

Hydroformylation of alkenes with rhodium catalyst in supercritical carbon dioxide

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Received 1 November 2005; accepted 16 November 2005

1-Octene, 1-decene and styrene have been hydroformylated using a CO₂-philic fluororous ligand associated with a rhodium catalyst. The effect of P/Rh molar ratio, partial pressure of CO/H₂ and total pressure of carbon dioxide were studied. When 1-octene was used as the substrate, high conversion and selectivity in aldehydes were observed using low rhodium concentration and low P/Rh ratios.

KEY WORDS: rhodium complexes; hydroformylation; supercritical; carbon dioxide; P-donor ligands.

1. Introduction

The hydroformylation of long chain alkenes is an important industrial process. The aldehydes obtained can be converted into plasticizer alcohols and biodegradable detergents [1]. The main disadvantage of this reaction is difficult separation of the reaction products from the catalyst at the end of the reaction due to the high boiling points of the aldehydes. Several strategies have been developed to solve this problem. The most successful one is to use a multiphase system consisting of two or more immiscible liquid phases. The catalyst is immobilised in the liquid phase while the substrate and the product(s) of the catalysed reaction are in the other phases [2].

In 1984, Rhône-Poulenc/Ruhr-Chemie initiated the first commercial process for the biphasic aqueous hydroformylation of propene [3–5]. This process produces 300,000 tones of butanal per year but it is not viable for long-chain alkenes because a certain solubility of the alkene in water is needed to obtain a high conversion [6].

In 1994, the concept of the fluororous biphasic system (FBS) was introduced by Horváth and Rábai and applied to the hydroformylation of 1-decene [7–9]. The FBS is based on the properties of fluororous solvents, which have a low affinity for non-fluorinated compounds. The catalyst, which contains ligands with fluororous chains, is therefore dissolved in the fluororous phase and the products can be separated by a simple decantation. Since then there has been increasing interest in the development of catalysts with high affinities for the

fluororous phase. Although the FBS has many advantages, it has not been applied at industrial level due to the high cost of the fluororous solvents.

Supercritical carbon dioxide (scCO₂) is an attractive green solvent and an alternative to conventional organic solvents. It is used successfully in industrial extraction processes [10]. scCO₂ can also be used as a solvent in homogeneous catalysis. [11]. Carbon dioxide has mild critical data ($T_c = 31^\circ\text{C}$, $P_c = 73.8$ bar) and is both environmentally friendly and relatively inexpensive. Supercritical carbon dioxide has gas-like properties, and gases such as H₂ and CO are highly soluble in it. For this reason, it is a good alternative solvent, especially in reactions in which the reagents are gases. ScCO₂ is a non-polar solvent, so modifications in catalytic systems are required to increase the solubility of the catalyst in the reaction media. The best results in terms of solubility have been achieved by introducing fluororous chains into the ligands [12]. Due to the tuneable properties of carbon dioxide, changing the pressure or temperature of the system could induce the selective precipitation of the catalyst system. The products and the substrate could then be separated from the catalyst by extraction with supercritical carbon dioxide [12, 13].

We recently reported the successful application of Rh catalysts using the fluororous ligand **1** (figure 1) in the hydrogenation [14] and hydroformylation [15] of alkenes using the FBS concept. The selectivity in aldehydes obtained in the hydroformylation of 1-octene using perfluoromethylcyclohexane was high (96%) and the activity was up to 1040 h⁻¹. When a biphasic perfluoromethylcyclohexane/toluene system was used, the system could be effectively recycled for two consecutive runs. In this study we report the use of this fluororous

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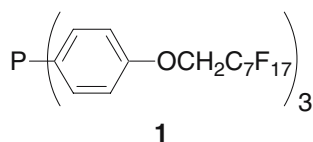


Figure 1. Ligand 1.

monophosphine $\text{P}(\text{C}_6\text{H}_4\text{-4-OCH}_2\text{C}_7\text{F}_{15})_3$ (**1**) in the rhodium catalytic hydroformylation of model alkenes using supercritical carbon dioxide as solvent.

2. Experimental

2.1. Solubility studies

The solubility studies were carried out in a Thar reactor (100 cm^3) equipped with sapphire windows and magnetic stirring. The autoclave was charged with ligand **1** (0.144 mmol), $[\text{Rh}(\text{acac})(\text{CO})_2]$ (0.048 mmol) and 1-octene (24 mmol). The reactor was pressurised with syn-gas and CO_2 , the system was heated and the total pressure was increased using a syringe pump. Solubility was monitored by visual inspection.

