# Rhodium complex of monodentate phosphite as a catalyst for olefins hydroformylation

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## ARTICLE INFO

## ABSTRACT

Rhodium complex of a novel monodentate bulky phosphite ligand, tri-1-naphthylphosphite is studied for the hydroformylation of dissimilar alkenes specifically, 1-hexene, styrene, and cyclohexene. The steric attributes of free ligand is investigated by cone angle. The effect of concentration of alkene as well as catalyst, ligand/Rh ratio, pCO and $pH_2$ on the rate of reaction has been studied. For 1-hexene and styrene, the initial rate was found to be zero order with respect to initial alkene concentration and first order with respect to catalyst concentration and $H_2$ partial pressure. For cyclohexene, the reaction was found to be first order with respect to the initial cyclohexene concentration and of slightly positive order with respect to $H_2$ partial pressure. The initial rate of hydroformylation of styrene (at 80 °C, 3.0 MPa syngas pressure) is ~3.9 times less than that of 1-hexene hydroformylation where as the rate of cyclohexene hydroformylation is ~87 times less than that of 1-hexene hydroformylation.

## 1. Introduction

Hydroformylation of olefins to aldehydes is one of the most imperative industrial reaction that use Co and Rh metal complexes as catalysts [1–3]. Rhodium complexes are the most proficient catalysts for hydroformylation reactions in terms of both activity and selectivity [4]. Rhodium–phosphine based catalyst system operates at lower temperature and pressure than earlier cobalt based catalyst system and now represents the most used catalyst system for hydroformylation reaction. To improve the selectivity and activity of catalytic reactions modified phosphine ligands have been investigated as they can modify the electronic and steric effect around the metal and thereby affect their catalytic activity/properties [5,6]. Consequently, recent developments in hydroformylation reaction are basically focused on the ligand synthesis methodology. In the recent years, use of phosphite ligands for the hydroformylation has received much attention and even used in commercial catalyst system in the place of triphenyl phosphine (TPP) [7]. Organophosphites are weak σ donors and strong π-acceptors, less sensitive toward oxidation, easy to synthesize and give high reaction rate than phosphines. Moreover phosphites as auxiliary ligands have been appeared in several reports [8–10]. Bulky monodentate phosphite ligands are known to show high activity in the hydroformylation

of olefins [11–15]. Van Rooy et al. showed a high reaction rate (TOF up to 1,60,000 h$^{-1}$ with moderated linearity of 65%) for the hydroformylation of 1-octene using Rh/Tris (2-*tert*-butyl-4-methyl-phenyl) phosphite system [15].

Efforts have been directed to understand kinetics and mechanism of the rhodium catalyzed hydroformylation reaction as these reactions are enormously sensitive to the experimental conditions employed. The available kinetic data for the Rh/PPh$_3$ system reveal the first-order dependence with respect to olefin and rhodium concentration and zero order on hydrogen partial pressure, implying that the slow step is either the coordination of the substrate to rhodium or the migratory insertion of the alkene into the Rh–H bond. However, the oxidative addition of hydrogen has been considered as the rate determining step in other reports employing the same catalytic system under different reaction conditions on the basis of the acceleration of the hydroformylation rate observed upon increasing the H$_2$ pressure. A comprehensive kinetic studies have also been performed for relatively few catalysts: rhodium system with bulky phosphites [11–15], HRh(CO)PPh$_3$ [16–19], phosphine-phosphite and diphosphite [20,21], and diphosphine [22] system, with 1,2,5-triphenyl-1H-phosphole [23], and a rhodium-triphenylarsine precatalyst [24].

In our endeavor to develop an effective catalytic system for the hydroformylation reactions, we have synthesized a novel modified monodentate phosphite ligand, which is very active towards hydroformylation of alkenes, gave high selectivity for aldehyde and low side products. Studies on the reaction kinetics of hydroformylation of alkenes using rhodium complex of this ligand is also done.

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## 2. Experimental

### 2.1. Materials

The ligand synthesis was performed using standard Schlenk technique under nitrogen atmosphere. THF was distilled from sodium/benzophenone prior to use. Toluene and hexane were purchased from Sigma–Aldrich as anhydrous grade material and used as received. Et$_3$N was distilled from sodium and stored under N$_2$. PCl$_3$ and 1-naphthol were obtained from S. D. Fine chemicals, India, and used as received. Rh(CO)$_2$(acac), alkenes namely 1-hexene, styrene, cyclohexene were purchased from Sigma–Aldrich Chemicals, USA and used as received. The syngas (99.8%) used was from Hydro Gas India Pvt. Ltd., India.

### 2.2. Instrumentation

All the reactions were performed in 100 mL stainless steel autoclave reactor (Autoclave Engineers, EZE–Seal Reactor, USA). $^{31}$PNMR spectra of complexes were measured in CDCl$_3$ solvent and 85% H$_3$PO$_4$ as an internal reference, on Bruker Avance 500 MHz FT-NMR. IR spectra were recorded using nujol mull and KBr pellet on Perkin-Elmer spectrum GX FT-IR system in the range 400–4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. CHN analysis has been done on Perkin-Elmer, 2400 C, H, N, S/O analyzer. Products were analyzed with Shimadzu GC-17A gas chromatograph (GC) using flame ionization detector (FID) having 5% diphenyl- and 95% dimethyl siloxane capillary column (60 m length, 0.25 mm diameter). Column temperature was initially kept at 50 °C for 5 min and then raised to 200 °C at 10 °C/min. Nitrogen was used as a carrier gas (1.2 mL/min). *n*-decane was used as internal standard and the GC was also calibrated using known amount of corresponding aldehydes.

### 2.3. Single crystal X-ray analysis

The crystallographic data and structural data for tri-1-naphthylphosphite (TNPST) are given in Tables 1 and 2, respectively. During X-ray measurement, crystal of suitable size was selected and immersed in partone oil, then mounted on the tip of a glass

**Table 1**
Crystal data and structure refinement for tri-1-naphthylphosphite.

| | |
|---|---|
| Empirical formula | C$_{30}$H$_{21}$O$_3$P |
| Formula weight | 460.44 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $a$ = 7.5142(7) Å, alpha = 106.7420(10)° |
| | $b$ = 10.8401(10) Å, beta = 97.794(2)° |
| | $c$ = 14.6310(13) Å, gamma = 92.854(2)° |
| Volume | 1125.73(18) A$^3$ |
| Z | 2 |
| Density (calculated) | 1.358 Mg/m$^3$ |
| Absorption coefficient | 0.154 mm$^{-1}$ |
| $F$(000) | 480 |
| Crystal size | 0.48 mm × 0.36 mm × 0.22 mm |
| Theta range for data collection | 1.47–28.34° |
| Index ranges | $-9 \leq h \leq 9$, $-13 \leq k \leq 13$, $-19 \leq l \leq 19$ |
| Reflections collected | 9679 |
| Independent reflections | 5104 [$R$(int) = 0.0240] |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9670 and 0.9298 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 5104/0/307 |
| Goodness-of-fit on $F^2$ | 1.064 |
| Final $R$ indices [$I > 2$ sigma($I$)] | R1 = 0.0616, wR2 = 0.1436 |
| $R$ indices (all data) | R1 = 0.0738, wR2 = 0.1526 |
| Largest diff. peak and hole | 0.730 and $-0.355$ e Å$^{-3}$ |

