Hydroformylation of olefins catalyzed by Rh(sox)(CO)₂–phosphorous ligand systems

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Abstract

Dicarbonylsalicylaldoximatorhodium $(Rh(sox)(CO)_2)$ combined with phosphorous ligands exhibits high activity for hydroformylation of olefins under mild conditions. The reaction rate and regioselectivity strongly depend on the phosphorous ligands and substrate. In the case of styrene, the branched aldehyde is the major product, almost pure 2-phenylpropanal can be afforded at 1.0 MPa. In the case of 1-hexene, *n*-aldehyde is predominant over *iso*-aldehyde. Diphosphine ligands are much more active than monophosphine ligands, but the latter give higher regioselectivity for *n*-aldehyde. Increasing the CO/H_2 ratio results in a decrease of reaction rate and the regioselectivity towards *n*-aldehyde, probably due to the formation of more hydridic LnRhH. These catalytic systems are inert for hydrogenation of olefins under hydroformylation reaction conditions, but isomerization of 1-hexene was found and it may be inhibited by an excess of phosphines. © 1998 Elsevier Science B.V.

Keywords: Hydroformylation; Rh catalyst; Salicylaldoximate ligand

1. Introduction

A challenge in homogeneously catalyzed reactions over transition metal complexes is to gain high selectivity through modification of the nature of the metal complexes and the additional ligands. Numerous efforts [1–4] have been made to increase the catalytic activity and selectivity under mild conditions. Rhodium complexes have been proved to be the best catalyst for good selectivity at low temperature and low pressure.

Recently, the use of chelating diphosphine [5], diphosphite [6–8], phosphine–phosphite [8] and P–N ligands [9] has received considerable attention. Generally, an enhancement in the hydroformylation regioselectivity of various alkenes has been observed when the chelating bidentate ligands were employed. In situ high pressure ^{1}H and ^{31}P{^{1}H} NMR and FT-IR studies have been conducted to elucidate the mechanism of hydroformylation reaction. Both spectroscopic [6,7] and kinetic data [10] indicate that $RhH(CO)_2L_2$, formed in situ from $Rh(acac)(CO)_2$ and phosphorous ligands, is responsible for the high selectivity in the hydroformylation reaction.

As a part of a program to study the reactivity of Rh complexes containing anionic chelate nitrogen–oxygen ligands and search for new se-

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lective hydroformylation catalyst at low pressure, we have previously reported [11–15] the hydroformylation of olefins catalyzed by Rh(N–O)(CO)$_2$ and Rh(N–O)(COD) together with phosphorous ligands at 1.0 MPa. It was found that high regioselectivity being up to 95% was given for styrene hydroformylation even in the presence of typical chelating phosphorous ligands. As a continuation, here we report the hydroformylation of styrene and 1-hexene using Rh(sox)(CO)$_2$ (sox = salicylaldoximate) as catalyst precursor. The hydroformylation of *N*-vinylpyrolidone and dicyclopentadiene are also described briefly.

2. Experimental

All reactions were carried out using standard Schlenk procedures under atmosphere of argon. Solvents were purified and dried according to standard methods. Rh(sox)(CO)$_2$ was prepared from [Rh(CO)$_2$Cl]$_2$ and sodium salicylaldoximate in THF at room temperature [15].

The atmospheric hydroformylation reactions were performed in 50 ml jacketed glass bottles at a constant pressure of 0.1 MPa. The reactor was evacuated, filled with CO and H$_2$, then the solution of catalyst and the appropriate phosphorous ligands in toluene were injected successively. The mixture was stirred for 20 min and the reaction was started by injection of olefins

through a self-sealing silicon rubber cap into the reactor. The temperature was regulated with circulating water and a thermostat. The reaction rate was monitored by a constant-pressure gas burette connected to the reactor.

The hydroformylation reactions at 1.0 MPa were performed in a 75 ml stainless steel autoclave. The autoclave was evacuated and filled with Ar. The solution of catalyst and olefins were injected into the autoclave through a ball-valve connected with the reactor. Then the autoclave was evacuated carefully and pressed with CO/H$_2$ to the required pressure. The temperature was maintained with an oil bath, and the contents of the autoclave was stirred at a magnetic stirrer. After the reaction was completed, the reactor was cooled to room temperature and the pressure was released carefully. A sample was taken and analyzed by GC immediately.

