Applied Organometallic Chemistry (1990) 4 369–374
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0268-2605/90/040369-06$05.00

Influence of the ligand structure on SLP-catalysed hydroformylation of propene

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Received 13 February 1990 *Accepted 12 May 1990*

Hydroformylation of propene was studied at 90–120 °C and 3–10 atm. The catalyst was hydrido(carbonyl)tris(triphenylphosphine)rhodium [$H(CO)Rh(PPh_3)_3$] supported on silica, in an excess of a liquid phosphine (P) ligand as solvent. The following series of ligands (P) was synthesized and studied in this application: $CH_3(CH_2)_nPPh_2$ ($n=3$, 7, 17), $(c-C_6H_{11})_xPPh_{3-x}$ ($x=0$, 1, 2) and also unsaturated allyl- and poly(butadienyl)-diphenylphosphines. The activity and regioselectivity of the catalysts are discussed in terms of the mobility and coordination ability of the ligands used. With the same electron density of the phosphorus atom, the activity of the catalysts increases with the mobility of the ligands. On the other hand, given the same mobility of the ligand, a lower electron density on phosphorus results in increased catalytic activity.

Keywords: Hydroformylation, SLP catalyst, tertiary phosphines, silica, immobilized catalyst

INTRODUCTION

Hydroformylation is an important industrial reaction catalysed by soluble transition-metal complexes and, therefore, it has been studied for several decades. However, new processes based on expensive modified rhodium catalysts require us to pay great attention to the activity, stability and re-use of the catalysts. However, the influence of ligand structure on the performance of hydroformylation catalysts has been examined systematically in only a few cases.[1]

One of the possible improvements in handling and re-use of hydroformylation catalysts is the application of supported liquid phase (SLP) catalysts which were studied in detail by Lyngby[2] and Delft[3] (see also references therein). Nevertheless, in spite of the promising performance of SLP catalysts, with only one exception[4] no interest has been shown to the influence of the structure of the solvent ligand on their catalytic behaviour.

As previously claimed,[5] the ligand is in excess as solvent (solvent ligand) and has multifunctional character which involves above all its mobility and coordination ability. In this work we concentrated our attention on the synthesis of a series of phosphines which allow these two features to be studied separately.

EXPERIMENTAL

Materials

Triphenylphosphine, benzene (Merck), diphenylchlorophosphine, dichlorophenylphosphine, alkyl halogenides (Fluka), carbon monoxide, propene and hydrogen were commercial products used without further purification. To ensure a constant ratio of the reactant gases for each series of experiments, as empty steel cylinder was filled with a mixture of the reactant gases and their relative proportions in the cylinder were determined by gas chromatographic analysis.

Reactivity of catalysts was tested in a stainless differential plug microreactor in exactly the same manner as reported previously[6] (the reaction rate of aldehyde formation is defined as molecules s^{-1} $(g\,Rh)^{-1}$ and the regioselectivity R as the ratio $r_{butanal}/r_{isobutanal}$).

Silica (Grace) was grounded, sieved and the fraction between 100 and 140 mesh was used as the support. The texture of the support was (mercury porosimeter Micrometrics Auto-pore 9230): total intrusion volume 1.26 $cm^3\,g^{-1}$, total pore area 570 $m^2\,g^{-1}$, mean pore diameter (volume) 7.6 nm, mean pore diameter (area) 5.5 nm, average pore diameter 8.8 nm, area in pores narrower

Table 1 Physical properties of the phosphines used

Phosphine	Mol. wt	^{31}P shift[a] (ppm)
Butyldiphenyl	242.8	−15.67
Octyldiphenyl	298.4	−15.73
Octadecyldiphenyl	438.6	−15.69
Allyldiphenyl	262.3	−15.34
Poly(butadienyl)diphenyl	1 970[b]	−(14.91 to 15.24)
Triphenyl	262.3	−4.71
Cyclohexyldiphenyl	268.3	−3.26
Dicyclohexylphenyl	274.4	+2.94

[a] Determined on a Varian 200 MHz spectrometer in hexadeuterobenzene corresponding to phosphoric acid. [b] Calculated from P content.

than 5 nm in diameter 183 $m^2 g^{-1}$. Allyldiphenylphosphine,[7] butyldiphenylphosphine,[8] cyclohexyldiphenylphosphine[8] and hydrido(carbonyl)tris(triphenylphosphine)rhodium[9] were prepared by the procedures as indicated.