2.2. Catalysis in supercritical carbon dioxide

Hydroformylation experiments were carried out in a Parr autoclave (25 cm^3) with magnetic stirring. The autoclave was equipped with a liquid inlet, a gas inlet, a CO_2 inlet and a thermocouple. An electric heating mantle kept the temperature constant. The complex $[\text{Rh}(\text{acac})(\text{CO})_2]$ (0.012 mmol) and the ligand (0.036 or 0.06 mmol) were placed in the autoclave. The autoclave was then evacuated, and the substrate 1-octene (6 mmol) was then added. The system was pressurised with CO/H_2 (1:1), and liquid CO_2 was introduced until a total pressure of 60 bar. The autoclave was heated to the desired temperature. When thermal equilibrium was reached, the total pressure was adjusted with a Thar syringe pump. After the reaction time, the autoclave was cooled to $-50\text{ }^\circ\text{C}$ and carefully vented. The final mixture was analysed by GC. The products were identified by GC-mass spectrometry.

To preactivate the catalyst, $[\text{Rh}(\text{acac})(\text{CO})_2]$ and ligand **1** were placed in the autoclave, the system was evacuated and pressurised with syn-gas and carbon dioxide, the system was heated to the desired value, and then more carbon dioxide was added. The system was stirred for 1 h, cooled to $-50\text{ }^\circ\text{C}$ and depressurised. The substrate was then added and the system was pressurised again. All preactivations were carried out under the same reactions conditions.

Gas chromatography analyses were performed in a Hewlett-Packard 5890A in an HP-5 (5% diphenylsilicone/95% dimethylsilicone) column ($25\text{ m}\times 0.2\text{ mm } \varnothing$) for separation of the products.

3. Results and discussion

3.1. Solubility studies

We studied the solubility of the catalytic system $\text{Rh}/\mathbf{1}$ in supercritical carbon dioxide. The solubility studies were performed in a Thar 100 ml autoclave equipped with sapphire windows and solubility was established by visual inspection. The catalytic precursor $[\text{Rh}(\text{acac})(\text{CO})_2]$ ($0.48\cdot 10^{-3}\text{ M}$), the phosphine **1** ($\text{P}/\text{Rh}=3$) and 1-octene (24 mmol) were placed in the autoclave, which was then pressurised with CO/H_2 , 10 bar (1:1) and finally with carbon dioxide. The solubility behaviour was studied by increasing the temperature and total pressure of carbon dioxide progressively using a syringe pump. The mixture became a solubilised one-phase transparent yellow system at $80\text{ }^\circ\text{C}$ and 200 bar of total pressure at a density of approximately 0.6 g ml^{-1} (figure 2a). When the autoclave was cooled down, the two phases were recovered without apparent decomposition (figure 2b).

3.2. Hydroformylation reactions

To investigate the efficiency of the fluorous phosphine **1** in rhodium-catalysed hydroformylation, we chose 1-octene (**2**), 1-decene (**3**) and styrene (**4**) as model substrates for the hydroformylation of 1-alkenes (Scheme 1) in supercritical carbon dioxide.

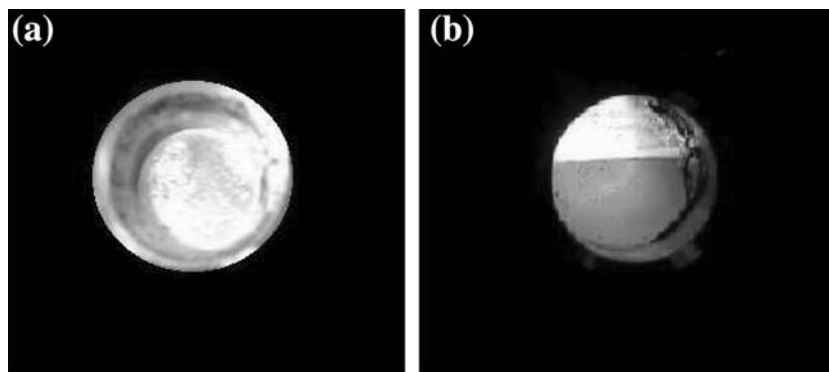
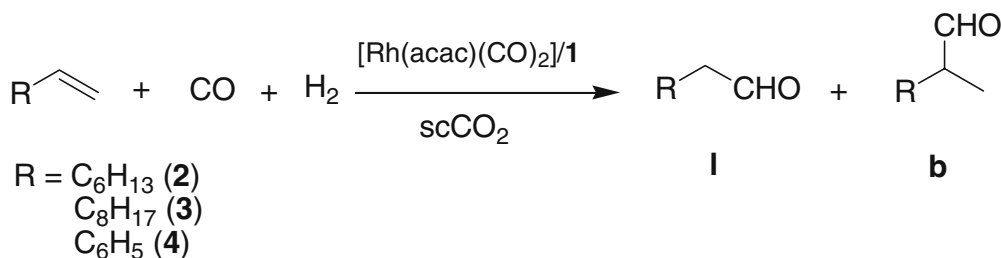


