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Comparison of "on water" and solventless procedures in the rhodium-

catalyzed hydroformylation of diolefins, alkynes, and unsaturated alcohols

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Graphical abstract



Highlights

- 1. Highly efficient hydroformylation was performed under solventless conditions.
- 2. Dialdehydes were formed selectively in "on water" hydroformylation of dienes.
- 3. Linear aldehyde was obtained from phenylacetylene in "on water" conditions.
- 4. Solventless conditions facilitated formation of linear aldehydes from alcohols.

Abstract

Catalytic systems containing $Rh(acac)(CO)_2$ or Rh/PAA (PAA = polyacrylic acid) and hydrophobic phosphine (PPh₃) were used in the hydroformylation of diolefins, alkynes, and unsaturated alcohols under solventless and "on water" conditions. The total yield of dialdehydes obtained from 1,5-hexadiene and 1,7-octadiene reached 99%, and regioselectivity towards linear dialdehydes was higher in the "on water" system. The tandem hydroformylation-hydrogenation of phenylacetylene led to the formation of saturated aldehydes (3-phenylpropanal and 2phenylpropanal) at 98% conversion with a good regioselectivity towards the linear aldehyde in the "on water" reaction. In contrast, solventless conditions appeared better in the hydroformylation of 1-propen-3-ol. 4-Hydroxybutanal, formed in this reaction with an excellent selectivity, was next transformed to tetrahydrofuran-2-ol via a ring-closure process. Cyclic products were also obtained in hydroformylation of 1-buten-3-ol. In reaction of undec-1-ol and 2-allylphenol linear aldehydes were formed with the yield 69-87%. The hydroformylation of 3buten-1-ol performed under "on water" conditions showed very good regioselectivity towards a linear aldehyde, 5-hydroxypentanal. Further cyclization of the aldehyde to tetrahydropyran-2-ol was observed.

Keywords: hydroformylation; on water; rhodium; solventless

1. Introduction

The hydroformylation of olefins is one of the most important homogeneously catalyzed industrial processes with about nine million tons of aldehydes produced annually. Hydroformylation was discovered by Otto Roelen in 1938. However, this reaction is still extensively studied as a highly attractive process to produce aldehydes and alcohols [1].

"On water" and solventless methods of performing catalytic reactions are gaining significant attention in green chemistry due to their advantages as environmentally friendly procedures. In most cases, reactions occur smoothly giving pure products with high selectivity and a high reaction rate. These procedures are also very attractive from the economic point of view because they enable the elimination of environmentally harmful, toxic, and flammable organic solvents [2-7].

The term "on water" means catalytic reactions performed with reactants insoluble in water [5, 36].

It was shown that hydrophobic effect, observed when water was used as a solvent, could enhance the rate of organic reactions [8-10].

The hydroformylation of diolefins produces a mixture of mono- and dialdehydes, saturated and unsaturated, linear and branched [11, 12]. Dialdehydes are valuable intermediates for the production of a range of commercially significant products such as diamines [13], bicarboxylic acids and their derivatives [14, 15], alicyclic and heterocyclic compounds having different structures, [16] and cross-linking agents for polymers, such as proteins, polysaccharides, and other functionalized macromolecular compounds [17–21]. The hydroformylation of diolefins has been carried out in organic solvents [11, 22–28] and in $scCO_2$ [29]. However, attempts to

hydroformylate diolefins under "on water" or solventless conditions have not been reported till now.

In contrast to the hydroformylation of alkenes, studies on the hydroformylation of alkynes are still underdeveloped. [1, 30–33]. The hydroformylation of phenylacetylene, carried out by Goettmann *et al.* [31] in an organic solvent with a zirconia-silica catalyst, gave 23% conversion to enals. The same reaction was reported in a patent [34], Rh(acac)(CO)₂ in scCO₂ being used as a catalyst. Here, the reaction products were 3-phenylpropanal (62%), 2-phenylpropanal (18%), and styrene (20%) at 80% conversion.

4-Hydroxybutanal could be obtained by the hydroformylation of allyl alcohol. It could next be reduced to 1,4-butanediol, an important component in the synthesis of plastics. Often, 4-hydroxybutanal undergoes cyclization to substituted 2-hydroxytetrahydrofuran [35–37].

We have recently developed protocols for the hydroformylation of olefins "on water" and under solventless conditions which give excellent selectivity to aldehydes at a very high activity of Rh catalyst [38].