**Table 2**
Selected bond lengths (Å) and angles (°) for tri-1-naphthylphosphite.

| Bond lengths (Å) | | Bond angles (°) | |
|---|---|---|---|
| P(1)–O(1) | 1.646(6) | O(2)–P(1)–O(3) | 101.86(8) |
| P(1)–O(2) | 1.613(6) | O(2)–P(1)–O(1) | 97.92(8) |
| P(1)–O(3) | 1.641(6) | O(3)–P(1)–O(1) | 94.71(8) |
| O(1)–C(1) | 1.393(3) | C(1)–O(1)–P(1) | 118.95(14) |
| O(2)–C(11) | 1.400(3) | C(11)–O(2)–P(1) | 127.77(14) |
| O(3)–C(21) | 1.392(3) | C(21)–O(3)–P(1) | 124.72(14) |
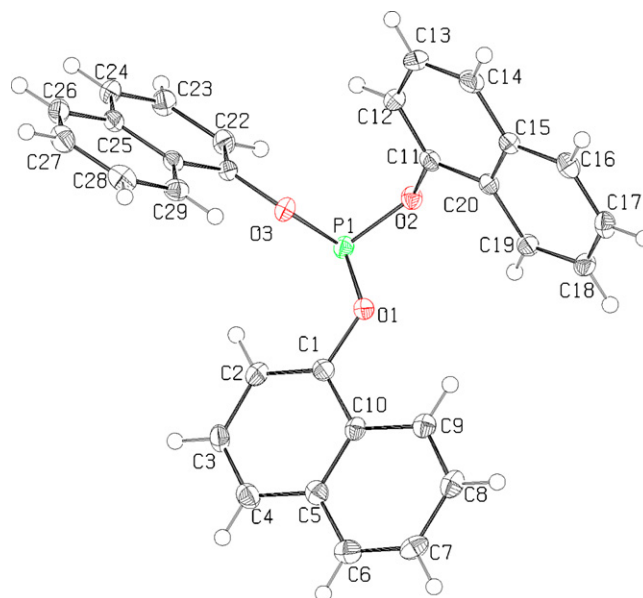


**Fig. 1.** ORTEP diagram of tri-1-naphthylphosphite.

fiber and cemented using epoxy resin. Intensity data for all three crystals were collected using Mo K$\alpha$ ($\lambda$ = 0.7107 Å) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector at 100 K. The data integration and reduction were processed with SAINT [25] software. An empirical absorption correction was applied to the collected reflections with SADABS [26] using XPREP. The structure was solved by direct method using SHELXTL [27] and was refined on $F^2$ by the full-matrix least-squares technique using the SHELXL-97 [28] program package. Graphics are generated using PLATON [29] and MERCURY 1.3. [30]. ORTEP diagram of TNPST and proposed structure of HRh(CO)$_3$L complex are given in Figs. 1 and 2, respectively.

### 2.4. Catalytic reaction

In typical hydroformylation experiment, required amount of catalyst, ligand, substrate, solvent were charged into stainless steel autoclave 100 mL reactor. The stirrer was adjusted to 1000 rpm. The reactor was flushed with nitrogen three times followed by flushing
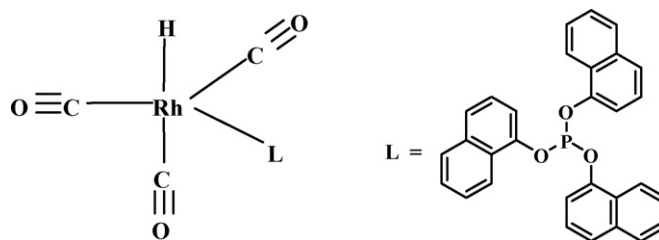


**Fig. 2.** Proposed structure of HRh(CO)$_3$L.

syngas twice at room temperature after which reactor was brought to reaction temperature and pressurized with syngas at desired pressure. The reaction was initiated by stirring; reaction started immediately as was evidenced by a pressure drop and accompanied increase of the temperature. After desired reaction time, the stirring was stopped and reactor was cooled down to room temperature, depressurized, flushed with $N_2$ and opened to collect final sample for a GC analysis.

## 2.5. Kinetic study

For kinetic studies, liquid samples were withdrawn during the experiment at regular intervals and analyzed for reactants and products in order to check the material balance. The reproducibility of the experiments was found to be in a range of ±5–7%.

The initial reaction rate was calculated within 15–20% conversion of alkenes to avoid inference form the products. The turnover frequency is defined as

$$\text{TOF} = \frac{\text{number of moles of product form}}{\text{number of moles of rhodium} \times \text{h}}$$

In order to study effect of parameters like concentration of alkene as well as catalyst, ligand/Rh ratio and partial pressure of CO and $H_2$, the hydroformylation experiments were carried out by varying these parameters.

## 2.6. Synthesis of Ligand and characterization

A dried Schlenk flask was placed under inert atmosphere and then charged with 9.87 g (0.069 mol) of 1-naphthol, 10.5 mL (0.075 mol) of $Et_3N$ and 80 mL of THF. The solution was cooled to −78 °C and $PCl_3$ 2 mL (0.023 mol) was added drop wise under stirring at the same temperature over 10 min. A colorless precipitate formed immediately. After 10 min, the mixture was allowed to warm to room temperature and stirred additionally for 3 h. After 3 h, a thick suspension of light yellow solid was obtained. The precipitate was filtered off and washed with dry THF (2× 35 mL). The filtrates were combined and were evaporated in vacuo yielding crude ligand as oil. The crude ligand was washed with chilled hexane and was concentrated in vacuo, ligand was solidified on cooling at 0 °C. Yield: 6.03 g, 57%. ^{31}P NMR ($CDCl_3$): δ 132.8 ppm, ^{1}H NMR ($CDCl_3$): δ 7.0–8.2 ppm (m, 7H, aromatic).

## 2.7. Synthesis of in situ Rh–TNPST complex and characterization

A solution of 0.015 g (0.058 mmol) of $Rh(CO)_2(acac)$ in 25 mL toluene was prepared under inert atmosphere. To this solution was then added 0.160 g (0.348 mmol) of the TNPST ligand. Evolution of CO was observed immediately and the mixture was stirred for 30 min. The solution was placed under 3.0 MPa syngas pressure at 80 °C and stirred 30 min. After 30 min a sample was withdrawn for IR and NMR analysis. The IR spectrum shows three peaks at, 2063, 2044, 2012 $cm^{-1}$. ^{31}P NMR ($CDCl_3$): doublet at δ 138.2 ppm, J (P-Rh) = 241 Hz. The mono ligand complex could not be isolated and has only been observed under syngas environment [14]. Bases on the ^{31}P NMR and IR data, the probable structure of the in situ form Rh–TNPST complex in the presence of syngas is given in Fig. 2 where three CO molecules are coordinated with rhodium metal along with one TNPST ligand and hydrogen.

