

# Hydroformylation of hex-1-ene in supercritical carbon dioxide catalysed by rhodium trialkylphosphine complexes

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**Triethylphosphine complexes of rhodium catalyse the hydroformylation of hex-1-ene in supercritical carbon dioxide at rates similar to those obtained in toluene, but with a slightly improved n : i ratio; using trioctylphosphine, much lower rates are observed.**

Supercritical carbon dioxide is potentially an excellent solvent for carrying out homogeneous catalytic reactions because it is easily separated from the catalyst and the products and is environmentally benign.<sup>1,2</sup> In addition, the high solubility of gases (totally miscible with scCO<sub>2</sub>) means that problems associated with transport of gases across interfaces are removed and the gas-like nature of the medium means that diffusion is much faster than in solution reactions.

Extensive studies have been made of hydroformylation of alkenes using [Co<sub>2</sub>(CO)<sub>8</sub>]<sup>3,4</sup> but there have been problems with studying the more active and selective rhodium based species because the triarylphosphine complexes that are usually employed in liquid phase reactions have very low solubility in scCO<sub>2</sub>.<sup>5</sup> A brief report has appeared in which this problem has been overcome by derivatising the aryl groups with fluorinated chains.<sup>6</sup>

We now report that simple trialkylphosphines such as PEt<sub>3</sub>, which are readily available, do not involve the use of costly fluorinated derivatives and have low molecular masses so the relatively small amounts can be employed, can provide highly active catalysts for the hydroformylation of hex-1-ene in scCO<sub>2</sub>. Trimethylphosphine complexes of ruthenium have been used for the hydrogenation of CO<sub>2</sub><sup>5</sup> and for the formation of DMF from CO<sub>2</sub>, hydrogen and dimethylamine in scCO<sub>2</sub>.<sup>7,8</sup>

Using a catalyst prepared *in situ* from [Rh<sub>2</sub>(OAc)<sub>4</sub>] and PEt<sub>3</sub>, complete conversion to C<sub>7</sub> aldehydes, with a trace of C<sub>7</sub> alcohols [total straight to branched (n:i) ratio = 2.4] is obtained within 2 h at 100 °C. ‡ [SAFETY WARNING: All reactions involving scCO<sub>2</sub> are carried out at very high pressures

(up to 250 bar). They should only be attempted in autoclaves that have been specially designed to withstand such pressures.] Comparison of the pressures within the autoclave during the heating period (10 min), with those obtained during heating an identical solution in the absence of catalyst shows that the onset of reaction occurs at 80 °C, and visual inspection through a sapphire window shows that the mixture becomes homogeneous (monophasic pale yellow solution) at *ca.* 70 °C. Table 1 lists the results of a series of different experiments and shows that the rate is very similar to that obtained with the same catalyst under identical conditions using toluene as the solvent, but the n : i ratio is slightly higher in scCO<sub>2</sub>. The reaction is retarded by addition of excess of PEt<sub>3</sub>, but enhanced by increased *p*<sub>CO</sub> or *p*<sub>H<sub>2</sub></sub>.

In the solution phase system, we have previously shown<sup>9</sup> that C<sub>7</sub> alcohols can be products of the hydroformylation of hex-1-ene, either formed in a sequential reaction (thf as solvent) or as primary products (alcoholic solvents). In the hydroformylation of hex-1-ene carried out in scCO<sub>2</sub>, C<sub>7</sub>-alcohols are products (*ca.* 8%) after 2 h reaction and become significant (31%) products after longer reaction times. Adding ethanol to the mixture does not increase the amount of alcohol produced, but somewhat reduces the overall rate. We have shown<sup>9</sup> that, in liquid phase reactions, protonation of an acyl intermediate by ethanol is the key step that leads to C<sub>7</sub> alcohol production. It is presumably the inability of scCO<sub>2</sub> to solvate the ionic species formed by the protonation, that prevents the direct formation of C<sub>7</sub> alcohols when the reaction is carried out in scCO<sub>2</sub> in the presence of ethanol. Interestingly, addition of the fluorinated alcohol, C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>OH, does lead to an increase in the amount of alcohol produced and to a higher reaction rate.