In this paper, we would like to report the application of these two protocols to the hydroformylation of diolefins, alkynes, and unsaturated alcohols. The catalytic systems contained a water-soluble immobilized catalyst, Rh/PAA, or a water-insoluble complex, Rh(acac)(CO)₂, with an excess of hydrophobic phosphine, PPh₃. The substrates, diolefins, phenylacetylene, and 1-hexyne, are insoluble in water, while allyl alcohols are miscible with water.

2. Experiment section

2.1. The general procedure of hydroformylation

Hydroformylation experiments were carried out in 100 mL (or 50 mL) stainless steel autoclaves provided with a manometer, a thermostat, a magnetic stirrer, and a gas inlet/outlet system. The catalyst, Rh(acac)(CO)₂ or Rh/PAA, and PPh₃ were placed in the autoclave. Then, 1.5 mL of substrate were introduced into the autoclave under a nitrogen atmosphere. In the case of experiments carried out on water, 1.5 mL of twice distilled water was added. The autoclave was closed, flushed with hydrogen (5 bar) three times, and thereafter pressurized with a synthesis gas (H₂: CO =1:1) to 10 bar (or 14 bar) and heated to 80 °C (or 60°C). After the reaction was finished, the autoclave was cooled to room temperature and the residual gases depressurized. The product mixture was immediately analyzed by NMR spectra, the catalyst was removed by StratospheresTM Spe, and the obtained products were identified by means GC and GC-MS.

Selected reaction mixtures were analyzed additionally using ¹H and ¹³C NMR.



Fig. 1. ¹H NMR and ¹³C NMR spectra (C₆D₆) of a) 1,7-octadiene and b) post-reaction mixture after the hydroformylation of 1,7-octadiene under solventless conditions



Fig. 2. ¹H NMR and ¹³C NMR spectra (C_6D_6) of a) phenylacetylene and b) solution obtained after the hydroformylation of phenylacetylene under solventless conditions.



Fig. 3. ¹H NMR and ¹³C NMR spectra (C_6D_6) of a) allyl alcohol and b) products after the hydroformylation of allyl alcohol under solventless condition at substrate to rhodium ratio 600.

3. Results and discussion

3.1. Hydroformylation of 1,7-octadiene

The hydroformylation of 1,7-octadiene was carried out in "on water" and solventless conditions, using rhodium precursors, Rh(acac)(CO)₂ (water-insoluble) and Rh/PAA (water-soluble), as

catalysts, with a 13-fold excess of hydrophobic phosphine (PPh₃). The possible reaction products are shown in Scheme 1 and the results are given in Table 1. In all experiments, the conversion of 1,7-octadiene was 100%. The main products were dialdehydes (1,10-decanedial **4** and 2-methylnonanedial **3**). Smaller amounts of 2,7-dimethyloctanedial **2** and 6-nonenal **1** (monoaldehyde isomerization product) were also formed. Interestingly, iso-dienes, possible isomerization products, were not formed under the hydroformylation reaction conditions.

The reaction under solventless conditions, performed by applying the catalytic system Rh(acac)(CO)₂/PPh₃, exhibited good selectivity to form dialdehydes.



Scheme 1: Hydroformylation of 1,7-octadiene

In the same reaction carried out under "on water" conditions, an increase in the 4/(2+3) ratio to 1.69 was noted (Table 1, entry 2). The "on water" hydroformylation of 1,7-octadiene, catalyzed by water-soluble Rh/PAA, showed even higher 4/(2+3) ratio, equal 3.28 (Table 1, entry 4). Thus, the catalyst Rh/PAA used in a water medium promoted regioselectivity towards the linear dialdehyde. It should be underlined here that the reaction with a Rh/PAA catalyst was slower and it took about 3 h, whereas already 1.5 h was enough to get a total conversion of 1,7-octadiene using Rh(acac)(CO)₂. The difference in the reaction rate can be related to the hydrophobic effect

expressed stronger when the catalyst is insoluble in water [8-10]. On the other hand application of the soluble catalyst resulted in the increase of the selectivity to the linear aldehyde.

The analysis of solventless, "on water" and in toluene reactions performed with a $Rh(acac)(CO)_2/PPh_3$ system (Table 1, entries 1, 2 and 3) led to the conclusion that there is not much difference in the three system, the results were very similar. In all cases the selectivity expressed as the (4/(2+3) ratio was significantly lower than with Rh/PAA as the catalyst (Table 1, entry 4).

