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## Selectivity of Rhodium-catalyzed Hydroformylation of 1-Octene in a Thermomorphic Solvent System

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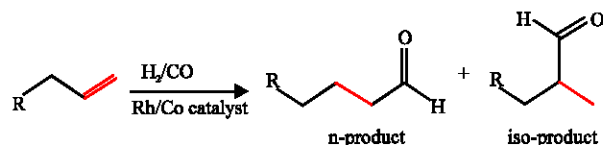
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**Abstract:** The use of temperature dependent multicomponent solvent (TMS) process, in which the catalyst remains as a residue in one of the liquid phases and the product goes preferably to the other liquid phase, can be an enabling strategy of commercial application of hydroformylation processes with high selectivity, efficiency and ease of product separation and catalyst recovery. This paper describes the isomer distribution of the formation of n-nonanal and 2-methyloctanal for the rhodium-catalyzed homogeneous hydroformylation of 1-octene using  $\text{HRh}(\text{CO})[\text{P}(\text{OPh})_3]_3$  catalyst in TMS-system consisting of propylene carbonate (PC), dodecane and 1,4-dioxane. Effects of the concentration of 1-octene and catalyst, temperature, composition of syngas ( $\text{H}_2/\text{CO}$ ), total pressure of syngas and ligand to catalyst  $[\text{P}(\text{OPh})_3/\text{HRh}(\text{CO})(\text{PPh}_3)_3]$  ratio on the selectivity of the nonylaldehyde products (n/iso ratio) have been measured. Highest selectivity for n-nonanal with average catalyst activity is observed at temperature of 363 K, equimolar of  $\text{CO}/\text{H}_2$ , total syngas pressure of 1.5 MPa and ligand/catalyst ratio of 12 in TMS composition of 0.1/0.3/0.6. This study is practically useful for the optimization of n-nonanal production by hydroformylation of 1-octene.

**Key words:** Hydroformylation, thermomorphic solvent systems, selectivity, 1-Octene, rhodium catalyst

### INTRODUCTION

One of the widely studied homogeneous catalyzed reactions, the hydroformylation reaction, provides a versatile route for the synthesis of a vast array of bulk and specialty chemicals, such as industrial solvents, biodegradable detergents, surfactants, lubricants and plasticizers (Bohnen and Cornils, 2003). The overall reaction can be represented by equation given below.



A cobalt- or rhodium-based catalyst is often used. The advantages of the rhodium catalyst system are mild reaction conditions, higher n:i (normal to iso) ratio of the products and higher activity. In general, a linear aldehyde is the desired product. It is known that hydroformylation of 1-octene, in the presence of rhodium-based catalyst, gives a mixture of two isomeric aldehydes namely, nonanal and 2-methyloctanal, although, under certain

conditions, small amounts of side products are formed. The problem of directing this reaction to give preferential formation of n-nonanal, owing to its greater practical importance, has mainly been mentioned in the open and patent literature. Little has been reported on how to influence the product distribution of isomeric aldehydes (Cornils, 1980; Gholap *et al.*, 1992; Piacenti *et al.*, 1991; Van Rooy *et al.*, 1995; Van Rooy *et al.*, 1996; Tijani and Ali, 2006). From the literature data, variations in the ratio of n-nonanal to 2-methyloctanal from 1.6 to 10.1 were observed under widely different conditions of temperature, catalyst concentration, ligand to catalyst mole ratio, solvent and partial pressures of carbon monoxide and hydrogen. The most influential parameter was found to be the partial pressure of carbon monoxide. The partial pressure of hydrogen has a small but reproducible effect on the product distribution. Temperature has a strong influence on the n/iso ratio, and conflicting results have been reported for the effect of catalyst concentration. Despite these investigations of the product distribution in the hydroformylation of 1-octene, the factors influencing the n-nonanal/2-methyloctanal ratio are still rather obscure (Van Rooy *et al.*, 1995). Also, detailed kinetics of these