## 2.8. Steric characteristics of ligand

The steric parameter of the ligand can be determined by cone angle known as the Tolman's cone angle according to Tolman's procedure [31] or the new approach develop by Muller et al. [32] We have calculated the cone angle of TNPST according to the Muller

procedure taking the metal-phosphorous distance and hydrogen atom radius as 2.28 and 0.3 A° respectively. Crystallographic data for TNPST has been used for the cone angle calculation. Crystallographic cone angle, $\Theta$, for TNPST was found as 166°.

## 3. Results and discussion

### 3.1. Hydroformylation of 1-hexene

The hydroformylation of 1-hexene was studied using $Rh(CO)_2(acac)$ as the catalyst precursor and TNPST as the ligand in the temperature range of 50–90 °C, total syngas pressure of 2.0–6.0 MPa and toluene as a solvent. The reaction products were 1-heptanal and 2-methylhexanal along with 2-hexene obtained by the isomerization of 1-hexene were analyzed by GC.

#### 3.1.1. Effect of temperature

The conversion and aldehyde selectivity data for Rh/TNPST catalyzed hydroformylation of 1-hexene performed at different temperatures (50–90 °C), under 3.0 MPa pressure, are given in Table 3. The reaction rate and isomerization increases with the increase in reaction temperature. However, aldehyde selectivity is found to decrease with increasing temperature. A slight increase in the $n/i$ ratio is also observed. For example, at 50 °C, reaction rate is $5.51 \times 10^3$ mol mol$_{Rh}^{-1}$ h$^{-1}$ and selectivity toward aldehyde is 92% where as at 90 °C, the rate increased up to $67.51 \times 10^3$ mol mol$_{Rh}^{-1}$ h$^{-1}$ with heptanal selectivity decreases to 75%. The decrease in aldehyde selectivity at higher temperature is mainly due to increase in the isomerized product (Table 3). The hydroformylation activity of internal alkene is less as compare to 1-alkene [12]. The amount of isomerization product increases from 8 to 25% as the temperature increases from 50 to 90 °C.

#### 3.1.2. Effect of ligand/Rh ratio

It is well recognized that catalytic activity varies nonlinearly as a function of phosphine concentration [33]. The rate increases as the phosphine concentration increases, until it reaches maxima. Further increase in the ligand concentration leads to lower rates due to the hindrance in the formation of the active species. Generally, the catalytic activity and the selectivity increase as the ligand/Rh ratio increases under the homogeneous condition. However, in this system, a decrease in the rate is observed with an increase in ligand/Rh ratio from 6.0 to 18.0 (Table 4). Therefore one can conclude that ligand/Rh ratio of 6.0 is sufficient to form an active catalyst and it is reasonably to state that under this system, the decreasing trend of the catalytic activity begins at lower ligand excess. This trend is also found in biphenyl based monodentate phosphite [34].

#### 3.1.3. Effect of initial 1-hexene concentration

The effect of 1-hexene concentration on the rate of hydroformylation was studied at 80 °C, 3.0 MPa syngas pressure, ligand/Rh of 6.0, and 0.23 mM rhodium precursor concentration by changing 1-hexene initial concentration from 1.86 to 3.02 M. At different

**Table 3**
Effect of temperature on Rh/tri-1-naphthylphosphite catalyzed hydroformylation of 1-hexene[a].

| Entry | Temp. (°C) | Initial rate, $r_i$ ($\times 10^3$ mol mol$_{Rh}^{-1}$ h$^{-1}$) | $S_{isomer}$ (%) | $S_{aldehyde}$ (%) | n/b |
|---|---|---|---|---|---|
| 1 | 50 | 05.51 | 8 | 92 | 63/37 |
| 2 | 60 | 17.37 | 10 | 90 | 66/34 |
| 3 | 70 | 29.71 | 11 | 89 | 68/32 |
| 4 | 80 | 59.46 | 14 | 86 | 70/30 |
| 5 | 90 | 67.51 | 25 | 75 | 65/35 |

[a] Reaction conditions: $[Rh(CO)_2(acac)] = 0.23$ mmol/L, P/Rh = 6.0, [1-hexene] = 2.79 mol/L, syngas pressure ($CO/H_2 = 1:1$) = 3.0 MPa, solvent (toluene) = 50 mL.

**Table 4**
Effect of P/Rh ratio on Rh/tri-1-naphthylphosphite catalyzed hydroformylation of 1-hexene[a].

| Entry | P/Rh | Initial rate, $r_i$ ($\times 10^3$ mol mol$_{Rh}^{-1}$ h$^{-1}$) | $S_{isomer}$ (%) | $S_{aldehyde}$ (%) | n/b |
|---|---|---|---|---|---|
| 1 | 3.0 | 28.88 | 12 | 88 | 67/33 |
| 2 | 6.0 | 29.71 | 11 | 89 | 68/32 |
| 3 | 12.0 | 23.48 | 10 | 90 | 71/29 |
| 4 | 18.0 | 21.35 | 8 | 92 | 72/28 |

[a] Reaction conditions: [Rh(CO)$_2$(acac)] = 0.23 mmol/L, [1-hexene] = 2.79 mol/L, syngas pressure (CO/H$_2$ = 1:1) = 3.0 MPa, temp. = 70 °C, solvent (toluene) = 50 mL.

1-hexene concentration (1.86–3.02 M), the reaction rate is independent of the alkene concentration and shows zero order dependency on the initial 1-hexene concentration (Table 5). Similar zero order dependency with respect to 1-alkene was reported using Rh/Tris (2-*tert*-butyl-4-methyl-phenyl) phosphite system [11]. However hydroformylation using HRhCO(PPh$_3$)$_3$ show substrate inhibited kinetics for 1-hexene. Generally, a positive order dependency on olefin has been reported till a critical substrate/catalyst ratio is reached, after that a negative or zero dependence is reported. The variation of the initial 1-hexene concentration scarcely influenced the normal to branch ratio.

### 3.1.4. Effect of initial rhodium precursor concentration

The study of effect of rhodium precursor concentration on the rate of hydroformylation reaction showed the increase in rate with an increase in the catalyst concentration (0.23–0.69 mM). The rhodium concentration was varied from 0.25 to 3.0 times of our standard rhodium precursor concentration 0.23 mM. The results are shown in Fig. 3, it is evident that the rate of formation of product is linearly proportional to the rhodium precursor concentration and gave first order dependency with respect to the rhodium concentration.