Table 1. Hydroformylation of 1,7-octadiene "on water", under solventless conditions and in toluene.

Entry	Solvent	Conversion	1(E and	2 %	3 %	4 %	4/(2+3)
		%	Z) %				
1	-	100	1	5	36	58	1.41
2	Water	100	3	4	32	61	1.69
3	Toluene	100	5	4	31	60	1.71
4 ^a	Water	100	10	6	15	69	3.28

Reaction conditions: 1,7-octadiene 1.5 mL (0.01 mol), water 1.5 mL or toluene 1.5 mL as solvent, $Rh(acac)(CO)_2$ (1.27 . 10⁻⁵ mol), PPh_3 (1.65 . 10⁻⁴ mol), P = 10 bar, T = 80 °C, time = 1.5 h, ^atime = 3 h and Rh/PAA as catalyst.

3.2. Hydroformylation of 1,5-hexadiene

In the hydroformylation of 1,5-hexadiene under solventless conditions, using the catalytic system Rh(acac)(CO)₂/PPh₃, the substrate was completely converted to dialdehydes. The main products were octane-1,7-dial (**4**), 64%, and 2-Me-heptane-1, 8-dial (**3**), 29%, (Scheme 2, Table 2, entry 1).



Scheme 2: Hydroformylation of 1,5-hexadiene

The same reaction carried out "on water" with the same catalyst showed an increase of the unsaturated monoaldehyde (1) amount from 4 to 14%. Simultaneously, the yield of branched dialdehydes (2 + 3) decreased from 32 to 23% with almost the same yield of the linear dialdehyde (4) (63%) (Table 2, entry 2). The results obtained by using toluene as a solvent were similar to solventless conditions with selectivity to linear aldehydes lower than in water (Table 2, entry 3 and 4). The best regioselectivity towards the linear dialdehyde, octane-1, 7-dial (4, 69%), was obtained by using the Rh/PAA catalyst in water (Table 2, entry 4). Similarly as in hydroformylation of 1,7-octadiene, the reaction in water was faster with insoluble Rh(acac)(CO)₂ than with soluble Rh/PAA.

For comparison, in the hydroformylation of 1,5-hexadiene and 1,7-octadiene, catalyzed by $Rh(acac)(CO)(PPh_3)/PPh_3$ in toluene, the total yield of the dialdehyde reached 100% after 3 h, and the l/b ratio was 1.8–2.1 [11]. The high yield of the dialdehyde was obtained in the hydroformylation of 1,5-hexadiene by Botteghi et al. [15], using the catalytic system $Rh(CO)(PPh_3)_3/Xantphos$ (1:3) in toluene, at 60 °C and 20 bar in a reaction time of 24 h. The catalytic system $Rh(acac)(CO)_2/$ tris(3,5-bis(trifluoromethyl)phenyl)phosphine was applied for

the hydroformylation of 1,5- hexadiene and 1,7-octadiene by S. Fujita et al. [29]. They received the total yield of dialdehydes 30% and 50% respectively in toluene, and 90% for both substrates in scCO₂ at 60 $^{\circ}$ C and 40 bar, in a reaction time of 2 h. The l/b ratio was 1.5 and 0.6 respectively. Thus, the good selectivity was obtained "on water" under relatively mild conditions.

Table 2.	Hydroform	vlation of	f 1,5-hexadiene	"on water",	under solventless	conditions and in	toluene.
	2	2	,	,			

Entry	solvent	Conversion	1 (E +	2 %	3 %	4 %	4/(2+3)
		%	Z) %				
1	-	100	4	3	29	64	2.0
2	Water	100	14	2	21	63	2.7
3	Toluene	100	10	3	27	60	2.0
4 ^a	Water	100	14	2	15	69	4.1

Reaction conditions: 1,5-hexadiene 1.5 mL (0.0126 mol), water 1.5 mL or toluene 1.5 mL as solvent, $Rh(acac)(CO)_2$ (1.58 . 10⁻⁵ mol), PPh_3 (2.05 . 10⁻⁴ mol), $T=80 \ ^{o}C$, H_2 : CO (1:1)= 10 bar, time = 1.5 h, ^a Rh/PAA as catalyst, time = 3 h.