individual reactions is lacking. Therefore, as a first step toward understanding the more complex problem of isomer distribution, the overall kinetics of the  $\text{HRh}(\text{CO})[\text{P}(\text{OPh})_3]_3$  catalyzed hydroformylation of 1-octene in TMS-system consisting of propylene carbonate (PC), dodecane and 1,4-dioxane was investigated and modeled (Shaharun *et al.*, 2010). The TMS-system is solvent mixture which changes thermally from biphasic to monophasic with distribution of the products and of the catalyst in the non-polar (dodecane) and polar phases (PC) thus simplifying the process of separation and recycling of the catalyst (Behr *et al.*, 2005; Behr and Roll, 2005; Behr and Fangewisch, 2003). We have also selected the optimum solvent composition as a practical one for further study based on the selectivity to nonanal, TOF value, percentage of Rh loss to nonpolar phase and yield of aldehyde (Shaharun *et al.*, 2010). In the present work, the objectives were to investigate the effect of process variables on the isomer distribution during the hydroformylation of 1-octene using  $\text{HRh}(\text{CO})[\text{P}(\text{OPh})_3]_3$  as a catalyst precursor. For this purpose, experiments were carried out under different operating variables with  $\text{HRh}(\text{CO})[\text{P}(\text{OPh})_3]_3$  catalyst in a TMS system consisting of three components – PC, n-dodecane and 1,4-dioxane. The variables included temperature, 1-octene and catalyst concentrations, composition of syngas ( $\text{H}_2/\text{CO}$ ), total pressure of syngas and ligand to catalyst  $[\text{P}(\text{OPh})_3/\text{HRh}(\text{CO})(\text{PPh}_3)_3]$  ratio.

## MATERIALS AND METHODS

**Materials:** 1-Octene, triphenylphosphite, propylene carbonate, dodecane and 1,4-dioxane, purchased from Merck, were of purity 98-99%. The chemicals were used without further purification. GC analysis did not show any peaks of impurities. Nitrogen and syngas (1:1  $\text{CO}/\text{H}_2$ ) were supplied by MOX, with a purity of 99.99%.

**Experimental setup and procedure:** The catalyst was prepared in situ by mixing a rhodium catalyst precursor,  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  (ABCR, Germany) and triphenylphosphite  $\text{P}(\text{OPh})_3$ . Experimental runs were conducted at four different temperatures (353, 363, 373 and 383 K), three total gas pressures (1.5, 2.0, 2.5 MPa), four  $\text{CO}/\text{H}_2$  pressure ratio (0.3, 1, 2 and 3), four molar ratio of  $\text{HRhCO}(\text{PPh}_3)_3$  catalyst to  $\text{P}(\text{OPh})_3$  ligand (10, 12, 14 and 16), catalyst concentrations varying from  $8.67 \times 10^{-5}$  to  $6.8 \times 10^{-4} \text{ kmol m}^{-3}$  (0.08 to  $0.63 \text{ g L}^{-1}$ ) and

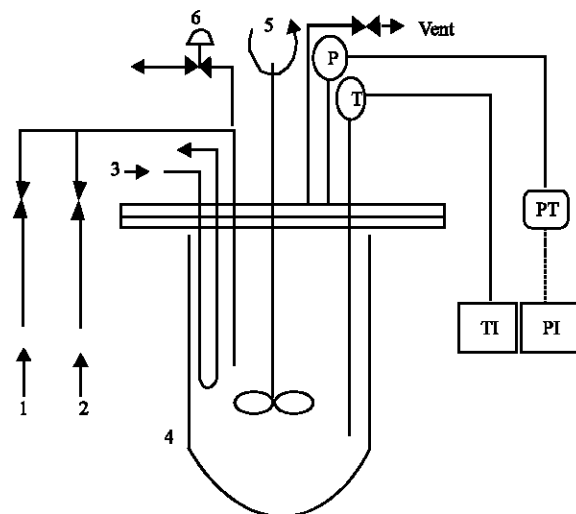


Fig. 1: Schematic of the experimental setup for kinetic studies: 1: Nitrogen, 2: Syngas ( $\text{CO}/\text{H}_2$ ), 3: Cooling water in, 4: High pressure reactor, 5: Stirrer, 6: Sampling valve, T: Thermocouple, P: Pressure gauge

1-octene concentration varying from 0.2 to 3.9 M. Hydroformylation of 1-octene was carried out in a stirred high pressure reactor (model: Parr 4843). A schematic of experimental set up is shown in Fig. 1.

