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Advantages of the solventless hydroformylation of olefins

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ABSTRACT

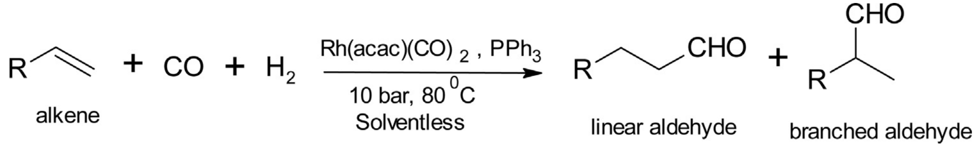
The hydroformylation of olefins using Rh(acac)$(CO)_2$ as a catalyst with the excess of PPh_3 was investigated at the temperature of 80 °C within the pressure range from 4 to 12 bar in a neat substrate, without a solvent. The conversion of 1-hexene was complete, with a linear-to-branched aldehyde ratio of ca. 10. Very good results were also obtained for 1-pentene and 1-octene. The catalytic performance of the Rh(acac)$(CO)_2$/PPh_3 catalytic system in hydroformylation under solventless conditions was better than that in toluene, owing to the high concentration of the reactants. Recycling experiments confirmed the good stability of the catalyst and its constant activity.

1. Introduction

Olefin hydroformylation, the addition of synthesis gas (CO/H_2) to a carbon–carbon double bond in the presence of a transition metal catalyst, is one of the most important homogeneously catalyzed industrial processes. The hydroformylation of 1-olefin yields a mixture of products, a linear *n*-aldehyde and a branched iso-aldehyde. These aldehydes can be easily converted into many industrially important secondary products, such as solvents, biodegradable detergents, soaps, fragrance, flavors, perfumes, pharmaceuticals, surfactants, lubricants, and plasticizers [1–7]. The hydroformylation reaction has been carried out in different reaction media such as organic solvents [8], aqueous-biphasic [9], supercritical CO_2 [10], or ionic liquids [5,11].

Solvent-free synthesis is one of the most important methods of green chemistry, which has recently become increasingly attractive. Among the expected benefits of solvent-free processes are cost savings, a high reaction rate, decreased energy consumption, the easy separation and purification of products, and a significant reduction in reactor size and capital investment. The solvent-free method has also been applied to hydroformylation [6,12]. In 2010, Monnereau et al. reported the application of the hemispherical Rh(acac)(1,3-calix-diphosphite) complex for this reaction with a very good activity. For example, 33% of 1-nonanol was obtained at 80 °C and 20 bar with TOF of 17,290 h^{-1} [6]. Colbey, Klosin, and Whiteker used a rhodium catalyst with (R,S)-BINAPHOS and (S,S)-kelliphos for the asymmetric hydroformylation of allyl cyanide under solvent-free conditions and found a high reaction rate [12]. Clarke and Roff used Rh(acac)$(CO)_2$ with 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phosphaadamantane for the hydroformylation of methyl acrylate under solvent-free conditions receiving high selectivity to the branched product [13].

In this paper, we report on the solventless hydroformylation of olefins using Rh(acac)$(CO)_2$ as a catalyst with an excess of PPh_3. This catalytic system is well known for the hydroformylation of olefins. However, all reported studies have been performed in organic solvents. It was interesting for us to check whether any improvement of the catalytic activity can be achieved by the elimination of the solvent from the catalytic system.



2. Experimental

2.1. Materials

The rhodium complex Rh(acac)$(CO)_2$ was prepared according to the literature [14].

Triphenylphosphine (PPh_3) was purchased from Avocado; 1-hexene and 1-pentene were purchased from Merck; 1-octene was

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Table 1
Hydroformylation of 1-hexene using $Rh(acac)(CO)_2/PPh_3$.

