uccessful research developments in homogeneous hydroformylation catalysts [1-4] has certainly been the exploitation of the effect that a ligand exerts on the electronic and steric properties of a metal complex. By tuning the electronic and steric properties of catalytically active metal ions, selectivities and rates can be dramatically altered. There are many examples for each metal in the periodic table, which show how the same metal can be used to catalyze different reactions, depending on the coordinated ligands. Ligands that have been utilized to induce changes, by variation of their structures include phosphines, amines, imines, alkoxides and cyclopentadienyl anions. Among the classes of ligands, which are able to coordinate to transition metal and form complex, phosphine and its derivatives are the most widely used. The only classes of ligands used in industrial hydroformylation plants are phosphines PR_3 ($R = C_6H_5$, n-C_4H_9), triphenylphosphine oxide and in some special cases phosphites, $P(OR)_3$. Phosphines and their coordination chemistry have been extensively studied [5]. Tolman introduced the cone angle (θ) and the electronic parameter (χ) to classify phosphine ligands with respect to their steric demand and coordination ability [6-7]. For chelating diphosphines, Casey has developed natural bite angle, based on molecular mechanics calculations [8-10]. The n/iso selectivities of aldehydes in oxo reactions are now predictable by the diphosphine structure and by their natural bite angle. Nitrogen-containing ligands such as amines, amides or *iso*-nitriles showed exclusively lower reaction rates in the oxo reactions, due to their strong coordination to the metal centre.

A number of papers and patent applications appear annually in the area of hydroformylation, many dealing with new phosphine structures, their modified derivatives and catalytic results obtained therewith. However, the literature on the effect of other Group V (As, Sb) ligands on the hydroformylation of olefins is scarce. As the electronic properties of triphenylarsine are similar to those of its phosphorous counterpart in their ligand behavior, it may be expected that triphenylarsine could also stabilize the lower oxidation state of transition metals, an important requirement for a ligand in hydroformylation reaction catalysts. The σ-donor/π-acceptor ratios for EPh_3 (E = P, As, Sb) ligands shows [11-12] the trend: $SbPh_3 > PPh_3 > AsPh_3$. Generally, the ligands with low σ-donor ability, favor faster reaction rates towards

ue to lower the σ-donor ability and thereby lower basicity, one should expect a faster rate of hydroformylation reaction with $AsPh_3$ ligand compared to those for PPh_3 and $SbPh_3$. Furthermore, recent reports [13-15] of higher catalytic activity of transition metal complexes of arsine for hydroformylation reactions encouraged us to study the comparative behavior of arsine and antimony metal complexes with respect to use of phosphine complexes of rhodium, cobalt and ruthenium metals in the hydroformylation reactions. The studies on hydroformylation of detergent-grade olefin, 1-dodecene, using triphenylamine, triphenylphosphine, triphenylarsine, triphenylantimony and triphenylbismuth as ligands, reported by Carlock [16] proves the superiority of triphenylphosphine over other group V ligands. However, this has been done only for rhodium and that too *in-situ*, i.e. without synthesizing the metal complexes.

In the present chapter, the results are reported on comparative studies on different transition metal-catalyzed hydroformylations of ethylene and 1-hexene using rhodium, cobalt, ruthenium and palladium complexes of triphenylphosphine, triphenylarsine and triphenylantimony.

3.2. Experimental

3.2.1. Materials

1-hexene (99.9%) and *n*-decane (99.9%) were procured from Sigma-Aldrich U.S.A. The ligand EPh_3 (E = P, As, Sb) and the metal salts: $RhCl_3.3H_2O$, $RuCl_3.3H_2O$, $K_2[PdCl_4]$ and $CoCl_2.6H_2O$, were purchased from E. Merck, India. Ethylene (99.5%) and syn-gas (99.8%) were procured from Hydro Gas Ltd. Mumbai, India and Alchemie Gases & Chemicals Pvt. Ltd. Mumbai, India, respectively. Organic solvents required for complex synthesis were purchased from Rankem, India and purified by reported methods [17].

3.2.2. Catalyst synthesis and characterization

Before describing the synthesis of the catalysts used for hydroformylation of ethylene and 1-hexene, it is worth to mention here, the reason for using the chloro complexes of rhodium. The hydroformylation activity of $RhCl(PPh_3)_3$ is in general known to be lower than that of $HRh(CO)(PPh_3)_3$ unless a strong base is added to remove the HCl formed during active catalyst formation with $RhCl(PPh_3)_3$. However, we have dies using $RhCl(PPh_3)_3$ and its corresponding analogues Ph$_3$)$_3$ complexes, since the metal complexes $HRh(CO)(AsPh_3)_3$ and $HRh(CO)(SbPh_3)_3$, which are the corresponding analogues of $HRh(CO)(PPh_3)_3$, were difficult to isolate and synthesize. To have proper comparison of effect of the ligands PPh_3, $AsPh_3$ and $SbPh_3$ in these complexes, it is appropriate to have all the complexes either as chloro or carbonyl complexes. As it was difficult to synthesize all the complexes as carbonyl complexes, we had opted for the chloro form for comparative studies.

$RhCl(PPh_3)_3$ [18], $RhCl(AsPh_3)_3$ [19], $RhCl(SbPh_3)_3$ [19] metal complexes, $RuCl_2(PPh_3)_3$ [20], $RuCl_3(AsPh_3)_2.CH_3OH$ [20], $RuCl_2(SbPh_3)_3$ [20] metal complexes, $PdCl_2(PPh_3)_2$ [21], $PdCl_2(AsPh_3)_2$ [21], $PdCl_2(SbPh_3)_2$ [21] metal complexes were prepared by reported procedures. The only known chloro complex of cobalt (Co) with Group V ligands is the $CoCl_2(PPh_3)_2$ [22]. The chloro-complexes of arsine and antimony of cobalt are not known and these are not separable at atmospheric conditions due to isomeric limitations [23]. Hence, to have proper comparative study, the complexes Co/PPh_3, $Co/AsPh_3$ and $Co/SbPh_3$ were prepared *in-situ* by mixing $CoCl_2.6H_2O$ and EPh_3 in 1:60 molar ratio in the autoclave reactor during conducting the hydroformylation experiments.