3.3. Hydroformylation of phenylacetylene and styrene

In the hydroformylation of phenylacetylene under solventless conditions by employing $Rh(acac)(CO)_2$ with a 13-fold excess of PPh₃, the conversion was 28% with high chemoselectivity of the hydrogenation product, styrene (17%) (Table 3, entry 1). In contrast, in the "on water" reaction 3-phenylpropanal (**3**) and 2-phenylpropanal (**4**) were mainly formed (Table 3, entry 2). Moreover, the total conversion was higher, 50%. High conversions, 98% and 94%, were obtained in water using $Rh(acac)(CO)_2$ and Rh/PAA respectively at 100 °C and 14 bar (Table 3, entries 5 and 6). Apparently, selectivity to the linear aldehyde, 3-phenylpropanal (**3**), was also satisfactory (Table 3, entry 5 and 6). The results clearly showed that the reactions

ran in two steps. The first step was the hydroformylation of phenylacetylene to produce unsaturated aldehydes (enals) followed by the second step involving the hydrogenation of enals to saturated aldehydes (as shown in Scheme 3). To make sure that the saturated aldehydes were through hydroformylation followed by hydrogenation, we performed the formed hydroformylation of styrene under the same conditions on water and under solventless conditions (Table 3 entries 7-11). The obtained results were completely different; the reaction was faster, and already in 1 h the conversion was complete (100%). Moreover, a higher regioselectivity to the branched aldehyde was noted. This is in agreement with our previous study on the hydroformylation of styrene on water and under solventless conditions [5, 38] as well as with results obtained by other Authors [1]. The application of different H_2 : CO ratio (1.5 : 1) changed only slightly the 3/4 ratio (Table 3, entries 10 and 11). Although formation of aldehydes by hydroformylation of styrene, product of hydrogenation of phenylacetylene, can not be completely ruled out, the remarkable difference in selectivity suggested hydroformylation of phenylacetylene as a first step of the reaction. Accordingly, saturated aldehydes were formed through hydroformylation of phenylacetylene to unsaturated aldehyde followed by hydrogenation.

The tandem hydroformylation/hydrogenation reaction of phenylacetylene exhibited a higher regioselectivity to the linear aldehyde in the "on water" reaction than under solventless conditions.



Scheme 3: Hydroformylation of phenylacetylene

Entry	Substrate	Solvent	t, h	Conversion%	1%	2%	3%	4%	3/4 ratio
1 ^a		-	22	28		17	4	7	0.6
2 ^a		Water	22	50	4	12	21	13	1.6
3	Phenyl	-	6	50	2	7	26	15	1.73
4	acetylene	-	22	97	1	3	49	44	1.1
5		Water	22	98	1	1	58	38	1.5
6 ^b		Water	19	94		2	53	39	1.4
7		-	1	100			21	79	0.26
8		Water	1	100			22	78	0.28
9 ^b	Styrene	Water	1	100			17	83	0.2
10 ^c		-	1	100		5 ^d	27	68	0.4
11 ^c		Water	1	100		5 ^d	25	70	0.36

Table 3. Hydroformylation of phenylacetylene and styrene using Rh(acac)(CO)₂ as a catalyst

Reaction condition: phenylacetylene (1.5 mL, 0.0137 mol) or styrene 1.5 mL as substrate, water (1.5 mL), [sub]/[Rh]=800, [L]/[Rh]= 13, T=100°C, P= 14 atm (H₂: CO = 1:1), ^a T=80°C, P= 10 atm (H₂: CO = 1:1), ^b Rh/PAA as catalyst, ^c P = 14 atm (H₂: CO = 1.5 : 1), ^d Ethylbenzene.

3.4. Hydroformylation of 1-hexyne

1-Hexyne reacted with moderate conversion and good chemoselectivity to saturated aldehydes (Table 4). Higher regioselectivity towards heptanal (linear aldehyde) was obtained in the water medium than under solventless conditions.

Table 4. Hydroformylation of 1-hexyne catalyzed by Rh(acac)(CO)₂ under solventless conditions

Entry	Solvent	Conversion	Heptanal %	2-Me-	l/b	Heptanoic acid
		%		hexanal %		
1 ^a	-	13	6	2	3.0	5
2	-	72	48	20	2.4	4
3	Water	68	50	14	3.6	4
4 ^b	Water	55	35	15	2.3	5

and on water

Reaction condition: 1-hexyne (0.013 mol), substrate/Rh = 800, $PPh_3/Rh = 13$, $(H_2:CO)(1:1) = 16$ bar, $T = 100 \,^{\circ}C$, water(1.5 mL), $^{a}(H_2:CO)(1:1) = 10$ bar, $T = 80 \,^{\circ}C$, $^{b}Rh/PAA$ as catalyst.

