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Hydroformylation of methyl methacrylate via "in-situ" phosphinerhodium catalysis

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Abstract

It has been shown that in hydroformylation of methyl methacrylate with rhodium phosphine catalysts prepared "in situ" the regioselectivity is very sensitive not only to the reaction conditions but also to the basicity of the phosphine and to the presence of added Et_3N. At low P/Rh ratio chlororhodium species are catalytically active. No side reactions have been detected.

Introduction

Hydroformylation of α,β-unsaturated esters, especially methyl methacrylate (MMA), has received much attention [1–7]. In addition to cobalt catalysts [5,6], several rhodium precursors Rh_2O_3, $[Rh(CO)_2Cl]_2$, $HRh(CO)(PPh_3)_3$ have been used, and the regioselectivity of the reaction studied. While with cobalt catalysts there is selective β-formylation [5,6], in the presence of rhodium complexes α-formylation is favoured and the branched aldehyde (methyl α-formylisobutyrate) is the major product. The ratio of the latter increases with increase in the P/Rh ratio and with increase in pressure but decreases with increase in temperature. With diphosphinerhodium catalysts, the size of the chelate ring formed influences the product distribution, and the aldehydes are accompanied by a considerable amount of the hydrogenation by-product. In all cases addition of Et_3N has only a small effect on the selectivity. In keeping with the findings by Wilkinson and his colleagues [8] it has been generally accepted that under hydroformylation conditions chlororhodium precursors are transformed into hydridorhodium complexes, the active species for the reaction. We describe here hydroformylation of MMA with very efficient phosphinerhodium catalysts prepared "in situ" and demonstrate the major role of the basicity of the phosphine and reveal the influence of added bases such as Et_3N on the selectivity.

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Table 1

Hydroformylation of methyl methacrylate with phosphinerhodium catalysts prepared "in situ" [a]

Catalyst	Temperature (°C)	Pressure (bar)	Conversion (%)	R_S [b] (%)
$[Rh(NBD)Cl]_2 + PPh_3$	150	80	100	53
$[Rh(NBD)Cl]_2 + PPh_3 + Et_3N$	150	80	100	22
$[Rh(NBD)Cl]_2 + PPh_3$	100	80	100	14
$[Rh(NBD)Cl]_2 + PPh_3 + Et_3N$	100	80	100	7
$[Rh(NBD)Cl]_2 + PBu_3$	100	80	84	51
$[Rh(NBD)Cl]_2 + PBu_3 + Et_3N$	100	80	100	11
$[Rh(NBD)Cl]_2 + PPh_3$	100	15	80	34
$[Rh(NBD)Cl]_2 + PPh_3 + Et_3N$	100	15	84	27
$[Rh(NBD)Cl]_2 + PPh_3 + (c\text{-}Hex)_2EtN$	100	15	79	24
$[Rh(NBD)Cl]_2 + PBu_3$	100	15	58	82
$[Rh(NBD)Cl]_2 + PBu_3 + Et_3N$	100	15	75	28
$[Rh(NBD)Cl]_2 + PBu_3 + (c\text{-}Hex)_2EtN$	100	15	76	26

[a] Rh/P/N/olefin = 1/2/15/20; $CO/H_2 = 1/1$; 1 mmol substrate in 5 ml benzene; reaction time 3 h.
[b] R_S (%) = $\frac{\text{methyl } \beta\text{-formylisobutyrate}}{\text{total aldehyde}} \times 100$.

Results and discussion

Hydroformylation of MMA with catalysts prepared "in situ" from $[Rh(NBD)Cl]_2$ and tertiary phosphines takes place readily in benzene solution without detectable side reactions. As tertiary phosphine ligands, the highly basic PBu_3, and the much less basic PPh_3 were chosen; this choice was based on our earlier experience with stereoselective hydrogenation of cyclic ketones [9] and regioselective hydroformylation of N-containing cyclic olefins [10], which revealed the strong influence of the basicity of the phosphine on stereo- and regio-selectivity. However, in the case of reactions of N-containing derivatives the substrate itself can play a role equivalent to that of Et_3N, creating some difficulties in the separation of the two factors of key importance, phosphine basicity and the effect of the nitrogen base. To avoid this problem in this work MMA, whose reactions are known to be exceptionally sensitive to reaction conditions, was selected as the substrate for hydroformylation. Under the conditions specified in Table 1, changing the reaction variables (CO/H_2 pressure, reaction temperature) resulted in a product distribution similar to that previously reported [3,7].