Entry	Conversion (%)	Hexane (g)	2-Hexene (%)	l (%)	b (%)	l/b	Acid (%)	TOF, (h^{-1})
1[a]	99.2	4	6.4	69.7	18.7	3.7	0.4	438
2[b]	99.5	2	10	77	8.5	9.1	2	970
3[c]	100	1.5	4.5	81	11	7.4	2	1330

Reaction conditions: 1-hexene (0.012 mol, 1.5 mL), [Rh] (2.9×10^{-5} mol), ($PPh_3 = 1.6 \times 10^{-4}$ mol) [1-hexene]/[Rh] = 420, [L]/[Rh] = 6.8, $T = 80\,^\circ C$, (H_2:CO)(1:1) = 10 bar, $t = 40$ min.

[a] Toluene as a solvent, $t = 90$ min.

[b] Solventless.

[c] Recycled catalyst from entry 2.

purchased from Sigma–Aldrich; Styrene was purchased from Alfa Aesar; hydrogen (H_2, 99.999%) and carbon monoxide (CO, 99.97%) were procured from Air Products. All chemicals were used without any additional purification.

2.2. Hydroformylation reaction

Hydroformylation experiments were carried out in 50 mL and in 100 mL stainless steel autoclaves provided with a manometer, a thermostat, and a magnetic stirrer. The 100 mL autoclave was equipped with a Teflon vessel. The catalyst $Rh(acac)(CO)_2$, PPh_3, and the substrate were introduced to the autoclave under a nitrogen atmosphere. The autoclave was closed, flushed with hydrogen (5 bar) three times, and then pressurized with synthesis gas (H_2:CO = 1:1) to 10 bar and heated to 80 °C for a specified time. After the reaction was finished, the autoclave was cooled to room temperature and depressurized. The products were analyzed by means GC and GC–MS.

2.3. Recycling of the catalyst

When the hydroformylation reaction was completed, the organic reaction products were separated from the catalyst by "vacuum transfer". New portion of olefin was added to the residue and the resulting mixture was introduced to the autoclave together with PPh_3. The autoclave was closed, flushed with hydrogen (5 bar) three times, and then pressurized with synthesis gas (H_2:CO = 1:1) to 10 bar and heated to 80 °C for a specified time.

2.4. Turnover frequency (TOF)

The turnover number (TON) is defined as the number of moles of substrate that a mole of catalyst can convert before becoming inactivated. Turnover frequency (TOF) is defined as molecules reacting per active site in unit time.

The TOF values were calculated as moles of the aldehyde/([mol of catalyst] × time); time (h) was estimated from the linear part of the graph presenting pressure drop vs. time. For example the TOF value in Table 1 entry 2 was calculated as following:

$$\mathrm{TON} = \frac{\text{amount of substrate (moles)}}{\text{amount of catalyst (moles)}} = \frac{0.012}{2.86 \times 10^{-5}} = 420$$

The method of estimation time from the linear part of the graph presenting pressure drop vs. time is illustrated in Fig. 1.

$$y = 0.5807x + 12.989$$

$$x = 22.4\ \text{min} = 0.37\ \text{h}$$

$$\mathrm{TOF} = \frac{\text{actualTON}}{\text{time(h)}} = \frac{359.1}{0.37} = 970\ \text{h}^{-1}$$

The actual TON at the 85.5% of aldehyde yield is:

$$\text{actualTON} = 420 \times 0.855 = 359.1$$

3. Results and discussion

3.1. Hydroformylation of 1-hexene

The hydroformylation of 1-hexene was investigated under solventless conditions using $Rh(acac)(CO)_2$ as a catalyst with a 6.8-fold excess of PPh_3 as a ligand. The reaction was very fast, and the complete conversion of the olefin was already achieved after 40 min. The selectivity to aldehyde was ca. 86%, the l/b ratio was 9.1, and TOF was 970 (Table 1, entry 2). The recycled catalyst in the presence of an excess of PPh_3 afforded the complete conversion of 1-hexene with a high yield of the aldehyde, 92%, (l/b ratio = 7.4), and a high TOF, 1330 h^{-1} (Table 1, entry 3). Under the same conditions, the reaction was performed using toluene as a solvent in order to compare the reaction rate and the catalytic outcome. The conversion of 1-hexene and the selectivity to aldehydes were high, ca. 99% and 88%, however, the l/b ratio was only 3.7 (Table 1, entry1). The reaction time was 90 min and the turnover frequency was 438 h^{-1}. The catalytic activity in the absence of a solvent was higher than in the experiment carried out in toluene, as was noted by other authors [6,15].