### 3.1.5. Effect of syngas pressure and variation of the pCO and pH$_2$

The catalytic hydroformylation reaction of Rh/TNPST system was studied at 70 °C at different syngas pressure. At 2.0 MPa syngas pressure, alkene isomerized product and hydroformylation products were found to be 23% and 77% respectively. With increase in the syngas pressure from 2.0 to 6.0 MPa, rate of reaction increases slightly and the n/i ratio also slightly affected. Increases in the rate with increase in pressure could be due to enhancement of availability of CO and H$_2$ at high pressure. Moreover, there is a significant decrease in the isomerization of alkene at higher pressure.
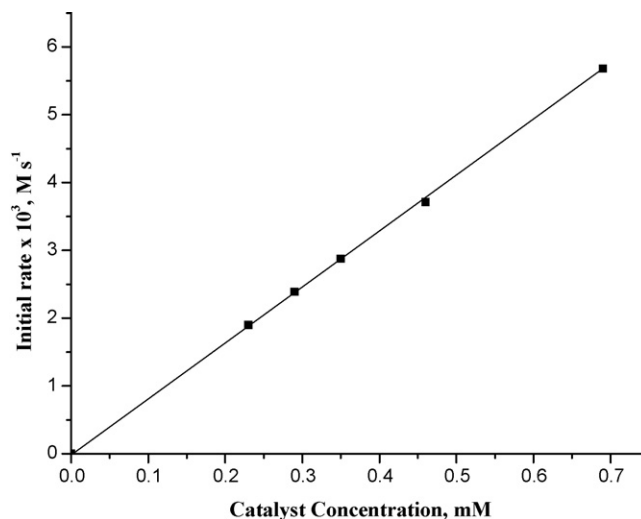
In general, the chemo selectivity to aldehydes is higher at low temperature, it decreases with an increase the temperature and syngas pressure; regioselectivity to linear aldehydes increases with increasing the temperature and slightly affected by the total syngas pressure. Lazzaroni et al. [35] have studied the influence of various reaction parameters (temp. 50–120 °C, and 40–200 atm) on the chemo- and regioselectivity of 1-hexene hydroformylation using Rh$_4$(CO)$_{12}$ as catalyst precursor. They concluded that at low temper-



**Fig. 3.** Effect of catalyst concentration on the rate of 1-hexene hydroformylation: reaction conditions: [1-hexene] = 2.79 mol/L, P/Rh = 6.0, syngas pressure (CO/H$_2$ = 1:1) = 3.0 MPa, temp. = 80 °C, solvent (toluene) = 50 mL.

ature, the formation of alkyl-rhodium intermediate is irreversible, however, at higher temperature it is reversible and β-elimination of hydride forms isomeric alkene. Moreover, at high temperature, regioselectivity to linear one increases as secondary alkyl-rhodium has higher tendency to undergo β-elimination than primary one (Scheme 1).

The effect of H$_2$ partial pressure on the rate of hydroformylation of 1-hexene was studied at 70 °C, with constant CO pressure (1.5 MPa), 2.79 M 1-hexene and 0.23 mM catalyst concentration by varying the H$_2$ partial pressure (2.5–4.5 MPa). The rate of hydroformylation of 1-hexene was found to increase on increasing the partial pressure of hydrogen, indicating first order dependency on H$_2$ partial pressure (Table 6), which suggest that the oxidative addition of hydrogen to the acylrhodium intermediate is the rate determining step. No considerable change in the n/i ratio is observed.

The effect of CO partial pressure on the rate of hydroformylation of 1-hexene was studied at 70 °C, with constant H$_2$ pressure (1.5 MPa), 2.79 M of 1-hexene and 0.23 mM catalyst concentration by varying the CO partial pressure (2.5–4.5 MPa). The hydroformylation reaction rate however shows an inverse dependency on the CO partial pressure (Table 6). The rate inhibition trend at higher CO partial pressure suggests the formation of inactive acyl species (RCO)Rh(CO)$_3$L. The CO present in the reaction mixture is consumed so fast that the diffusion of CO from the vapor into the solution becomes rate determining. With an increase in the CO pressure,

**Table 5**
Effect of initial 1-hexene concentration on Rh/tri-1-naphthylphosphite catalyzed hydroformylation of 1-hexene[a].

| Entry | 1-Hexene (M) | Initial rate, $r_i$ ($\times 10^3$ mol mol$_{Rh}^{-1}$ h$^{-1}$) | $S_{isomer}$ (%) | $S_{aldehyde}$ (%) | n/b |
|---|---|---|---|---|---|
| 1 | 1.86 | 58.32 | 14 | 86 | 70/32 |
| 2 | 2.33 | 57.47 | 14 | 86 | 70/30 |
| 3 | 2.79 | 58.75 | 15 | 85 | 70/30 |
| 4 | 3.02 | 56.27 | 17 | 83 | 69/30 |

Average initial rate = 57.71 $\times 10^3$ mol mol$_{Rh}^{-1}$ h$^{-1}$.

[a] Reaction conditions: [Rh(CO)$_2$(acac)] = 0.23 mmol/L, P/Rh = 6.0, syngas pressure (CO/H$_2$ = 1:1) = 3.0 MPa, temp. = 80 °C, solvent (toluene) = 50 mL.

**Table 6**
Effect of syngas pressure and variation of pCO and pH$_2$ on Rh/tri-1-naphthylphosphite catalyzed hydroformylation of 1-hexene[a].

| Entry | pCO | pH$_2$ | Initial rate, $r_i$ ($\times 10^3$ mol mol$_{Rh}^{-1}$ h$^{-1}$) | $S_{isomer}$ (%) | $S_{aldehyde}$ (%) | n/b |
|---|---|---|---|---|---|---|
| 1 | 10 | 10 | 22.51 | 23 | 77 | 72/28 |
| 2 | 15 | 15 | 29.71 | 11 | 89 | 68/32 |
| 3 | 20 | 20 | 35.22 | 10 | 90 | 66/34 |
| 4 | 25 | 25 | 38.88 | 8 | 92 | 66/34 |
| 5 | 15 | 25 | 42.73 | 11 | 89 | 66/34 |
| 6 | 15 | 35 | 57.76 | 10 | 90 | 66/34 |
| 7 | 15 | 45 | 76.07 | 10 | 90 | 66/34 |
| 8 | 25 | 15 | 24.89 | 10 | 90 | 65/35 |
| 9 | 35 | 15 | 22.79 | 8 | 92 | 66/34 |
| 10 | 45 | 15 | 16.09 | 8 | 92 | 66/34 |

[a] Reaction conditions: [Rh(CO)$_2$(acac)] = 0.23 mmol/L, P/Rh = 6.0, [1-hexene] = 2.79 mol/L, temp. = 70 °C, solvent (toluene) = 50 mL.
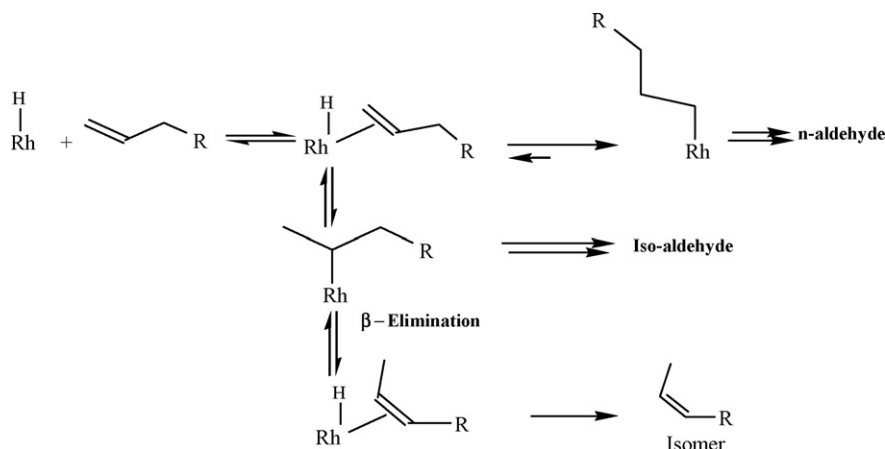
**Scheme 1.** Possible pathways for the 1-hexene coordinated rhodium complex.

the isomerization reaction suppressed and the $n/i$ ratio is slightly changed.

