Rhodium-catalysed hydroformylation of branched 1-alkenes; bulky phosphite vs. triphenylphosphine as modifying ligand

Annemiek Van Rooy [a], Jacques N.H. de Bruijn [a], Kees F. Roobeek [b], Paul C.J. Kamer [a], Piet W.N.M. Van Leeuwen [a,*]

[a] *Van 't Hoff Research Institute, Department of Inorganic Chemistry, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, Netherlands*

[b] *Koninklijke / Shell-laboratorium, Amsterdam (Shell Research), Badhuisweg 3, 1031 CM Amsterdam, Netherlands*

Abstract

The influence of alkyl substituents in 1-alkene substrates in the rhodium-catalysed hydroformylation in the presence of tris(2-tert-butyl-4-methylphenyl) phosphite has been studied and compared with that observed for the reaction involving the conventional PPh_3-modified catalyst. Hindered alkenes underwent hydroformylation at good rates (i.e. 1300 mol (mol Rh)$^{-1}$ h^{-1} for 3,3-dimethyl-1-butene as $T = 70°C$ and $P = 20$ bar (H_2–CO)); under mild conditions the rates were only slightly affected by the alkyl substituents. The selectivity towards the linear aldehyde increases progressively with substitution, from 66% for 1-octene up to 100% for 3,3-dimethyl-1-butene, and the proportion of isomerized alkenes remained substantial (up to 17.4% for allylcyclohexane). The differences between the two systems are explained in terms of the different kinetics observed for them.

Keywords: Rhodium; Hydroformylation; Alkenes

1. Introduction

The rhodium-catalysed hydroformylation of alkenes is a widely studied process [1]. Fundamental studies are directed towards gaining new insights into the reaction mechanism [2] and improving the rate and selectivity of the reaction using new modifying ligands. In recent years use of phosphites as modifying ligands has received much attention (especially in the patent literature), and monophosphites are now used in commercial catalyst systems [3], having replaced triphenylphosphine. It is commonly accepted that the mechanism proposed by Heck and Breslow [4] for cobalt hydroformylation also holds for the unmodified and phosphine-modified rhodium-containing systems. Overall it resembles the dissociative mechanism proposed by Wilkinson and coworkers [5]. Steric effects are very important in phosphine- and phosphite-modified rhodium-catalysed hydroformylation of alkenes; the rate of the hydroformylation falls with increasing steric hin-

drance in the ligand and the substrate [6], and at the same time the ratio of the normal to branched aldehyde rises. The reactivities of substrates decreases in the series 1-alkenes > substituted 1-alkenes ≫ internal alkenes. However, Van Leeuwen and Roobeek [7] and Jongsma et al. [8a] showed that otherwise unreactive alkenes can be hydroformylated in the presence of a bulky phosphite-modified catalyst under milder conditions than those usually used. They attributed this to the very large cone angle of the phosphite ligand, tris(2-tert-butyl-4-methylphenyl) phosphite ($\theta = 172°$); the nature of the active species is changed, resulting in increased reactivity. (This is in contrast with earlier reports [6a,9].) In particular, 1,2- and 2,2-dialkylalkenes are hydroformylated at higher rates when the bulky phosphite is used instead of triphenylphosphine [7], and it was recently shown that the bulky phosphite can be used in the hydroformylation of a range of substrates [8b]. We found that use of the bulky monophosphite gives rise to.a very active catalyst for the hydroformylation of alkenes such as 1-octene and styrene [10]. Very high rates were observed (up to 160000 mol (mol Rh)$^{-1}$ h^{-1} for 1-octene [10b]).

Table 1

Hydroformylation of various 1-alkenes with the triphenylphosphine-modified rhodium catalyst [a]

Substrate	Rate [b] (mol (mol Rh)$^{-1}$ h^{-1}) [b]	Linear aldehyde (%)	Isomer (%)	Order in alkene
1-Propene	4900	61.4	— [c]	(1)
1-Pentene	11300	78.4	—	(1)
1-Heptene	7100	76.6	—	(1)
4-Me-1-pentene	9300	78.0	—	(1)
4-Me-1-hexene	7700	77.3	—	(1)
4,4-Me$_2$-1-pentene	5300	85.0	—	(1)
3-Me-1-pentene	9600	91	—	(1)
3-Me-1-hexene	8800	90.7	—	(1)
3,3-Me$_2$-1-pentene	7600	99	—	(1)

[a] Conditions: $T = 90°C$; $P = 20$ bar (CO/H$_2$); [Rh(COD)OAc]$_2$ = 0.01 mmol; [PPh$_3$] = 0.20 mmol; [L]/[Rh] = 10; [alkene] = 10 mmol in 20 ml of benzene.

