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Hydrogenation and hydroformylation of C_4 unsaturated alcohols with an $[Rh(acac)(CO)_2]$/PNS catalyst in water solution (PNS = $Ph_2PCH_2CH_2CONHC(CH_3)_2CH_2SO_3Li$)

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Abstract

A catalytic system containing $[Rh(acac)(CO)_2]$ and water soluble phosphine PNS (PNS = $Ph_2PCH_2CH_2CONHC(CH_3)_2CH_2SO_3Li$) was used for the hydrogenation and hydroformylation of C_4 unsaturated alcohols: 1-buten-3-ol ($CH_2=CHCH(CH_3)OH$) **(1)**, 2-methyl-2-propen-1-ol ($CH_2=C(CH_3)CH_2OH$) **(2)** and 2-buten-1-ol ($CH_3CH=CHCH_2OH$) **(3)** in water. The most reactive substrate, **(1)**, with a terminal double bond, is hydrogenated at 313 K and 0.1 MPa of H_2 pressure giving 92% of 2-methyl-propanol after 4 h. The hydrogenation of **(2)** and **(3)** with, respectively, 74% and 65% yields was performed at 353 K and 0.5 MPa of H_2 pressure. The main products of the hydroformylation of **(1)**, **(2)** and **(3)** alcohols are 2-hydroxytetrahydrofuran derivatives formed by hydroxyaldehyde cyclization. The hydroformylation of **(1)** gave 81–95% of 2-hydroxy-5-methyl-tetrahydrofuran at 323–353 K and 1 MPa CO/H_2 regardless of the PNS concentration. In the hydroformylation of **(2)** and **(3)** the highest yield of products, respectively 92 and 77%, was achieved at 353 K, 1 MPa and [PNS]: [Rh] = 3. During the reaction a pH decrease was noted.

Keywords: Hydrogenation; Hydroformylation; Unsaturated alcohols

1. Introduction

Catalytic reactions carried out in biphasic systems in which the catalyst is dissolved in water phase and substrates and products in organic one have in recent years been the subject of increasing interest [1–7]. Such catalytic systems offer the possibility of easy catalyst–product separation (i.e., by decantation or extraction) and repeated use of the catalyst [8–10]. Water soluble rhodium catalysts can be obtained when water soluble phosphines like PNS = $Ph_2PCH_2CH_2CONHC(CH_3)_2CH_2SO_3Li$, are used as phosphorus ligands modifying a catalytic system. This phosphine was successfully applied in 1-hexene and methylacrylate hydroformylation with $[Rh(acac)(CO)_2]$ as a catalyst precursor [11,12].

In this paper the same catalytic system ($[Rh(acac)(CO)_2]$/PNS) is used in the hydrogenation and hydroformylation of C_4 unsatu-

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Table 1
Hydrogenation of $H_2C{=}CHCH(CH_3)OH$ (1-buten-3-ol) **(1)** catalyzed by the $Rh(acac)(CO)_2$ /PNS and $HRh(CO)(PPh_3)_3$ /PNS systems— products composition

[PNS]/[Rh]	Time (h)	Conversion (%)	A (%)[a]	B (%)[a]
$Rh(acac)(CO)_2$ / PNS				
3	2	38	35	3
3	4	100	93	7
5	2	22	19	3
5	4	65	59	6
$HRh(CO)(PPh_3)_3$ / PNS				
–	2	53.9	48.6	5.3
–	4	100	95.3	4.7
3	2	57.3	52.3	5.0
3	4	89.7	85.3	4.4
5	2	85.5	77.3	8.2
5	4	100	87.9	12.1

$[Rh] = 1.48 \times 10^{-2}$ M, T = 313 K, $p(H_2) = 0.1$ MPa.
[a]**A**, **B** - see Scheme 1.

rated alcohols. The hydroformylation of unsaturated alcohols is interesting from the practical point of view as it delivers different chemicals widely used in chemical industry. The hydroformylation products, hydroxyaldehydes, may be reduced to diols then used in polymer synthesis [13,14]. Hydroxyaldehydes with a short carbon chain may undergo cyclization to substituted tetrahydrofuran derivatives [15–17]. Cyclization is particularly privileged when the location of carbonyl and hydroxyl groups in relation to each other allows the formation of a five- or six-membered ring. For example, γ-hydroxyaldehydes produce 2-hydroxytetrahydrofuran derivatives, whereas β-hydroxyaldehydes form *m*-dioxane species [15]. During both, hydroformylation and hydrogenation reactions, competitive isomerization may occur leading to new unsaturated alcohols as well as to aldehydes or saturated ketones [18–20].