3.5. Hydroformylation of 1-propen-3-ol

The typical reaction products of 1-propen-3-ol hydroformylation, tetrahydrofuran-2-ol (1), 2methylprop-2-enal (2a), 2-methylpropanal (2b), and propanal (3), are presented in Scheme 4. 4-Hydroxybutanal undergoes fast cyclization to tetrahydrofuran-2-ol, and it was found only in this form in the reaction mixture.



Scheme 4: Hydroformylation of 1-propen-3-ol

The results collected in Table 5 show that the hydroformylation of 1-propen-3-ol catalyzed by the Rh(acac)(CO)₂/PPh₃ system gave an excellent regioselectivity towards linear aldehydes and 56% of cyclization product, tetrahydrofuran-2-ol (1), was formed within 3.5 h (Table 5, entry 1). Quite different results were obtained in water, where the conversion increased to 83 and 85% with the application of the catalyst precursors Rh(acac)(CO)₂ and Rh/PAA respectively. However, simultaneously, the 1/(2a+2b) ratio, illustrating reaction selectivity, decreased to 1.5 and 0.7 respectively (Table 5, entries 2 and 3). The change of the substrate-to-rhodium ratio from 800 to 600 and reducing pressure from 14 to 12 bar resulted in an enhancement of the reaction rate and an increase in chemoselectivity (Table 5, entries 1 and 4). Lower chemoselectivity was obtained by applying Rh/PAA as catalyst under solventless condition (Table 5, entry 5).

Table 5. Hydroformylation of 1-propen-3-ol "on water" and under solventless conditions catalyzed by

entry	Sub:Rh	Solvent	t, h	Conversion	1%	(2a+2b)%	1/(2a+2b)	3%	4 ^d %
				%					
1 ^a	800	-	3.5	57	56				1
2 ^a	800	Water	4	83	45	31	1.5		7
3 ^{a,c}	800	Water	4	85	32	49	0.7		4
4 ^b	600	-	2.5	92	83	3	27.7	2	4
5 ^{b,c}	600	-	3	75	52	9	5.7	6	8

Rh(acac)(CO)₂/PPh₃ system

Reaction condition: $[PPh_3]/[Rh] = 6$, $T = 80 \ ^{\circ}C$, ^a allyl alcohol (1.5 mL), solvent 1.5 mL P = 14 bar, ^b allyl alcohol (0.82 mL), P = 12 bar, ^c Rh/PAA as catalyst, ^d unidentified product.

3.6. Hydroformylation of 3-buten-1-ol

The hydroformylation of 3-buten-1-ol led to the expected products, 5-hydroxypentanal and 4-hydroxy-2-methylbutanal, undergo cyclization to tetrahydropyran-2-ol (1) and 4-methyltetrahydrofuran-2-ol respectively (2) (Scheme 5).



Scheme 5: hydroformylation of 3-buten-1-ol

At 60 °C and 10 bar, the conversion of 3-buten-1-ol was 73%, and the selectivity to products **1** and **2** was 52% (1/2 ratio = 5.5) (Table 6, entry 1). Conversion and regioselectivity increased (1/2 ratio = 10) with pressure increased to 14 bar (Table 6, entry 2). At an elevated temperature (80 °C), conversion to **1** and **2** increased to 84%; however, the **1**/2 ratio decreased to about 4 as a result of the higher amount of the branched product (Table 6, entry 3).

In a water medium, at 80 °C and 14 bar, the hydroformylation of 3-buten-1-ol catalyzed by $Rh(acac)(CO)_2/PPh_3$ was less efficient although good selectivity was noted (Table 6, entry 4). Under the same conditions, Rh/PAA performed much better giving the highest yield of **1** (82%) selectivity (Table 6, entry 5).

entry	Solvent	Conversion%	t, h	1%	2%	1/2	3%	4%	5%
1 ^a	-	73	1.5	44	8	5.5	9	6	6
2 ^b		96	2.5	60	6	10	9	11	10
3°	-	97	2	67	17	4	4	6	3
4 ^c	Water	86	3.2	69	8	8.6	4	5	
5 ^{c,d}	Water	94	3	82	9	9	1	1	1

Table 6. Hydroformylation of 3-buten-1-ol "on water" and under solventless conditions

Reaction condition: 3-buten-1-ol (1.5 mL), water (1.5 mL), [substrate: Rh] = 800, [PPh_3 : Rh] = 6, ^{*a*} T = 60 ^{*o*}C, P = 10 bar, ^{*b*} T = 60 ^{*o*}C, P = 14 bar, ^{*c*} T = 80 ^{*o*}C, P = 14 bar, ^{*d*} Rh/PAA as a catalyst.