### 3.2. Hydroformylation of styrene

The hydroformylation of styrene gave two regio-isomers namely branched (2-phenyl propionaldehyde) and linear aldehyde (3-phenyl propionaldehyde) under employed reaction conditions. Effect of different parameter on the rate of hydroformylation of styrene is discussed below.

#### 3.2.1. Effect of temperature

In order to elucidate the influence of the reaction temperature on the rate of hydroformylation of styrene, other reaction parameters were kept constant as: syngas pressure of 3.0 MPa, ligand/Rh = 6.0, styrene concentration of 1.40 M and catalysts concentration of 0.23 mM. Reaction temperature was varied from 50 to 80 °C. With an increasing temperature, the rate of hydroformylation reaction increases and excellent chemo selectivity towards aldehydes was observed (Table 7). At low reaction temperature, formation of branched regio-isomer predominates. The formation of branched aldehyde decreases with an increase in reaction temperature. In the Rh-catalyzed hydroformylation of styrene and p-substituted styrene, the branched regio-isomer prevalence over the linear one is well known [36] showing an anomalous regioselectivity as compared with that observed in case of 1-alkens.

Rhodium carbonyl catalyzed hydroformylation of styrene as a function of temperature and pressure have been reported by Lazzaroni et al. [37]. Under employed reaction conditions, the branch isomer decreases with an increase in the reaction temperature. CO or $H_2$ partial pressure also affects the region-selectivity of the reaction. These results have been simplified on the basis of the isomerization of the branch alkyl rhodium intermediate to linear one, preferential by high temperature that reducing the branch to linear

isomer ratio. The isomeric ratio found at room temperature strongly favors the branched isomer which has been also supported by the deuteroformylation experiments [38].

#### 3.2.2. Effect of ligand/Rh ratio

The effect of L/Rh ratio on the rate of styrene hydroformylation was studied at 70 °C, 3.0 MPa syngas pressure and 1.4 M styrene concentration by varying L/Rh ratio 3.0 to 18.0. The data show that with an increase in ligand/Rh ratio from 6.0 to 18.0, there is decrease in the reaction rate. However, aldehyde selectivity and b/n ratio increases (Entry 1: L/Rh 3.0, initial rate, $r_i$ (mol mol$_{Rh}^{-1}$ h$^{-1}$) $10.17 \times 10^3$, b/n 77/23; Entry 2: L/Rh 6.0, initial rate, $r_i$ $10.96 \times 10^3$, b/n 78/22; Entry 3: L/Rh 12.0, initial rate, $r_i$ $7.83 \times 10^3$, b/n 81/19; Entry 4: L/Rh 18.0, initial rate $r_i$ $5.21 \times 10^3$, b/n 83/17). The decrease in the rate may be due to enhance stability of the active species with the increase of ligand/Rh ratio.

#### 3.2.3. Effect of initial styrene concentration

The initial styrene concentration was systematically varied from 0.93 to 1.86 M at 80 °C with 3.0 MPa syngas pressure, ligand/Rh = 6.0 and 0.23 mM catalyst concentration. The rate of hydroformylation was found to be zero order with respect to the initial styrene concentration in the range of 0.93 to 1.86 M (Table 8). The zero order dependence on styrene has also been reported for the hydroformylation of styrene catalyzed by $Rh_4CO_{12}$ [35] and HRhCO(PPh$_3$)$_3$ [19]. According to the Scheme 2, the addition of olefin to form the olefin–Rh complex is an equilibrium step. The equilibrium may be attained even at lower concentration of styrene leadings to zero order dependence. The observed average initial reaction rate of styrene $14.89 \times 10^3$ mol mol$_{Rh}^{-1}$ h$^{-1}$ is approximately 3.9 times lower than that of the rate of 1-hexene hydroformylation. Similar results were obtained in case of Rh/Tris (2-tert-butyl-4-methyl-phenyl) phosphite system [11]. However, this result is in contrast

**Table 7**
Effect of temperature on Rh/tri-1-naphthylphosphite catalyzed Hydroformylation of styrene[a].

| Entry | Temp. (°C) | Initial rate, $r_i$ ($\times 10^3$ mol mol$_{Rh}^{-1}$ h$^{-1}$) | $S_{aldehyde}$ (%) | b/n |
|---|---|---|---|---|
| 1 | 50 | 2.77 | >99 | 90/10 |
| 2 | 60 | 6.53 | >99 | 85/15 |
| 3 | 70 | 10.96 | >99 | 78/22 |
| 4 | 80 | 15.14 | >99 | 73/27 |

[a] Reaction conditions: [Rh(CO)$_2$(acac)] = 0.23 mmol/L, P/Rh = 6.0, [styrene] = 1.40 mol/L, syngas pressure (1:1) = 3.0 MPa, solvent (toluene) = 50 mL.

**Table 8**
Effect of initial styrene concentration on Rh/tri-1-naphthylphosphite catalyzed hydroformylation of styrene[a].

| Entry | Styrene (M) | Initial rate, $r_i$ ($\times 10^3$ mol mol$_{Rh}^{-1}$ h$^{-1}$) | $S_{aldehyde}$ (%) | b/n |
|---|---|---|---|---|
| 1 | 0.93 | 14.61 | >99 | 68/32 |
| 2 | 1.16 | 14.95 | >99 | 73/27 |
| 3 | 1.40 | 15.14 | >99 | 73/27 |
| 4 | 1.86 | 14.87 | >99 | 72/28 |

Average initial rate = $14.89 \times 10^{-3}$ mol mol$_{Rh}^{-1}$ h$^{-1}$.