According to the recent studies of biphasic systems, the pH of the reaction mixture is one of the factors determining reaction rate and the yield of hydroformylation products. For instance, in 1-octene hydroformylation with $[RhCl(COD)]_2$/TPPTS (TPPTS = trisodium salt of tri-(*m*-sulfophenyl)-phosphine) a fivefold increase of the reaction yield was observed with the change of the pH of the water phase from 7 to 10 [21].

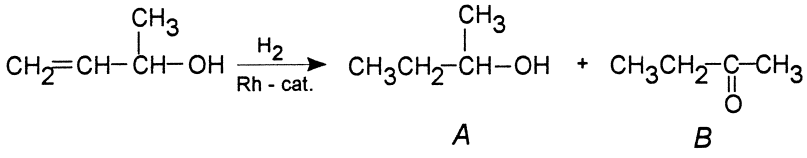
The main goal of this paper is to report on studies of the effect of pH on hydrogenation and hydroformylation of unsaturated alcohols and the optimization of reaction parameters such as reaction temperature, H_2 or CO/H_2 pressure and phosphorus ligand concentration. The catalytic system contained $[Rh(acac)(CO)_2]$ as a catalyst precursor, PNS as a phosphorus ancillary ligand and C_4 unsaturated alcohols as substrates.

The following C_4 alcohols (of the same general formula but different construction of the carbon chain) were selected for detailed studies: 1-buten-3-ol ($CH_2{=}CHCH(CH_3)OH$) **(1)**, 2-methyl-2-propen-1-ol ($CH_2{=}C(CH_3)CH_2OH$) **(2)**,2-buten-1-ol ($CH_3CH{=}CHCH_2OH$) **(3)**.

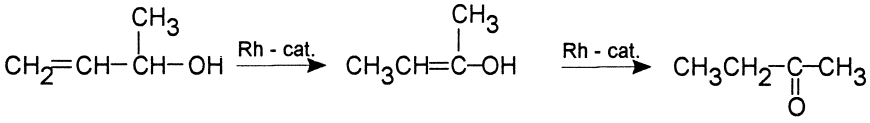
2. Results and discussion

2.1. Hydrogenation of 1-buten-3-ol ($H_2C{=}CHCH(CH_3)OH$) (1)

Hydrogenation reactions were carried out in water in which alcohol **(1)** is well soluble. At mild conditions (temp. 313 K, H_2 pressure 0.1 MPa) alcohol **(1)** is hydrogenated with a good yield (Table 1)—after 4 h 93% of 2-methyl-propanol **(A)** as the hydrogenation product and 7% of 2-butanon **(B)** as the product of alcohol isomerization (Scheme 1) were obtained. The complex $[HRh(CO)(PNS)_3]$ was found in the



Scheme 1.



Scheme 2.

reaction medium by $^{31}P\{^{1}H\}$ NMR ($\delta = 29.7$ ppm, $J_{Rh-P} = 151$ Hz) and ^{1}H NMR ($\delta = -10.5$ ppm) spectra [11].

Alcohol isomerization to ketone is a side reaction accompanying hydrogenation with the enol as an intermediate state (Scheme 2) [15,16].

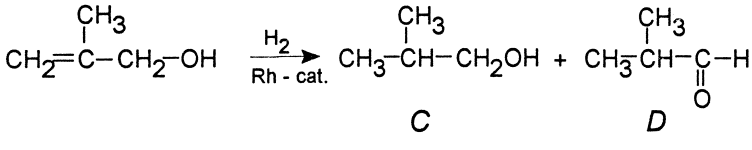
An increase of phosphine (PNS) concentration caused decrease of alcohol hydrogenation from 93% of 2-methyl-propanol **(A)** at [PNS]/[Rh] = 3 to 59% at [PNS]/[Rh] = 5 (Table 1). The observed decrease of the hydrogenation yield may be caused by the steric hindrance of bulky PNS phosphine making coordination of alcohol to the catalyst difficult. The alternative explanation could be the competition between alkene and the phosphine in the coordination to rhodium.

The hydrogenation of **(1)** was also studied with the $[HRh(CO)(PPh_3)_3]$/PNS system, in which two ancillary ligands, PPh_3 and PNS, are present. The complex $[HRh(CO)(PPh_3)_3]$ itself is a good catalyst of the hydrogenation of **(1)** and the addition of PNS phosphine causes a small change of selectivity: a decrease of the yield of 2-methyl-propanol **(A)** and a small increase of the ketone **(B)** yield (Table 1). At the ratio [PNS]/[Rh] = 5 the reaction runs faster in comparison to the hydrogenation reaction carried out in the presence of $[HRh(CO)(PPh_3)_3]$ only (Table 1). This can be illustrated by comparison of the reaction product composition after 2 h in reactions catalyzed with only $[HRh(CO)(PPh_3)_3]$ (48.6% of **(A)**) and that in the presence of a fivefold excess of PNS (77.3% of **(A)**). The effect of reaction yield increase with increase of PNS concentration is different than that observed in reactions with the $[Rh(acac)(CO)_2]$ complex, where only 19% of **(A)** was obtained at $[Rh(acac)(CO)_2]$/5 PNS.