Figure 2. (a) Soluble catalyst precursor in one phase system at $80\text{ }^\circ\text{C}$ and 200 bar, (b) Precipitation of catalyst precursor at $50\text{ }^\circ\text{C}$ and 135 bar.



Scheme 1.

Hydroformylation reactions were carried out using the *in situ* formed catalyst precursor $[\text{Rh}(\text{acac})(\text{CO})_2]/\mathbf{1}$ at 0.48 mM concentration. Using 1-octene (**2**) as the substrate, we studied the influence of P/Rh ratio, temperature, partial pressure of CO/H₂ and total pressure on the activity of the reaction. The results are summarised in table 1.

At 10 bar of CO/H₂, 200 bar of total pressure, 80 °C and with a P/Rh molar ratio of 3 (entry 1, table 1), conversion was very low, though the system was soluble under these conditions. The selectivity in aldehydes was also very low and the major products obtained were 2-octene isomers. This low conversion may be due to the lack of formation of the active species, since a period of induction, as reported for low donor phosphite systems, was probably needed [16]. Therefore, to form the active species in the supercritical solvent, we decided to conduct an experiment by heating the system at 80 °C,

10 bar of CO/H₂ and scCO₂ up to 200 bar of total pressure for 1 h (entry 2, table 1). The autoclave was then cooled to −50 °C and depressurised, and the substrate was introduced. CO/H₂ and carbon dioxide were again charged and the reaction was allowed to proceed for 1 h. Conversion and aldehyde selectivity increased by up to 49% and 74%, respectively.

Increasing the P/Rh molar ratio to 5 (entry 3, table 1) increased total conversion but also decreased both aldehyde selectivity and regioselectivity. To prevent the formation of isomerisation products by-elimination, we decreased the temperature to 60 °C while maintaining the P/Rh ratio at 5 (entry 4, table 1). We observed a decrease in conversion, a lower selectivity in aldehydes and no further improvement in the *l/b* ratio.

We studied the effect of partial pressure of CO/H₂ at a P/Rh ratio of 3. Increasing the partial pressure to 20 bar (1:1) increased selectivity in aldehydes (86%) and

Table 1
Hydroformylation of **2–4** using $[\text{Rh}(\text{acac})(\text{CO})_2]/\mathbf{1}$ in scCO₂^a

Entry	Alkene	P/Rh	<i>t</i> (h)	P(CO/H ₂) (atm)	<i>T</i> (°C)	<i>P</i> _{tot} (atm)	Conv. (%) ^b	<i>S</i> _{ald} (%) ^c	<i>l/b</i>	<i>S</i> _i (%) ^d
1	2	3	1	5/5	80	200	4	50	70/30	41
2 ^e	2	3	1	5/5	80	200	49	74	76/24	26
3 ^e	2	5	1	5/5	80	200	66	64	68/32	36
4 ^e	2	5	1	5/5	60	200	29	57	66/34	43
5 ^e	2	3	1	10/10	80	200	66	86	76/24	14
6 ^e	2	3	1	10/10	100	200	47	60	77/23	40
7 ^e	2	3	1	10/10	80	250	40	72	73/27	28
8 ^e	2	3	1	10/10	100	250	73	74	76/23 ^f	26
9 ^e	2	3	1	20/20	80	200	76	74	72/23	26
10 ^{g,h}	2	5	1	20/20	80	40	68	96	74/26	4
11 ^{e,h}	2	5	1	20/20	80	200	32	38	64/36	61
12 ⁱ	2	5	1	20/20	80	40	97	98	73/23	2
13 ^e	3	3	3	10/10	80	200	94	60	71/29	40
14 ^{e,j}	4	3	3	10/10	80	200	31	87	28/62	–

^aReaction conditions: *V* = 25 ml, $[\text{Rh}(\text{acac})(\text{CO})_2] = 0.48 \cdot 10^{-3}$ M, 1-octene:Rh = 500.

^b% Conv = total conversion of alkene.

^c% *S*_{ald} = selectivity in aldehydes.