Fig. 1 shows the reaction rate of 1-hexene hydroformylation, estimated by the pressure drop.

The effect of synthesis gas pressure on the hydroformylation of 1-hexene under solventless conditions was studied at 4, 6, and 8 bar at a temperature of 80 °C. The results, summarized in Table 2, show that the conversion of 1-hexene decreased from 87% to 44% when the CO/H_2 pressure changed from 8 to 2 bar. Simultaneously, the yield of aldehydes decreased from 66.4% to 22% with an increase in isomerization reaction yield due to the not sufficient amount of synthesis gas. However, the l/b ratio increased from 10.2 to 22 when the CO/H_2 pressure was reduced from 8 to 2 bar. Such an effect was expected, because linear aldehyde formation is favored at a lower pressure [16].

In order to study the effect of the [1-hexene]/[Rh] ratio on the reaction course, the amount of the olefin changed to achieve a

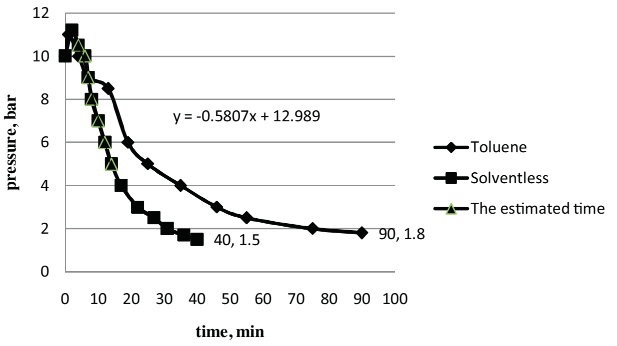


Fig. 1. Pressure drop during hydroformylation of 1-hexene in a solventless system and in toluene at [1-hexene]/[Rh] = 420, [Rh] = (2.9×10^{-5} mol), [L]/[Rh] = 6.8, $T = 80\,^\circ C$, (H_2:CO)(1:1) = 10 bar. The estimated time means the time used for calculations of TOF value.

Table 2
Effect of the pressure on the hydroformylation of 1-hexene under solventless conditions.

Entry	P(bar)	Conversion (%)	2-Hexene (%)	l (%)	b (%)	l/b	Acid(%)	TOF, (h^{-1})
1	8	86.5	13	66.4	6.5	10.2	0.6	757
2	6	69	22	44	3	14.7		322
3	4	44	21	22	1	22		163

Reaction conditions: 1-hexene (0.012 mol, 1.5 mL), [Rh] (2.9×10^{-5} mol), PPh_3 = (1.6×10^{-4} mol) [1-hexene]/[Rh] = 420, [PPh_3]/[Rh] = 6.8, T = 80 °C, (H_2:CO)(1:1), t = 40 min.

Table 3
Effect of the [1-hexene]/[Rh] ratio on the hydroformylation of 1-hexene under solventless conditions.

Entry	[1-Hexene]/[Rh]	Conversion (%)	Hexane (%)	2-Hexene (%)	l (%)	b (%)	l/b	Acid(%)	TOF, (h^{-1})
1[a]	1000	98		11	74	10	7.4	3	1945
2[a]	1500	99		12	68	17	4	2	2327
3[a]	2000	97		8	71	15	4.7	3	4062
4[a]	3000	100	4	22	56	16	3.5	2	3299
5[b]	3000	100	1	3	72	23	3.1	1	4353
6[b]	4000	99	1	2	72	23	3.1	1	2403
7[b]	5000	99	2	2	71	23	3.1	1	3056

Reaction conditions: [PPh_3]/[Rh] = 13, T = 80 °C, (H_2:CO)(1:1) = 10 bar.
[a] t = 60 min, autoclave 50 mL.
[b] t = 80 min, autoclave 100 mL.