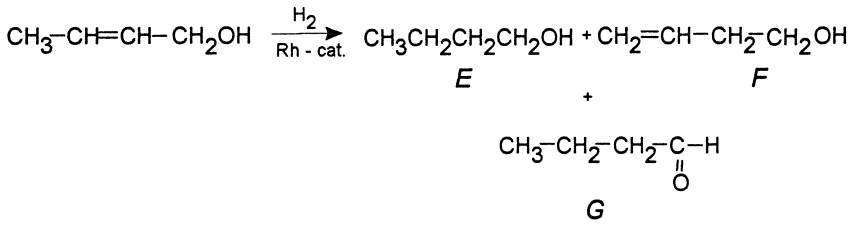
$^{31}P\{^{1}H\}$ NMR studies of the mixture containing $[HRh(CO)(PPh_3)_3]$ + 4 PNS in a THF solution show the total substitution of PPh_3 with the formation of $[HRh(CO)(PNS)_3]$ species. In the $^{31}P\{^{1}H\}$ NMR spectrum, besides the doublet from the hydride complex, the signal of uncoordinated PPh_3 at -4.8 ppm is observed. However, at reaction conditions probably both rhodium complexes, with PPh_3 and with PNS, exist and the observed catalytic activity is the combined effect of the activity of both complexes.

*2.2. Hydrogenation of 2-methyl-2-propen-1-ol ($CH_2=C(CH_3)CH_2OH$) **(2)** and 2-buten-1-ol ($CH_3CH=CHCH_2OH$) **(3)***

Rather limited solubility of both alcohols, **(2)** and **(3)**, in water may explain their lower reactivity towards dihydrogen as compared with alcohol **(1)**. The hydrogenation reaction products at 0.1 MPa H_2, 313 K and after 4 h are as follows: 5.5% of 3-methyl-propanol **(C)** for alcohol **(2)** and 6.9% of butanol **(E)** for **(3)**



Scheme 3.



Scheme 4.

(Scheme 3, Scheme 4 , Tables 2 and 3). The introduction of a cosolvent (EtOH) to improve miscibility of reaction components did not increase the reaction yield (Tables 2 and 3).

However, a significant increase of the hydrogenation yield of alcohols **(2)** and **(3)** was obtained by the elevation of temperature to 333 K or 353 K, and dihydrogen pressure to 0.5 MPa. The increase of dihydrogen pressure from 0.1 to 0.5 MPa at 313 K causes the increase of the hydrogenation yield of alcohol **(2)** from 3% to 48% **(C)** (Scheme 3 and Table 2). To obtain a similar yield (45%) of alcohol **(3)** hydrogenation, it is necessary to apply higher temperature (333 K) (Table 3). Besides the hydrogenation products (**(C)** and **(E)**, respectively), some amounts of proper aldehydes (**(D)** and **(G)**), products of the isomerization of **(2)** and **(3)**, were found (Schemes 3 and 4), (Tables 2 and 3). Hydrogenation reactions were carried out at pH 9 caused by the basicity of phosphine (PNS). Changes of pH generally have a minor effect on the composition of reaction products at 313 K, but it is more advantageous to perform the reaction at higher pH. For example increasing pH to ca. 10 (by adding KOH to the reaction mixture) in the hydrogenation of **(2)** causes

Table 2
The products of 2-methyl-2-propen-1-ol ($H_2C=C(CH_3)CH_2OH$) **(2)** hydrogenation reaction catalyzed by $[Rh(acac)(CO)_2]$/PNS

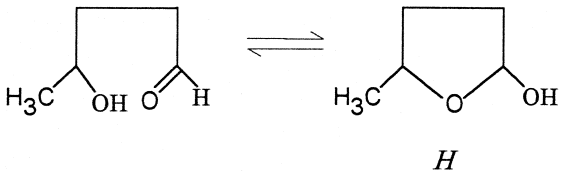
Conversion (%)	C (%)*	D (%)*
Reactions under 0.1 MPa		
3.4	3.4	–
3.0	3	–
5.5[a]	5.5	–
16.6[b]	7.6	9
4.0[c]	4	–
3.0[d]	1.5	1.5
Reactions under 0.5 MPa		
52.6	48.3	4.3
63.4[e]	54.4	9
82.6[f]	74	8.6
78.7[f,g]	60.5	18.2

$[Rh]=1.48\times10^{-2}$ M, [PNS]: $[Rh]=3$, $T=313$ K, $p(H_2)=0.1$ MPa, 2 h.
[a]4 h.
[b]pH ca. 10 by addition of KOH.
[c]Reaction carried out at presence of EtOH, $[EtOH]/[H_2O]=4{:}6$.
[d]$[EtOH]/[H_2O]=6{:}4$.
[e]333 K.
[f]353 K.
[g]Reaction carried out at the presence of specially neutralized phosphine PNS.
*C, D - see Scheme 3.