The hydroformylation products were identified by a Hitachi M-80 MS-GC instrument and analyzed by a Shangfen 103 gas chromatograph (Shanghai Analytical Instruments) equipped with a flame ionization detector and a 2 m OV-101 column.

3. Results and discussion

3.1. Hydroformylation of styrene

The hydroformylation of styrene was examined using Rh(sox)(CO)$_2$ as catalyst precursor

Table 1
Hydroformylation of styrene[a]

Ligand	P/Rh (mol/mol)	Pressure (MPa)	Time (h)	Conv. (%)	Regioselectivity (%)	
					2-phenylpropanal	3-phenylpropanal
PPh$_3$	2	0.1	7	3.0	70.2	29.8
	5	0.1	7	4.8	75.9	24.1
dppe	2	0.1	7	29.9	92.8	7.2
	5	0.1	7	40.7	93.2	6.8
PPh$_3$	2	1.0	5	98.0	99.7	—[b]
	5	1.0	5	73.0	99.5	0.5
dppe	2	1.0	4	91.0	99.7	—[b]
	5	1.0	4	36.0	99.7	—[b]

[a]60°C, CO/H$_2$ = 1, toluene 8 ml, styrene 2 ml, Rh(sox)(CO)$_2$ 2.0×10^{-5} mol.
[b]Not detectable.

in the presence of triphenylphosphine and 1,2-bis(diphenylphosphino)ethane (dppe) under 0.1 and 1.0 MPa. The results are presented in Table 1. The complex alone was inactive for the hydroformylation of styrene even at elevated temperature, GC showed no aldehyde was produced in both the cases of 0.1 and 1.0 MPa. However, the combination of $Rh(sox)(CO)_2$ and Ph_3P or dppe catalyze the styrene hydroformylation smoothly, which gives 2-phenylpropanal and 3-phenylpropanal, no ethylbenzene was observed.

It can be seen from Table 1, the reaction rate and regioselectivity strongly depend on the phosphorous ligands and reaction pressure. Under atmospheric pressure, higher reaction rate and regioselectivity towards branched aldehyde was observed in the case of chelating ligands. An increase of the P/Rh ratio causes an enhancement of the hydroformylation reaction rate. The branched aldehyde, 2-phenylpropanal, was obtained as the major product with high regioselectivity being 93% when the P/Rh ratio was 5. The use of monophosphine led to a rather low reaction rate and a poor regioselectivity of 2-phenylpropanal. The P/Rh ratio has little influence on the regioselectivity. The effect of the P/Rh ratio is similar to that in other hydroformylation reactions catalyzed by $Rh(N-O)(CO)_2$ type complexes [11,14]. These catalytic systems are one of the rare examples [16] in which regioselectivity are not affected by the P/Rh ratio. For styrene hydroformylation, $Rh(sox)(CO)_2$ behaves similarly as $Rh(sox)(COD)$ does, which was reported [14] by us previously. This result indicate that COD may be substituted by CO under hydroformylation conditions.

It is interesting to note that when the total pressure of CO and H_2 was raised from 0.1 to 1.0 MPa, almost pure 2-phenylpropanal was afforded in both the cases of PPh_3 and dppe, independent of the P/Rh ratio. When the pressure was 1.0 MPa, the yield of aldehyde had declined to 36.0% from 91.0% and to 73.0% from 98.0% for dppe and PPh_3 separately, with

the increase of the P/Rh ratio from 2 to 5. At the pressure of 1.0 MPa, the P/Rh ratio has a negative effect on the reaction rate, which is just contrary to that at 0.1 MPa. This implies that a slightly excess of phosphine ligand is enough to form the unidentified active species. Unexpectedly, the regioselectivity of 2-phenylpropanal was increased greatly when the total pressure was raised especially in the case of PPh_3. At present, we do not understand why the raising of CO/H_2 pressure has such an enhancement of regioselectivity. Whether the nature of the active species changes with variation of total pressure is not clear.

Considering that $Rh(sox)(CO)_2$ together with dppe exhibits high regioselectivity and activity, the chelating nature of salicylaldoximate and dppe must be an important factor.

