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Catalytic conversions in water Part 19. Smooth hydroformylation of *N*-allylacetamide in mono- and biphasic aqueous media

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Dedicated to Professor Henri Brünner on the occasion of his 65th birthday

Abstract

The Rh/tppts (tppts = $P(C_6H_4$-*m*-$SO_3Na)_3$) catalysed hydroformylation of *N*-allylacetamide in water proceeds at a much faster rate and in a much higher selectivity (> 99%) towards the aldehydes, 4-acetamidobutanal and 2-methyl-3-acetamidopropanal, than the Rh/PPh_3 catalysed reaction in organic solvents, such as THF, toluene and methanol. In water, at 90°C and 50 bar H_2/CO, turnover frequencies (TOF) > 10.700 h^{-1} were observed. Unfortunately, both catalysts exhibited a rather low regioselectivity (linear/branched (l/b) ratio = 1.1–1.5) which for Rh/tppts was found not to depend on the temperature, pressure, or ligand concentration. By using phosphate buffers the optimum pH of the aqueous reaction mixture was found to be pH 7.0. Under basic conditions (pH 11.0), the l/b ratio increased to l/b = 6.5, while the overall selectivity towards the aldehydes decreased to 41%. In a toluene/water biphasic system, due to the presence of water, the selectivity towards the aldehydes remained > 99%. Although Rh/PPh_3 (operating in the organic phase) was less active compared to Rh/tppts (operating in the aqueous phase), Rh/PPh_3 could easily be separated from the aqueous product layer. The hydrophobic Rh/Xantphos catalyst (Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) afforded a product mixture with l/b ratios up to 20 and could be recycled in five consecutive runs without loss in activity.

Keywords: Hydroformylation; Rhodium/phosphine complexes; *N*-Allylacetamide

1. Introduction

The hydroformylation of olefins is one of the most intensively studied reactions in the field of homogeneous catalysis [1]. Of all transition metal complexes that were found to catalyse this reaction, rhodium/phosphine complexes are generally preferred due to their high activity and high selectivity towards the linear aldehydes. The high atom efficiency of the reaction, combined with the availability of these highly active and selective catalysts, that operate under mild reaction conditions, makes the production of aldehydes by hydroformylation of olefins environmentally friendly and economically attractive.

In most Rh-catalysed processes the feedstock is restricted to non-functionalised olefins with the C=C bond preferably in the terminal position, as in the case of propene, styrene and 1-octene. Aldehydes containing hetero-atom substituents are convenient building blocks in organic synthesis [2], but unfortunately, their preparation by hydroformylation of a hetero-atom functionalised olefin is generally cumbersome [3]. Even in the presence of large amounts of catalyst and under harsh reaction conditions the hydroformylation proceeds slowly, while intra- or intermolecular condensation reactions afford side products, such as acetals, hemiacetals, imines, etc. [4]. In short: the hydroformylation pathway for the preparation of aldehydes with hetero-atom substituents is rather unpractical.

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Table 1
The hydroformylation of *N*-allylacetamide in organic and aqueous media

Exp. [a]	Catalyst	Solvent	Time (min)	Conv. (%)	Yield (%)	l/b ratio	TOF [b] (h^{-1})
1/1	Rh/PPh_3	THF	360	99.9	88.7	1.5	589
1/2	Rh/PPh_3	Toluene	240	99.3	92.7	1.5	712
1/3	Rh/PPh_3	MeOH	180	98.6	92.3	1.2	1342
1/4	Rh/tppts	H_2O	45	98.9	97.9	1.3	3891
1/5	Rh/tppts	MeOH	180	99.9	93.4	1.1	1239
1/6	Rh/tppts	$MeOH/H_2O$ [c]	120	99.9	95.3	1.1	1459

[a] Reaction conditions: 0.010 mmol $[Rh(acac)(CO)_2]$, 0.25 mmol ligand, 25 mmol *N*-allylacetamide, 70°C, 10 bar H_2/CO (1/1), 1000 rpm, 125 ml total reaction volume.
[b] Initial reaction rate in mol product per mol catalyst per hour.
[c] $MeOH/H_2O = 1/1$ (v/v), 125 ml total.

Recently, we reported that the hydroformylation of *N*-allylacetamide proceeds smoothly in high selectivity when the reaction is conducted in water, employing the water-soluble Rh/tppts catalyst (tppts = $P(C_6H_4$-*m*-$SO_3Na)_3$), or in an inverted aqueous biphasic catalytic system in which the catalyst resides in the organic phase [5]. The linear aldehyde, 4-acetamidobutanal, is an intermediate in the synthesis of *N*-acetyl-5-methoxytryptamine (melatonin), a human hormone which regulates sleep. Mortreux and coworkers reported that the hydroformylation of acrylic esters, such as methyl acrylate, also proceeds faster in a biphasic toluene/water medium with Rh/tppts compared to the Rh/PPh_3 catalysed reaction in neat toluene [6]. It seems that water is an ideal solvent for the hydroformylation of hetero-atom substituted olefins. Herein we report a detailed investigation of the hydroformylation of *N*-allylacetamide in single phase aqueous media, as well as in toluene/water mixtures.