Table 3
The products of 2-buten-1-ol ($CH_3CH=CHCH_2OH$) **(3)** hydrogenation reaction catalyzed by $[Rh(acac)(CO)_2]$/PNS system

Conversion (%)	E (%)*	F (%)*	G (%)*
Reactions carried out under 0.1 MPa			
7.7[a]	5	1.7	1
9.2[d]	6.9	–	2.3
Reactions carried out under 0.5 MPa			
1	1	–	–
55.5[e]	45	1	9.5
87.5[f]	65	0.5	22
10.8[b,f]	5.8	2	3.0

$[Rh]=1.48\times10^{-2}$ M, [PNS]: $[Rh]=3$, T = 313 K, 2 h.
[a]Reactions carried out at the presence of EtOH, $[EtOH]/[H_2O]=4{:}6$.
[b]Reactions carried out at the presence of specially neutralized PNS phosphine.
[d]4 h.
[e]333 K.
[f]353 K.
*E, F, G - see Scheme 4.



H

Scheme 5.

reaction yield increase from 3 to 7.6% (Table 2). The effect of pH change is much more significant at 353 K, particularly for alcohol **(3)**, where the decrease of pH from 9 to 7 causes a decrease of product **(E)** yield from 65 to 5.8%. For alcohol **(2)** the yield of product **(C)** decreased from 74 to 60% with pH decrease.

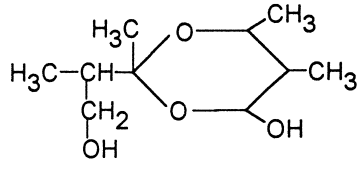
The addition of KOH not only changes the pH value but also transforms PNSLi to PNSK salt. On the basis of the investigations discussed above one may conclude that for best results the reactions should be carried out at pH ≥ 9 or with the application of PNSK or PNSNa instead of PNSLi.

*2.3. Hydroformylation of 1-buten-3-ol **(1)**, 2-methyl-2-propen-1-ol **(2)**, 2-buten-1-ol **(3)** with an [Rh(acac)(CO)$_2$] / PNS catalytic system*

*2.3.1. Hydroformylation of 1-buten-3-ol ($CH_2=CHCH(CH_3)OH$) **(1)***

The main product of the hydroformylation of **(1)** is a cyclic compound **(H)** (2-hydroxy-5-methyl-tetrahydrofuran) formed as the result of γ-hydroxyaldehyde cyclization (Scheme 5).

Additionally, besides the product **(H)** some amounts (1–6%) of a compound **(I)** formed as the product of the condensation of two molecules of β-aldehydes were found (Scheme 6). Both compounds were identified by GC-MS and ^{1}H NMR spectra and compared with those published previously [16].



I

Scheme 6.

After 2 h over 90% of the product 2-hydroxy-5-methyl-tetrahydrofuran **(H)** was obtained regardless of phosphine concentration ([PNS]/[Rh] = 3–8). The temperature decrease to 323 K causes a minor decrease of the reaction yield from 94% to 81% (at 353 K) (Table 4).

*2.3.2. Hydroformylation of 2-methyl-2-propen-1-ol ($H_2C=C(CH_3)CH_2OH$) **(2)** and 2-buten-1-ol ($CH_3CH=CHCH_2OH$) **(3)***

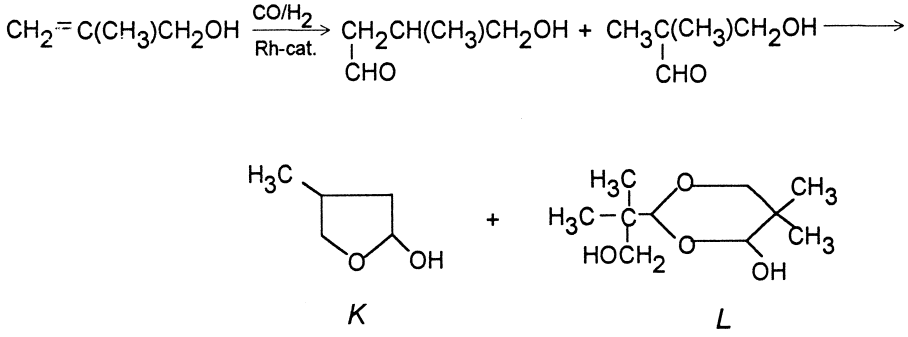
The main products of the hydroformylation of alcohols **(2)** and **(3)** are cyclic compounds—2-hydroxytetrahydrofuran derivatives (**(K)** and **(M)**) analogous to the compound **(H)** identified in hydroformylation reactions of alcohol **(1)** (Schemes 7 and 8). Hydroformylation reactions of alcohols **(2)** and **(3)** are significantly slower as compared with alcohol **(1)**, particularly at 333 K. The highest yield of alcohol **(2)** hydroformylation product **(K)** (Scheme 7) is 50% (Table 5) and that of alcohol **(3)** **(M)** ca. 72% (Scheme 8 and Table 6). Small amounts of condensation of products of two molecules of β-aldehydes (compounds **(L)** and **(N)**) were found in reaction products.