Octyl- and octadecyl-diphenylphosphines were prepared by the reaction of 0.3 mol of diphenylchlorophosphine in 100 ml of diethyl ether with 0.35 mol of octyl- or octadecyl-magnesium bromide in 900 ml of diethyl ether respectively. Similarly, by the reaction of 0.1 mol of phenyldichlorophosphine with 0.25 mol of cyclohexylmagnesium bromide, dicyclohexylphenylphosphine was obtained. In all three cases the reaction mixtures were then refluxed for 1 h, then degassed water was added the organic layer separated and the product distilled or recrystallized.

Poly(butadienyl)diphenylphosphine was prepared by a recently proposed procedure,[10] as follows.

A two-litre polymerization autoclave equipped with a stirrer and a cooling evidence device was flushed with nitrogen and filled with 1085 g of t-butyl methyl ether and 0.2 mol of butyllithium in 200 ml of hexane. Then a total of 300 g of butadiene was introduced during 0.5 h at a temperature from −2 to +28°C. After stirring for 15 min, 0.165 mol of chlorodiphenylphosphine was added at −5°C, followed by 0.9 cm^3 of methanol which decolourized the reaction mixture. The organic layer was then separated and washed twice with 0.8 litres of 1:10 methanol/water mixture. The solution of poly(butadienyl)diphenylphosphine was concentrated and all the volatile substances were removed under high vacuum at 190°C. The physical properties of the phosphines, along with their NMR ^{31}P shifts, are summarized in Table 1.

Preparation of the catalysts

Four procedures for the preparation of the SLP catalysts were used. (Rhodium complex = hydrido(carbonyl) tris(triphenylphosphine)rhodium)

(a) Mixing of 1 g of silica, 0.6 g of triphenylphosphine or cyclohexyldiphenylphosphine and 0.03 g of a rhodium complex was carried out in the same way as described previously.[6]

(b) A total of 1 g of silica was treated with 0.6 g of cyclohexyldiphenylphosphine dissolved in 4 cm^3 of benzene; then the benzene was evaporated *in vacuo* with shaking. The treated support was then mixed with 0.03 g of a rhodium complex.

(c) To a mixture of 1 g of silica, 0.6 g of a phosphine and 0.03 g of rhodium complex, 4 cm^3 benzene were added. After the ligand and complex had been dissolved, the contents were repeatedly evaporated and filled with nitrogen. Then benzene was evaporated *in vacuo* with shaking.

(d) The catalyst was prepared as in (c) but the amount of the rhodium complex was such that the Rh/P ratio was kept constant at 1:70.

Procedures (c) and (d) were performed with exclusion of air;[11] also, subsequent handling of catalysts including filling the microreactor was performed under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Before discussing the results the following facts must be taken into account. After addition of the ligand L to hydrido(carbonyl)tris(triphenylphosphine)rhodium, an equilibrium between the free ligand L and the rhodium complex is established. In the liquid phase this equilibrium is established rather quickly. In our case, due to the great excess of ligand L, it would very likely be shifted to the right[6] (Eqn [1]):

$$\mathrm{HRh(CO)(PPh_3)_3} \underset{-\mathrm{PPh_3}}{\overset{+\mathrm{L}}{\leftrightarrow}} \mathrm{HRh(CO)L(PPh_3)_2} \underset{-\mathrm{PPh_3}}{\overset{+\mathrm{L}}{\leftrightarrow}} \mathrm{HRh(CO)L_2(PPh_3)} \underset{-\mathrm{PPh_3}}{\overset{+\mathrm{L}}{\leftrightarrow}} \mathrm{HRh(CO)L_3} \qquad [1]$$