[a] Reaction conditions: [Rh(CO)$_2$(acac)] = 0.23 mmol/L, P/Rh = 6.0, syngas pressure (CO/H$_2$ = 1:1) = 3.0 MPa, temp. = 80 °C, solvent (toluene) = 50 mL.
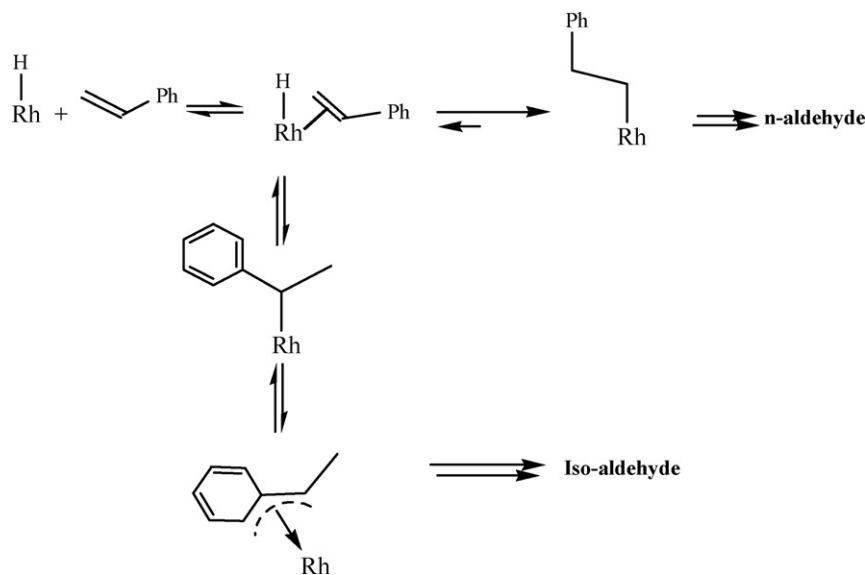
**Scheme 2.** Possible pathways for the interaction of styrene with rhodium complex.

with results obtained with $Rh_4CO_{12}$ [39] and $HRh(CO)(PPh_3)_3$ [40] as catalyst.

### 3.2.4. Effect of initial rhodium precursor concentration

To study the effect of rhodium precursor concentration on the rate of hydroformylation of styrene. The rhodium precursor concentration was varied (0.23–0.69 mM) at 70 °C under 3.0 MPa syngas pressure and ligand/Rh = 6.0, 1.40 M styrene concentration. The rate of hydroformylation of styrene was found to be linearly dependent with respect to the rhodium precursor concentration. (Entry 1: rhodium precursor concentration 0.23 mM, initial rate, $r_i$ $0.7 \times 10^3$ M s$^{-1}$; Entry 2: rhodium precursor concentration 0.29 mM, initial rate, $r_i$ $0.875 \times 10^3$ M s$^{-1}$; Entry 3: rhodium precursor concentration 0.35 mM, initial rate, $r_i$ $1.05 \times 10^3$ M s$^{-1}$; Entry 4: rhodium precursor concentration 0.46 mM, initial rate $r_i$ $1.35 \times 10^3$ M s$^{-1}$; Entry 5: rhodium precursor concentration 0.69 mM, initial rate $r_i$ $2.05 \times 10^3$ M s$^{-1}$). The first order dependence with respect to catalyst is consistent with increase in the active rhodium species concentration with increase in the catalyst precursor concentration. Similar result was also found for $HRh(CO)(PPh_3)_3$ catalyzed hydroformylation of styrene reported by Nair et al. [19].

### 3.2.5. Effect of syngas pressure and variation of pCO and pH$_2$

The rate of reaction of styrene hydroformylation increases with an increase of syngas pressure from 3.0 to 5.0 MPa, but the regioselectivity is slightly affected. The increase in CO partial pressure shows a typical substrate inhibited kinetics. This may be due to the decrease in active species concentration at high CO partial pressure resulting in the decrease in the rate reaction. The observation of negative order dependence with CO partial pressure was also reported for other olefins substrate [11,19].

With an increase H$_2$ partial pressure, the rate of hydroformylation of styrene (the partial pressure of H$_2$ varied from 2.5 to 4.5 MPa in hydroformylation experiments performed at 70 °C and 1.5 MPa constant pressure of CO) was found to be increased. The partial pressure of H$_2$ has strong effect on the rate of hydroformylation of styrene; these results are shown in Table 9. First order dependency on hydrogen indicated that the oxidative addition of H$_2$ to the acyl rhodium intermediate species is the rate determining step.

### 3.3. Hydroformylation of cyclohexene

In order to check catalytic performance of Rh/TNPST system in the cyclic alkene, cyclohexene was chosen as the substrate which yield only one hydroformylation product because it remain unchanged upon isomerization. The chemo-selectivity to aldehydes is >99% in all cases.

It is known that the hydroformylation of cyclic alkenes is rather difficult due to their internal double bonds. Thus for all the catalytic systems, the observed catalytic activities are lower than the activities which were found for 1-alkenes.

### 3.3.1. Effect of temperature

In order to study the effect of temperature on the rate of cyclohexene hydroformylation, experiments were performed under varying temperatures (70–100 °C) maintaining constant ligand/Rh ration, cyclohexene, catalyst concentration and 3.0 MPa syngas pressure. In (Table 10), the influence of the reaction temperature on the rate is presented. The rate of reaction increases as increasing the reaction temperature going from 70 to 100 °C, the reaction proceeds faster by a factor of approximately 6.

### 3.3.2. Effect of initial cyclohexene concentration

The effect of initial cyclohexene concentration on the rate of hydroformylation of cyclohexene was studied at 80 °C, 0.23 mM cat-

**Table 9**
Effect of syngas pressure and variation of pCO and pH$_2$ on Rh/tri-1-naphthylphosphite catalyzed hydroformylation of styrene[a].

| Entry | pCO | pH$_2$ | Initial rate, $r_i$ ($\times 10^3$ mol mol$_{Rh}^{-1}$ h$^{-1}$) | $S_{aldehyde}$ (%) | b/n |
|---|---|---|---|---|---|
| 1 | 15 | 15 | 10.96 | >99 | 78/22 |
| 2 | 20 | 20 | 13.04 | >99 | 80/20 |
| 3 | 25 | 25 | 16.70 | >99 | 80/20 |
| 4 | 15 | 25 | 16.17 | >99 | 82/18 |
| 5 | 15 | 35 | 25.04 | >99 | 84/16 |
| 6 | 15 | 45 | 28.96 | >99 | 85/15 |
| 7 | 25 | 15 | 8.88 | >99 | 80/20 |
| 8 | 35 | 15 | 7.31 | >99 | 82/18 |
| 9 | 45 | 15 | 4.18 | >99 | 81/19 |

[a] Reaction conditions: [Rh(CO)$_2$(acac)] = 0.23 mmol/L, P/Rh = 6.0, [styrene] = 1.40 mol/L, temp. = 70 °C, solvent (toluene) = 50 mL.