We have also studied other trialkylphosphine ligands. Replacing one ethyl group in PEt<sub>3</sub> with a fluorinated chain (–CH<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>F<sub>13</sub>) increases the reaction rate, presumably because of electron density changes on the rhodium rather than

**Table 1** Conditions and yields of products from the hydroformylation of hex-1-ene catalysed by rhodium complexes‡

Solvent	Phosphine	[Rh]/mmol dm <sup>-3</sup>	<i>p</i> <sub>CO</sub> /bar	<i>p</i> <sub>H<sub>2</sub></sub> /bar	<i>t</i> /h	Aldehydes <sup>a</sup> (%)	Heptanol (%)	n : i	TOF/Rh <sup>-1</sup> h <sup>-1</sup>
Toluene	PEt <sub>3</sub>	6.58	20	20	1	74	4.8	2.1	53
scCO <sub>2</sub>	PEt <sub>3</sub>	6.54	10	20	1	56	1	2.4	38
scCO <sub>2</sub>	PEt <sub>3</sub> <sup>b</sup>	6.48	10	20	1	23	—	2.2	16
scCO <sub>2</sub>	PEt <sub>3</sub>	6.43	10	10	1	38	—	2.5	27
scCO <sub>2</sub>	PEt <sub>3</sub>	6.57	5	20	1	35	—	2.6	24
scCO <sub>2</sub>	PEt <sub>3</sub>	6.48	20	20	1	82	2.3	2.4	57
scCO <sub>2</sub>	PEt <sub>3</sub>	6.52	20	20	2	89	8.1	2.5	
scCO <sub>2</sub>	PEt <sub>3</sub>	6.58	20	30	22	54	28 <sup>c</sup>	2.5	
scCO <sub>2</sub> /EtOH <sup>d</sup>	PEt <sub>3</sub>	6.48	20	20	1	60	3	2.4	44
scCO <sub>2</sub> /R <sub>f</sub> OH <sup>d,e</sup>	PEt <sub>3</sub>	6.42	20	20	1	82	11	2.5	62
scCO <sub>2</sub>	PEt <sub>2</sub> R <sub>f</sub> <sup>e,f</sup>	6.45	20	20	1	81	—	2.4	58
scCO <sub>2</sub>	P(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub>	6.57	5	10	2	8.2	—	3.3	2.7
scCO <sub>2</sub>	P(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub>	6.56	5	20	2	12	—	3.9	4.2
scCO <sub>2</sub>	P(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub>	6.69	10	10	2	17	1.5	2.8	6.3
scCO <sub>2</sub>	P(C <sub>8</sub> H <sub>17</sub> ) <sub>3</sub>	6.61	15	10	2	20	2.3	2.8	7.5

<sup>a</sup> Traces of isomerised alkenes are also observed. <sup>b</sup> 0.2 cm<sup>3</sup>. <sup>c</sup> 2-Methylhexanol (3%) and hexane are also observed. <sup>d</sup> 2 cm<sup>3</sup>. <sup>e</sup> R<sub>f</sub> = C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH<sub>2</sub>. <sup>f</sup> 90 °C.

changes in solubility (both reactions are fully homogeneous). Using tri-*n*-octylphosphine, the rate is very much reduced, two phases are apparent in the system and higher *n* : *i* ratios (up to 3.9) are obtained with low  $p_{\text{CO}}$ , although the conversion is low. We have shown that higher *n* : *i* ratios can be obtained at low conversion in the solution phase system.<sup>9</sup>

We conclude that hydroformylation of hex-1-ene can be successfully carried out in  $\text{scCO}_2$  using rhodium based catalysts containing cheap, readily available trialkylphosphine ligands, and that different chemoselectivities can be observed from those observed under some conditions in organic solvents.

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## Notes and References

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‡ Reactions were carried out in a 36 cm<sup>3</sup> Hastelloy autoclave fitted with a mechanical stirrer and a sapphire base for visual observation of the contents. All manipulations were carried out under nitrogen.  $[\text{Rh}_2(\text{OAc})_4]$  (0.052 g, 0.1176 mmol) was dissolved in  $\text{PEt}_3$  (0.1 cm<sup>3</sup>, 0.67 mmol) to give a red solution. Degassed hex-1-ene (2 cm<sup>3</sup>, 16 mmol) was added and the mixture transferred into the autoclave, pressurised with  $\text{CO}$  and  $\text{H}_2$  and stirred at room temperature for 1 h. Liquid  $\text{CO}_2$  was then transferred into the autoclave using a cooled head hplc pump to give a total pressure 65 bar above that of the  $\text{CO-H}_2$ . The autoclave was then heated for the desired reaction time, with the pressure and temperature being monitored

throughout. After the reaction, the autoclave was allowed to cool in dry ice to  $-50$  °C. The  $\text{CO}_2$  was vented and the liquid product, typically 1.8 cm<sup>3</sup>, was collected and analysed by GLC (quantitative analysis) and GC-MS (identification of products). <sup>31</sup>P NMR studies of the final liquid indicated that the major species in solution is  $[\text{RhH}(\text{CO})_2(\text{PEt}_3)_2]$ .<sup>9</sup>

For reactions in toluene, the reaction was carried out in the same autoclave using half the amounts of all the reagents, 17 cm<sup>3</sup> of toluene and the same gas pressure. This ensures that all the concentrations are the same as in the  $\text{scCO}_2$  experiments and that the pressure drop for the same percentage conversion of substrate is also the same.

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