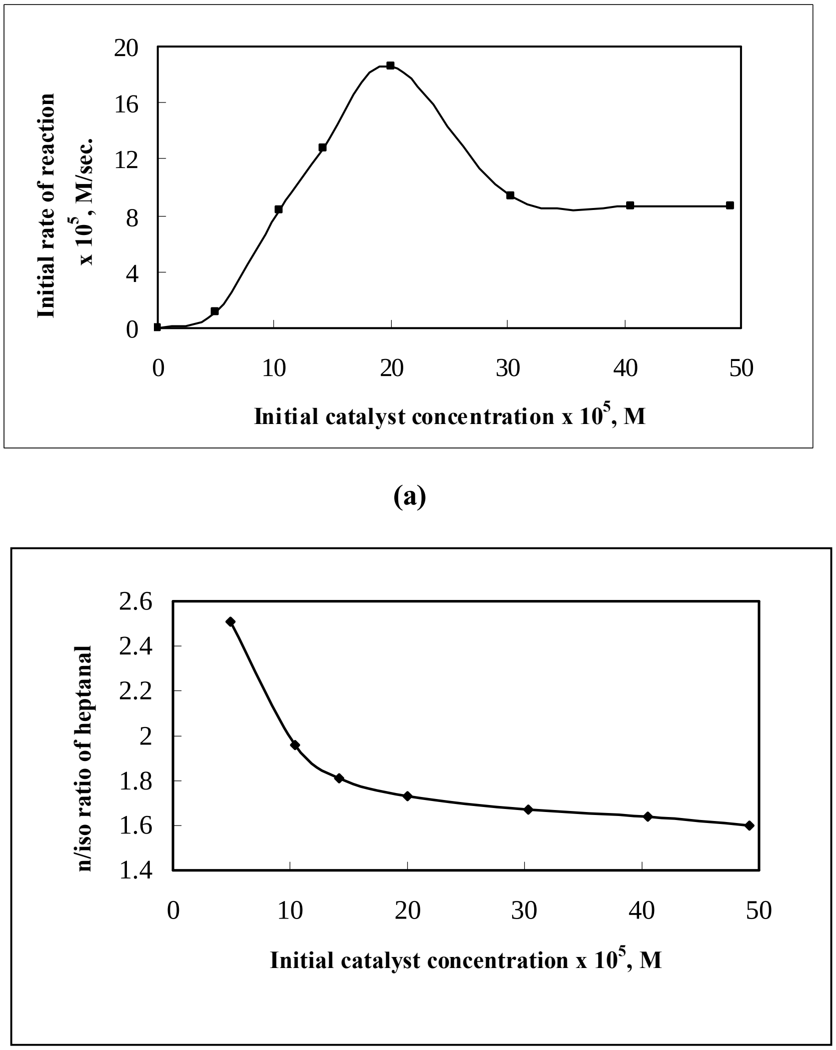
onsequently, the polarity of M-H bond will increase [19- the extent of Markownikov addition. Hence, the enhanced concentration of π-acidic $AsPh_3$, favors Markownikov addition lowering n/iso ratio for the aldehydes.



**(a)**

**(b)**

**Figure 4.7.** Effect of catalyst concentrations on hydroformylation reaction at [1-hexene] = 0.5 M; [catalyst] = 4.92 x $10^{-5}$ to 49.2 x $10^{-5}$ M; p(CO) = 19.73 bar; $p(H_2)$ = 19.73 bar; Temperature = $80^0$C and agitation speed = 850 rpm.

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### e of carbon monoxide on reaction rate

ssure of carbon monoxide on the rate of hydroformylation of 1-hexene using $RhCl(AsPh_3)_3$ catalyst was studied at $20x10^{-5}$ M concentration of catalyst and 0.5 M, 1-hexene concentration, at partial pressure of hydrogen 19.73 bar and $80^0C$ temperature. The partial pressure of carbon monoxide varied from 2.0 to 24.67 bar. The rates of hydroformylation increases up to certain limit and followed by a decrease on further increasing the CO partial pressure (Figure 4.8a). A rate inhibition trend at higher partial pressure of CO confirms the formation of hydroformylation inactive acyl species, $(RCO)Rh(CO)_2(AsPh_3)_2$ and/or $(RCO)Rh(CO)_3(AsPh_3)$. At higher partial pressure of CO, the concentration of hydroformylation inactive acyl species is higher and an inhibited kinetics was observed. The rate of hydroformylation is also reported [23] to increase with decrease in basicity of the ligand. Hence, some deviation from the conventional mechanistic pathway of hydroformylation reaction may be expected with $Rh/AsPh_3$ catalyst system than those for $Rh/PPh_3$ system. Additionally, Erkey et al. [22] have also reported, in the case of less basic ligands, there may be some possibility of shifting of rate determining step. The first possibility is that the rate-determining step is the dissociation of CO from species 1 (Scheme 4.1.). The alkyl intermediate species 5 (Scheme 4.1.) becomes more dominant species as the basicity of ligand decreased. This was attributed to a shift in the rate-determining step from dissociation of CO from species 1 to a step after formation of species 5 (Scheme 4.1.) for less basic intermediate complex because of weakening of Rh-carbonyl bond due to decreased basicity of ligand.