[b] Initial rates.

[c] Not detected.

2. Results and discussion

We have extended this study to branched 1-alkenes in order to find out how substituents in the alkene affect reaction rate. We have also obtained additional information on the effects of similar changes in substitution for hydroformylation with conventional triphenylphosphine-modified catalyst. Most of the substrates have been studied previously in hydroformylation with triphenylphosphine as ligand, but owing to the range of conditions used in the past [11], we have repeated several of the reactions under conditions that allow comparison with the results obtained with the bulky phosphite ligand.

Results are presented in Table 1 for the triphenylphosphine modified rhodium carbonyl catalyst and in Table 2 for the tris(2-tert-butyl-4-methylphenyl) phosphite-modified catalyst. Steric hindrance by the substrates increases on going from unsubstituted alk-1-enes to mono- and di-4-substituted alk-1-enes, to mono-3- and finally di-3-substituted alk-1-enes. The reaction temperatures were chosen such that comparable rates were obtained, and the reaction rates could be measured with the same reliability for both the catalyst systems and the progress of the reaction could be monitored by taking samples. Thus a temperature of 70°C was used for the bulky phosphite system and a temperature of 90°C for the triphenylphosphine system. Whether the anion of the precursor is acetate or acetylacetonate has no effect. The reactions for triphenylphosphine were conducted in benzene, which is a slightly better solvent, in order to avoid catalyst precipitation [2c].

Hydroformylation rates of the same order of magnitude are observed for all the substrates varying from 1300 mol (mol Rh)$^{-1}$ h^{-1} for 3,3-dimethyl-1-butene to 16000 mol (mol Rh)$^{-1}$ h^{-1} for vinylcyclohexane with the bulky phosphite-modified catalyst (70°C; 20 bar (H$_2$-CO); initial rates). It can be seen that, when account is taken of the different reaction temperatures ($T = 90°C$ for PPh$_3$, and $T = 70°C$ for the bulky phos-

Table 2

Hydroformylation of various 1-alkenes with the tris(2-tert-butyl-4-methylphenyl) phosphite-modified rhodium catalyst [a]

Substrate	Rate (mol (mol Rh)$^{-1}$ h^{-1})	Linear aldehyde (%)	Isomer (%)	Order in alkene
1-Octene	12500	66	8.8	(0)
1-Dodecene	6600	63	18.5$_b$	(0)
4-Me-1-pentene	8800	64	—	(0)
Allyl-cyclohexane	8800	66	17.4	(0)
4,4-Me$_2$-1-pentene	5400	79	15.1	(0)
Vinyl-cyclohexane	16000	78	16.3	(0)
3,3-Me$_2$-1-butene	1300 [c]	100	— [d]	(1)

[a] Conditions: $T = 70°C$; $P = 20$ bar (CO-H$_2$); [Rh(CO)$_2$Acac] = 0.002 mmol; [phosphite] = 0.02 mmol; [L]/[Rh] = 10; [alkene] = 15 mmol in 20 ml of toluene.
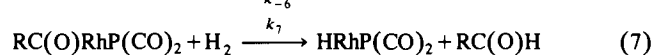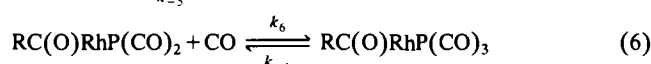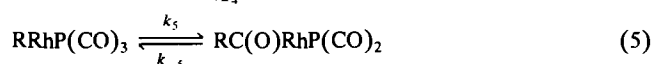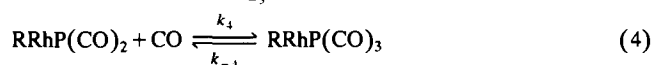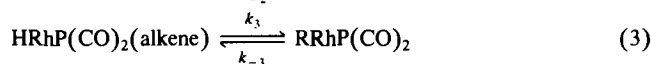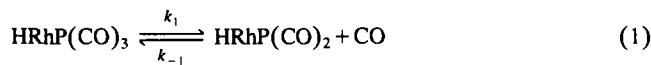
[b] Not detected.

[c] Initial rate.

[d] Not possible.

phite [1]), the catalyst derived from the bulky phosphite is much more active. An increase in the reaction temperature by 10°C raises the rate by a factor of about 2. For both catalysts, the rate falls with increasing chain length of the unsubstituted 1-alkenes, as was found for unmodified cobalt- and rhodium-catalysed hydroformylation by Wender et al. [12] and Heil and Markó [13] respectively. Propene does not fall in this sequence, probably because it is present in both gaseous, and liquid forms under the conditions used.