FT-NMR (^{1}H, ^{31}P) and FT-IR spectroscopy for the characterization of metal complexes were done by using Bruker Avance DPX 200MHz FT-NMR and Perkin Elmer Spectrum GX FT-IR systems, respectively. C, H and N elemental analyses were done on Perkin Elmer CHNS/O 2400 analyzer. The results of catalyst characterization are given in Table 3.1.

different metal complex catalysts

	FT-IR з(M-E),* (cm^{-1})	^{31}P-FT-NMR, (ppm)	C, H, N analyses calculated (found)
$RhCl(PPh_3)_3$	512	51.5, 53.9 (d)[#]	C: 70.1 (69.7) H: 4.9 (5.1)
$RhCl(AsPh_3)_3$	472	-	C:61.3 (58.8) H: 4.9 (5.1)
$RhCl(SbPh_3)_3$	449	-	C: 54.1 (53.0) H: 3.8 (3.2)
$RuCl_2(PPh_3)_3$	517	43.1 (s)[§]	C: 67.7 (67.0) H: 4.7 (4.3)
$RuCl_3(AsPh_3)_2.CH_3OH$	474	-	C: 52.2 (52.1) H: 4.0 (4.1)
$RuCl_2(SbPh_3)_3$	451	-	C: 52.7 (52.4) H: 3.7 (3.3)
$PdCl_2(PPh_3)_2$	506	41.4 (s)[Ȧ]	C: 61.6 (61.4) H: 4.3 (4.2)
$PdCl_2(AsPh_3)_2$	468	-	C: 54.7 (54.3) H: 3.8 (3.7)
$PdCl_2(SbPh_3)_2$	442	-	C: 48.9 (48.7) H: 3.4 (3.5)

Abbreviations: *M = metals (Rh, Ru or Pd), E = ligands (P, As or Sb), [#]Coupling constants, J (Rh-P) = 196.2 Hz in C_6D_6, [§]in CD_2Cl_2, [Ȧ]in $CDCl_3$.

3.2.3. Hydroformylation reaction

3.2.3.1. The autoclave reactor

All the experiments of hydroformylation of 1-hexene and ethylene were carried out in 100 ml stainless steel autoclave reactor (Autoclave Engineers, U.S.A.) equipped with a controlling unit. The details about the autoclave reactor, operational and safety procedures for conducting hydroformylation reactions have already been described in Chapter 2, Section 2.2.7.1.

-hexene

ylation experiment, the known amounts of 1-hexene, catalyst and *n*-decane dissolved in solvent (benzene, 50 ml) were charged in the autoclave. The reactor was then brought to the desired reaction temperature. Then CO and H_2 gases were successively were supplied to the autoclave reactor upto desired pressures. The hydroformylation reaction was initiated by starting the magnetic stirrer. After the set reaction time, the reaction was quenched by disconnecting the gas-supply to the reactor. The autoclave was then cooled to ambient temperature and the reaction mixtures were analyzed by gas chromatography.

3.2.3.3. Hydroformylation of ethylene

The known amounts of catalyst dissolved in solvent (benzene, 50 ml) were charged in the autoclave. The autoclave was twice flushed with nitrogen prior to introducing ethylene gas upto pre-decided pressure. The reactor was then brought to the desired reaction temperature. After that, CO and H_2 gases were introduced successively to the reactor upto desired pressures. The hydroformylation reaction was initiated by starting the stirrer. After the set reaction time, the autoclave was cooled to ambient temperature, and pressure drops were noted carefully, since in the case of ethylene, a gaseous reactant, the conversions were calculated in terms of total pressure-drops during the course of the hydroformylation reaction.

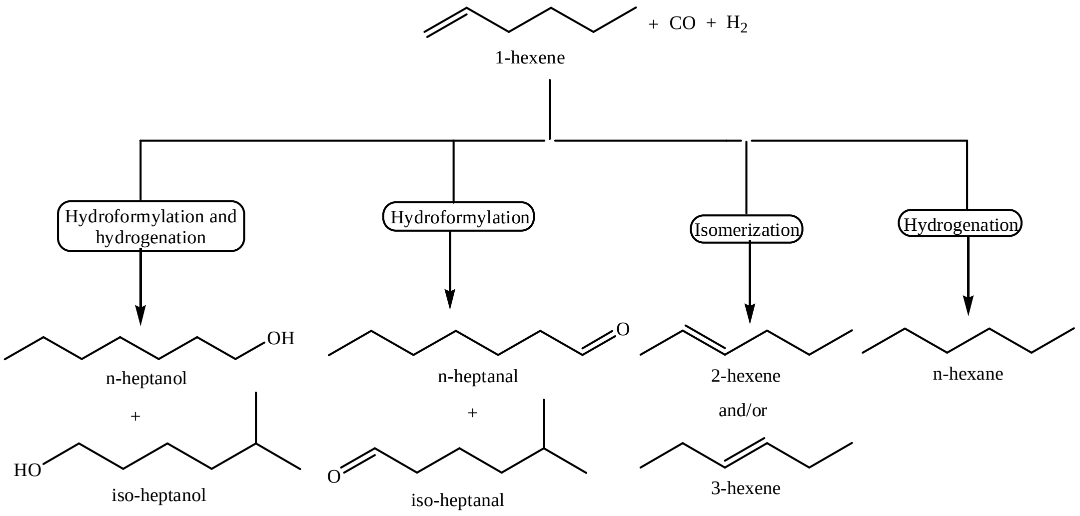
3.2.4. Reaction product analysis

The reaction product analysis was carried out using gas chromatography (GC) (Shimadzu 17A, Japan); the instrument has a 5% diphenyl and 95% dimethyl siloxane universal capillary column (60m length and 0.32mm diameter) and a flame ionization detector (FID). The initial column temperature was increased from 40 to 200^0C at the rate of 10^0C/min. Nitrogen gas was used as the carrier gas. The temperatures of the injection port and FID were kept constant at 200^0C during product analysis. The retention times for different compounds were determined by injecting pure compounds under identical gas chromatography conditions. *n*-Decane was used as an internal standard for GC analysis.

er comparative studies between the ligands of same transition metals, the hydroformylation reaction conditions were optimized with PPh_3 ligand of a particular metal and then hydroformylation reactions were conducted with $AsPh_3$ and $SbPh_3$ ligands with same metal under identical experimental conditions.

3.3.1. Hydroformylation of 1-hexene

The hydroformylation of 1-hexene (Table 3.2.) gave heptanal as main product, n-hexane as hydrogenation product and isomerized products of 1-hexene as minor products in the case of rhodium and cobalt complexes, whereas in the case of ruthenium complexes, hydrogenated n-hexane along with n-heptanal were the main products. The formation of alcohols (heptanols) was observed only in the case of rhodium complexes.