1000–5000-fold excess over rhodium. The obtained results listed in Table 3 indicate that the conversion of 1-hexene was very high and practically not influenced by the [1-hexene]/[Rh] ratio. Selectivity to the aldehyde increased with the increasing amount of 1-hexene mainly because the formation of 2-hexene, the isomerization product diminished. The l/b ratio decreased from 7.4 to 3.1 when the [1-hexene]/[Rh] ratio increased. It is worth to note here that results obtained in two autoclaves (50 mL and 100 mL) are slightly different as a result of different volume of CO/H_2 and different rate of heat transfer. It is illustrated by the curves of pressure changes in time for two experiments performed at S/C = 3000 (Table 3, Fig. 2). The products composition was also different and, for example, more of 2-hexene was formed in smaller autoclave (Table 3).

Fig. 2 shows the pressure drop vs. time at different [1-hexene]/[Rh] ratios. As expected, the pressure drop was faster at a lower [1-hexene]/[Rh] ratio, 1000–3000. Next, due to the low concentration of the catalyst, the reaction rate decreased, and the prolongation of the reaction time to ca. 80 min. was necessary to achieve a high conversion Fig. 2.

3.2. Hydroformylation of 1-octene

The solventless hydroformylation of 1-octene was carried out using the same catalytic system, Rh(acac)$(CO)_2$/PPh_3. When the first run was finished (entry 1), the products were removed by “vacuum transfer”, and new portions of 1-octene and PPh_3 were added to the remaining catalyst to start the second run (entry 2). The procedure was repeated and next reaction was performed with the same catalyst (entry 3). Table 4 summarizes the obtained results for recycling the catalyst in the solventless hydroformylation of 1-octene, which indicate the good stability of the catalyst with no significant loss in activity and selectivity during five sequential runs.

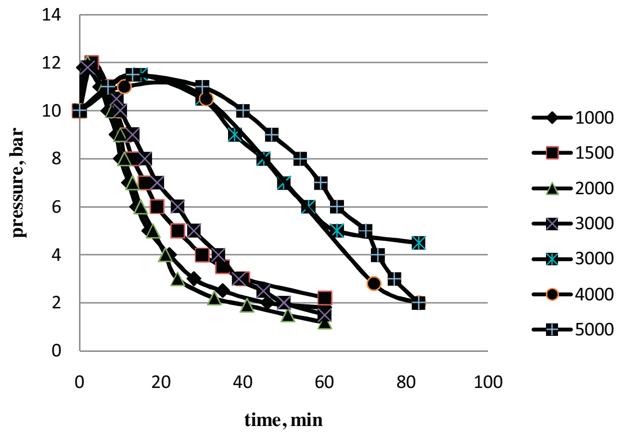


Fig. 2. Graph depicting pressure drops with time for the hydroformylation of 1-hexene catalyzed by Rh(acac)$(CO)_2$/PPh_3 under solventless conditions at different [1-hexene]/[Rh] ratios. [PPh_3]/[Rh] = 13, T = 80 °C, (H_2:CO)(1:1) = 10 bar. Reactions were performed in 50 mL and 100 mL autoclaves according to Table 3.

The catalyst recovered was investigated for the hydroformylation of 1-octene under solventless conditions five times, the conversion of 1-octene slightly decreased from 97% (Table 4, entry 1) to 81% (Table 4, entry 5). Selectivity to a linear aldehyde was almost the same, changing from about 72% to 66%. The yield of the branched aldehyde was 17% (Table 4, entry 1) and then decreased to

Table 4
Hydroformylation of 1-octene using Rh(acac)$(CO)_2$/PPh_3 without a solvent.