The reactor was equipped with an automatic temperature control system, which consisted of an external electric heating jacket and an internal cooling loop. A pressure transducer-monitor system with high precision was also connected to the reactor for on-line measurement of reactor pressure in the course of semi-batch Hydroformylation reaction. The feed mixture (solvents, 1-octene and catalyst; volume = 220 mL) was taken in the preheated reactor. The reactor was purged with nitrogen and syngas successively, and then adjusted to the desired temperature. It was pressurized with an equimolar mixture of  $\text{CO}$  and  $\text{H}_2$  to a desired total pressure which was maintained constant during the whole run. The stirrer was set at 450 rpm while the reaction continued. Liquid samples were withdrawn and analyzed at regular time intervals to follow the progress of the reaction. The analysis of reactants and products was carried out on GC-2010 chromatograph equipped with flame ionization detector and a 5% phenylmethyl siloxane capillary column (30 m x 0.32 mm ID, 3.0  $\mu\text{m}$ ). Initial experiments were repeated three times to check for reproducibility. Measurements are, in general, reproducible within a maximum of 10% but mostly within a few percent.

**RESULTS AND DISCUSSION**

**Effect of catalyst concentration:** The regioselectivity for linear aldehyde increased with the increase of catalyst loading. The n-product was favoured under all conditions studied even though the regioselectivity to n-nonanal decreased with time. Selectivity increased from 3.2 to 5.8 to 7.1 to 9 as  $\text{HRh}(\text{CO})[\text{P}(\text{OPh})_3]_3$  increased from  $(0.0866 \text{ to } 0.18 \text{ to } 0.35 \text{ to } 0.68) \times 10^{-3} \text{ kmol m}^{-3}$ . This could be attributed to the ratio of phosphite ligand (L) to rhodium metal affecting the coordination equilibrium of catalytic active species. According to the catalytic cycle of hydroformylation, with the increase of the ratio of phosphite ligand to rhodium metal, the rhodium metal complex converted from  $\text{HM}(\text{CO})_2\text{L}$  to  $\text{HM}(\text{CO})\text{L}_2$  and then to  $\text{HM}(\text{CO})\text{L}_3$ , among which  $\text{HM}(\text{CO})\text{L}_2$  was the main active species exhibiting higher catalytic activity and selectivity. Similar observation was reported before in the case of hydroformylation of 1-octene at 10 bar and 353 K, where the addition of excess ligand ( $\text{PPh}_3/\text{Rh} = 5:1$  molar ratio) systematically led to high rates of hydroformylation and high selectivity with reduced rates of isomerization and hydrogenation of the olefin (Huang *et al.*, 2004). With 0.68 mM  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ , the yield of total aldehyde were 95% with n/iso ratio of 9.3 and 9.0 in dodecane and propylene carbonate phases, respectively as shown in Fig. 2. In addition only 1.6% of 2-octene and 0.5 % of 1-octane were observed after 2.0 h. The percentage yield of aldehyde distributed into the nonpolar phase was found to be in the range of 89.5 to 93.3%.

**Effect of temperature:** Increases in temperature have a detrimental effect on the n:iso ratio. The reaction temperature can significantly influence the distribution of products due to enhanced isomerization of the double bond of the substrate olefin and the dissociation of ligand from the catalytic complexes at higher temperatures (Van Leeuwen, 2004). As presented in Fig. 3, the selectivity of the reaction decreased from 11.5 to 10 to 8.5 to 8 (in dodecane phase) as temperature increased from 353 to 363 to 373 to 383 K. The percentage yield of aldehyde dropped significantly from 90 to 72% with respect to an increase of temperature from 363 K to 373 K. In addition at the higher temperature (373 K) an orange colour develops in the reaction mixture due to the decomposition of the triphenylphosphite ligand which simultaneously affects the activity and stability of catalyst (van Leeuwen and Claver, 2000). A higher temperature decreases the n/iso ratio as the isomerization of 1-octene into other internal octenes are favorable at