Hydroformylation of 1-buten-3-ol gave a cyclic product, 2-hydroxy-5-methyltetrahydrofuran (1), as the main one. Interestingly, under solventless conditions it was formed with 99% yield. In water the selectivity was lower and 17-18% of alcohol was transformed to the branched aldehyde, identified in a cyclic form (2). The results were almost the same with $Rh(acac)(CO)_2$ and with Rh/PAA.



Scheme 6: Hydroformylation of 1-buten-3-ol

entry	Solvent	Conversion%	1%	2%
1	-	99	97	-
2	Water	98	77	18
3 ^a	Water	99	78	17

Table 7. Hydroformylation of 1-buten-3-ol "on water" and under solventless conditions

Reaction condition: water (1.5 mL), [substrate: Rh] = 500, [PPh_3 : Rh] = 13, T= 80 °C, P = 10 bar, 3h, ^a Rh/PAA as a catalyst.

3.7. Hydroformylation of 5-hexen-1-ol and undec-1-ol

The solventless hydroformylation of 5-hexen-1-ol was carried out using $Rh(acac)(CO)_2$ with a 6-fold excess of PPh₃ at a substrate-to-rhodium ratio of 800, 10 bar, and 80 °C. As expected, linear and branched hydroxy aldehydes (7-hydroxyheptanal and 6-hydroxy-2-methylhexanal) were formed without the formation of cyclic acetals [39, 40] (Scheme 7).



Scheme 7: Hydroformylation of 5-hexen-1-ol

The hydroformylation of undec-1-ol performed at 14 bar resulted in formation of 73-87% of 12hydroxydodecanal (linear product) and 11-12% of the branched one, 11-hydroxy-2-methylundecanal. The results obtained under solventless conditions and "on water" were very similar.

Table 8. Hydroformylation of undec-1-ol "on water" and under solventless conditions

entry	Solvent	Conversion	12-hydroxydodecanal %	11-hydroxy-2-
		%		methylundecanal 2%
1	-	100	85	11
2	Water	95	73	12
3 ^a	Water	100	87	11

Reaction condition: water (1.5 mL), [substrate: Rh] = 500, [PPh_3 : Rh] = 13, T= 80 °C, P = 10 bar, 3h, ^a Rh/PAA as a catalyst.

3.8. Hydroformylation of 2-allylphenol

2-Allylphenol was hydroformylated to the linear aldehyde, 4-(2-hydroxyphenyl)butanal (1), with the yield 70-80% at 14 bar. The branched aldehyde undergo cyclization to 2-methylchroman-2-ol (2). The selectivity to the linear product was higher in water, l/b = 4, than under solventless conditions (l/b = 2.2). At the lower pressure, 10 bar, conversion was only 44% and comparable amounts of linear and branched products were formed.



Scheme 8: Hydroformylation of 2-allylphenol

entry	Solvent	Conversion	4-(2-hydroxyphenyl)butanal	3-methylchroman-2-ol
		%	(1) %	(2) %
1	-	44	24	20
2^{a}	-	100	69	31
3 ^a	Water	100	80	20
4 ^{a,b}	Water	100	70	30

Table 9. Hydroformylation of 2-allylphenol

Reaction condition: water (1.5 mL), [substrate: Rh] = 500, [PPh_3 : Rh] = 13, T= 80 °C, P = 10 bar, 3h, ^a 14 bar, ^bRh/PAA as a catalyst.

3.9. Rhodium species formed during hydroformylation

Rhodium species present in the reaction mixture were identified by means of ¹H NMR measurements. The ³¹P NMR (500 MHz) spectrum measured after the hydroformylation reaction

of diolefins, alkynes, and unsaturated alcohols showed the presence of a doublet at 32.2 ppm (J(Rh-P) = 135 Hz), assigned to $HRh(CO)_2(PPh_3)_2$ [41].