The dependence of n/iso ratio of formation of heptanal is shown in Figure 4.8b. For $Rh/AsPh_3$ system, the n/iso ratio of heptanal was found to decrease on increasing partial pressure of CO. The n/iso ratio drops down from 2.5 to 1.7 on increasing the partial pressure of CO from 2.00 to 24.67 bar The highest n/iso ratio of heptanal was obtained at lowest partial pressure of CO. Generally, it is assumed that at low partial pressure of CO, the metal centre becomes sterically more crowded. Accordingly, the formation of *n*-aldehyde is favored through *anti*-Markownikov addition.

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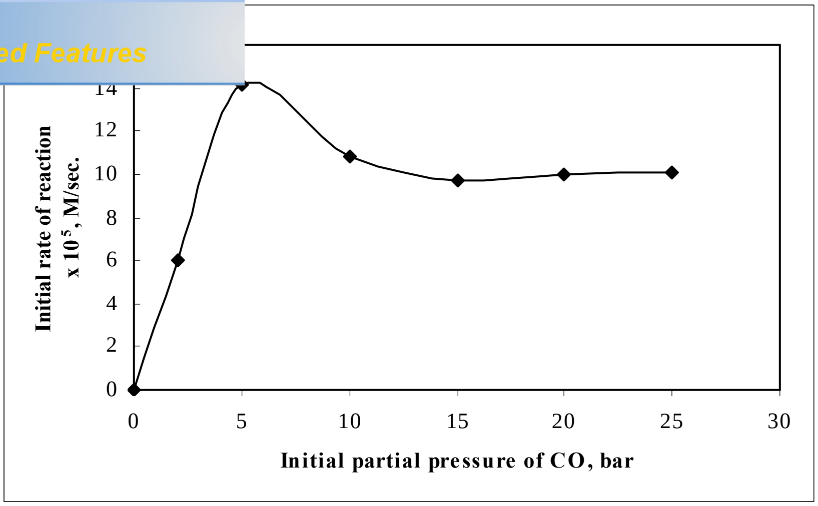
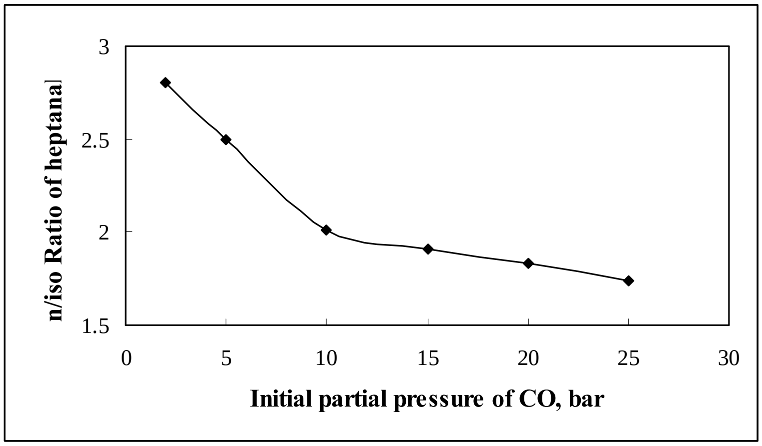


**(a)**



**(b)**

**Figure 4.8.** Effect of partial pressure of carbon monoxide on hydroformylation reaction at [1-hexene] = 0.5 M; [catalyst] = 20.00 x $10^{-5}$ M; p(CO) = 2.00ï 24.67 bar; p($H_2$) = 19.73 bar; Temperature = $80^0$C and agitation speed = 850 rpm.

### 4.3.5. Effect of partial pressure of hydrogen on reaction rate

The effect of partial pressure of hydrogen on the rate of hydroformylation of 1-hexene using $RhCl(AsPh_3)_3$ catalyst was studied at $20x10^{-5}$ M concentration of catalyst, 0.5 M 1-hexene concentration, at partial pressure of carbon monoxide 19.73 bar and $80^0$C temperature. The partial pressure of hydrogen was varied from 4.93 to 29.61 bar. The rate of hydroformylation was found (Figure 4.9a) to increase on increasing partial pressure of hydrogen. The observed first-order dependence of rate of hydroformylation of 1-hexene using $RhCl(AsPh_3)_3$ as a catalyst with respect to partial pressure of hydrogen confirms,

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ition of hydrogen to acyl complex $(RCO)Rh(CO)(AsPh_3)_2$
luring the complete catalytic cycle.