Scheme 3.1. Possibility of the reactions and products formed during 1-hexene hydroformylation

vity data of different catalysts for 1-hexene hydroformylation

		ion (%)	Selectivity (%)			
			Isomerization products	Hydrogenation products	Heptanal	n/iso
1	$RuCl_2(PPh_3)_3$	12	0	60	40	-
2	$RuCl_3(AsPh_3)_2$ $.CH_3OH$	23	0	46	54	-
3	$RuCl_2(SbPh_3)_3$	20	0	44	56	-
4	$Co/PPh_3{}^*$	30	0	0	100	3.1
5	$Co/AsPh_3{}^*$	30	14	0	86	2.6
6	$Co/SbPh_3{}^*$	18	12	4	84	2.9
7	$RhCl(PPh_3)_3$	100	1	0	86	1.0
8	$RhCl(AsPh_3)_3$	100	0	0	85	0.8
9	$RhCl(SbPh_3)_3$	99	10	20	68	2.0

Reaction conditions: 1-hexene = 2.0g, *n*-decane = 0.5g, *Co: EPh_3 (E= P, As, Sb) = 1:60 (molar ratio), *Solvent = acetonitrile, [Cat] = 0.08 mmol, reaction pressure = 60 bar, CO: H_2 = 1:1, reaction temperature = 80^0C, reaction time = 420 min.

3.3.1.1. Ruthenium complexes as catalyst systems

Ruthenium complexes are well known for their potential to hydrogenate -C=C- double bond of olefins [24-27]. However, ruthenium, due to its variable oxidation states, is also being well studied for homogeneous hydroformylation reaction after rhodium and cobalt metals [28-30]. With ruthenium complexes, the conversion of 1-hexene is higher for Ru/$AsPh_3$ system compared to Ru/PPh_3 and Ru/$SbPh_3$ system (Table 3.2., Run 1, 2, 3). Hydrogenation of 1-hexene is highest for Ru/PPh_3 system with no isomerization activity observed for any system. Almost comparable selectivities of heptanal were obtained for Ru/$AsPh_3$ and Ru/$SbPh_3$ systems; the values were higher than that for Ru/PPh_3 system. The Ru/EPh_3 systems gave only *n*-heptanal as hydroformylated product without the formation of *iso*-heptanal. Hence, for ruthenium complexes, the activity of

Ph_3. One of the reasons for the low hydroformylation

der syn-gas atmosphere, may be due to the formation of inactive species $HRuCl(CO)_2(PPh_3)_2$ and $RuCl_2(CO)_2(PPh_3)_2$ [31]. However, Wilkinson et al. [32] have also reported, $RuCl_2(PPh_3)_3$ catalyzed-hydroformylation of 1-hexene at 120°C and 100 bar of syn-gas pressure, where they also have observed the formation of maximum hydrogenation product during the hydroformylation of 1-hexene.

3.3.1.2. Cobalt complexes as catalyst systems

Under identical experimental conditions, the order of selectivity of heptanal by cobalt complexes was observed to be $Co/PPh_3 > Co/AsPh_3 > Co/SbPh_3$ (Table 3.2., Run 3, 4, 5) with the highest n/iso ratio for the PPh_3 ligand. The 1-hexene conversions are nearly same for arsine and phosphine complexes, followed by antimony complexes. Although n-hexane formation was not detected in the case of phosphine and arsine complexes of cobalt but 4% n-hexane formation was obtained in the case of an antimony complex of cobalt. In the case of the $Co/AsPh_3$ system, the isomerization of 1-hexene is 14% (Table 3.2., Run 5). On the other hand, both isomerization and hydrogenation of 1-hexene were observed for $Co/SbPh_3$ system (Table 3.2., Run 6). However, with Co/PPh_3 system neither of the side reactions was observed.

3.3.1.3. Rhodium complexes as catalyst systems

$RhCl(PPh_3)_3$ is a highly efficient and industrially established catalyst for hydroformylation reaction. Wilkinson et al. [33-34] have extensively studied the synthesis, characterization and its catalytic activity in the hydroformylation of various olefins. Its analogues, $RhCl(AsPh_3)_3$ and $RhCl(SbPh_3)_3$ were also prepared by them [19]. However, their catalytic activities towards hydroformylation reactions are not much reported. In the present investigations, it is observed that these catalysts gave 99-100% conversions in terms of concentrations of 1-hexene under employed reactions conditions (Table 3.2., Run 7, 8, 9). Isomerization and hydrogenation of 1-hexene are completely suppressed with Rh/PPh_3 and $Rh/AsPh_3$ systems (Table 3.2., Run 7, 8). However, significant isomerization and hydrogenation activity are observed for $Rh/SbPh_3$ system (Table 3.2., Run 9). The selectivity of aldehydes is nearly equal for phosphine and for arsine systems. The difference, which makes Rh/PPh_3 better than $Rh/AsPh_3$ system, is a higher n/iso ratio of heptanal (Table 3.2.) for the former. The highest n/iso ratio can also t the low selectivity of aldehydes and high isomerization nake it a less effective catalyst.

3.3.1.3.1. The comparative studies of 1-hexene hydroformylation with the Rh/EPh$_3$ systems under optimum conditions

In order to confirm the above observations (Table 3.2, Run 7, 8, 9), we have carried out additional experiments, with Rh/EPh$_3$ (where E = P, As, Sb) systems under their optimum conditions for the hydroformylation of 1-hexene. We have studied the effects of variation of pressure at 50^{0}C using Rh/EPh$_3$ systems as catalyst. At 50^{0}C and 10 bar syn-gas pressure, Rh/AsPh$_3$ system gave, the highest conversion, followed by Rh/SbPh$_3$ and Rh/PPh$_3$ systems (Table 3.3., Run 1, 2, 3). The selectivity obtained for heptanal was also higher with Rh/AsPh$_3$ than with the corresponding phosphine and antimony systems. However, the regioselectivity was highest for Rh/PPh$_3$ and Rh/SbPh$_3$ systems, as they gave only n-heptanal as product and the n/iso ratio of heptanal was 2.89 for Rh/AsPh$_3$ system (Table 3.3., Run 2). The side reactions, like isomerization (40%) and hydrogenation (17%), were also observed to be low for Rh/AsPh$_3$ system under employed reaction conditions as compared to other system studied.