4. Conclusions

In conclusion, the hydroformylation of diolefins, alkynes, and unsaturated alcohols was investigated for the first time under solventless conditions and in "on water" reactions by applying the catalytic systems Rh/PAA (water-soluble) and Rh(acac)(CO)₂ (water-insoluble) with an excess of a commercially available and inexpensive hydrophobic phosphine (PPh₃) ligand. The main advantage of the studied procedures was complete elimination of the organic solvent.

We demonstrated that the hydroformylation of diolefins can be very efficiently performed in water, where the dialdehydes were the desired products obtained in excellent yields with excellent selectivities. Regioselectivity towards the linear aldehyde increased in the "on water" reaction. It can be therefore suggested that aggregation of hydrophobic PPh₃ molecules around the active rhodium center facilitates formation of linear alkyl and acyl intermediates and, finally, linear aldehydes are produced.

We also demonstrated that such methodologies can be applied for alkynes to produce saturated aldehydes in high yield and selectivity. Saturated aldehydes, the final reaction products, were obtained through hydroformylation followed by hydrogenation. Good regioselectivity towards the linear aldehyde was found in the "on water" reaction.

We also demonstrated that the hydroformylation of unsaturated alcohols can be carried out very efficiently in water, and under solventless conditions. In the hydroformylation of 1-propen-3-ol, an excellent chemoselectivity and regioselectivity towards tetrahydrofuran-2-ol under solventless

conditions was obtained. In contrast, the hydroformylation of 3-buten-1-ol exhibited a better regioselectivity towards tetrahydropyran-2-ol in "on water" reaction than under solventless conditions.

Hydroxyaldehydes produced during the hydroformylation of 1-propen-3-ol, 3-buten-1-ol and 1buten-3-ol (short chain) undergo transformation to cyclic acetals, whereas the hydroformylation of 5-hexene-1-ol and undec-1-ol (long chain) leads to hydroxyaldehydes without the formation of cyclic acetals.

The influence of water on the hydroformylation of unsaturated alcohols can be related to their hydrophobic or hydrophilic properties. For example, the selectivity enhancement was not observed in hydroformylation of water-soluble 1-propen-3-ol while for 2-allylphenol higher selectivity was noted in water.

The performed studies indicate that the final composition of hydroformylation performed in water depends on hydrophobic effect comprising aggregation of substrate molecules and aggregation of hydrophobic phosphine used as modifying ligand.

References

- (a) A. M. Trzeciak and J. J. Ziółkowski, Coord. Chem. Rev., 883 (1999) 190–192; (b) A. M. Trzeciak, Hydroformylation in: Comprehensive Inorganic Chemistry II: from elements to applications, ed. J. Reedijk and K. Poeppelmeier, Elsevier, Amsterdam, 2013, vol. 6, p. 25; (c) A. Behr and P. Neubert, Applied Homogeneous Catalysis, Wiley-VCH, Weinheim, 2012; (d) Rhodium Catalysed Hydroformylation, ed. P. W. N. M. van Leeuwen and C. Claver, Kluwer Academic Publisher, Dordrecht, 2000.
- (a) V. M. Kolb, Astrobiology: An Evolutionary Approach, CRC Press, 2014. (b) P. Tundo,
 A. Perosa and F. Zecchini, Methods and Reagents for Green Chemistry: An Introduction,
 John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 2007.
- 3. O. Diebolt, C. Muller and D. Vogt, Catal. Sci. Technol., 2 (2012) 773-777.
- 4. S. L. Desset, S. W. Reader and D. J. Cole-Hamilton, Green Chem., 11 (2009) 630-637.
- 5. W. Alsalahi and A. M. Trzeciak, RSC Adv., 4 (2014) 30384- 30391.
- 6. L. Monnereau, D. Sémeril, and D. Matt, Eur. J. Org. Chem., (2010) 3068- 3073.
- 7. P. J. Walsh, H. Li, and C. A. de Parrodi, Chem. Rev., 107 (2007) 2503-2545.
- 8. R. Breslow, Acc. Chem. Res., 24 (1991) 159-164.
- 9. D.C. Rideout, R. Breslow, J. Am. Chem. Soc., 102 (1980) 7816-7817.
- M.B. Gawande, V.D.B. Bonifacio, R. Luque, P.S. Branco, R.S. Varma, Chem. Soc. Rev., 42 (2013) 5522-5551
- 11. A. M. Trzeciak and J. J. Ziółkowski, J. Organomet. Chem., 464 (1994) 107-111.
- H. J.V. Barros, C. C. Guimaraes, E. N. dos Santos and E. V. Gusevskaya, Catal. Commun., 8 (2007) 747- 750.
- 13. P. Eilbracht, C. L. Kranemann and L. Barfacker, Eur. J. Org. Chem., (1999) 1907-1914.