Ethanol added to the system as a cosolvent, like in case of hydrogenation, did not change

Table 4
The products of 1-buten-3-ol, ($H_2C=CHCH(CH_3)OH$) **(1)** hydroformylation catalyzed by [Rh(acac)(CO)$_2$]/PNS system

[PNS]/[Rh]	Conversion (%)	H (%)*	I (%)*	A (%)*
3	98	92	6	–
5	99	94	3	2
8	100	95	3	2
3[a]	93	91	2	–
5[a]	100	95	3	2
8[a]	98	95	1	2
5[b]	86	81	–	5

[Rh] = 1.48×10^{-2} M, [alc.]/[Rh] = 390, $p(H_2+CO)$ = 1 MPa, pH_2/pCO = 1, 2 h, 353 K.
[a] 3 h, 333 K.
[b] 3 h, 323 K.
* **H** - see Scheme 5, **I** - see Scheme 6, **A** - see Scheme 1.



Scheme 7.

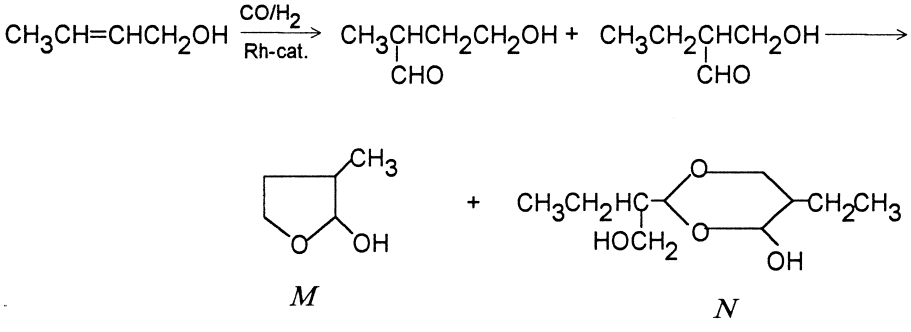
the reaction yield, and was found useless since over 333 K both alcohols form a one-phase system with water.

In contrast to the hydroformylation of **(1)**, in reactions of alcohols **(2)** and **(3)** a prevailing effect of phosphine concentration on reaction yield was observed and the highest yield was found at the ratio [PNS]/Rh = 3 (Tables 5 and 6). Further increase of phosphine concentration caused a decline of alcohol conversion (Figs. 1 and 2).

The optimal ratio [PNS]/[Rh] is 3 for both reaction systems, which is in agreement with the formation of an active catalyst form with the formula $[HRh(CO)(PNS)_3]$. A lower concentration of phosphine is not sufficient for hydrido complex formation whereas a higher concentration of PNS may hinder substrate coordination to the active centres on the rhodium catalyst. Since in the hydroformylation of alcohol **(1)**, a dependence on PNS concentration was not observed, it may be suggested that in the case of alcohols **(2)** and **(3)** steric hindrance of the substrates plays a very essential role.

*2.3.3. Effect of pH on the hydroformylation of alcohol **(3)** ($CH_3CH=CHCH_2OH$)*

To find the effect of H^+ concentration on the hydroformylation of alcohol **(3)**, the pH of the reaction mixture (normally alkaline from PNS) was changed in the range 6.5–9.5 by adding an appropriate amount of H_2SO_4 or NaOH. Hydroformylation reactions were carried out for 2 h at optimal phosphine concentration ([PNS]/[Rh] = 3). It was found, that the hydroformylation reaction rate measured as the rate of CO/H_2 pressure drop increases with pH increase (Fig. 3). The same applies to changes in alcohol conversion (Table 7). The best results (100% of alcohol conversion) were obtained at pH = 9. A



Scheme 8.