Table 3.3. Comparative studies of Rh/EPh$_3$ catalysts in hydroformylation of 1-hexene at 10 bar syn-gas pressure

Run	Catalyst	Conversion (%)	Selectivity (%)			
			Isomerization Products	Hydrogenation product	Heptanal	n/iso
1	$RhCl(PPh_3)_3$	23	72	18	10	-
2	$RhCl(AsPh_3)_3$	58	40	17	43	2.89
3	$RhCl(SbPh_3)_3$	48	63	23	14	-

Reaction Conditions: 1-hexene = 2.0 g, *n*-decane = 0.5 g, [Rh/EPh$_3$] = 0.018 mmol, reaction pressure = 10 bar, CO: H_2 = 1:1, reaction temperature = 50^{0}C, reaction time = 300 min.

At 28 bar syn-gas pressure and 50^{0}C reaction temperature, the Rh/EPh$_3$ systems showed the highest activity (Table 3.4., Run 1, 2, 3). Once again the Rh/AsPh$_3$ system gave the highest conversion (100%), followed by the values for Rh/SbPh$_3$ (70%) and Rh/PPh$_3$

nal was also highest for Rh/AsPh$_3$, followed by Rh/PPh$_3$
so ratio for heptanal was observed again for Rh/AsPh$_3$ system (Table 3.4., Run 2). Under the employed reaction conditions, isomerization and hydrogenation followed the trend: SbPh$_3$>PPh$_3$>AsPh$_3$.

Table 3.4. Comparative studies of rhodium metal catalysts for hydroformylation of 1-hexene at 28 bar syn-gas pressure

Run	Catalysts	Conversion (%)	Selectivity (%)			
			Isomerization Products	Hydrogenation product	Heptanal	n/iso
1	RhCl(PPh$_3$)$_3$	40	23	7	70	2.79
2	RhCl(AsPh$_3$)$_3$	100	14	3	83	1.41
3	RhCl(SbPh$_3$)$_3$	70	32	12	56	3.88

Reaction Conditions: 1-hexene = 2.0 g, *n*-decane = 0.5g, [Rh/EPh$_3$] = 0.018 mmol, reaction pressure = 28 bar, CO: H$_2$ = 1:1, reaction temperature = 50^{0}C, reaction time = 300 min.

The effects of metal/ligand ratio on the hydroformylation of 1-hexene using Rh/EPh$_3$ system have also been studied at 28 bar syn-gas pressure and 50^{0}C (Figure 3.5). It was observed that the conversion of 1-hexene decreases with the increase of metal/ligand ratio, except for the Rh/SbPh$_3$ system (Figure 3.5a) as the rate of reaction decreases on increasing metal/ligand ratio [33-34]. On the other hand, the selectivity of heptanal increases on increasing the metal/ligand ratio (Figure 3.5b), except for Rh/AsPh$_3$ system. It was observed that the n/iso ratio increases on increasing the metal/ligand ratio for all the Rh/EPh$_3$ systems (Figure 3.5c). However, the extent of increment in the n/iso is different for each Rh/EPh$_3$ system. Additionally, it is interesting to note that the n/iso ratio is always lower for Rh/AsPh$_3$ system than those of Rh/PPh$_3$ and Rh/SbPh$_3$ systems under each metal/ligand ratio studied.

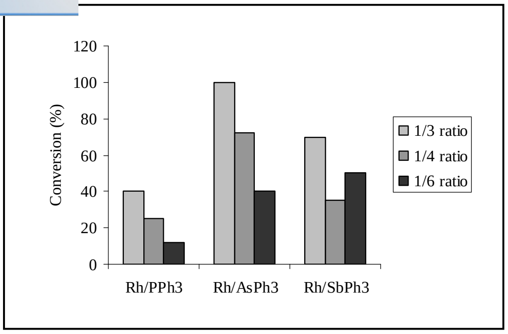


Figure 3.5a

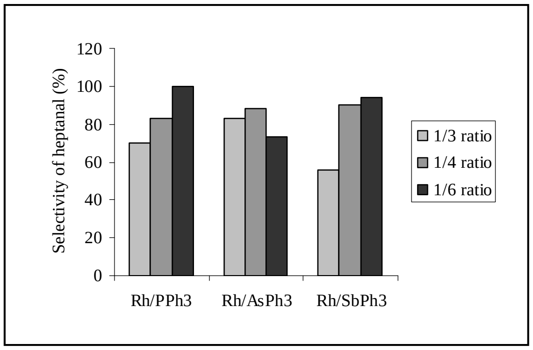


Figure 3.5b

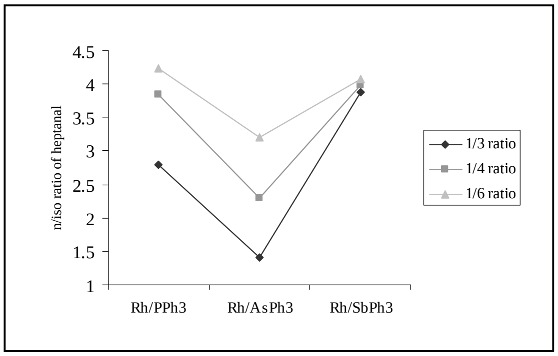


Figure 3.5c

Figure 3.5. Effect of the metal/ligand ratio on the conversion (Figure 3.5a), selectivity of heptanal (Figure 3.5b) and n/iso ratio (Figure 3.5c) towards the hydroformylation of 1-hexene using Rh/EPh_3 system.

Reaction Conditions: 1-hexene = 2.0g, *n*-decane = 0.5g, [Rh/EPh_3] = 0.018 mmol, reaction pressure = 28 bar, CO: H_2 = 1:1, reaction temperature = 50^0C, reaction time = 300 min.

n 1-hexene hydroformylation using $RhCl(AsPh_3)_3$ as a

The kinetic studies in 1-hexene conversion using $RhCl(AsPh_3)_3$ as a catalyst for hydroformylation reaction (at 60 bar and 80°C) showed that 100% 1-hexene is consumed within 5h. The selectivity of *n*-heptanal is maximum at 2h (Figure 3.6a), after which the formation of an *iso*-heptanal is also substantial. The n/iso ratio (Figure 3.6b) for the heptanal decreases rapidly with the increase in the reaction time.