For the PPh₃-modified catalyst, for a given chain length, the rate decreases with increasing steric hindrance by the substituents. Interestingly, two methyl groups in the 4-position have a larger effect than one in the 3-position. Location of the substituents closer to the reacting double bond increases the proportion of linear aldehydes (e.g. 78.4% for 1-pentene and 99% for 3,3-dimethyl-1-pentene; a high selectivity in the case of the latter substrate was observed previously for an unmodified catalyst [6b]). No isomerization products were detected. For all substrates first-order dependence of the rate on the alkene concentration was observed, indicating that addition of the alkene in the rhodium centre is the rate-determining step.

For the bulky phosphite-modified catalyst the effects of the substituents or of their positions are not clearcut, except for the reaction of 3,3-dimethyl-1-butene, for which 100% of the normal aldehyde is formed. The yield of isomerized alkenes varied from 0 for 4-methyl-1-pentene or 3,3-dimethyl-1-butene to 18.6% for dodecene. 3,3-Dimethyl-1-butene shows a kinetic behaviour different from that observed for the other substrates; for the 3,3-disubstituted 1-alkene, the steric hindrance is especially large, causing the addition of alkene to the rhodium centre to become rate limiting, a first-order rate dependence on the alkene concentration being observed. For 1-octene the rate was independent of the substrate concentration down to very low concentrations [10b], and this was the case for most of the substituted 1-alkenes.

The results can be explained in terms of the structures of the active catalyst complexes and the associated kinetic behaviour [2]. When a sufficient excess of PPh₃ is present, the active rhodium triphenylphosphine complex initially bears three-coordinated phosphine ligands

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[1] For the tris(2-tert-butyl-4-methylphenyl) phosphite ligand is was desirable to lower the reaction temperature in order to take samples. However, comparison remains difficult as for the PPh₃ ligand all the reactions are first order in alkene concentration, while the bulky phosphite catalyst shows a zeroth-order dependence on substrate concentration for most of the alkenes.

[2] We have not attempted to derive analytical kinetic expressions for the catalyst systems. The difference between the two systems is most convincingly shown when the kinetic behaviour is considered in a qualitative way (see also [10b]).

$$HRhP(CO)_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HRhP(CO)_2 + CO \tag{1}$$

$$HRhP(CO)_2 + alkene \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HRhP(CO)_2(alkene) \tag{2}$$

$$HRhP(CO)_2(alkene) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} RRhP(CO)_2 \tag{3}$$

$$RRhP(CO)_2 + CO \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} RRhP(CO)_3 \tag{4}$$

$$RRhP(CO)_3 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} RC(O)RhP(CO)_2 \tag{5}$$

$$RC(O)RhP(CO)_2 + CO \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} RC(O)RhP(CO)_3 \tag{6}$$

$$RC(O)RhP(CO)_2 + H_2 \overset{k_7}{\longrightarrow} HRhP(CO)_2 + RC(O)H \tag{7}$$

Scheme 1. Proposed mechanism of hydroformylation in the presence of the tris(2-tert-butyl-4-methylphenyl) phosphite-modified rhodium catalyst.

(HRh(CO)L₃ (a) (L = PPh₃)). It was concluded in earlier studies [2a] that one PPh₃ has to dissociate after which the alkene can coordinate to the relatively crowded rhodium centre. This is supported by the order of the reaction with respect to the concentration of CO, which is only −0.1. This coordination step is rate determining, implying that the rate depends on the degree of steric hindrance in the incoming substrate. With HRh(CO)(PPh₃)₃ and HRh(CO)(PPh₃)₂ + PPh₃ present in equilibrium, the rate expression is

$$r = \frac{K_1 k_2 [Rh_t][alkene]}{K_1 + [L]} \tag{1}$$

The regioselectivity is determined in the fast migration that follows.

The bulky phosphite forms a complex that contains only one ligand (HRh(CO)₃L (b) (L = tris(2-tert-butyl-4-methylphenyl) phosphite)) [8a]. This complex has a very strong tendency to lose CO owing to the high electron-accepting ability of the ligand ($\chi = 29$). Loss of CO leaves HRhL(CO)₂ (Scheme 1), which is more electronegative and less sterically hindered than HRh(CO)L₂. Even sterically hindered alkenes can coordinate readily, resulting in high reaction rates. The slowest step is now the last step in the reaction cycle, the hydrogenolysis reaction, and when $K_6 \gg 1$ in the following equation (which has been derived in [10b]);

$$r = \frac{k_7[H_2][Rh_t]}{K_6[CO]} \tag{2}$$

Whether complex a or b is formed depends on the cone angle θ and the π acidity of the ligand. Small and medium phosphorus ligands usually give complexes analogous to a ($\theta_{PPh3} = 145°$), while those with large cone angles ($\theta_{bulky\ phosphite} = 172°$) only give complexes analogous to b. Those with low χ values (electron donating) form a stronger metal–phosphorus-bond and

hence a complex such as **a** is readily formed. On the contrary, a strongly electron-withdrawing ligand (e.g. $P[OCH(CF_3)_2]_3$ [7]) will not give stable complexes containing three phosphorus ligands and a species such as **b** is obtained.