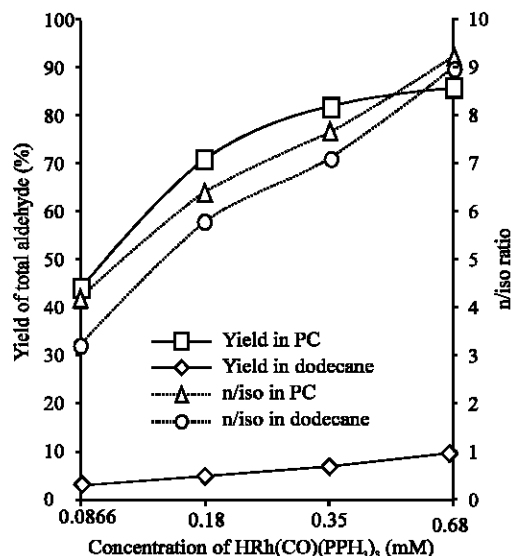


Fig. 2: Effect of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  concentration on the yield of total aldehyde and selectivity. Reaction conditions:  $P = 1.5 \text{ MPa}$ ,  $y_{\text{H}_2}/y_{\text{CO}} = 1/1$ ,  $T = 363 \text{ K}$ ,  $1\text{-octene} = 1.9 \text{ kmol m}^{-3}$ ,  $\text{P}(\text{OPh})_3/\text{HRh}(\text{CO})(\text{PPh}_3)_3 = 12$ ,  $\text{PC}/\text{dodecane}/1,4\text{-dioxane} = 0.30/0.10/0.60$

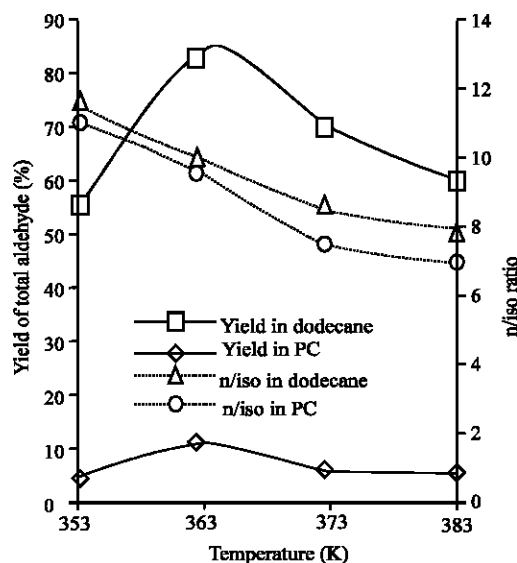


Fig. 3: Effect of temperature on the yield of total aldehyde and selectivity. Reaction conditions:  $P = 1.5 \text{ MPa}$ ,  $y_{\text{H}_2}/y_{\text{CO}} = 1/1$ ,  $\text{HRh}(\text{CO})(\text{PPh}_3)_3 = 6.8 \times 10^{-4} \text{ kmol.m}^{-3}$ ,  $1\text{-octene} = \text{kmol m}^{-3}$ ,  $\text{P}(\text{OPh})_3/\text{HRh}(\text{CO})(\text{PPh}_3)_3 = 12$ ,  $\text{PC}/\text{dodecane}/1,4\text{-dioxane} = 0.30/0.10/0.60$

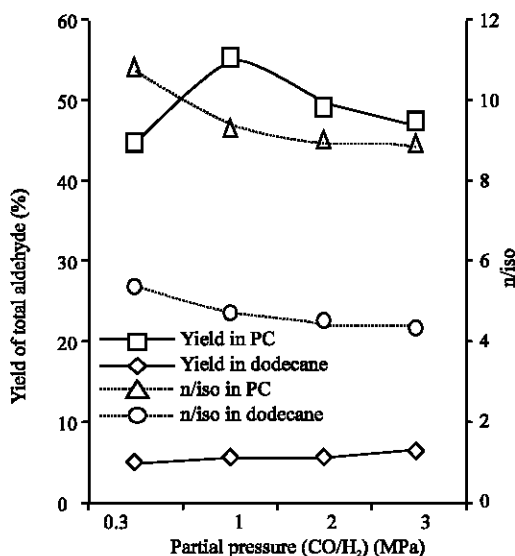


Fig. 4: Effect of CO/H<sub>2</sub> ratio on the yield of total aldehyde and selectivity. Reaction conditions: p = 1.5 MPa, HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> = 2.1 × 10<sup>-4</sup> kmol m<sup>-3</sup>, 1-octene = 1.9 kmol m<sup>-3</sup>, P(OPh)<sub>3</sub>/HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> = 12, PC/deodecane/1,4-dioxane = 0.30/0.10/0.6017, temperature = 363 K