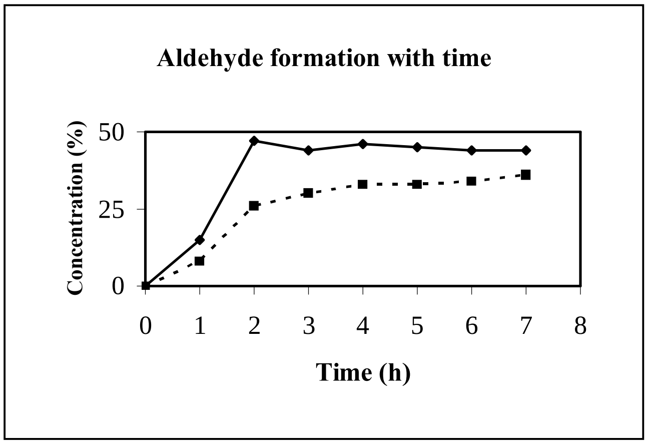


Figure 3.6a (Smooth lines = *n*-heptanal, Dashed lines = *iso*-heptanal)

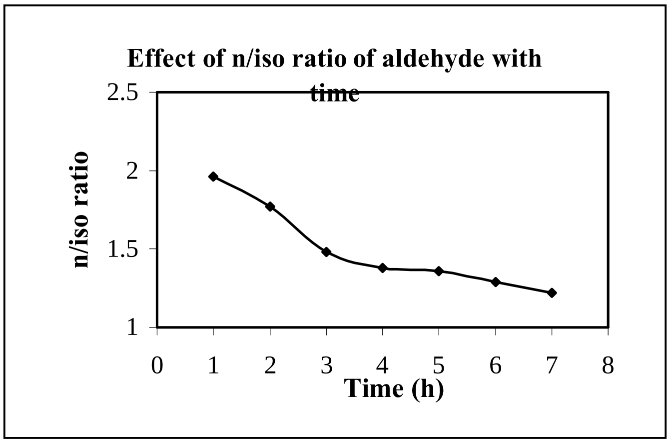


Figure 3.6. Plots of heptanal formation versus time (h) (Figure 3.6.a) and n/iso ratio of aldehyde versus time (Figure 3.6.b) using $RhCl(AsPh_3)_3$ as a catalyst towards hydroformylation of 1-hexene.

Reaction Conditions: 1-hexene = 2.0g, *n*-decane = 0.2g, [$RhCl(AsPh_3)_3$] = 0.02 mmol, reaction pressure = 60 bar, CO: H_2 = 1:1, reaction temperature = 80^0C.

on of $RhCl(AsPh_3)_3$ concentration in 1-hexene

Hydroformylation of 1-hexene was studied at constant pressure (60 bar) and temperature (80°C) by varying the catalyst concentration in the range $2x10^{-3}$ to $10x10^{-3}$ mmol (Figure 3.7a). Towards lower concentrations of the catalyst, the formation of aldehydes was found to be increased on increasing the catalyst concentration, and approached saturation towards higher concentration. On the other hand, the highest n/iso ratio was obtained with the lowest catalyst concentration (Figure 3.7b).

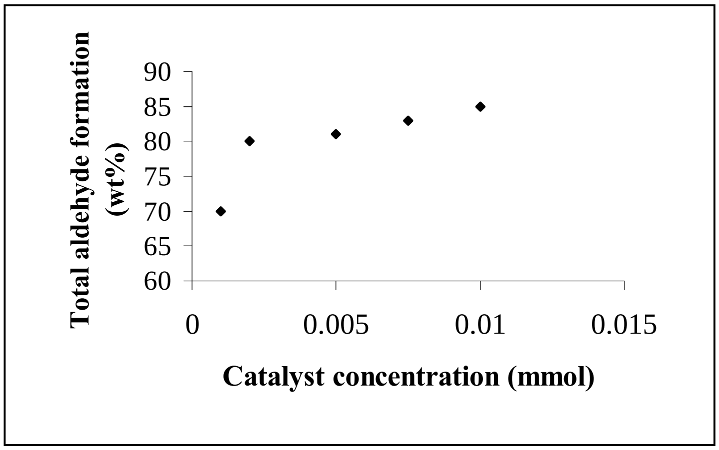


Figure 3.7a

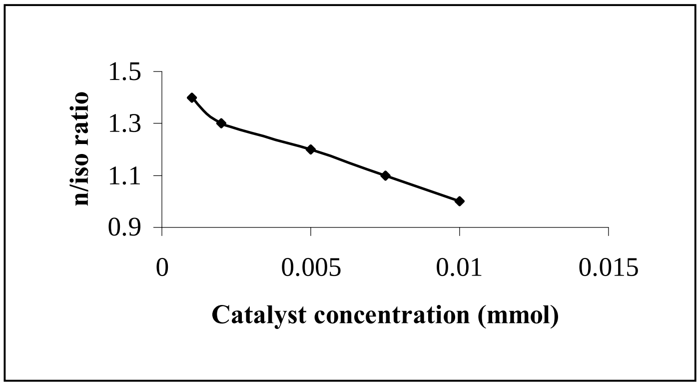


Figure 3.7b

Figure 3.7. Dependence of heptanal formation (Figure 3.7a) and n/iso ratio of aldehyde (Figure 3.7b) on the $RhCl(AsPh_3)_3$ concentration toward hydroformylation of 1-hexene.

Reaction Conditions: 1-hexene = 2.0g, *n*-decane = 0.2g, reaction pressure = 60 bar, CO: H_2 = 1:1, reaction temperature = 80^0C, reaction time = 300 min.

n reaction pressure in $RhCl(AsPh_3)_3$ catalyzed-

The effect of pressure was investigated for the $RhCl(AsPh_3)_3$ catalyzed-hydroformylation of 1-hexene and the corresponding results are given in Table 3.5. As shown in the table, at low pressure (10 bar) only 33% oxo product, 54% n-hexane and 13% isomerized products were observed. As the pressure increased, there is an increase in the oxo products formation with decrease in the hydrogenation and isomerization reactions under employed reaction conditions.

Table 3.5. Effect of variation of reaction pressure in $RhCl(AsPh_3)_3$ catalyzed-hydroformylation of 1-hexene

Run	Pressure (bar)	Conversion (%)	Selectivity (%)			
			Isomerization products	Hydrogenation products	Heptanal	n/iso
1	60	100	4	8	78	1.0
2	40	100	6	15	71	1.0
3	20	98	10	46	40	1.0
4	10	98	13	54	31	1.3

Reaction Conditions: 1-hexene = 2.0 g, *n*-decane = 0.2 g, [Cat] = 0.01 mmol, CO: H_2 = 1:1, reaction temperature = 80^0C, reaction time = 300 min.