**Table 10**
Effect of Temperature on Rh/tri-1-naphthylphosphite catalyzed hydroformylation of cyclohexene[a].

| Entry | Temperature (°C) | Initial rate, $r_i$ (mol mol$_{Rh}^{-1}$ h$^{-1}$) | $S_{aldehyde}$ (%) |
|---|---|---|---|
| 1 | 70 | 208 | >99 |
| 2 | 80 | 660 | >99 |
| 3 | 90 | 940 | >99 |
| 4 | 100 | 1240 | >99 |

[a] Reaction conditions: [Rh(CO)$_2$(acac)] = 0.23 mmol/L, P/Rh = 6.0, [cyclohexene] = 0.23 mol/L, syngas pressure (1:1) = 3.0 MPa, solvent (toluene) = 50 mL.
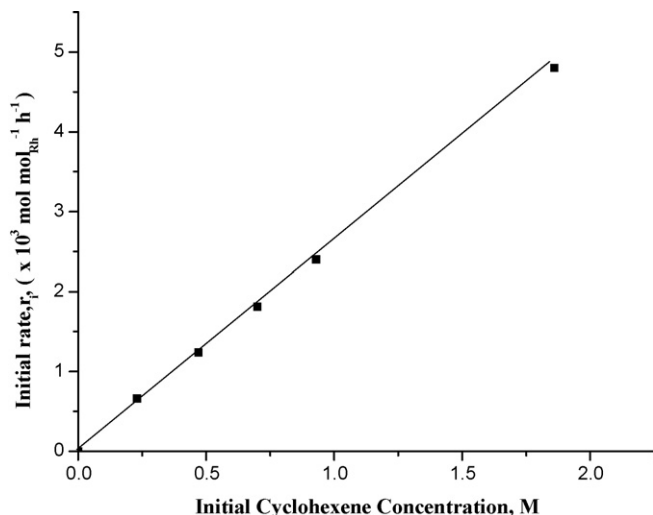


**Fig. 4.** Effect of initial cyclohexene concentration on the rate of cyclohexene hydroformylation; reaction conditions: [Rh(CO)$_2$acac] = 0.23 mol/L, P/Rh = 6.0 syngas pressure (CO/H$_2$ = 1:1) = 3.0 MPa, temp. = 80 °C, solvent (toluene) = 50 mL.

alyst concentration, and 3.0 MPa syngas pressure by varying the cyclohexene concentration from 0.23 to 1.86 M. The plot of initial rate vs. initial cyclohexene concentration (Fig. 4) shows a straight line which clearly indicated that the reaction rate of cyclohexene hydroformylation is first order with respect to the initial cyclohexene concentration. The hydroformylation rate of internal alkene is known to be much slower than the hydroformylation rate of 1-alkenes, found approximately 87 times lower than for 1-hexene.

### 3.3.3. Effect of syngas pressure and variation of pCO and pH$_2$

The rate of hydroformylation of cyclohexene increases slightly as the total syngas pressure increases. The rate of reaction was also found to be increase with an increase in the partial pressure of H$_2$ but in this case slightly positive effect was found while reverse trend was observed in case when partial pressure of CO was increased (Table 11).

**Table 11**
Effect of syngas pressure and variation pCO and pH$_2$ on Rh/tri-1-naphthylphosphite catalyzed hydroformylation of cyclohexene[a].

| Entry | pCO | pH$_2$ | Initial rate, $r_i$ (mol mol$_{Rh}^{-1}$ h$^{-1}$) | $S_{aldehyde}$ (%) |
|---|---|---|---|---|
| 1 | 15 | 15 | 660 | >99 |
| 2 | 20 | 20 | 695 | >99 |
| 3 | 25 | 25 | 721 | >99 |
| 4 | 15 | 25 | 726 | >99 |
| 5 | 15 | 35 | 738 | >99 |
| 6 | 15 | 45 | 834 | >99 |
| 7 | 35 | 15 | 521 | >99 |
| 8 | 45 | 15 | 460 | >99 |
| 9 | 55 | 15 | 382 | >99 |

[a] Reaction conditions: [Rh(CO)$_2$(acac)] = 0.23 mmol/L, P/Rh = 6.0, [cyclohexene] = 0.23 mol/L, temp. = 80 °C, solvent (toluene) = 50 mL.

## 4. Mechanism aspect

The common accepted mechanism for hydroformylation reaction, so called dissociative mechanism has been proposed by several authors [41–43], for both modified and unmodified cobalt and rhodium complexes as a catalyst. Evans et al. [43] have proposed dissociative and associative type of mechanism. The dissociative type mechanism is, however, considered to be the major pathway. The rhodium complex modified with triphenylphosphine forms a active species like HRh(CO)$_2$L$_2$, in case phosphine is replaced by bulky phosphite ligand, one would expect more steric hindrance around the metal center which can effect the alkene addition resulting in the lower reaction rate. However Van Rooy et al. [11] have reported the use of the bulky phosphite, tris(o-t-butylphenyl)phosphite as a ligand and observed high reaction rate for the variety of substrates. The high reactivity is explained by the formation of mono ligated rhodium phosphite complex, HRh(CO)$_3$L, on the basis of in situ IR and NMR studies. Bulky phosphites are weak σ donor and strong π acceptor than phosphine ligand. Generally strong σ donor ligands impart high electron density on the metal center and hence substantial back donation to CO whereas ligand with π acceptor capabilities compete with CO for the electron back donation, therefore electron density around metal center decreases and as a result reaction rate increases due to facile CO dissociation and easily alkene association.

At high reaction rate, generally the reaction is governed by mass transfer and hence the lack of CO dissolved in the liquid phase leads to formation of unsaturated Rh species which can isomerizes the olefin. When all terminal alkenes are converted into aldehydes, the internal alkenes start to participate in the hydroformylation as a result, the high isomerization give low n/i ratio.

TNPST is bulkier and sterically hindered ligand as compare to TPP (cone angle of TNPST is 166° while for TPP is 145°) and this may give rise to an active species containing only one bulkier phosphite ligand around rhodium resulting in the formation of HRh(CO)$_3$L, (L = tri-1-naphthylphosphite) intermediate species which is confirmed by in situ IR and NMR analysis. The FT-IR spectrum of in situ prepared Rh/bulky phosphite (TNPST) complex under syngas environment and in absence of substrate gives IR stretching vibrations at 2063, 2044, 2012 cm$^{-1}$ which clearly indicate that three carbonyl group coordinate with rhodium center along with one TNPST (L) as ligand. Similar IR observation has been reported by Jongsma et al. [14] wherein they reported the in situ IR spectrum during the hydroformylation of cyclooctene corresponding to reactive species HRh(CO)$_3$L, {L = tris(o-t-butylphenyl)phosphite} the observed carbonyl frequencies during hydroformylation reaction were 2093, 2043 and 2013 cm$^{-1}$. Therefore, on the basis of experimental result and based on the reported literature on hydroformylation mechanisms using bulky ligand, the proposed mechanism for the rhodium catalyzed hydroformylation using bulky phosphite, tri-1-naphthylphosphite, as ligand is depicted below (Fig. 5).

## 5. Rate expressions for the hydroformylation of alkenes catalyzed by Rh/phosphite

Extensive literature have appeared in the hydroformylation reaction system dealing with catalyst based on unmodified or modified Rh-complex of PPh$_3$ but only a few reports are there on kinetics aspect based on rhodium modified by bulky monophosphite ligand [11,12].

Various rate equations have been given by different authors depending on the reaction condition for the phosphine modified rhodium catalyst; the reaction rate dependence on the different reaction parameter is as follow:

(i) first order with catalyst concentration,
(ii) first order in pH$_2$,
(iii) at low olefin concentration, positive order and at high olefin concentration negative order,
(iv) at low CO partial pressure, positive order and at high CO partial pressure negative order,
(v) at low ligand concentration, positive order and at high ligand concentration zero order.