Phosphines of different basicities had significantly different influences on the normal/branched aldehyde ratio. Addition of Et_3N to each catalytic system enhanced the activity and increased the proportion of the α-formylated product. No significant change in R_S * or in the reaction rate occurred when Et_3N was replaced by $(c\text{-}Hex)_2EtN$, and this indicates that Et_3N does not act simply as a stabilising ligand.

In the following experiments the influence of the P/Rh ratio on selectivity was investigated with and without added Et_3N (Fig. 1). Under the conditions used the aldehyde distribution varied over a wide range, but in the absence of Et_3N there are

* R_S is the ratio of methyl β-formylisobutyrate/total aldehyde.

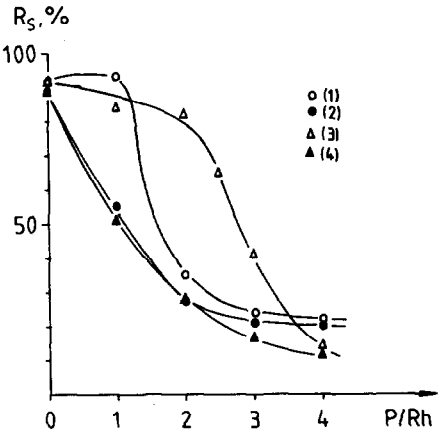

Fig. 1. Influence of the phosphine/Rh ratio on the regioselectivity of hydroformylation; reaction conditions: 100 °C, 15 bar ($CO/H_2 = 1/1$); Rh/N/MMA = 1/15/20; 3 h. (1) $[Rh(NBD)Cl]_2 + PPh_3$, (2) $[Rh(NBD)Cl]_2 + PPh_3 + Et_3N$, (3) $[Rh(NBD)Cl]_2 + PBu_3$, (4) $[Rh(NBD)Cl]_2 + PBu_3 + Et_3N$.

again significant differences between the effect of the catalyst system containing PPh_3 and PBu_3. Increase in the P/Rh ratio led to increase in the branched aldehyde in each case. Addition of Et_3N almost eliminated the differences in regioselectivity.

As can be seen from Fig. 2 the increase in the Et_3N/Rh ratio also led to a marked increase in the α-selectivity.

Our observations can be accounted for in terms of the assumptions that Et_3N brings about HCl abstraction in both catalytic systems and that there is an equilibrium between the chlororhodium carbonyl derivatives and the monohydridorhodium carbonyl species (eq. 1). At low P/Rh ratios and in the absence of

$$RhCl(CO)P_2 \overset{H_2}{\rightleftharpoons} H_2RhCl(CO)P_2 \overset{Et_3N}{\rightleftharpoons} HRh(CO)P_2 \qquad (1)$$

Et_3N, the chloro complexes are active, and give the methyl β-formylisobutyrate. At higher P/Rh ratios (the ratio being different for each phosphine) chloride abstrac-

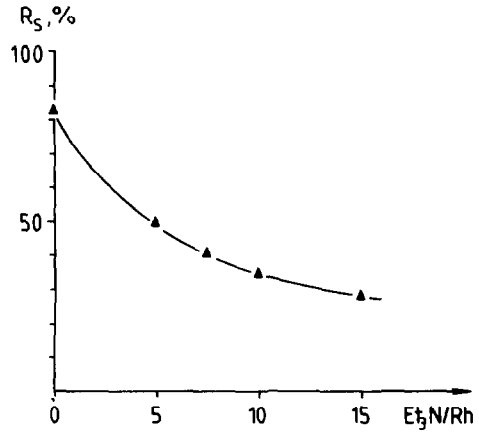

Fig. 2. Influence of the Et_3N/Rh ratio on the regioselectivity of hydroformylation; reaction conditions: 100 °C, 15 bar ($CO/H_2 = 1/1$); 3 h; $Rh/PBu_3/MMA = 1/2/20$.

Table 2

Hydroformylation of methyl methacrylate with substituted $Rh_4(CO)_{12}$ catalysts [a]

Catalyst	Rh/P/N	Conversion (%)	R_S (%)
$Rh_4(CO)_{12}$	1/0/0	98	94
$Rh_4(CO)_{12} + PPh_3$	1/1/0	93	28
$Rh_4(CO)_{12} + PPh_3 + Et_3N$	1/1/15	90	30
$Rh_4(CO)_{12} + PBu_3$	1/1/0	70	15
$Rh_4(CO)_{12} + PBu_3 + Et_3N$	1/1/15	65	15
$Rh_4(CO)_{12} + PBu_3$	1/2/0	58	10
$Rh_4(CO)_{12} + PBu_3 + Et_3N$	1/2/15	51	9

[a] 100 °C; 15 bar ($CO/H_2 = 1/1$); 3 h.

tion occurs even in the absence of the base, and monohydridophosphinorhodium carbonyl are active, transforming MMA mainly into the branched aldehyde.