Entry	Conversion (%)	Octane (%)	2-Octene (%)	l (%)	b (%)	l/b	Acid (%)	TOF (h^{-1})
1	96	2	5	71	17	4	1	703
2	94		7	72	12	6	3	606
3	92		4	73	12	6.1	3	421
4	90		5	71	10	7.1	4	356
5	81		5	66	9	7.3	1	330
6[a]	100	3	5	72	20	3.6		545

Reaction conditions: 1-octene (0.01 mol, 1.5 mL), [Rh] (2.3×10^{-5} mol), (PPh_3 = 1.6×10^{-4} mol), [1-octene]/[Rh] = 440, [PPh_3]/[Rh] = 6.8, T = 80 °C, (H_2:CO)(1:1) = 10 bar, t = 1 h.
[a] Toluene as solvent.

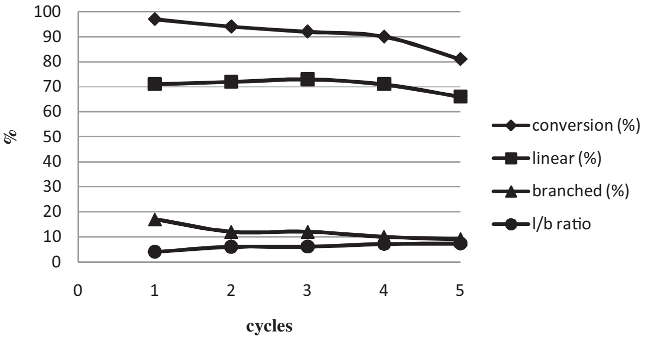


Fig. 3. Plot of the conversion of 1-octene, yield of aldehydes (linear and branched), and the l/b ratio vs. the number of cycles, for the hydroformylation of 1-octene under solventless conditions. 1-octene (0.01 mol, 1.5 mL), [Rh] (2.3×10^{-5} mol), ($PPh_3 = 1.6 \times 10^{-4}$ mol), [1-octene]/[Rh] = 440, [PPh_3]/[Rh] = 6.8, $T = 80\,^\circ C$, (H_2:CO) (1:1) = 10 bar, $t = 1$ h.

Table 5
Hydroformylation of 1-pentene using $Rh(acac)(CO)_2$ without a solvent.

Entry	Conversion (%)	Time (h)	Pentane (%)	2-Pentene (%)	b (%)	l (%)	l/b	Acid (%)	TOF (h^{-1})
1	95.4	1	0.5	5.4	11.5	76.4	6.6	1.6	1512
2	99.5	1.5	0.1	1.8	12.7	80.6	6.4	4.3	634
3	96	1.5	0.4	3.7	11.7	77.9	6.7	2.3	526
4	97.8	2	0.1	1.5	11.1	83.7	7.6	1.4	379
5[a]	96	1	2	5	19	70	3.7		1237

Reaction condition: 1-pentene (0.0137 mol, 1.5 mL), [Rh] (1.7×10^{-5} mol), [PPh_3] (1.03×10^{-4} mol), [1-pentene]/[Rh] = 800, [PPh_3]/[Rh] = 6, $T = 80\,^\circ C$, (H_2:CO)(1:1) = 10 bar.

[a] Toluene as solvent.

Table 6
Solventless hydroformylation of styrene using $Rh(acac)(CO)_2/PPh_3$.

Entry	Conversion (%)	P (bar)	Ethylbenzene (%)	l (%)	b (%)	l/b	TOF (h^{-1})
1	68	10	7	22	39	0.6	250
2	97	12	2	35	60	0.6	524
3[a]	96	12	2	33	61	0.5	415

Reaction condition: styrene (0.013 mol, 1.5 mL), [Rh] (2.9 × 10–5 mol), [PPh3] (2×10^{-4} mol) [styrene]/[Rh] = 440, [PPh_3]/[Rh] = 6.8, $T = 80\,^\circ C$, (H2:CO)(1:1), $t = 2$ h

[a] Toluene as solvent.