The effect of n/iso ratio of formation of heptanal is shown in Figure 4.9b. Unlike Rh/$PPh_3$ system [19-20], the n/iso ratio of aldehyde decreases on increasing partial pressure of hydrogen. The n/iso ratio of heptanal falls from 2.8 to 1.9 on increasing partial pressure of hydrogen from 4.93 to 29.61 bars. In the present experimental runs, it was observed that lower partial pressure of hydrogen (<9.87 bar) favors side reactions, because at lower partial pressure of hydrogen, concentration of carbon monoxide is sufficient (at 19.73 bar) in the reactor, which inhibits the formation of the active species and hence the hydroformylation reaction becomes slow. Higher partial pressure of hydrogen gives the higher rate of reaction because of more active species formation. The selectivity for aldehyde formation was increased on increasing the partial pressure of hydrogen. At lower partial pressure of hydrogen, the aldehydes formation was low due to above mentioned and discussed reasons.

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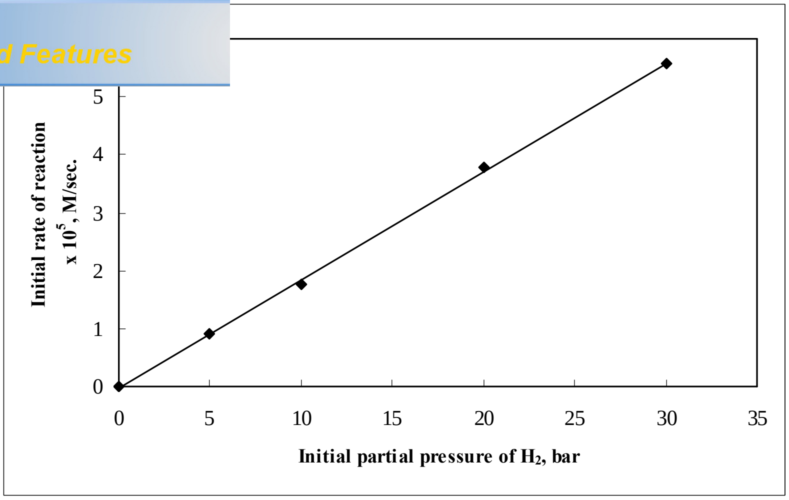

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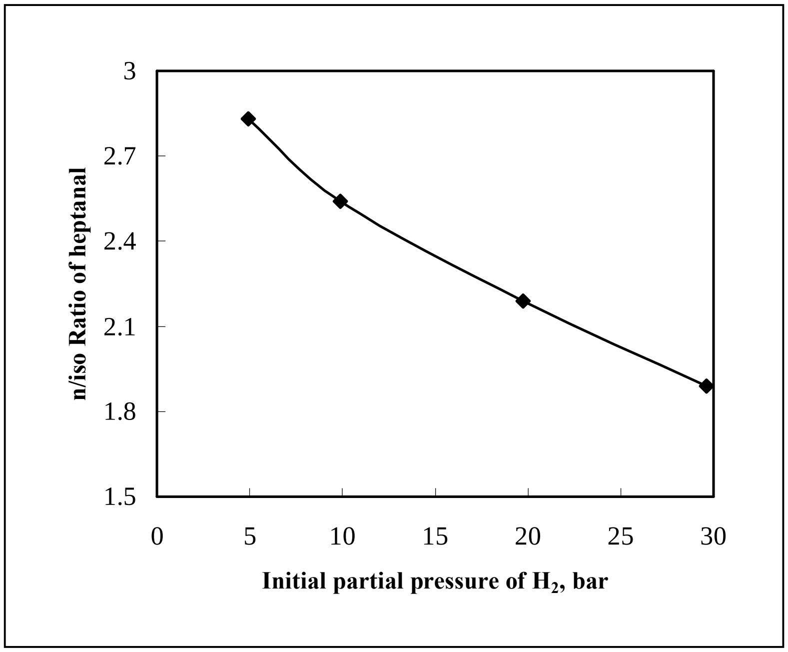

**(b)**

**Figure4.9.** Effect of partial pressure of hydrogen on hydroformylation reaction at [1-hexene] = 0.5 M; [catalyst] = 20.00 x $10^{-5}$ M; p(CO) = 19.73 bar; p($H_2$) = 4.93 - 26.61 bar; Temperature = $80^0$C and agitation speed = 850 rpm.

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### due to heat treatment

of $HRh(CO)(PPh_3)_3$ [14-18] in the absence of $H_2$ and CO leads to stable rhodium cluster which is inactive towards hydroformylation reactions. Under hydroformylation reaction conditions, other products such as benzaldehyde, benzene, and diphenylpropylphosphine are found, which are due to deactivation of the catalyst. In present case, the deactivation studies for the catalyst $RhCl(AsPh_3)_3$ have done under hydroformylation reaction conditions. The results obtained are given in Table 4.4.