3.2. Hydroformylation of 1-hexene

At first, we have examined the effect of phosphorous ligands on the catalytic activity of $Rh(sox)(CO)_2$ for the hydroformylation of 1-hexene under atmospheric pressure. The results were listed in Table 2.

The results show the combination of $Rh(sox)(CO)_2$ with chelate ligands forms highly active species. The yield of total aldehyde ($n + iso$ heptanal) being 93.6% can be achieved in

Table 2
Hydroformylation of 1-hexene at 0.1 MPa[a]

Ligand	P/Rh (mol/mol)	TOF[b] (min^{-1})	Conv. (%)	Regioselectivity (%)	
				n-heptanal	iso-heptanal
$P(OPh)_3$	2	0.33	12.0	73.3	26.7
	5	∼ 0	0	0	0
PPh_3	2	0.67	28.9	80.7	19.3
	5	0.45	13.1	80.8	19.2
dppe	2	1.62	37.2	51.0	49.0
	5	0.45	48.9	52.2	47.8
dppp	2	1.66	93.6	48.2	51.8
	5	0.56	65.0	42.2	57.8

[a] 60°C, $CO/H_2 = 1$, toluene 9 ml, 1-hexene 1 ml, $Rh(sox)(CO)_2$ 2.0×10^{-5} mol.
[b] Turnover frequency defined as mol 1-hexene converted per mole of catalyst per minute.

Table 3
C_6 components distribution in hydroformylation of 1-hexene[a]

Ligands	P/Rh	Distribution of C_6 components (%)				
		1-hexene	hexane	*trans*-2-hexene	*cis*-2-hexene	3-hexene
P(OPh)$_3$	2	15.7	1.8	48.4	22.1	0
	5	92.8	2.6	2.0	0	2.6
PPh$_3$	2	59.7	2.1	5.1	2.6	1.6
dppe	2	39.9	2.4	12.5	0	8.1
	5	36.8	4.3	4.5	3.9	1.6
dppp	2	3.4	1.3	1.2	0	0.6
	5	32.5	1.6	0.9	0	0

[a] For the reaction conditions see the notes in Table 2.
(1-hexene + 2-hexene + 3-hexene + hexane + C_7 aldehyde)% = 100%.

the case of dppp (1,3-bis(diphenylphosphino) propane), however, the *n/iso* ratios are nearly one by using diphosphine ligands. The use of PPh$_3$ resulted in a better regioselectivity towards *n*-heptanal, although the reaction rate is much slower than that in the case of diphosphines. Generally, an increase of the P/Rh ratio causes a decline of the initial reaction rate (described as turnover frequency), but no significant change in the *n/iso* ratio was observable. The data of regioselectivity suggest that the chelate diphosphine favor the formation of branched aldehyde and the monodentate ligands favor the formation of linear aldehyde for both styrene and 1-hexene.

The GC analysis show isomerization of 1-hexene to 2-hexene and 3-hexene occurs in 1-hexene hydroformylation. Table 3 gives the distribution of C_6 components in the mixture. As can be observed in Table 3, the hexane concentration has almost no increase after hydroformylation for 10 h, hence hydrogenation of 1-hexene can almost be neglected. However, the isomerization reaction of 1-hexene is of significance in some cases, especially for P(OPh)$_3$. The isomerization can be inhibited greatly by the presence of excess phosphorous ligands. For instance, the yield of isomerization products (2-hexene and 3-hexene) was reduced from 70.5% to 4.6% when the P(OPh)$_3$/Rh ratio was increased from 2 to 5. Phosphite ligands induce more isomerization of terminal olefins in Rh-

catalyzed hydroformylation than phosphine ligands do, which was also reported by Trzeciak and Ziólkowski [17].

The low reaction rate of the P(OPh)$_3$ modified catalyst may be partially assigned to the isomerization reaction, because the catalyst is inert for the hydroformylation of internal alkenes under these mild conditions. The hydroformylation and isomerization of 1-hexene were both suppressed by the excess of phosphorous ligands.