This assumption was supported also by an IR spectroscopic study. At low P/Rh ratios, the IR spectra (determined both in a high pressure IR cell [11] and at normal pressure) showed that most of the catalyst was in the form of $RhCl(CO)_2P$ and $RhCl(CO)P_2$ complexes. ($P = PPh_3$: ν(CO) 2088, 2002 cm^{-1}; ν(Rh–Cl) 290 cm^{-1} and ν(CO) 1965 cm^{-1}; ν(Rh–Cl) 313 cm^{-1}, respectively; $P = PBu_3$: ν(CO) 2084, 1990 cm^{-1}; ν(Rh–Cl) 283 cm^{-1} and ν(CO) 1944 cm^{-1}; ν(Rh–Cl) 316 cm^{-1}). When Et_3N was added or the P/Rh ratio was considerably increased, the spectra showed that hydrido species were present ($P = PPh_3$; ν(CO) 1980 cm^{-1}; $P = PBu_3$; ν(CO) 1960 cm^{-1}).

The role of Et_3N was also studied indirectly by adding Et_3N to substituted rhodium carbonyl catalysts (Table 2). Under these conditions mainly the branched aldehyde was formed, even at low P/Rh ratios, and none of the catalytic systems was influenced by the base.

In view of our results (Fig. 1) in the presence of Et_3N it seemed likely that $HRh(CO)(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, and $RhCl(PPh_3)_3$ behave very similarly in hydroformylation, and this was confirmed experimentally (Table 3). Our results are in accordance with the qualitative observations made by Wilkinson and his colleagues [8]. When $RhCl(CO)(PPh_3)_2$ or $RhCl(PPh_3)_3$ is used as precursor, the HCl abstraction is rather slow in the absence of Et_3N, and this is reflected in the distribution of the aldehyde isomers. When the catalyst is prepared "in situ" from

Table 3

Hydroformylation of methyl methacrylate with various catalysts [a]

Catalyst	R_S (%)
$HRh(CO)(PPh_3)_3$	25
$HRh(CO)(PPh_3)_3 + Et_3N$	26
$RhCl(CO)(PPh_3)_2 + 1\ PPh_3$	39
$RhCl(CO)(PPh_3)_2 + 1\ PPh_3 + Et_3N$	29
$RhCl(PPh_3)_3$	49
$RhCl(PPh_3)_3 + Et_3N$	28
$\frac{1}{2}[Rh(NBD)Cl]_2 + 2\ PBu_3$	82
$\frac{1}{2}[Rh(NBD)Cl]_2 + 2\ PBu_3 + Et_3N$	28

[a] 100 °C; 15 bar (CO/H_2 1/1); 3 h; Rh/N/olefin 1/15/20.

basic phosphines, at low P/Rh ratios HCl abstraction does not occur in the absence of the base and the regio-selectivity of the active chloro complex is different.

Experimental

Materials

Benzene was dried and distilled under argon. The catalyst precursors $[Rh(NBD)Cl]_2$, $HRh(CO)(PPh_3)_3$, $Rh_4(CO)_{12}$, $RhCl(CO)(PPh_3)_2$, $RhCl(PPh_3)_3$ were prepared by standard methods [12–15]. The phosphines were purchased from Fluka, and methyl methacrylate from Aldrich.

Hydroformylation reaction

In a typical experiment, a solution of $[Rh(norbornadiene)Cl]_2$ (11.6 mg) and 0.1 mmol phosphine in 5 ml benzene was kept under argon in a Schlenk tube for 10 min. The solution thus obtained was injected together with 1 mmol of substrate into a 20 ml stainless steel autoclave (equipped with a shaking device) flushed with argon.

A 1/1 mixture of purified carbon monoxide and hydrogen was introduced up to 15 bar and the temperature raised to 100 °C. After 3 h shaking the autoclave was rapidly cooled, the gases discharged, and the mixture analysed by GLC. GLC analyses were performed on a HP5830 chromatograph equipped with a 25 m × 0.25 mm i.d. glass capillary column coated with OV-1 and OV-17 mixed stationary phase and a flame-ionization detector. Argon was used as carrier gas and the column temperature was programmed from 50 to 250 °C at 10 °C/min. The aldehydes formed were identified by ^1H NMR spectroscopy after fractional distillation. ^1H NMR spectra were recorded in $CDCl_3$ on a Varian CFT-20 spectrometer. IR spectra were recorded on SPECORD IR-75 and DIGILAB-FS100 spectrophotometers.

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