3.3.1.3.5. Effect of variation of reaction temperature in $RhCl(SbPh_3)_3$ catalyzed-hydroformylation of 1-hexene

The variation of reaction temperature using $RhCl(SbPh_3)_3$ as a catalyst for hydroformylation of 1-hexene was also studied and results are given in Table 3.6. There is a decrease in the hydroformylation products and an increase in the hydrogenation activity on increasing the reaction temperature.

reaction temperature in hydroformylation of 1-hexene using

Run	Temperature (^{0}C)	Conversion (%)	Selectivity (%)			
			Isomerization products	Hydrogenation products	Heptanal	n/iso
1	60	80	10	13	77	2.48
2	80	98	6	24	65	1.62
3	100	92	20	51	29	2.76
4	120	96	21	60	19	2.33

Reaction Conditions: 1-hexene = 2.0g, *n*-decane = 0.5g, $[RhCl(SbPh_3)_3]$ = 0.01 mmol, CO: H_2 = 1:1, overall reaction pressure = 40 bar, reaction time = 300 min.

ylene

f ethylene catalyzed by palladium, ruthenium, cobalt and rhodium complexes of PPh_3, $AsPh_3$ and $SbPh_3$ were investigated at 60-80 bar pressures and 150^0C and the results obtained are listed in Table 3.7. A representative plot of drop of total pressure in the reactor with time during hydroformylation of ethylene catalyzed by Co/$AsPh_3$ system is shown in Figure 3.8. Similar plots were made for all the studied catalyst systems and their slopes were used to evaluate the rates of drop in pressure (-d[P]/dt) (P = total pressure) given in Table 1, during hydroformylation.

Table 3.7. Conversions and selectivity data of different catalysts for ethylene hydroformylation

Run	Catalysts	Pressure (bar)	Conversion[f] (%)	Propanal (%)	-d[P]/dt (bar/h)
1	$PdCl_2(PPh_3)_2$ [a]	70 [d]	38	70	1.60
2	$PdCl_2(AsPh_3)_2$ [a]	70 [d]	36	97	1.75
3	$PdCl_2(SbPh_3)_2$ [a]	70 [d]	21	19	0.45
4	$RuCl_2(PPh_3)_3$ [b]	60 [e]	12	19	0.78
5	$RuCl_3(AsPh_3)_2 . CH_3OH$ [b]	60 [e]	67	44	2.79
6	$RuCl_2(SbPh_3)_3$ [b]	60 [e]	21	37	1.46
7	Co/PPh_3 [a*]	80 [c]	20	44	0.21
8	Co/$AsPh_3$ [a*]	80 [c]	57	95	1.23
9	Co/$SbPh_3$ [a*]	80 [c]	15	72	0.43
10	$RhCl(PPh_3)_3$ [a]	80 [c]	88	94	11.2
11	$RhCl(AsPh_3)_3$ [a]	80 [c]	80	93	7.97
12	$RhCl(SbPh_3)_3$ [a]	80 [c]	62	90	6.52

Reaction Conditions: [a]Time = 12h, [b]Time = 9h, [c]$p(C_2H_4) + p(CO+H_2) = (30 + 50)$ bar, [d]$p(C_2H_4) + p(CO+H_2) = (30 + 40)$ bar, [e]$p(C_2H_4) + p(CO+H_2) = (30 + 30)$ bar, [catalyst] = 2.0 mmoles, T = 150^0C, *Co: EPh_3 (E= P, As, Sb) = 1:60 (molar ratio), [f]conversions were calculated by total pressure drop during hydroformylation reaction.

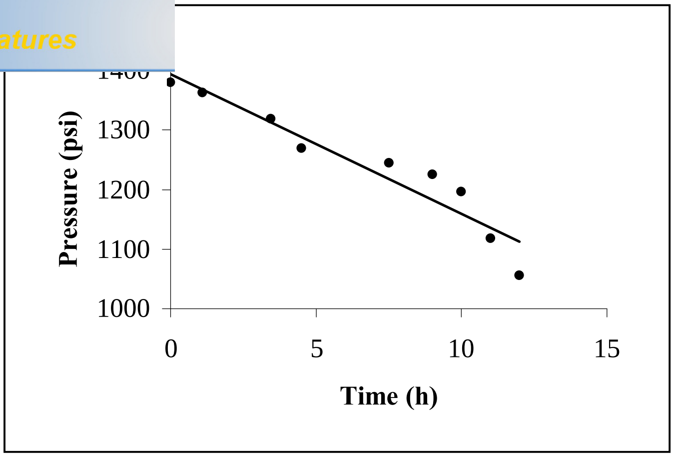


Figure 3.8. Plot of pressure versus time, showing the drop in pressure during the ethylene hydroformylation reaction of ethylene at reaction temperature = 150^{0}C, Co/AsPh$_3$ = 1:60 (molar ratio), p(C_2H_4) = 30 bar and p(CO+H_2) = 50 bar.

3.3.2.1. Palladium complexes as catalyst systems

Under identical experimental conditions, the order for selectivity of propanal by palladium complexes was observed to be AsPh$_3$ > PPh$_3$ > SbPh$_3$ (Table 3.7., Run 1, 2, 3). The conversions of ethylene are nearly equal for arsine and phosphine complexes of palladium, followed by an antimony complex. The rates of pressure-drops (-d[P]/dt) was higher for Pd/AsPh$_3$ system than those for Pd/PPh$_3$ and Pd/SbPh$_3$ systems.

3.3.2.2. Ruthenium complexes as catalyst systems

Under identical experimental conditions, ruthenium metal complexes showed higher conversion and selectivity for Ru/AsPh$_3$ system followed by Ru/SbPh$_3$ and Ru/PPh$_3$ systems (Table 3.7., Run 4, 5, 6). The rate of pressure-drops (-d[P]/dt) were again higher for Ru/AsPh$_3$ system than those for Ru/SbPh$_3$ and Ru/PPh$_3$ systems.

3.3.2.3. Cobalt complexes as catalyst systems

Under identical experimental conditions, with the cobalt metal complexes the conversion was higher for AsPh$_3$ ligand than PPh$_3$ and SbPh$_3$ ligands. However, selectivity propanal follows rather different trend as AsPh$_3$ > SbPh$_3$ > PPh$_3$ (Table 3.7., 7, 8, 9) and the rate of the pressure-drops (-d[P]/dt) was also higher for Co/AsPh$_3$ than those for Co/SbPh$_3$ and Co/PPh$_3$ systems.

catalyst systems

are known to be highly active catalytic systems for hydroformylation reactions, follow somewhat different trend than previously studied metal systems with ethylene substrate. Under identical experimental conditions, the activities of Rh/PPh_3 system were observed to be better than Rh/$AsPh_3$ and Rh/$SbPh_3$ systems, however, the values of the selectivity of propanal, were comparable for Rh/PPh_3 and Rh/$AsPh_3$ systems (Table 3.7., Run 10, 11, 12). The rate of pressure-drops (-d[P]/dt) was also observed to be highest for Rh/PPh_3 system than those for Rh/$AsPh_3$ and Rh/$SbPh_3$ systems.