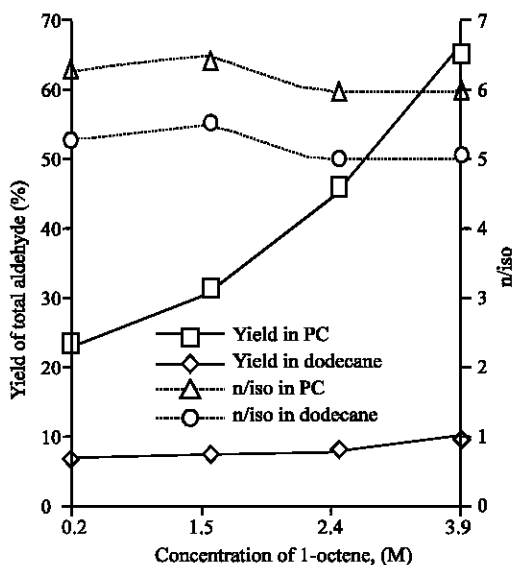


Fig. 5: Effect of 1-octene concentration on the yield of total aldehyde and selectivity. Reaction conditions: p = 1.5 MPa, y<sub>H<sub>2</sub></sub>/y<sub>CO</sub> = 1/1, HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> = 1.73 × 10<sup>-4</sup> kmol · m<sup>-3</sup>, P(OPh)<sub>3</sub>/Hrh(CO)(PPh<sub>3</sub>)<sub>3</sub> = 12, PC/dodecane/1,4-dioxane = 0.30/0.10/0.60, temperature = 363 K

higher temperatures. The resulting higher concentrations of the branched octenes adversely affect the n/iso ratio.

**Effect of CO/H<sub>2</sub> ratio:** The effect of composition of syngas on the total yield of aldehyde and the selectivity are presented in Fig. 4. A decrease in the partial pressure of CO increased the selectivity of the linear aldehyde but a decrease in the total yield of aldehydes was observed. The selectivity of the reaction decreased from 10.8 to 9.45 to 9.0 to 8.9 (in dodecane phase) as the molar ratio of CO/H<sub>2</sub> changed from 0.3 to 1 to 2 to 3. A sudden increase of the total yield of aldehydes was observed when equimolar ratio of CO/H<sub>2</sub> was used. The negative-order dependence with CO in a certain range of partial pressures appears to be a common feature in hydroformylation reaction, using HRh(CO)(PPh<sub>3</sub>) as a catalyst. As proposed by Evans *et al.* (1968) the inhibition in the hydroformylation rates at higher CO pressures is mainly due to the formation of (RCO)Rh(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and/or (RCO)Rh(CO)<sub>2</sub>(PPh<sub>3</sub>) species which are unreactive toward hydrogen. These species are likely to be formed by equilibrium reactions, thus reducing the effective concentration of the active catalytic species. The equilibrium leading to the formation of unreactive species will be more pronounced at higher pressures of CO causing a sharp decrease in the total yield of aldehydes and rate of reaction as observed in this work. At lower partial pressures of CO, the formation of these species is expected to be negligible, and therefore a positive-order dependence of the rate on P<sub>CO</sub> is observed. Regeneration of rhodium hydrides from dormant rhodium species formed by impurities is another cause for the positive rate response to raising the H<sub>2</sub> pressure.

**Effect of 1-Octene concentration:** As shown in Fig. 5, a higher concentration of 1-octene increases the total yield of aldehydes but the n/iso ratio in the product or non-polar phase was in the range 6.0-6.5 and did not differ significantly. An increase in the 1-octene concentration resulted in a higher reaction rate and conversion of 1-octene, while the linear aldehyde selectivity remains unaffected. The increase in olefin concentration will predictably cause an increase of the addition of olefin to the active catalyst species, to form the alkyl complex and hence will cause enhancement in the rates of reaction as observed.