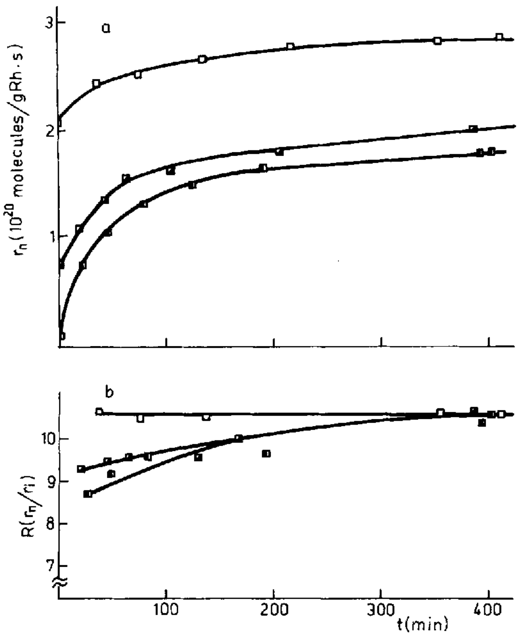

Figure 1 Rate of n-butanal formation and regioselectivity as a function of preparation ($T = 374$ K; $p_{tot} = 0.5$ MPa; ligand = cyclohexyldiphenylphosphine. □, Preformed catalyst; ◩, mixed; ◧, impregnated support, then mixed.

In the presence of a support, the situation is much more complicated, and the phosphine is expected to interact strongly with the support.[12,13] Moreover, it has been shown that rhodium complexes also interact with the surface of the support.[14] Finally, it should be taken into account that the pores of silica are not uniform. This material always contains micropores which are difficult for reactants to enter (one-third of the surface area of the support used is formed by pores with diameter smaller then 5 nm). Therefore, in spite of the fact that SLP-catalysed hydroformylation[12,13] is not controlled by diffusion between gas and liquid phase, it was expected that *formation and stabilization* of SLP *catalysts* under the conditions used would be a slow process, in which diffusion of the rhodium complex and phosphine ligands and their mobility would play an important role. Therefore, great attention has been paid to the time dependence of reaction rates.

At first, it was necessary to compare the methods of synthesis of the catalysts. Three curves in Fig. 1 (a and b) reflect the behaviour of catalysts based on (cyclohexyl)diphenylphosphine which were prepared by (a) mixing of the support, the ligand and the rhodium complex, (b) treatment of the support with dissolved ligand and subsequent mixing with the rhodium complex, and (c) treatment of the support with the solution of the rhodium complex and the ligand [methods (a), (b), (c)—see Experimental section].

At the beginning of the reaction, the highest reaction rate was achieved when the support was treated with the solution of the rhodium complex and excess of the ligand; a lower rate was found when both the ligand and the rhodium complex were outside the support, and the lowest activity was exhibited by the catalyst in which the ligand was 'hidden' inside support pores and was not available for interaction with hydrido(carbonyl)-tris(triphenylphosphine)rhodium. However, after several hours the regioselectivity of all three catalysts was the same. This indicates that the active complex is identical in these cases and that, after a sufficiently long reaction time, reaction rates would tend to be the same.