3.3.2.5. The effect of variation of reaction temperature in ethylene hydroformylation using Co/$AsPh_3$ as a catalyst system

In order to get better insight some additional experiments have also been carried out in hydroformylation of ethylene using Co/$AsPh_3$ catalyst system. The effects of variation of the reaction temperature in ethylene hydroformylation reactions (Table 3.8.) were studied with the Co/$AsPh_3$ catalyst system. The conversion and the selectivity of propanal both were observed to increase on increasing the reaction temperature from 100^0 to 150^0C (Run 1, 3, 4, Table 3.8.) in 12 h reaction time. However, the conversion and comparable selectivity of propanal, which were obtained at 150^0C, can also be achieved at 100^0C but at longer reaction time (Run 2, 4, Table 3.8.).

Table 3.8. Effect of variation of reaction temperature on Co/$AsPh_3$ system catalyzed-hydroformylation of ethylene

Run	Temperature (^{0}C)	Conversion (%)	Propanal (%)	Time (h)
1	100	44	76	12
2	100	56	98	21
3	125	52	85	12
4	150	57	95	12

Reaction Conditions: Co/$AsPh_3$ = 1:60 (molar ratio), p(C_2H_4) = 30bar, p(CO+H_2) = 50 bar, Solvent = Benzene (40 ml).

ion of metal/ligand ratio of Co/AsPh$_3$ in ethylene

During the studies of the variations metal/ligand ratio with Co/AsPh$_3$ catalytic system it was observed that conversion and selectivity of propanal both increases on varying the Co/AsPh$_3$ molar ratio from 0.1 to 0.016 at 100^{0}C (Table 3.9.). The conversion and selectivity of propanal both were low for 1/60 molar ratio of Co/AsPh$_3$ than what it was observed in Table 3.7. with same molar ratio. One of the possible reasons may due to the differences in the reaction temperature applied.

Table 3.9. Effect of variation of metal ligand ratio of Co/AsPh$_3$ in hydroformylation of ethylene

Run	Co/AsPh$_3$ (molar ratio)	Conversion (%)	Propanal (%)
1	1/10	39	69
2	1/20	41	76
3	1/40	44	81
4	1/60	44	93

Reaction Conditions: p(C_2H_4) = 30 bar, p(CO+H_2) = 50 bar, Solvent = Benzene (40ml), Reaction Temperature = 100^{0}C and Reaction Time = 12 h.

exene and ethylene

The conversion and selectivity data of the various metals with PPh_3, $AsPh_3$, $SbPh_3$ ligands showed that, as expected, rhodium complexes are more efficient than cobalt and ruthenium and palladium complexes in the hydroformylation of both 1-hexene (Table 3.2.) and ethylene (Table 3.7.). This may be due to the greater ease of oxidative addition of molecular hydrogen to the rhodium(I)acyl complex during the catalytic cycle. Moreover, cobalt(I)/ruthenium(II)/palladium(II) intermediates formed during hydroformylation catalytic cycle (of 1-hexene and ethylene) require more severe conditions for continuation of cycle (i.e. for dissociation) than those required for rhodium(I) intermediate [33-34].

One more observable difference among the different metal systems was the n/iso ratio of the heptanal formed in 1-hexene hydroformylation reactions (Table 3.2.). For the cobalt system, the n/iso ratio is higher than that for the rhodium system; in the case of ruthenium, only normal aldehyde is formed under the employed reaction conditions. There are a number of contradicting reports [35] on this aspect. However, the possible sources of isomeric aldehyde formation during hydroformylation reactions include olefin isomerization, regioselectivity addition of olefin to the hydridometalcarbonyl intermediate complex and isomerization of the acylmetalcarbonyl during the catalytic cycle. Additionally, the n/iso ratio of aldehydes also depends on the ligand/metal ratio [35] since steric bulkiness at the metal center favors normal aldehydes, due to *anti*-Markownikov addition of olefin on the metal center. In the present case, the ligand/metal ratio is too higher for the cobalt system than for the rhodium system; this, in turn, may be responsible for a higher n/iso for the former system than for the latter.

For comparing the hydroformylation activity of different ligands for a particular metal, one has to look into the σ- and π-character of ligands and their influence on the steps involved in the hydroformylation reaction cycle. The elementary step in the hydroformylation reaction cycle, which is sensitive to the electronic properties, viz., σ- and π-character of ligands, is the ligand association-dissociation equilibrium:

$$\rightleftharpoons \quad HM(CO)_n\,(EPh_3)_{m-1} \; + \; EPh_3 \qquad (3.1)$$

Where n, m = 2 or 3 depending on the metal used, and E = P, As or Sb.

The shift of equilibrium (3.1) towards the right hand side gives the hydrido complex $HM(CO)_n(EPh_3)_{m-1}$, which is an active intermediate for the hydroformylation reactions, therefore; the rate of hydroformylation reaction is strongly influenced by ease of dissociation of ligand EPh_3. The σ-donor and π-acceptor character of EPh_3 ligand will be the governing factor for the dissociation of M-EPh_3 bond. Tucci [36] has also reported that the rate of olefin hydroformylation reaction is strongly dependent on the ligand basicity (i.e. the ligand of low basic character supports faster a rate of hydroformylation reaction). As discussed earlier, σ-basicity is lower for $AsPh_3$ than for PPh_3 and $SbPh_3$. Lower σ-basicity and high π-acidity character of As in $AsPh_3$ is further augmented by its higher electronegativity compared to those of P and Sb atoms (the Allred-Rochow type electronegativity of P: 2.06, As: 2.20 and Sb: 1.82). From the above discussion, one may conclude that $SbPh_3$ and PPh_3 stabilize the M-EPh_3 bond more than $AsPh_3$ does, this was further confirmed by cyclic voltammetry (CV) [37] studies for the ruthenium(II) complexes of PPh_3 and $AsPh_3$: $RuCl_2(CO)_2(AsPh_3)_2$ and $RuCl_2(CO)_2(PPh_3)_2$. In these complexes, M-E bond is more labile in $RuCl_2(CO)_2(AsPh_3)_2$ than in $RuCl_2(CO)_2(PPh_3)_2$.