Table 5
Hydroformylation of 2-methyl-2-propen-1-ol, ($H_2C = C(CH_3)CH_2OH$) **(2)** in the system $[Rh(acac)(CO)_2]$/PNS

[PNS]/[Rh]	Conversion (%)	K (%)*	L (%)*	C (%)*
0	–	–	–	–
1	71	56	14	1
2	86	76	8	2
3	93	91	–	2
4	88	78	8	2
5	65	60	4	1
8	33	32	–	1
3[a]	52	50	–	2
5[a]	14	12	2	–
8[a]	5	3	2	–

$[Rh] = 1.48 \times 10^{-2}$ M, [alc.]/[Rh] = 390, 353 K, 2 h, $p(H_2 + CO) = 1$ MPa, $pH_2/pCO = 1$.
[a] 333 K, 3 h.
* **K**, **L** - see Scheme 7, **C** - see Scheme 3.

similar positive effect of a higher pH on reactions has also been found by other authors [20].

2.4. Stability of the $[Rh(acac)(CO)_2]$ / PNS catalytic system

The stability of catalytic systems was studied for alcohol **(3)** hydroformylation with an $[Rh(acac)(CO)_2]$/PNS catalytic system in which the ratio of [PNS]/[Rh] = 3. The post-reaction mixture forms a biphasic system in which both phases are coloured (the water phase is orange whereas the organic phase is claret). This may

Table 6
Hydroformylation of 2-buten-1-ol, ($CH_3CH = CHCH_2OH$) **(3)** with $[Rh(acac)(CO)_2]$/PNS system

[PNS]/[Rh]	Conversion (%)	M (%)*	N (%)*	E (%)*	G (%)*
2	55	40	4	2	9
3	99	77	1	12	9
4	79	57	–	14	8
5	67	49	–	9	9
8	33	24	–	8	1
3[a]	85	72	–	3	10
5[a]	38	24	8	1	5
8[a]	9	7	–	1	1

$[Rh] = 1.48 \times 10^{-2}$ M, [alc.]/[Rh] = 390, 353 K, 2 h, $p(H_2 + CO) = 1$ MPa, $pH_2/pCO = 1$.
[a] 333 K, 3 h.
* **M**, **N** - see Scheme 8, **E**, **G** - see Scheme 4.

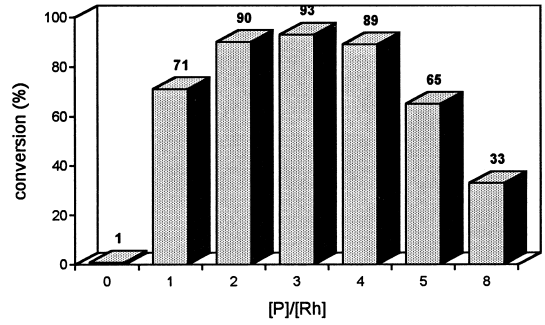


Fig. 1. Effect of [PNS]/[Rh] concentration ratio on conversion of $CH_2 = C(CH_3)CH_2OH$ **(2)** at 353 K.

suggest that hydroformylation occurs also in both phases, which explains the almost 100% conversion of alcohol. Since the rhodium catalyst as well as the hydroformylation reaction products are present in both phases, simple separation by decantation of catalyst from reaction products was not possible. The water phase containing some amounts of the catalyst was used again for the hydroformylation of a new portion of alcohol but only 6% conversion was observed. The same result (ca. 6% conversion) was obtained for a water phase from which reaction products were extracted by the application of Et_2O or CH_2Cl_2. The stability of the catalytic system $[Rh(acac)(CO)_2]$/PNS during the course of the hydroformylation reaction was tested in an experiment in which a new portion of alcohol **(3)** was added to the post-reaction mixture to conduct the next hydroformylation reaction trial. The conversion of alcohol in such

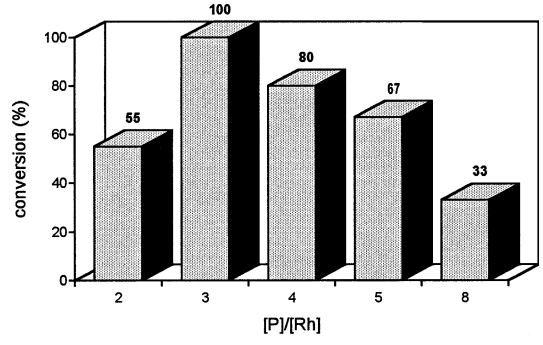


Fig. 2. Effect of [PNS]/[Rh] concentration ratio on conversion of $CH_3CH{=}CHCH_2OH$ **(3)** at 353 K.