**Table 4.4.** The consumption of 1-hexene with time after pre-heat treatment of the catalyst $RhCl(AsPh_3)_3$

| Time (minutes) | Concentration of 1-hexene (M) | | | | | |
|---|---|---|---|---|---|---|
| | $80^{0}$C/ 1.0h | $100^{0}$C / 0.5h | $150^{0}$C/ 0.5h | $150^{0}$C/ 1.0h | $200^{0}$C/ 0.5h | $200^{0}$C/ 1.0h |
| 0 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| 60 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| 120 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 | 0.50 |
| 180 | 0.28 | 0.33 | 0.37 | 0.41 | 0.50 | 0.50 |
| 240 | 0.10 | 0.14 | 0.18 | 0.23 | 0.50 | 0.50 |
| 300 | 0.06 | 0.08 | 0.17 | 0.20 | 0.39 | 0.49 |

*Reaction Conditions*: [1-hexene] = 0.50 M [catalyst] = 20.00 x $10^{-5}$ M, p(CO) = 19.73 bar, p($H_2$) = 19.73 bar and agitation speed = 850 rpm.

The consumption of 1-hexene is zero upto 120 minutes after heat treatment for each temperature. The activity of the catalyst $RhCl(AsPh_3)_3$ was highly dependent on the temperature and time of pre-heat treatment under syn-gas atmosphere (Table 4.4.). For example, after 180 minutes of hydroformylation reaction the consumption of 1-hexene is highest for the catalyst pre-heated at $80^{0}$C and is zero after pre heating at $200^{0}$C. Only the slight consumption of 1-hexene at 300 minutes was observed at $200^{0}$C, which was sufficient time to consume all the 1-hexene in the case of hydroformylation with the catalyst not subjected to heat treatment. Chaudhari et al. [18] have also studied the deactivation of $HRh(CO)(PPh_3)_3$ after heat treatment in syn-gas atmosphere. They

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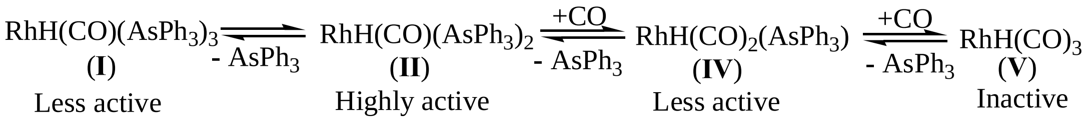
temperature of pre-heat treatment, the conversion (or eased significantly but the rate of hydroformylation, was enhanced. In the present case, however, we found the consumption of 1-hexene decreased on increasing the temperature of the pre-heat treatment but the initial rate of hydroformylation of 1-hexene was zero, irrespective of temperature of heat-treatment. Hence, it can be concluded that the tendency to regenerate the catalyst is more difficult for Rh/$AsPh_3$ system than that of Rh/$PPh_3$ system; hence, Rh/$AsPh_3$ system is more susceptible towards the temperature of heat-treatment.

As the ligand $AsPh_3$ is less basic than $PPh_3$, the dissociation of the ligand via following equilibrium is most favorable in presence of syn-gas and temperature. The existence of inactive species (V) does not have any spectroscopic evidence; however, due to weak interaction between Rh-$AsPh_3$, the removal of all the ligands can be expected from the rhodium metal in presence of syn-gas atmosphere on heat-treatment at higher temperature.



$$\underset{\text{(I)}}{RhH(CO)(AsPh_3)_3} \underset{-\,AsPh_3}{\rightleftharpoons} \underset{\text{(II)}}{RhH(CO)(AsPh_3)_2} \underset{-\,AsPh_3}{\overset{+CO}{\rightleftharpoons}} \underset{\text{(IV)}}{RhH(CO)_2(AsPh_3)} \underset{-\,AsPh_3}{\overset{+CO}{\rightleftharpoons}} \underset{\text{(V)}}{RhH(CO)_3}$$

The formation of dimmer or cluster of the catalyst $RhCl(AsPh_3)_3$ is also one of the most favorable possibilities under syn-gas atmosphere and pre-heat treatment temperature. Since the basicity of the ligand $AsPh_3$ is lower than that of $PPh_3$, the tendency of donation of electron pairs towards rhodium metal from ligand $AsPh_3$ always would be lower than ligand $PPh_3$. The electron deficiency on the rhodium metal will be the favorable conditions for formation of dimmer or cluster species. However, to understand the mechanism of the deactivation of Rh/$AsPh_3$ system further spectroscopic studies are promising.