From the above facts one can conclude that (i) formation of the catalyst and the stabilization of its activity is a rather slow process in which diffusion of the ligand and the rhodium complex in and out of the pores and interaction with the support play an important role; (ii) in agreement with our previous results,[5] high activity of the catalyst is contingent on effective access of the ligand to the rhodium centre [otherwise the catalyst prepared by method (b) would not exert the lowest activity]. Therefore the catalysts were prepared by method (c) (a constant loading of the liquid phase and constant concentration of rhodium on the support) and (d) (a constant loading of the liquid phase and a constant PRh ratio). Similarly, in all the cases the loading of 0.6 g of the ligand per g of the support was used as in the previous studies.[5,6]

Five curves in Fig. 2 (a and b) illustrate the influence of the ligand structure of the activity and selectivity of the catalysts. It should be stressed that the butyl-, octyl-, octadecyl-, allyl- and poly(butadienyl)-diphenylphosphine exert almost the same ^{31}P NMR shift near -15 ppm (Table 1). This shows that the electron density on phosphorus of these phosphines is nearly the same. Furthermore, steric requirements of the ligands for coordination are also similar as two substitutents are phenyl groups and the third one differs only in the length of the chain. Hence, the coordination ability of these ligands seems to be almost identical and variations in the activity and selectivity are then caused mostly by the different mobilities of ligands and their ability to form an

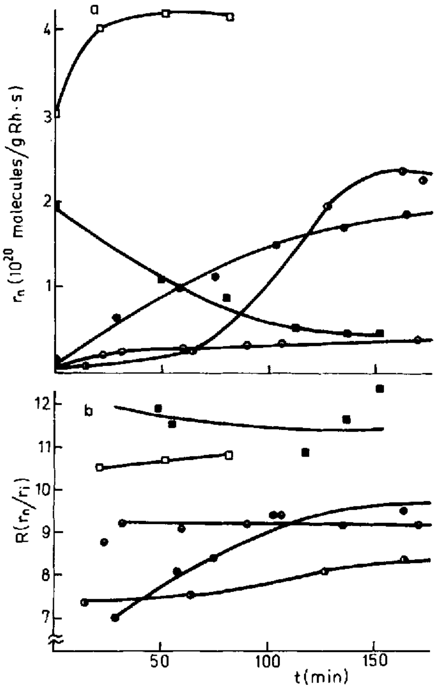

Figure 2 Rate of n-butanal formation and regioselectivity as a function of ligand ($T = 393$ K; $p_{tot} = 0.31$ MPa; $CO:C_3H_6:H_2 = 1.5:1.1:1$). □, Cyclohexyldiphenylphosphine; ■, poly(butadienyl)diphenylphosphine; ●, butyldiphenylphosphine; ◑, allyldiphenylphosphine; ⊖, octyldiphenylphosphine.

effective excess in the vicinity of the rhodium complex inside pores of the support.

Figure 2 (a and b) demonstrates that for phosphines of similar electron density, the catalytic activity decreases with the length of the alkyl substitutent in alkyldiphenylphosphines, i.e. it decreases with decreasing mobility. Several remarks should however be presented.

The catalyst based on octyldiphenylphosphine is obviously less active than that based on butyldiphenylphosphine, with the catalyst containing octadecyldiphenylphosphine being practically inactive. However, the catalyst with allyldiphenylphosphine as the ligand, which at the beginning of the reaction is inactive, after some time (2–3 h) shows somewhat higher activity compared with the catalyst containing butyldiphenylphosphine. We believe that this is due to the fact that at the beginning of the reaction allyldiphenylphosphine can act as 9 bidentate ligand, partly entering the coordination sphere of rhodium with its unsaturated double bond. This bond could under reaction conditions by hydrogenated (or hydroformylated), after which the ligand behaves as propyldiphenylphosphine in both catalyst activity and selectivity. On the other hand, poly(butadienyl)diphenylphosphine, which contains the polymeric unsaturated substituent, is probably being crosslinked and thus quite immobilized. Therefore, the complex with this ligand shows markedly decreased activity. The high divergence in the determination of regioselectivity is probably due to experimental errors when this catalyst is almost inactive. The best ligand from this series is cyclohexyldiphenylphosphine. As its electron density on the phosphorous atom differs from the other ligands and as it is similar to that of triphenylphosphine, it will be discussed later.