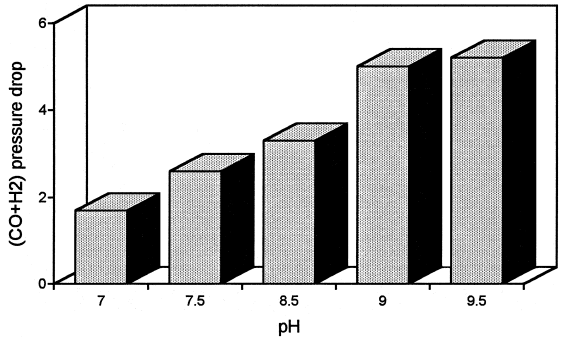


Fig. 3. Effect of pH of reaction mixture on the $(CO + H_2)$ pressure drop measured as the difference of pressure at the beginning and at the end of reaction.

an experiment was only 40% after 2 h, much lower than in the first trial (100%).

It was found that pH changes during a reaction are responsible for the activity loss of the catalytic system. The reaction mixture pH of ca. 9 at the beginning slowly decreased during reaction to ca. 5. The pH decrease can be explained by formation of acidic form of PNS phosphine (PNSH) in reaction with alcohol. The conversion of PNS into an acidic form was also observed during the heating of PNS in ethanol. The reaction, accompanied by a pH drop, seems to be the general reaction of phosphine lithium salts with alcohols.

Measurements of pH during the hydroformylation reaction showed that pH drops from 9 to 7 during the first 30 min of reaction, when the highest pressure drop ($\Delta p = 3.5$ atm) is also observed. During the next 20 min. pH decreases to 6.5 and finally reaches 5.5 after ca. 2 h of the hydroformylation reaction. The small pressure drop ($\Delta p = 1.5$ atm) means much lower substrate conversion. From the data collected in Table 7 one may conclude that the low pH value (ca. 5) of the post-reaction mixture was the main reason for the low conversion of alcohol in the repeated hydroformylation experiment with the same catalyst.

The low activity of the system in an acidic medium is probably caused by the decomposition of reactive rhodium–hydrido form of catalyst, which was earlier proved for systems containing carboxylic acids [22]. On the other hand, raising pH to 9 by adding NaOH to the post-reaction mixture without reaction product separation reactivates the catalyst and alcohol conversion increases to ca. 60% in a repeated experiment.

These experiments showed that the alkalization of the post-reaction mixture is necessary for the re-use of the catalytic system [Rh(acac)$(CO)_2$]/PNS in unsaturated alcohol hydroformylation. It is worth noting that during the hydroformylation of 1-hexene a pH drop was not observed and the same catalytic system was used several times without a loss of activity [12].

3. Experimental

[Rh(acac)$(CO)_2$] [23], [HRh(CO)$(PPh_3)_3$] [24] and PNS [11] were prepared according to methods described in literature.

3.1. Hydrogenation reactions

Hydrogenation reactions at 0.1 MPa of H_2 were performed in a glass thermostatted reactor ($v = 70$ cm^3) with magnetic stirring. Reactions under a higher pressure (0.5 MPa) were performed in a steel autoclave ($v = 50$ cm^3) at 333 or 353 K with magnetic stirring. Reagents were

Table 7
Conversion of 2-buten-1-ol, ($CH_3CH{=}CHCH_2OH$) **(3)** in hydroformylation reaction catalyzed by the system [Rh(acac)$(CO)_2$]/PNS at [PNS]/[Rh] = 3 depending on pH of reaction mixture

pH	pH fixed addition of	Conversion of $CH_3CH{=}CHCH_2OH$ (%)
6.5	H_2SO_4	20
7	Neutral form of PNS	33
8.5	Neutral form of PNS + NaOH	54
9	Neutral form of PNS + NaOH	90
9.5	PNS	100

introduced in a dinitrogen atmosphere. After the reaction the reactor or autoclave was cooled and the liquid sample was vacuum distilled and analysed by GC-MS.

In all reactions 1 cm^3 of alcohol, 0.00766 g (2.96×10^{-5} mol) of [Rh(acac)$(CO)_2$], ([alcohol]/[Rh] = 390) and 1 cm^3 of water were used. The amount of PNS was 0.03551 g or 0.066 g in reactions at [PNS]: [Rh] = 3 or 5, respectively. The rhodium catalyst and phosphine were weighted and introduced to the reactor in small teflon vessels.

3.2. Hydroformylation reactions

Hydroformylation reactions were carried out in a steel autoclave ($v = 50$ cm^3) (with a magnetic stirrer) under 1 MPa of $CO/H_2 = 1$ gas mixture. In each experiment, 0.5 cm^3 of alcohol, 0.5 cm^3 of water and 0.00383 g (1.48×10^{-5} mol) of [Rh(acac)$(CO)_2$] were used. The concentration of the rhodium catalyst in all experiments was 1.5×10^{-2} M at [alcohol]/[Rh] = 390. The total volume of the solution in the autoclave was constant, which means that corresponding amounts of acid or base were introduced in added water portion so that the total volume was 1 cm^3. All reagents were introduced into the autoclave in a dinitrogen atmosphere. The autoclave was purged twice with dihydrogen and subsequently filled with H_2 up to 0.5 MPa and with CO up to 1 MPa. After the reaction the autoclave was cooled and the reaction products were vacuum distilled and analysed by the GC-MS method.