### 4.4. Kinetic modeling

Due to the complexities involved regarding the variation of the rate with different parameters in hydroformylation reactions, it is important to develop a suitable rate models to describe the intrinsic kinetics of the hydroformylation reactions. The rate equation proposed by Natta and Ercoli [24] is not adequate to represent the above results and may be applicable in a narrow range of operating conditions only. As discussed in the experimental section, the rates of hydroformylation were calculated under a various

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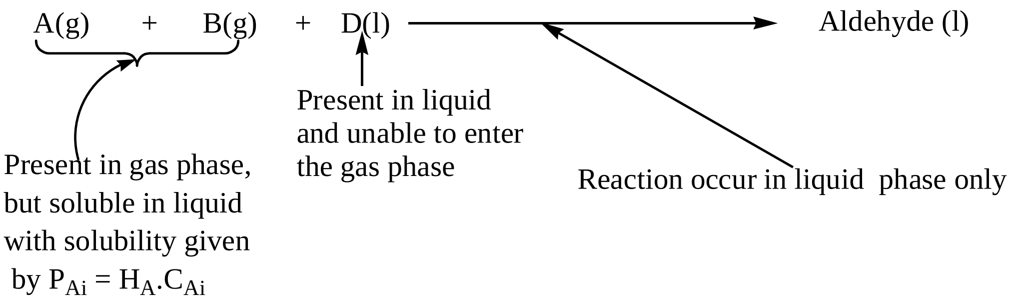
ıs. In order to develop a suitable rate model representing
re analyzed for the significance of mass transfer resistance.

The hydroformylation can be represented as an irreversible reaction of following type of complex kinetics:



Since the concentration of the olefin is usually in large excess compared to dissolved concentration of hydrogen and carbon monoxide and catalyst concentration remains constant, it can be assumed that there is negligible reduction of olefin and catalyst concentration at any point in the liquid phase [21]. The following assumptions were made:

a) the gas side mass transfer resistance is negligible since gases are in their purest forms,
b) Henryôs law is applicable,
c) application of semi batch mode,
d) the reaction takes place only in liquid phase.

In order to evaluate the effect of mass transfer on a homogeneous catalytic reaction, equation have been derived for the enhancement factor, which is defined as

$$\phi = \left(\frac{\text{rate of uptake of } C_n \text{ when reaction occurs}}{\text{rate of uptake of } C_n \text{ for straight mass transfer}}\right)$$

where, n = A, $A_i$, B or $B_i$.

Since the agitation speed (850 rpm), has no effect upon the 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 carbon monoxide and hydrogen at the respective conditions.

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nd $\phi_2$ were calculated as [5],

$$\phi_1 = \frac{R}{k_1 a\ A_i} \qquad (4.4)$$

$$\phi_2 = \frac{R}{k_1 a\ B_i} \qquad (4.5)$$

Where, R represents the rate of hydroformylation, $k_1a$ is the gas-liquid mass transfer coefficient. The evaluation of $\phi_1$ and $\phi_2$ requires knowledge of $k_1a$, $A_i$ and $B_i$, which can be calculated by solubilities of the hydrogen and carbon monoxide in addition to rate data. The Henry's law constants [6] ($H_A$ = 906.9 barM$^{-1}$, $H_B$ = 230.2 barM$^{-1}$) are used to calculate $A_i$ and $B_i$, respectively. The value of the $k_{1a}$ were obtained by the following correlations

$$k_{la} = \left(\frac{N^2\ Di^2}{Dt^{1.5}}\right)^{1.95} \qquad (4.6)$$

$$k_a = \left(\frac{N\ Di^2}{Dt^{1.6}} - 0.45\right) \qquad (4.7)$$

The values of $\phi_1$ and $\phi_2$ calculated for all the rate data were found to be less than 0.10 in each case. 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.

For the purpose of the quantitative analysis of the relationship between different factors and the reaction rate, various empirical models were attempted. However, it is more meaningful to derive rate models based on the actual mechanism of hydroformylation, assuming oxidative addition of hydrogen to acylrhodium species 7 (Scheme 4.1.) as the rate-controlling step.