9–10% (Table 4, entries 4 and 5). As a result, the linear-to-branched ratio increased from 4 to 7.3, probably due to the increasing excess of the ligand in the system (Fig. 3).

3.3. Hydroformylation of 1-pentene

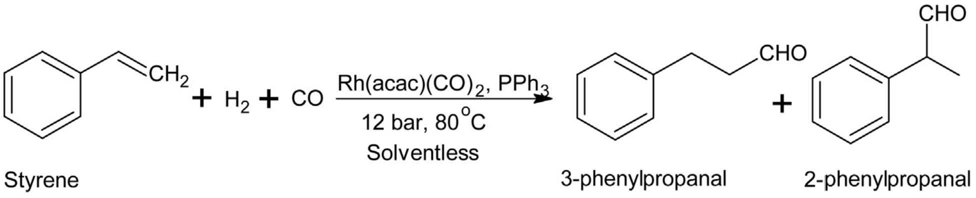
The hydroformylation of 1-pentene was performed under solventless conditions using the same catalytic system, $Rh(acac)(CO)_2/PPh_3$. Similarly as in the case of other olefins, the catalyst was reused four times with the addition of PPh_3 in each run. The results presented in Table 5 show that the conversion of 1-pentene and selectivity to aldehydes remained approximately constant in this series. It is worth noting that good conversion was also obtained in toluene; however, the l/b value was remarkably lower, amounting to 3.7. Under solventless conditions, l/b varied from 6.4 to 7.6.

3.4. Hydroformylation of styrene

As expected, the hydroformylation of styrene using Rh-phosphine as a catalyst led principally to the branched aldehyde (2-phenylpropanal) [6,17]. The solventless hydroformylation of styrene at 80 °C and 10 or 12 bar of CO/H_2 resulted in 61% aldehyde yield in the first run and 95% in the second one performed with the same catalyst. The l/b ratio was 0.6, whereas it was 0.5 in reaction in toluene Table 6

3.5. Rhodium species formed during hydroformylation

In order to identify rhodium species present in the reaction mixture, NMR measurements were performed. The ^{31}P NMR (300 MHz) spectrum measured after hydroformylation reaction showed the presence of two doublets at 40 ppm (J(Rh-P) = 156 Hz) and at 32.2 ppm (J(Rh-P) = 135 Hz), assigned to $HRh(CO)(PPh_3)_3$ and to $HRh(CO)_2(PPh_3)_2$ respectively. The intensity of the doublet originated from $HRh(CO)(PPh_3)_3$ increased during storage of the solution for a few hours under nitrogen atmosphere. Conversely, signals of $HRh(CO)_2(PPh_3)_2$ were observed in a fresh sample.



4. Conclusions

The hydroformylation of three olefins, 1-hexene, 1-pentene, and 1-octene catalyzed by Rh(acac)$(CO)_2$/PPh_3 under solventless conditions at 80 °C and 10 bar exhibited a high rate and selectivity of aldehydes. The formation of a linear aldehyde was particularly favored at a low pressure. The hydroformylation of 1-hexene was faster than hydroformylation of 1-pentene and 1-octene and proceeded with the high l/b, 9.1. The catalyst could be easily recovered after the removal of products by "vacuum transfer" and used five times without the loss of activity. During recycling the l/b ratio decreased in reaction of 1-hexene, whereas increase of l/b ratio was observed for 1-pentene and 1-octene. As a results, recycled catalyst formed aldehydes with similar l/b ratio, ca. 7, for three olefins studied. The results obtained under solventless conditions were better than in toluene considering both the reaction rate and selectivity. Solventless hydroformylation was also successfully performed for styrene.

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