^d% *S*_i = selectivity in isomerised products.

^ePreactivation of catalyst.

^fLess than 0.5% of ethylhexanal was detected.

^gSolvent = C₇F₁₄, see reference [15].

^h $[\text{Rh}(\text{acac})(\text{CO})_2] = 1.6 \cdot 10^{-3}$ M, *S*:Rh = 2000.

ⁱSolvent = toluene, ligand = PPh₃, see reference [15].

^jThirteen percent ethylbenzene was also formed.

conversion (66%) (entry 5 versus entry 2 in table 1). When we increased the temperature to 100 °C (entry 6 in table 1) while keeping the other parameters constant, we observed a drop in both conversion and aldehyde selectivity.

The total pressure of carbon dioxide and the temperature can also affect the reactivity of the system since these parameters also affect the density [11, 17]. At the same partial pressure of 20 bar of CO/H₂, and by increasing the total pressure of carbon dioxide to 250 bar at 80 °C (entry 7 versus entry 5, table 1), we observed a decrease in conversion and in aldehyde selectivity. Increasing the temperature to 100 °C (entry 8 versus entry 6 in table 1) and applying a higher pressure of carbon dioxide led to better conversion (73%) and aldehyde selectivity (74%). The approximate density of the system at 250 bar and 100 °C (entry 8, table 1) was 0.6 g ml⁻¹, whereas the density at 200 bar and 100 °C (entry 6, table 1) was 0.5 g ml⁻¹. When we compared these densities with those calculated for the system at 200 bar and 80 °C ($d=0.6$ g ml⁻¹) (entry 5, table 1) and at 250 bar and 80 °C ($d=0.7$ g ml⁻¹) (entry 7, table 1), we found that the best conversions and aldehyde selectivities were obtained when the density of the system was around 0.6 g ml⁻¹.

Increasing the partial pressure of CO/H₂ up to 40 bar (1:1) (entry 9, table 1) gave higher conversion but slightly decreased aldehyde selectivity.

Optimisation of the conditions therefore showed that the best results (66% conversion and 86% selectivity in aldehydes) were obtained at a P/Rh molar ratio of 3, 20 bar of CO/H₂ and 200 bar total pressure.

The Rh/I system was also used in the rhodium-catalysed hydroformylation of 1-octene (**2**) in fluoros systems [15]. The best results in FBS were obtained at a P/Rh ratio of 5 and a rhodium concentration of 1.6×10^{-3} M (entry 10, table 1). To compare both solvents as reaction media, we performed a catalytic experiment in scCO₂ using the same conditions as those in FBS. Under the same conditions, the fluoros system provided the best results. However, when we compared the best results for both systems (entry 5 versus entry 10, table 1), we noticed that similar conversions and regioselectivities could be obtained using scCO₂ but with the added advantage that the catalyst concentration, P/Rh molar ratio and CO/H₂ partial pressure can be much lower. The selectivity in scCO₂ was about 10% lower. When we compared the results obtained using the catalyst precursor [Rh(acac)(CO)₂]/PPh₃ in toluene (entry 12, table 1), though conversion and selectivity were lower in scCO₂, we found that under suitable conditions this solvent can clearly replace toluene.

The Rh/I system was also applied to the hydroformylation of 1-decene (**3**) and styrene (**4**) (entries 13 and 14 in table 1). When 1-decene (**3**) was used as the

alkene, conversion was high but selectivity in aldehydes was moderate. The *n*/iso ratios were similar to those obtained with 1-octene (**2**) under the same reaction conditions. Styrene (**4**) was also hydroformylated with low conversion (31%), though aldehyde selectivity was high (87%) and the *l*/*b* ratio was moderate.

4. Conclusion

Ligand **1** associated with [Rh(acac)(CO)₂] afforded an active catalyst in the hydroformylation of olefins in scCO₂. The results showed that the system was more active at low rhodium concentrations with low P/Rh ratios. At low CO/H₂ pressure, conversions were low. However, increasing the partial pressure up to 20 bar led to high conversions. Higher partial pressures slightly decreased aldehyde selectivity. The density of the system clearly influences the conversion and selectivity in aldehydes. The best results were obtained at densities close to 0.6 g ml⁻¹. Comparative results showed that scCO₂ can replace fluoros systems and, though conversion and selectivity were lower than when [Rh(acac)(CO)₂]/PPh₃ was used, this system could also be used as a catalyst precursor.

Acknowledgment

We thank the *Ministerio de Educación, Cultura y Deporte* (CTQ2004-03831/PPQ) for financial support.

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