3.3. Analyses

The yields of aldehydes (*n* and *iso*) were determined by GC-MS (Hewlett Packard 5890II + Hewlett Packard 5971A, column Hewlett Packard 5.25 m × 0.2 mm × 0.33 m).

The MS data for reaction products are as follows.

1-Methyl-propanol, A: 72 (15); 59 (24); 57 (9); 55 (2); 50 (1); 46 (1); 45 (100); 44 (13); 43 (54); 42 (4); 41 (12); 39 (3); 32 (4); 31 (11); 29 (13); 27 (9); 26 (2); 18 (2).

2-Butanon, B: 72 (M^+, 24); 57 (7); 45 (3); 44 (2); 43 (100); 42 (5); 41 (1); 39 (1); 29 (12); 28 (2); 27 (8); 25 (2).

4-Methyl-propanol, C: 72 (11); 59 (2); 57 (2); 56 (4); 55 (6); 45 (2); 44 (4); 43 (100); 42 (62); 41 (57); 40 (2); 39 (12); 38 (3).

2-Methyl-propanal, D: 72 (M^+, 44); 57 (3); 55 (2); 54 (1); 53 (1); 51 (1); 44 (5); 43 (100); 42 (8); 41 (69); 40 (3); 39 (16); 38 (3); 37 (2); 30 (1); 29 (24); 28 (11); 27 (32); 26 (3).

Butanol, E: 73 (M^+, 2); 57 (6); 56 (100); 55 (16); 46 (1); 45 (5); 44 (3); 43 (50); 42 (28); 41 (60); 40 (4); 39 (11).

3-Buten-1-ol, F: 72 (M^+, 6); 71 (2); 57 (11); 54 (4); 50 (1); 44 (11); 43 (23); 42 (90); 41 (34); 40 (6); 39 (25); 38 (2); 32 (40); 31 (47); 29 (8); 28 (100); 27 (10); 18 (16); 17 (2).

Butanal, G: 72 (M^+, 61); 71 (6); 57 (28); 55 (1); 54 (3); 53 (2); 45 (3); 44 (100); 44 (77); 42 (11); 41 (57); 40 (4); 39 (20); 38 (5); 37 (3); 32 (4); 31 (1); 29 (44); 28 (24); 27 (39); 26 (5); 25 (1); 18 (3).

2-Hydroxy-4-methyl tetrahydrofuran, K: 102 (M^+, 1); 101 (2); 85 (2); 72 (19); 69 (4); 58 (16); 57 (69); 56 (100); 55 (17); 45 (3); 44 (6); 43 (20); 41 (59); 40 (5); 39 (17).

L (Scheme 7): 142 (1); 112 (5); 101 (5); 86 (6); 85 (100); 84 (5); 67 (9); 57 (19); 56 (9); 55 (6); 43 (7); 41 (15); 39 (3).

L′ (isomer of L): 112 (1); 101 (8); 86 (6); 85 (100); 67 (11); 57 (21); 56 (18); 55 (34); 43 (12); 41 (18); 39 (9).

2-Hydroxy-3-methyl-tetrahydrofuran, M: 101 (1); 86 (3); 85 (49); 83 (1); 71 (15); 67 (2); 61 (32); 59 (4); 57 (12); 56 (100); 55 (22); 54 (2); 53 (3); 45 (4); 43 (26); 42 (3); 41 (63); 40 (3); 39 (12); 38 (1).

M′ (isomer of M): 101 (1); 84 (13); 72 (9); 57 (54); 56 (100); 55 (46); 54 (1); 53 (7); 45 (1); 44 (10); 43 (28); 42 (1); 41 (63); 40 (1); 39 (22).

N (Scheme 8): 142 (1); 111 (1); 101 (2); 86 (5); 85 (100); 84 (7); 83 (2); 71 (1); 67 (3); 58 (1); 57 (6); 56 (33); 55 (13); 53 (1); 47 (1); 43

(24); 42 (1); 41 (23); 40 (1); 39 (6). Instruments used for IR measurements: FT-IR Nicolet Impact 400; for ^{1}H and ^{31}P NMR, Bruker 300 (121.5 MHz for ^{31}P).

4. Note added in proof

In the course of redaction of this manuscript a report of allyl alcohol hydrogenation with rhodium water-soluble catalysts appeared [25].

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