For bulky monodentate phosphite modified rhodium catalyst, the high reaction rate is observed and the rate depends on the following parameters:

(i) first order with catalyst concentration,
(ii) first order in pH$_2$,
(iii) zero order with olefin concentration (in case of 1-alkene), in case of cyclic alkene positive order is found,
(iv) at low CO partial pressure, positive order and at high pressure negative order,
(v) at low ligand concentration, positive order and at high ligand concentration zero order dependence on ligand concentration.

Hydroformylation of 1-alkene using rhodium complex modified with bulky phosphite ligand gives very high rate as compare to the modified rhodium complex by TPP and unmodified rhodium complex, moreover comparison of ligand is difficult because TPP modified system is first order with respect to 1-olefin initial concentration.

The hydroformylation of styrene using rhodium complex modified by bulky phosphite ligand is some what slower than 1-hexene and initial rate (at 80 °C, 3.0 MPa syngas pressure) for styrene hydroformylation was found approximately 3.9 time slower than initial rate of 1-hexene hydroformylation while the hydroformylation of cyclohexene was found even slow than 1-alkene due to internal double bond and initial rate (at 80 °C, 3.0 MPa syngas pressure, 0.23 M initial cyclohexene concentration) for cyclohexene hydroformylation was found ~87 times slower than 1-hexene but this comparison has limitation because initial rate of cyclohexene hydroformylation is first order with respect to the initial cyclohexene concentration.

As described earlier, Lazzaroni et al. [37] have showed that the degree of isomerization depends on the reaction conditions. Coordination of alkene to rhodium form two alkyl species like linear alkyl species and branch alkyl species, at high temperature branch alkyl species gives back to 1-alkene or 2-alkene while linear alkyl species is irreversible because the isomerization reaction has a higher free energy of activation than hydroformylation. Therefore at high temperature, the proportion of isomeric product is expected to increase with an increase in the reaction temperature but in the case of styrene, at low temperature branch species is predominated due to the resonance stabilization of branched species. At high temperature, the branch species convert back to styrene by β-elimination while in the case of 1-alkene isomerization occurred which give 2-alkene which is hydroformylated to branched aldehyde products.

## 5.1. Rate equation for 1-hexene and styrene

By considering the catalytic cycle described in Fig. 5, some important steps based on actual mechanism is simplified and rate



**Fig. 5.** Propose mechanism for Rh/tri-1-naphthylphosphite catalyzed hydroformylation of alkenes.

**Scheme 3.** (a) Important reaction steps based on actual mechanism to derive rate equation for Rh/tri-1-naphthylphosphite catalyzed hydroformylation of 1-hexene and styrene; (b) reaction scheme based on actual mechanism to derive rate equation for Rh/tri-1-naphthylphosphite catalyzed hydroformylation of cyclohexene.

equation for hydroformylation of 1-alkene can be derived applying the equilibrium approximation. A first order dependency on the hydrogen partial pressure indicated that the oxidative addition of hydrogen to the acylrhodium intermediate species is the rate controlling step.

Therefore, from reaction (4) (Scheme 3a) the rate of reaction is given as

$$\text{rate} = kC_4[H_2] \tag{I}$$

Since, the total concentration of the catalyst species known as

$$C_T = C_1 + C_2 + C_3 + C_4 + C_5$$

$$C_T = \frac{C_1([CO] + K_1 + K_1K_2[ole] + K_1K_2K_3[ole][CO]}{+ K_1K_2K_3K_4[CO]^2[ole])}{[CO]} \tag{II}$$

Then, rate Eq. (I) becomes,

$$\text{rate} = \frac{kK_1K_2K_3C_T[H_2][CO][ole]}{([CO] + K_1 + K_1K_2[ole] + K_1K_2K_3[ole][CO]}{+ K_1K_2K_3K_4[CO]^2[ole])}$$

$$\text{rate} = \frac{\mathbf{k}C_T[H_2][CO][ole]}{([CO] + K_1 + X + Y[CO] + Z[CO]^2)} \tag{III}$$

where $\mathbf{k} = kK_1K_2K_3$, $X = K_1K_2[ole]$, $Y = XK_3$, $Z = XK_3K_4$.

The rate Eq. (III) is consistent with our proposed mechanism for the hydroformylation of olefin using rhodium bulky phosphite catalyst, indicating a first order dependency of $[H_2]$ and $[Rh]$, and negative order with high partial pressure of CO. This rate equation is also rather similar to that reported by Nair et al. for the hydroformylation of styrene catalyze by HRhCO $(PPh_3)_3$ [19].

### 5.2. Rate equation for cyclohexene

A first order dependency on the initial cyclohexene concentration indicated that the coordination of cyclohexene to rhodium species $(C_2)$ is the rate controlling step.

Therefore, from reaction (2) (Scheme 3b) the rate of reaction is given as

$$\text{rate} = KC_2[\text{cyclohexene}] \tag{IV}$$

Since, the total concentration of the catalyst species known as

$$C_T = C_1 + C_2$$

$$C_2 = \frac{K_1C_T}{K_1 + [CO]} \tag{V}$$

Then, rate Eq. (IV) becomes,

$$\text{rate} = \frac{KK_1C_T[\text{cyclohexene}]}{K_1 + [CO]} \tag{VI}$$

The above rate Eq. (VI) explains both the observed orders in the rhodium precursor and cyclohexene and the negative order with CO. The above rate Eq. (VI) for hydroformylation of cyclohexene is also similar to that reported by Leeuwen et al. for the hydroformylation of cyclohexene catalyze by Rh/tris(2-*tert*-butyl-4-methylphenyl) phosphite [11].

## 6. Conclusions

Rhodium complex modified with monodentate bulky phosphite ligand, TNPST was found to be effective catalytic system for hydroformylation of 1-alkenes which give high TOF under mild condition.

A very high initial rate is obtained for 1-hexene with reasonable regioselectivity of 2.33. The selectivity for the linear product increases with temperature up to 80 °C but for temperature > 80 °C, selectivity decreases due to high isomerization. While in the case of styrene, initial reaction rate is lower than 1-hexene, the selectivity for the branch isomer decreases with increasing temperature, but found high at low temperature and higher pressure. In the case of 1-hexene and styrene, reaction shows first order dependence on $H_2$ partial pressure indicating that the rate controlling step is the reaction of $H_2$ with the acylrhodium complex while for cyclohexene, reaction was found to be first order with initial cyclohexene concentration indicating that the addition of cyclohexene to the rhodium hydride complex is rate determining step. Moreover, in rhodium bulky phosphite system, the main catalytic active species

is HRh(CO)$_3$L, (characterized by NMR and IR spectroscopy) where only one phosphite ligand is coordinated to Rh center instead of two, as in the case of rhodium/TPP system. These observations indicate that the behavior of the bulky modified system is different from that of the modified TPP system but is similar to HRh(CO)$_4$ system.

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