Usually, hydrogenation of olefins is often observed under the hydroformylation conditions. Rh(sox)(CO)$_2$ did not display hydrogenation activity. Probably the formation of rhodium acyl intermediate from CO insertion is much more favored to the hydrogenolysis of the rhodium alkyl intermediate.

Table 4 shows the results of 1-hexene hydroformylation under 1.0 MPa, the effect of PPh$_3$ and dppe were tested comparatively. Increasing

Table 4
Hydroformylation of 1-hexene at 1.0 MPa[a]

Ligand	P/Rh (mol/mol)	Time (h)	Conv. (%)	Regioselectivity (%)	
				2-heptanal	3-heptanal
PPh$_3$	2	4	65.5	72.2	27.8
	5	4	98.0	71.0	29.0
dppe	2	5	69.1	70.0	30.0
	5	5	45.0	45.0	55.0

[a] 60°C, CO/H$_2$ = 1, toluene 9 ml, 1-hexene 1 ml, Rh(sox)(CO)$_2$ 2.0×10^{-5} mol.

the pressure of CO/H_2 (1:1) significantly accelerates the hydroformylation, the highest conversion of 1-hexene reached 98% when Ph_3P/Rh was 5. Similar to styrene hydroformylation, a higher pressure of CO/H_2 promotes the formation of branched aldehyde and the n/iso ratio was lowered with an increase of total pressure.

The H_2/CO ratio is also an important factor to influence the hydroformylation rate and regioselectivity. The effect of the H_2/CO ratio on the hydroformylation of 1-hexene was examined at 1.0 MPa, the results were summarized in Table 5. While the total pressure stays constant, the hydroformylation reaction is significantly suppressed with increasing CO/H_2 ratio. The 1-hexene conversion decreased sharply from 98% to 9.1% when the CO/H_2 ratio was increased from 1/1 to 1/4 at the pressure of 1.0 MPa. The regioselectivity is also dependent on the CO/H_2 ratio, a higher H_2 concentration favors the formation of normal aldehyde. Increasing the CO partial pressure gives rise to a poor conversion and greater amounts of branched aldehyde, which indicate a LnMH species with a more hydridic character has been produced. The interpretation has been commonly accepted [1]. On the other hand, the coordination of dppe and dppp to Rh should produce poor hydridic Rh–H intermediates, thus higher n/iso ratios should be afforded for 1-hexene hydroformylation. However, they give the inverse result. It seems that the effect of the

sox ligand should be considered except the electron donating ability of phosphine ligands.

3.3. Hydroformylation of functional olefins

The catalyst system $Rh(sox)(CO)_2$-phosphine is so active that under atmospheric pressure it catalyze the hydroformylation of some inert functional olefins which usually require elevated temperature and pressure. The products of N-vinylpyrolidone hydroformylation are intermediates of some important natural and biologically active compounds. The reaction was ever reported by Kóllar et al. [18] which was conducted at 8.0 MPa and gave 30% of the linear aldehyde. Our catalytic system can work at atmospheric pressure and more than 20 mol aldehyde per mol of catalyst was obtained. Furthermore, the catalyst shows exceptionally high regioselectivity, only linear aldehyde can be detected by gas chromatography.

Under the same conditions, dicyclopentadiene can also be hydroformylated to its corresponding aldehyde which was used as a starting materials of new resins [19,20]. Within 6 h, more than 30 mol aldehyde per mole of rhodium can be afforded. GC-MS analysis showed only one double bond participated in the reaction; no bisaldehyde was detectable.

The results mentioned above show that $Rh(sox)(CO)_2$ is a good catalytic precursor for olefin hydroformylation under very mild conditions. $Rh(sox)(CO)_2$ can be easily prepared from the commercial compound $[Rh(CO)_2Cl]_2$. Therefore, the hydroformylation affords a convenient route to synthesize 2-phenylpropanal and some functional aldehyde. Furthermore, the regioselectivity can be controlled through the choice of phosphorous ligands.