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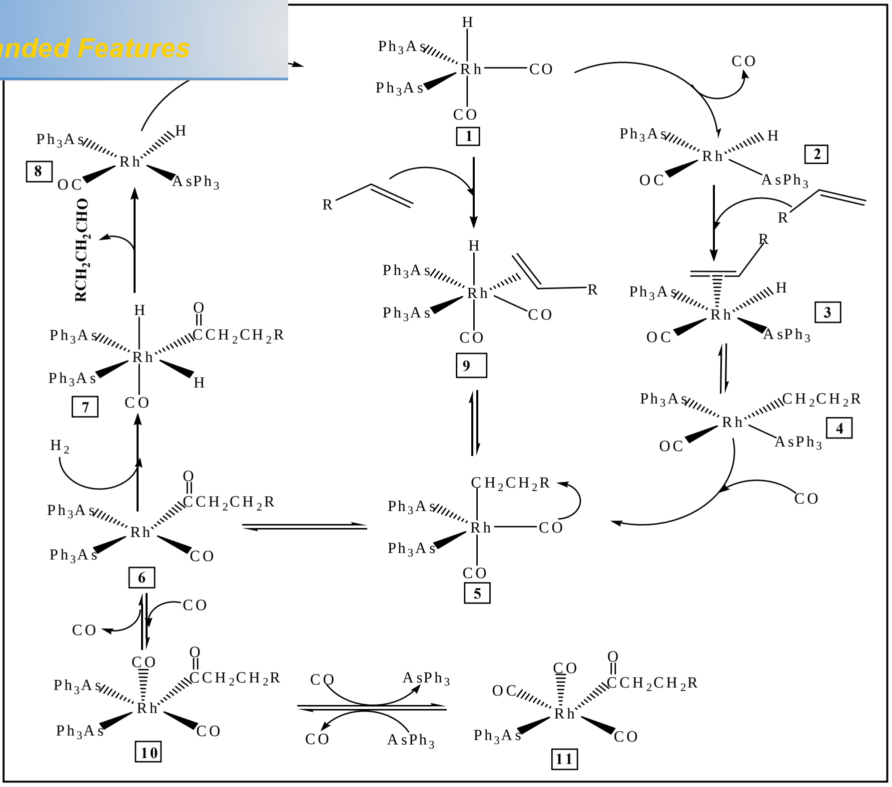

**Scheme 4.1.** Mechanistic pathway of hydroformylation reaction

$$HRh(CO)(AsPh_3)_3 \rightleftharpoons \underset{C_1}{HRh(CO)(AsPh_3)_2} + AsPh_3 \qquad (1)$$

$$HRh(CO)(AsPh_3)_2 + CO \overset{K_{11}}{\rightleftharpoons} \underset{C_2}{HRh(CO)_2(AsPh_3)_2} \qquad K_{11} = \frac{k_1}{k_{-1}} = \frac{C_2}{C_1\,[CO]} \qquad (2)$$

$$HRh(CO)_2(AsPh_3)_2 + \text{1-hexene} \overset{K_{12}}{\rightleftharpoons} \underset{C_3}{Rh(acyl)(CO)(AsPh_3)_2} \qquad K_{12} = \frac{C_3}{C_2\,[\text{1-hexene}]} \qquad (3)$$

$$Rh(acyl)(CO)(AsPh_3)_2 + H_2 \xrightarrow{k} \underset{C_1}{HRh(CO)(AsPh_3)_2} + \text{Aldehyde} \qquad \text{rate} = k\,C_3\,[H_2] \qquad (4)$$

$$Rh(acyl)(CO)(AsPh_3)_2 + CO \overset{K_{13}}{\rightleftharpoons} \underset{C_4}{Rh(acyl)(CO)_2(AsPh_3)_2} \qquad K_{13} = \frac{C_4}{C_3\,[CO]} \qquad (5)$$

$$Rh(acyl)(CO)_2(AsPh_3)_2 + CO \overset{K_{14}}{\rightleftharpoons} \underset{C_5}{Rh(acyl)(CO)_3(AsPh_3)} + AsPh_3 \qquad K_{14} = \frac{C_5\,[L]}{C_4\,[CO]} \qquad (6)$$

**Scheme 4.2.** Some important reaction steps based on actual mechanism

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ydrogen to the acylrhodium carbonyl species is considered
therefore, from reaction (4) (Scheme 4.2.) the rate of reaction is given as

$$\text{rate} = kC_3[H_2] \qquad (4.8)$$

The concentration $C_3$ is unknown, therefore, $C_3$ is replaced by $C_1$ from the reaction (1) to (3) (Scheme 4.2.). The concentration of dissociated ligand is very low so equation (1) can be neglected. Therefore, equation (4.8.) becomes,

$$\text{rate} = kK_{11}K_{12}[\text{1-hexene}][H_2][CO]C_1 \qquad (4.9)$$

The total concentration of the catalyst species known as

$$C = C_1 + C_2 + C_3 + C_4 + C_5 \qquad (4.10)$$

Where, C is the concentration of catalyst charged.

The concentration of $C_2$ to $C_6$ expressed in terms of $C_1$ from (Scheme 4.2.) and by putting in equation (4.10),

$$C = (C_1 + K_{11}[CO]C_1 + K_{11}K_{12}[CO][\text{1-hexene}]C_1 + K_{11}K_{12}K_{13}[CO]^2[\text{1-hexene}]C_1 + K_{11}K_{12}K_{13}K_{14}[CO]^3[\text{1-hexene}]C_1)$$

and subsequently,

$$C_1 = C/(1 + K_{11}[CO] + K_{11}K_{12}[CO][\text{1-hexene}] + K_{11}K_{12}K_{13}[CO]^2[\text{1-hexene}] + K_{11}K_{12}K_{13}K_{14}[CO]^3[\text{1-hexene}])$$