- 14. M. Morikawa, Bull. Chem. Soc. Jpn., 37 (1964) 379-380.
- 15. C. Botteghi, C. D. Negri, S. Paganelli and M. Marchetti, J. Mol. Chem. A: Chem., 175 (2001) 17-25.
- P. Eilbracht, L. Bärfacker, C. Buss, C. Hollmann, B. E. Kitsos-Rzychon, C. L. Kranemann, T. Rische, R. Roggenbuck and A. Schmidt, Chem. Rev., 99 (1999) 3329- 3365.
- J. Gawroński, M. Brzostowska, M. Kwit, A. Plutecka, and U. Rychlewska, J. Org. Chem., 70 (2005) 10147- 10150.
- H. Yamamoto, H. Tanisho, S. Ohara and A. Nishida, Int. J. Biol. Macromol. 14 (1992) 66-72.
- J. P. Draye, B. Delaey, A. V. de Voorde, A. V. D. Bulcke, E. Bogdanov, and E. Schacht, Biomaterials 19 (1998) 99- 107.
- 20. J. Z. Knaul, S. M. Hudson and K. A. M. Creber, J. Polym. Sci. Part B, Polym. Phys., 37 (1999) 1079- 1094.
- V. Crescenzi, G. Paradossi, P. Desideri, M. Dentini, F. Cavalieri, E. Amici and R. Lisi, Polym. Gel. Network, 5 (1997) 225-239.
- 22. A. M. Trzeciak, J. J. Ziółkowski, J. Organomet. Chem., 479 (1994) 213- 216.
- S. Bertozzi, N. Campigli, G. Vitulli, R. Lazzaroni and P. Salvadori, J. Organomet. Chem. 487 (1995) 41- 45.
- 24. A. M. Trzeciak, J. J. Ziółkowski and R. Choukroun, J. Mol. Catal. A: Chem., 110 (1996) 135-139.
- 25. T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki and H. Takaya, Tetrahedron 53 (1997) 7795-7804.

- 26. S. Fujita, S. Fujisawa, B. M. Bhanage, Y. Ikushima and M. Arai, Eur. J. Org. Chem., (2004) 2881-2887.
- 27. G. Liu and M. Garland, J. Organomet. Chem. 608 (2000) 76-85.
- 28. S. Yu, Y. Chie, X. Zhang, L. Dai and X. Zhang, Tetrahedron Letters, 50 (2009) 5575–5577.
- 29. S. Fujita, S. Fujisawa, B. M. Bhanage and M. Arai, Tetrahedron Letters 45 (2004) 1307– 1310.
- 30. V. Agabekov, W. Seiche and B. Breit, Chem. Sci., 4 (2013) 2418- 2422.
- 31. F. Goettmann, P. L. Floch and C. Sanchez, Chem. Commun., (2006) 180-182.
- 32. B. G. V. d. Hoven and H. Alper, J. Org. Chem., 64 (1999) 9640- 9645.
- 33. Y. Ishii, K. Miyashita, K. Kamita and M. Hidai, J. Am. Chem. Soc., 119 (1997) 6448- 6449.
- 34. I. Ojima and H. Urata, Process for hydrocarbonylations in supercritical carbon dioxide, WO 1999050214 A1, 7 Oct 1999.
- 35. C. U. Pittman, Jr., and W. D. Honnick, J. Org. Chem., 45 (1980) 2132-2139.
- E. Mieczyńska, A. M. Trzeciak and J. J. Ziółkowski, J. Mol. Catal. A: Chem., 148 (1999) 59-68.
- 37. I. I. F. Boogaerts, D. F. S. White and D. J. Cole-Hamilton, Chem. Commun., 46 (2010) 2194-2196.
- 38. W. Alsalahi and A.M. Trzeciak, J. Mol. Catal. A: Chem., 408 (2015) 147-151.
- J. T. Sullivan , J. Sadula , B. E. Hanson , R. J. Rosso, J. M. Catal. A: Chem., 214 (2004) 213-218.
- 40. A. M. Trzeciak, E. Wolszczak and J. J. Ziółkowski, New J. Chem., 20 (1996) 365-370.
- 41. C. Bianchini, H. M. Lee, A. Meli, and F. Vizza, Organometallics, 19 (2000) 849-853.