Since Eq. (2) (applicable to the bulky phosphite-modified catalyst) does not include the alkene concentration substituents would not be expected to affect the reaction rate. However, we observed some influence of the chain length, as also was found by Heil and Markó [13] for the unmodified rhodium carbonyl catalyst (145°C; 25 bar) for which a rate equation analogous to that of the bulky phosphite system applies. Apparently, the reaction with hydrogen does not take place at the same rate for all substrates. Probably the steric hindrance by the alkyl group in $RhL(CO)_2C(O)R$ affects the rate of the hydrogenolysis step. Nevertheless, the coordination of the alkene remains fast compared with the hydrogenolysis of the acylrhodium intermediate, and the slowness of the hydrogenolysis step allows the β-H elimination that causes isomerization to take place. The importance of the reaction depends on the reaction temperature and pressure. For the neohexene substrate, the substituents are evidently so large that the rate-limiting step is changed, as indicated by the fact that the rate law is (as derived in [10b]).

$$r = \frac{K_1 k_2 [Rh_t] [alkene]}{K_1 + [CO]} \quad (3)$$

(step (a) in Scheme 1 being treated as a pre-equilibrium process) and branched aldehydes are absent from the products. In this case, the rate in the presence of the bulky phosphite-modified catalyst depends on the alkene concentration, as for the PPh_3 system, and as in the case for other substrates such as cyclohexene, which coordinate less easily to the rhodium centre [10b].

3. Conclusions

We have shown that the structure of the catalyst has a large influence on the activity and selectivity of the modified rhodium carbonyl hydroformylation catalyst. When the triphenylphosphine ligand is used, it forms a catalyst complex for which coordination of the alkene is rate determining. As a consequence, lower rates are observed for hindered alkenes, and the product selectivity rises sharply with increase in the number of substituents on the alkene. When the tris(2-tert-butyl-4-methylphenyl) phosphite-modified catalyst is used, the rate of hydroformylation remains independent of the substrate concentration, even for highly substituted substrates, but the selectivity towards formation of normal aldehydes remains fairly low. Use of this system also results in more isomerization of the alkene.

4. Experimental details

4.1. General comments

Gas–liquid chromatography analyses were carried out with a DB-1 column in a Carlo Erba GC 6000 Vega series 2 chromatograph.

Carbon monoxide 3.0, hydrogen 3.0 and synthesis gas 5.0 were obtained from Prax Air. $Rh(CO)_2Acac$ was purchased from Johnson–Matthey, triphenylphosphine and triphenylphosphite from Aldrich and Janssen, and nonane, decane and undecane from Aldrich, they were all used as received. Alkenes were purchased from Aldrich (1-octene, 1-dodecene, vinylcyclohexane and 3,3-diMe-1-butene), or prepared by published procedures (allylcyclohexane, 4-Me-1-pentene and 4,4-diMe-1-pentene) [14] and freed from hydroperoxides by percolation through neutral alumina. $[Rh(COD)OAc]_2$ and tris(2-tert-butyl-4-methylphenyl) phosphite were prepared by published methods [10b,15].

4.2. Hydroformylation

Hydroformylation experiments were performed in a 181 ml stainless steel autoclave, equipped with a magnetic stirrer and containing a glass beaker. Hydroformylation with the triphenylphosphine catalyst was performed with $[Rh(COD)OAc]_2$ as the catalyst precursor and undecane as the internal standard and with benzene as the solvent in order to prevent precipitation of the catalyst. For reaction in the presence of tris(2-tert-Bu-4-Me-phenyl) phosphite, $Rh(CO)_2Acac$ was used as the catalyst precursor (a change from OAc to Acac made no difference in the catalyst performance). Decane was used as the internal standard and, because of the higher solubility of this catalyst, in this case toluene could be used as the solvent. The autoclave was charged with the precursor rhodium complex, the ligand, the internal standard and the solvent. The reactor was pressurized and brought to the required temperature; and the reaction was then initiated by adding the substrate. Samples were taken at intervals from the reaction mixture quenched with $P(OPh)_3$ to prevent isomerization of the alkene and analysed by GLC. In the case of the PPh_3-containing catalyst, the initial reaction rates were calculated from the pressure drop because the reactions were all of first order with respect to the alkene concentration.

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