**Effect of the total pressure of syngas:** The effect of total pressure (y<sub>H<sub>2</sub></sub>/y<sub>CO</sub> = 1/1) on the total yield of aldehyde and the selectivity is presented in Fig. 6. In general, an increase in the total pressure decreased the selectivity of the linear aldehyde. Analysis of the non-polar product

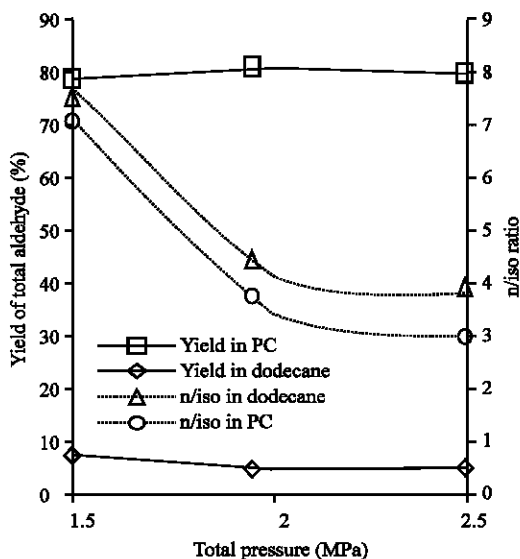


Fig. 6: Effect of total pressure on the yield of total aldehyde and selectivity. Reaction conditions:  $y_{H_2}/y_{CO} = 1/1$ ,  $HRh(CO)(PPh_3)_3 = 6.8 \times 10^{-4} \text{ kmol m}^{-3}$ , 1-octene =  $1.9 \text{ kmol m}^{-3}$ ,  $P(OPh)_3/HRh(CO)(PPh_3)_3 = 12$ , PC/dodecane/1,4-dioxane =  $0.30/0.10/0.60$ , temperature = 363 K

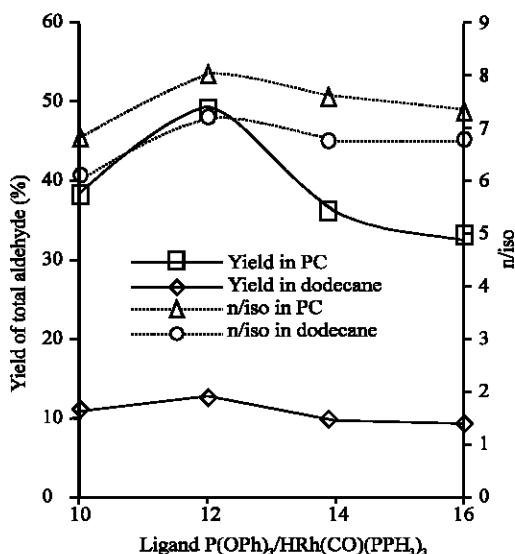


Fig. 7: Effect of  $P(OPh)_3/HRh(CO)(PPh_3)_3$  ratio on the yield of total aldehyde and selectivity. Reaction conditions:  $p = 1.5 \text{ MPa}$ ,  $HRh(CO)(PPh_3)_3 = 2.1 \times 10^{-4} \text{ kmol m}^{-3}$ , 1-octene =  $1.9 \text{ kmol m}^{-3}$ ,  $P(OPh)_3/HRh(CO)(PPh_3)_3 = 12$ , PC/dodecane/1,4-dioxane =  $0.30/0.10/0.60$ , temperature = 363 K

phase revealed that the n/i ratio decreased from 7.7 at total pressure of 1.5 MPa to 4.23 at 2 MPa and 3.8 at 2.5 MPa. According to Wilkinson, the increase in total pressure led to an increase of catalytic activity (Evans *et al.*, 1968). However, side-hydrogenation and isomerization of isomerization of 1-octene also increased at a pressure above 1.5 MPa, which made the selectivity for nonanal drop correspondingly.