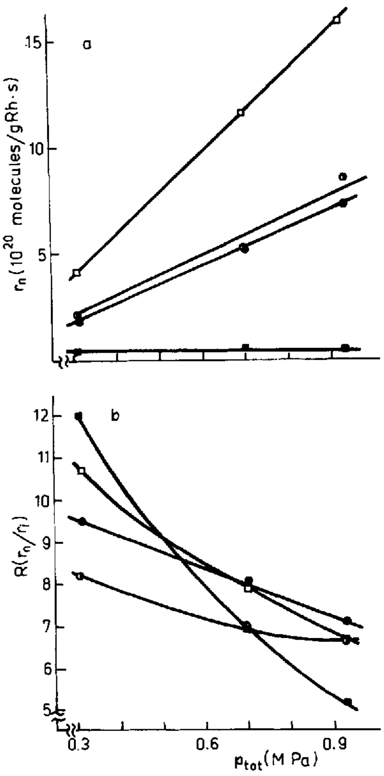

Figure 3 Rate of n-butanal formation and regioselectivity as a function of the total pressure of the reactants ($T = 393$ K; $CO:C_3H_6:H_2 = 1.5:1.1:1$). □, Cyclohexyldiphenylphosphine; ■, poly(butadienyl)diphenylphosphine; ●, butyldiphenylphosphine; ◑, allyldiphenylphosphine.

In Fig. 3 (a and b) depicted the dependence of the total reaction rate and the regioselectivity on the total pressure of the reactants. For inactive, probably immobilized, catalysts with poly(butadienyl)diphenylphosphine the total reaction order is zero and the regioselectivity decreases sharply with increasing total pressure. The total reaction

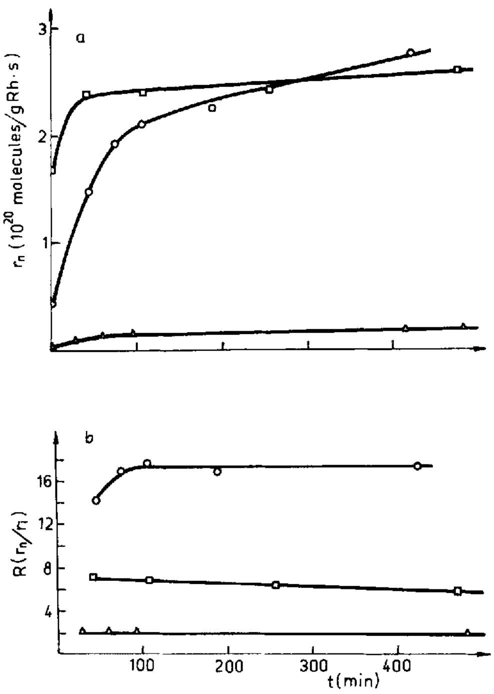

Figure 4 Rate of n-butanal formation and regioselectivity as a function of $(C_6H_{11})_xPPh_{3-x}$ ligand ($T = 373$ K; $p_{tot} = 0.5$ MPa; $COC_3H_6H_2 = 1.4{:}1{:}1.2$). ○, $x = 0$; □, $x = 1$; △, $x = 2$.

orders for the catalysts containing butyl-, allyl- and cyclohexyl-diphenylphosphine are approximately 1.2, 1.2 and 1.3, respectively. This is in good agreement with the reaction order reported for SLP-catalysed hydroformylation with triphenylphosphine ligand under similar conditions (1.76—Ref. 5; 1.2—Ref. 15). The regioselectivity decreases as usual[1] with increasing reaction rate. Decrease in regioselectivity with increasing total reaction pressure is more pronounced in the case of cyclohexyldiphenylphosphine, compared with butyl or allyl analogues.