On putting the values of $C_1$ in terms of C in equation (4.9), the rate would be,

$$\text{rate} = k[\text{1-hexene}][H_2][CO][C]/(1 + K_{11}[CO] + K_{11}K_{12}[CO][\text{1-hexene}] + K_{11}K_{12}K_{13}[CO]^2[\text{1-hexene}] + K_{11}K_{12}K_{13}K_{14}[CO]^3[\text{1-hexene}]) \qquad (4.11)$$

According to Arrhenius equation,

$$k = k_0e^{-Ea/RT}$$

After considering the activation energy term, the rate equation (4.11) becomes,

$$\text{rate} = k_0e^{-Ea/RT}[\text{1-hexene}][H_2][CO][C]/(1 + K_{11}[CO] + K_{11}K_{12}[CO][\text{1-hexene}] + K_{11}K_{12}K_{13}[CO]^2[\text{1-hexene}] + K_{11}K_{12}K_{13}K_{14}[CO]^3[\text{1-hexene}]) \qquad (4.12)$$

Where $K_1$, $K_2$, $K_3$, $K_4$ are the constants, derived from the equilibrium constants of each of the steps in the reaction mechanism, thus these constants are dependent upon reaction temperature. E is the activation energy.

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re evaluated from the rate model (4.11) by a non-linear a modified Levenberg-Marquart (LM) algorithm. In the present case the nonlinear regression was used, the guess values of the constants in the denominator were first obtained using the sets of rate data in which only a single parameter was varied. Based on the minimized sum of squares of the errors ($\phi_{min}$), between calculated and experimental rates, the best-fit model. $\phi_{min}$ was calculated as,

$$\phi\text{min} = \sum_{i=1}^{N} (\text{rate}_{\text{calc(i)}} - \text{rate}_{\text{exp(i)}})^2 \qquad (4.13)$$

It was found that the experimental data were not fitted properly in equation (4.11) which is evidenced by having minimized sum of root mean squares error ($\phi_{min}$) between experimental and calculated rates upto 26%. As this model was not found suitable for present system this means that the rate determining step is not only oxidative addition of $H_2$ on the acyl species 7 (Scheme 4.1.). Additionally, the experimental results as discussed earlier (in the effects of, 1-hexene concentration and partial pressure of CO) also gave indication of shifting of the rate-determining step.

Some other highly complicated rate models with a large number of parameters can also be derived if various steps are assumed as rate controlling steps and different simplifications are adopted. In the present case, more unknown parameters should be evaluated from experimental data and unreliable parameter values would be obtained. Therefore, it is preferred to introduce simplified semi-empirical rate equations, which are consistent with the observed reaction behavior. Various empirical rate equations were taken into consideration in this work and the semi-empirical rate model (4.14) was found to be the best representing the experimental data.

$$\text{rate} = \frac{4008.22 * [A]^{0.75} * [B] * C^{0.35} * D}{((1 + 102.0 * [B] + 10.99 * D)^3 * D)} \qquad (4.14)$$

which, have minimized sum of root mean squares deviation (variance), $2.98\text{x}10^{-7}$, and an average error ($\phi_{min}$) between experimental and calculated rates was found to be 11.6 % (Figure 4.10.).

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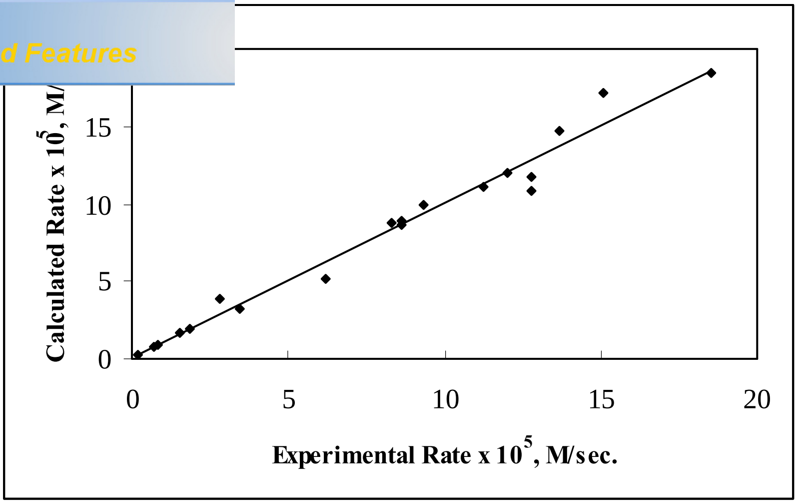

**Figure 4.10.** Comparison of hydroformylation reaction rates calculated from the empirical model (4.14) with experimental data.