**Effect of ligand to catalyst [ $P(OPh)_3/HRh(CO)(PPh_3)_3$ ] ratio:** On the basis of the above catalytic results in 1-octene hydroformylation, an excess of  $P(OPh)_3$  was added to  $HRh(CO)(PPh_3)_3$ , and the effects of  $P(OPh)_3$  at 15 bar ( $H_2/CO = 1$ ) and 363 K was investigated. It is clearly seen from Fig. 7 that addition of excess  $P(OPh)_3$  systematically leads to great increases in the ratio of n/iso aldehydes when the molar ratio of  $P(OPh)_3:Rh$  is in the range of 10-12 and eventually dropped thereafter. The need for excess ligand (L) arises from the facile Rh-L dissociation equilibrium shown in Fig. 8 (van Leeuwen and Claver, 2000). As the concentration of  $P(OPh)_3$  increases, the formation of inactive catalyst  $HRhL_3$  lowers the total yield. In addition, at high  $P(OPh)_3$  concentrations, where the catalyst resting state is  $(P(OPh)_3)_3Rh(CO)H$ , phosphite dissociation must occur to form the coordinatively unsaturated intermediates. This dissociation is suppressed by increased  $P(OPh)_3$  concentration, which serves to reduce the concentration of active Rh species in the catalytic cycle.

Alkene complexation may also be accelerated or become more favored thermodynamically. Migratory insertions are not particularly sensitive to electronic properties of the ligand, but it is important to note that oxidative addition will slow down when electron-withdrawing ligands are used (Broussard *et al.*, 1993).  $HRh(CO)(P(OPh)_3)_2$  presents a greater steric hindrance than  $PPh_3$  for the coordination of 1-octene to the rhodium center and thus can lead to lower rates of the 1-octene reactions. The greater steric hindrance relatively favours anti-Markownikov addition (van Leeuwen and Claver, 2000), which can produce more nonanal than 2-methyloctanal and 2-octene. The addition of excess  $PPh_3$  makes a significant impact on the enhancement of catalytic activity and selectivity of rhodium complexes for 1-octene hydroformylation (Deshpande *et al.*, 1993). Consistent with the results reported with other rhodium complex systems for 1-octene hydroformylation, our catalyst systems in the presence of excess  $P(OPh)_3$  ( $P(OPh)_3:Rh=12:1$  molar ratio) show a marked increase in the n/iso aldehyde ratio and great decreases in the activities for the formation

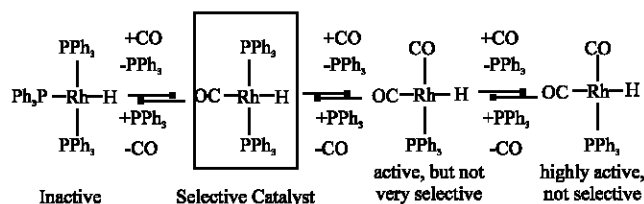


Fig. 8:  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  dissociation equilibrium

of 2-octene and n-octane. The increase in the n/iso aldehyde ratio and the suppression of the side reactions of 1-octene are mainly due to strong steric effect of  $\text{P}(\text{OPh})_3$ . However, the increase in the activity for the formation of aldehydes by addition of excess  $\text{PPh}_3$  or  $\text{P}(\text{OPh})_3$  remains unclear.

### CONCLUSIONS

The selectivity behavior for the formation of isomeric nonaldehydes have been studied in the hydroformylation of 1-octene using the homogeneous  $\text{HRh}(\text{CO})[\text{P}(\text{OPh})_3]_3$  catalyst precursor. The effects of various operating parameters on the n/iso ratio have been investigated. Experimental results show that the shift of equilibria between various active species with varied reaction conditions seems to be a determining factor in the hydroformylation reactions. Low ligand/metal ratios and high syngas pressure lead to the formation of unmodified rhodium carbon species with the characteristic of high reaction rates and low selectivities. Isomerization and hydroformylation were in competition in the reaction of 1-octene. Hydroformylation of isomerization products (2-octene, 3-octene) disturbs the initial linear aldehyde selectivity. This disturbance should be taken into consideration for process improvement. Moreover, the n/iso ratio was found to increase with increases in catalyst concentration and partial pressure of  $\text{H}_2$  but decreased with increase in temperature, total pressure and partial pressure of CO. No significant change was observed in the selectivity by varying the concentration of the substrate, 1-octene. The maximum n/iso ratio measured over the range of experimental conditions used was 11.5. In the hydroformylation of 1-octene using TMS-system of PC/dodecane/1,4-dioxane, highest selectivity for n-nonanal with average activity is observed at temperature of 363 K, equimolar of  $\text{CO}/\text{H}_2$ , total syngas pressure of 1.5 MPa, ligand/catalyst ratio of 12 and TMS composition of 0.1/0.3/0.6. Such information is useful for the preferential production of n-nonanal.

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