From previous results it follows that the mobility of the ligand plays an important role. We hence investigated also SLP catalysts containing phosphines of the type $(c\text{-}C_6H_{11})_xPPh_{3-x}$ ($x = 0$, 1, 2). In this series, the molecular weight of ligands and the size of substituents on the phosphorus are almost the same in the whole set. Therefore, on assuming that the mobility of ligands is approximately the same, changes in the activity and selectivity of the catalysts containing these ligands should be resulting from the different electron densities and complexing abilities of the ligands.

The performance of these catalysts is shown in Figs 4 (a and b) and agrees with the assumption that the ^{31}P NMR shift reflects the electron density on the phosphorous and that a positive value means a lower electron density. The most active catalysts are those with triphenylphosphine and cyclohexyldiphenylphosphine, i.e. ligands of similar basicity (Table 1). For triphenylphosphine both the activity and regioselectivity is in excellent agreement with literature data (i.e. $r = 2.1 \times 10^{20}$ molecules s^{-1} (g Rh)$^{-1}$ for SLP catalyst on macroporous silica;[15] 2.2×10^{20} molecules s^{-1} (g Rh)$^{-1}$ for homogeneous hydroformylation;[16] and regioselectivity approximately 15 for SLP catalyst under corresponding conditions[5]). Figure 5 gives the Arrhenius plots for the rates of n- and iso-butanal formation with cyclohexyldiphenylphosphine as the solvent ligand. The straight lines are based on the points corresponding to 363 K, 373 K and 383 K. The deviation at 393 K demonstrates the deactivation of the catalysts at the higher temperature.

The slope of the lines ($-E_a/R$) is -9857 K for n-butanal and -7857 K for isobutanal (corresponding to an activation energy of 82 kJ mol^{-1} for n-butanol and 65 kJ mol^{-1} for isobutanol) implies that regioselectivity increases with temperature. The above activation energies agree well with the values reported for SLP-catalysed hydroformylation using triphenylphosphine as the ligand [79.1 kJ mol^{-1} (Ref. 15) and $E_{a,n} = 64$ kJ mol^{-1}, $E_{a,iso} = 53$ kJ mol^{-1} (Ref. 5)].

Dicyclohexylphenylphosphine with a lower electron density on phosphorus is a much poorer ligand for SLP-catalysed hydroformylation, in spite of the fact that for the homogeneous process dicyclohexylphenylphosphine was recently claimed[17] as the ligand giving stable catalysts. It is

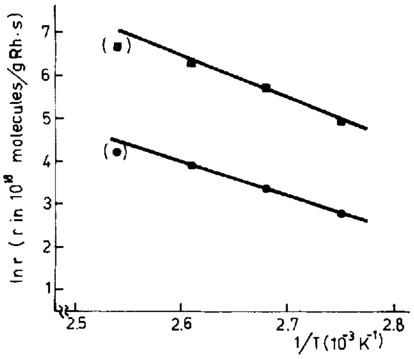

Figure 5 Arrhenius plot for (⊗) isobutanal and (☒) n-butanal formation ($p_{tot} = 0.5$ MPa; $COC_3H_6H_2 = 1{:}1.7{:}2.3$; cyclohexyldiphenylphosphine ligand) $E_n = 82$ kJ mol^{-1}, $E_{iso} = 65$ kJ mol^{-1}.

of interest that homogeneous hydroformylation under different conditions [dicyclohexylphenylphosphine(acetylactonato)dicarbonylrhodium = 65:1; 110°C, *ca* 5 atm, dimethylformamide as the solvent] gave almost the same regioselectivity (n-butanalisobutanol = 1.2) as obtained in this work.

butanal : isobutanol = 1.2) as obtained in this work.

Acknowledgement We are grateful to Dr Jan Schraml for scanning and interpreting NMR spectra, Dr Peter Schneider for texture measurements and Marie Czakoova, MS, for technical assistance (all from the Institute of Chemical Process Fundamentals).

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