Our results are not completely in agreement with that of similar catalyst $Rh(acac)(CO)_2$ and commonly used $[Rh(CO)_2Cl]_2$. This can be due to the different nature of the active species. $[Rh(CO)_2Cl]_2$ alone and its combination with phosphines are inactive for styrene and 1-hexene

Table 5
Effect of H_2/CO ratio on the hydroformylation of 1-hexene[a]

H_2/CO	Time (h)	Conv. (%)	Regioselectivity (%)	
			n-heptanal	iso-heptanal
5/1	3	91.2	76.5	24.4
2/1	4	98.0	72.2	27
1/1	4	98.0	71.0	29.0
1/2	5	36.4	70.0	30.0
1/4	6	9.1	70.0	30.0

[a]$PPh_3/Rh(sox)(CO)_2 = 5$, others are the same as noted in Table 4.

hydroformylation under atmospheric pressure and 60°C, although it is known that these complexes are effective catalysts under elevated pressure. However, they are useful hydrogenation catalysts at 1 atm of H_2. It has also been proved that the Rh(acac)$(CO)_2$–phosphine system catalyzes hydrogenation of olefins under H_2/CO or H_2 atmosphere. Hydrogenation of styrene was not observed using Rh(sox)$(CO)_2$ or its mixture with various phosphorous ligands at 1 atm of H_2. These observations suggest that the salicylaldoximate ligand plays a predominant role in the active species and the Rh(sox) fragment seems to be maintained, although the nature of the catalytically active species is not clear. Furthermore, the IR of Rh(sox)$(CO)_2$ in toluene showed no changes under atmosphere of H_2 even for days, whereas black precipitate was observed when Rh(acac)$(CO)_2$ and $[Rh(CO)_2Cl]_2$ were exposed to H_2 for several hours. This fact also supports the proposal of Rh(sox) existence in the reaction.

Acknowledgements

References

[1] B. Cornils, in: J. Falbe (Ed.), New Synthesis with Carbon Monoxide, Springer Verlag, New York, NY, 1980, pp. 1–225.

[2] P. Kalck, Y. Peres, J. Jenck, Adv. Organomet. Chem. 32 (1991) 121.

[3] L. Alvila, T.A. Pakkanen, O. Krause, J. Mol. Catal. 84 (1993) 145.

[4] H. Yamashita, B.L. Roan, T. Sakakura, M. Tanaka, J. Mol. Catal. 81 (1993) 255.

[5] A.M. Trzeciak, J.J. Ziólkowski, R. Choukroun, J. Organomet. Chem. 525 (1996) 145.

[6] B. Moasser, W.L. Gladfelter, D.C. Roe, Organometallics 14 (1995) 3832.

[7] A. van Rooy, P.C.J. Kamer, P.W.N.M. van Leeuwen, N. Veldman, A.L. Spek, J. Organomet. Chem. 494 (1995) C15.

[8] K. Nozaki, T. Nanno, H. Takaya, J. Organomet. Chem. 527 (1997) 103C.

[9] C. Basoli, C. Botteghi, M.A. Cabras, G. Chelucci, M. Marchetti, J. Organomet. Chem. 488 (1995) C20.

[10] A. van Rooy, E.N. Orji, P.C.J. Kammer, P.W.N.M. van Leeuwen, Organometallics 14 (1995) 34.

[11] W. Chen, Y. Xu, S. Liao, D. Yu, Acta Chim. Sin. 50 (1992) 601.

[12] W. Chen, Y. Xu, S. Liao, D. Yu, Cuihua Xuebao (Chin. J. Catal.) 13 (1992) 483.

[13] W. Chen, S. Liao, Y. Xu, Heteroat. Chem. 3 (1992) 539.

[14] W. Chen, Y. Xu, S. Liao, J. Mol. Catal. 88 (1994) 277.

[15] W. Chen, Y. Xu, S. Liao, Transition Metal Chem. 19 (1994) 413.

[16] C. Bergounhou, D. Neibecker, R. Réau, J. Chem. Soc. Chem. Commun. (1988) 1370.

[17] A.M. Trzeciak, J.J. Ziólkowski, J. Mol. Catal. 43 (1988) 335.

[18] L. Kollar, B. Heil, P. Sándor, J. Organomet. Chem. 379 (1989) 191.

[19] D.L. Hunter, S.E. Moore, P.E. Garrou, R.A. Dubois, Appl. Catal. 19 (1985) 259.

[20] D.L. Hunter, S.E. Moore, R.A. Dubois, P.E. Garrou, Appl. Catal. 19 (1985) 275.