### 4.5. Effect of temperature and activation energy

The effects of variation of the reaction temperature on the rate of hydroformylation of 1-hexene was also studied at the constant, concentrations of catalyst (20.0x10$^{-5}$ M) and 1-hexene (0.5 M) and partial pressures of hydrogen (19.73 bar) and carbon monoxide (19.73 bar) by varying the reaction temperature from 60 to 100$^0$C. The rate of reaction was increased with increasing temperature at cost of selectivity towards aldehyde and n/iso aldehyde ratio (Figure 4.11.). The formation of by product generally increased at higher temperature. The n/iso ratio is found to fall from 2.8 to 1.4 on increasing the reaction temperature. At higher temperatures, it can be expected that the steric factors decrease significantly and thermal motion increases, resulting in increase in the polarity of the M-H bond, which thereby favors Markownikov addition [19-20]. The earlier workers [22], for Rh/$PPh_3$ system, also reported the enhanced formation of iso-aldehyde with increasing reaction temperatures.

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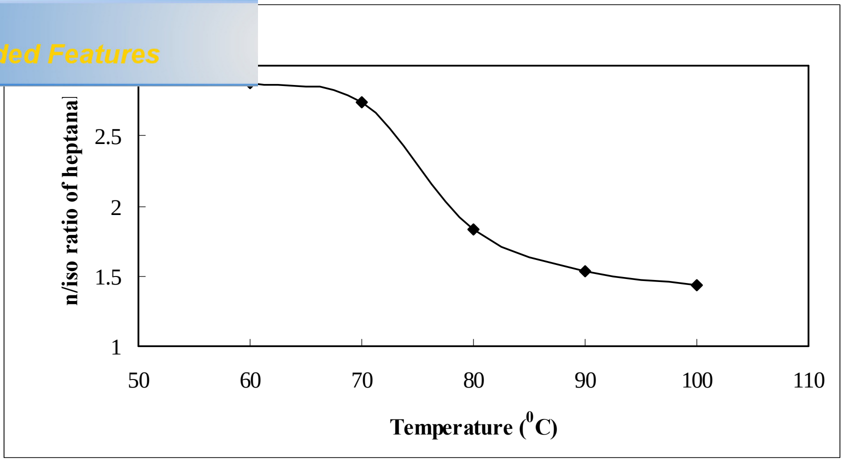

**Figure 4.11.** Effect of variation of the reaction temperature on the n/iso heptanal at [1-hexene] = 0.5 M; [catalyst] = 20.00 x $10^{-5}$ M; p(CO) = 19.73 bar; p($H_2$) = 19.73 bar and agitation speed = 850 rpm.

Activation energy calculated by plotting ln(k) v/s (1/T) (Figure 4.12.) for hydroformylation of 1-hexene using $RhCl(AsPh_3)_3$ as a catalyst was found to be 10.2 kcal/mol, which is less than the reported (28 kcal/mol) value for Rh/$PPh_3$ system [5]. The calculated value of pre-exponential factor is $1.62x10^6$. However, it was worthy to note that the conventional straight line in Arrhenius plot was not observed in the present case. The lower activation energy was observed at higher reaction temperature and vise versa. The entropy of activation computed by using Eyring equation for the studied range of temperature, found to be -48.5±1 cal/(K mol) indicated that the catalyst system is favorable being associated with significant low entropy.

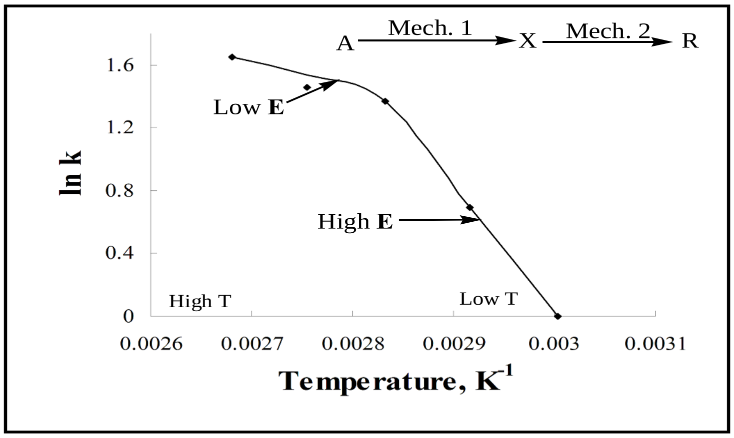

**Figure 4.12.** Arrhenius plot for activation energy

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for the multiple reactions [25], like hydroformylation, a

temperature indicates a shift in controlling mechanism of the reaction and consequently a change of rate determining step. The observed substrate-inhibited kinetics for 1-hexene concentration and CO partial pressure under employed kinetic conditions supports the above statement. Moreover, the average error between experimental and calculated rates upto 26% was observed when the oxidative addition of $H_2$ to acyl intermediate 7 (Scheme 4.2.) was considered as a rate determining step. These experimental and theoretical observations indicated a change in mechanistic pathway for the homogeneous hydroformylation of 1-hexene using $RhCl(AsPh_3)_3$ as a catalyst. However, spectroscopic experiments could give more light to confirm the exact pathway of hydroformylation of 1-hexene using $RhCl(AsPh_3)_3$ as a catalyst.

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