Hence, equilibrium (3.1) shifts more towards the right, when the ligand is $AsPh_3$ than when it is PPh_3 or $SbPh_3$. The formation of hydroformylation active hydrido $HM(CO)_n(EPh_3)_{m-1}$ species is favored by $AsPh_3$ ligand more than by PPh_3 and $SbPh_3$. Therefore, theoretically one should expect higher activity for hydroformylation reaction with M/$AsPh_3$ system than with M/PPh_3 and M/$SbPh_3$ systems. However, during the comparative studies of hydroformylation of 1-hexene (Table 3.2.) and ethylene (Table 3.7.) we found that M/$SbPh_3$ is least active and that the activities are comparable for M/PPh_3 and for M/$AsPh_3$ systems under employed reaction conditions.

A significant difference observed between the hydroformylation reactions of 1-hexene (Table 3.2.) and ethylene (Table 3.7.) during the comparative studies of different ligands with rhodium metal was that the trends of activities were quite different for both the substrates as shown bellow:

on and selectivity follow the trend,

$\approx$ Rh/Ph$_3$As > Rh/Ph$_3$Sb

However, for ethylene,

Rh/Ph$_3$P > Rh/Ph$_3$As > Rh/Ph$_3$Sb (conversion)

Rh/Ph$_3$P $\approx$ Rh/Ph$_3$As > Rh/Ph$_3$Sb (selectivity)

As concluded in above discussions that higher activity is expected for hydroformylation reaction with M/AsPh$_3$ system than with M/PPh$_3$ and M/SbPh$_3$ systems. However, in ethylene hydroformylation reactions, the conversion obtained was somewhat higher for Rh/PPh$_3$ than those for Rh/AsPh$_3$ systems. The discrimination of the trend observed may be due to the presence of ethylene as a substrate. In the case of the lower gaseous olefins like ethylene, the interaction of Rh/PPh$_3$ system with olefins is higher than those for Rh/AsPh$_3$ system; hence, higher conversion was obtained in the former than latter case. This is also supported by the fact that the Rh/PPh$_3$ system is highly active and industrially established catalytic system for hydroformylation of lower olefins like ethylene and propylene is not preferred for the higher olefins like 1-hexene. On both industrial and academic level, the cobalt catalytic systems are the favored for higher olefin hydroformylation reactions.

It has also been observed during the comparison of the metal with different metal/ligand systems in the hydroformylation of 1-hexene (Table 3.2.) that the M/AsPh$_3$ system always gave a lower n/iso ratio than the M/PPh$_3$ and M/SbPh$_3$ systems for all the metals studied. In this case, too, electronic factors or steric factors of the ligands or some combination of both would play a crucial role in determining the n/iso ratio of aldehydes during hydroformylation reaction of 1-hexene. The formation of alkyl complex via addition of olefin to the hydridometal complex HM(CO)$_n$(EPh3)$_{m-1}$ may be Markownikov or *anti*-Markownikov and only the latter leads to formation of normal aldehydes. The mode of addition will depend on the polarity of M-H bond [33-34]; enhanced polarity favors Markownikov addition. The presence of a ligand of high π-acidity such as AsPh3, which will increase the polarity of M-H bond, will further increase the extent of Markownikov addition and hence lower the n/iso ratio for the aldehydes.

During the study of pressure effects for hydroformylation of 1-hexene at 50^{0}C (Table 3.3. and Table 3.4.) using Rh/EPh$_3$ as catalyst, it was observed that, with the ectivity, there is a decrease in n/iso on increasing the ar. These observations are in accordance with the recent report on high-pressure effects in hydroformylation reactions [38].

It was interesting to note that both the conversion and selectivity were higher for Rh/AsPh$_3$ system than for Rh/PPh$_3$ and Rh/SbPh$_3$ systems under the identical experimental conditions and reaction time. Such as difference means that, the rate of reaction is faster for the Rh/AsPh$_3$ system than for Rh/PPh$_3$ and Rh/SbPh$_3$ systems. The above observation is in accordance with the assumption (made in Introduction section) and hence the equilibrium (3.1) shifts more towards the right when ligand is the AsPh$_3$ than when it is PPh$_3$ or SbPh$_3$. The reason for the lowest n/iso ratio of heptanal for Rh/AsPh$_3$ system may be due to the presence of the highly π-acidic AsPh$_3$ ligand. The Rh/AsPh$_3$ system always gave higher conversion and higher selectivity values with lower n/iso ratio than Rh/PPh$_3$ and Rh/SbPh$_3$, even with different metal/ligand ratios (Figure 3.5.). The Rh/SbPh$_3$ system does not show consistency in the observations, probably due to the presence of mixtures of complexes of RhCl(SbPh$_3$)$_3$ under syn-gas atmosphere [19].

The effect of variation of catalyst concentration of Rh/AsPh$_3$ system (Figure 3.7.) showed that on increasing the catalyst concentration, aldehyde formation gave increasing trend. The result obtained for n/iso ratio was in contrast to that observed for Rh/PPh$_3$ system. This is attributed to the enhanced amount of π-acidic AsPh$_3$ with increased catalyst concentration, which favors formation of *iso*-heptanal and hence lower n/iso ratios for the aldehydes.

The results obtained by variation of overall reaction pressure, using Rh/AsPh$_3$ as a catalyst for the hydroformylation of 1-hexene, are shown in Table 3.5. The n/iso ratio is constant from 60 bar to 20 bar overall reaction pressures and increased at 10 bar. The formation of by-products (isomerization and hydrogenation of 1-hexene) increased with decreased hydroformylation activity by lowering the overall reaction pressure. However, it is well known that Rh/PPh$_3$ shows an excellent hydroformylation activity even at 1 atm pressure [33-34]. This is assignable due to slightly more stable hydroformylation active-intermediates for Rh/AsPh$_3$ system at mild pressure, which requires somewhat more severe conditions for dissociation than that of, with Rh/PPh$_3$ system. The intermediates d reaction temperature (80^0C) employed are sufficient to ubstrate; hence enhanced the formation of byproducts.

The results obtained by varying reaction temperature using Rh/$SbPh_3$ system as a catalyst for hydroformylation of 1-hexene under employed reaction conditions are given in Table 3.6. A decrease in the selectivity of oxo product and increase in the hydrogenation activity were found on increasing the reaction temperature. Wilkinson et al [19] have studied the interaction of Rh/$SbPh_3$ complexes with CO and H_2 and have reported that Rh/$SbPh_3$ system undergoes to formation of mixtures of complexes. Hence, the antimony complexes of rhodium are less acquiescent to study than either the phosphine or the arsine analogues.

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