2. Results and discussion

2.1. Hydroformylation of N-allylacetamide in various solvents

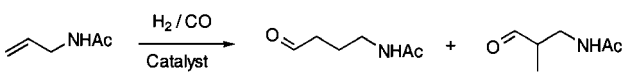
The Rh/PPh_3 catalysed hydroformylation of *N*-allylacetamide was tested in a number of selected organic solvents. Immediately prior to the beginning of the experiment, the catalyst precursor solutions were conveniently prepared in situ, by combining a freshly prepared solution of $[Rh(acac)(CO)_2]$ (acac = acetylacetonate) in the desired solvent with a solution of PPh_3. The reactions started without an induction period and the rates were found to increase in the order: THF < toluene < methanol as solvent (Table 1, Scheme 1). The selectivity towards the aldehydes, 4-acetamidobutanal and 2-methyl-3-acetamidopropanal, increased in the same order.

In contrast with non-functionalised olefins, *N*-allylacetamide has a high water solubility, which implies that the reaction might proceed smoothly in water, in the presence of a water-soluble catalyst. Hence, we prepared the catalyst in situ by adding a methanolic solution of $[Rh(acac)(CO)_2]$ to a solution of tppts in water. The bright yellow solution that is formed upon mixing can be used at once, unlike when the water-insoluble $[Rh(acac)(CO)_2]$ was added as a solid to an aqueous solution of tppts, which requires a much longer complexation time (usually 45 min). The presence of a small amount of methanol (1.0 ml) is considered not to have a significant effect on the reaction.

Indeed, the reaction in water proceeded smoothly; at 70°C and 10 bar of H_2/CO (1:1 (v/v)) a nearly quantitative conversion of *N*-allylacetamide was achieved in 45 minutes using as little as 0.04% (mol/mol) catalyst (Exp. 1/4). The selectivity towards the aldehydes was > 99%. In methanol, the Rh/tppts catalyst was found to be slightly less active compared to Rh/PPh_3, which suggests that the sulfonate substituents on the tppts ligand have only a minor effect on the performance of the catalyst. In a 1:1 mixture of water and methanol (Exp. 1/6) the Rh/tppts catalysed reaction was faster compared to the reaction in neat methanol, again showing that the presence of water has an accelerating effect on the reaction.

As can be seen from the reaction profile of experiment 1/4 (Fig. 1) the reaction starts immediately, without induction period. We conclude that, after replacement of the nitrogen by a mixture of H_2 and CO, during the heating up period, all of the catalyst precursor was converted into the catalytically active complexes. This was confirmed by the absence of the yellow colour of the precursor complexes in the sample taken at $t = 0$.

It has previously been established for the Rh/tppts catalysed aqueous biphasic hydroformylation of non-



Scheme 1. The hydroformylation of *N*-allylacetamide.

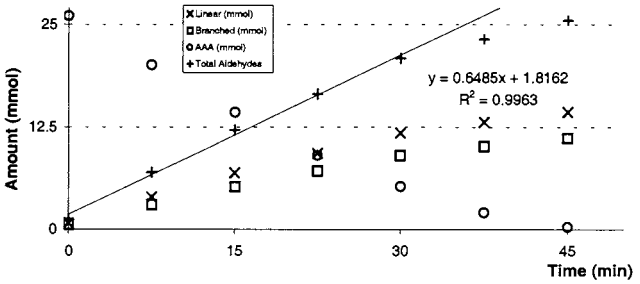


Fig. 1. Reaction profile of exp. 1/4 (Table 1).

functionalised olefins, such as propene, that the mechanism involves the initial formation of $[Rh(H)(CO)(tppts)_3]$ [7]. Dissociation of one of the phosphines and olefin coordination are followed by the insertion of the olefin into the Rh–hydride bond, affording a Rh–alkyl complex. Migratory insertion of CO affords a Rh–acyl intermediate, which undergoes an oxidative addition of H_2. Reductive elimination of the aldehyde and recombination with the phosphine gives back the initial Rh–hydride complex. We expect that in the hydroformylation of *N*-allylacetamide a similar mechanism is operative.

2.2. The effect of pressure, temperature and ligand concentration

Increasing the pressure of the reactant gasses H_2 and CO had a minor negative effect on the reaction rate, but the rate increased dramatically with the temperature to an initial turnover frequency (TOF) of 10.714 h^{-1} at 90°C and 50 bar. When the ligand concentration was increased from 0.8 to 4.0 mmol l^{-1} (10 to 50 equiv. per rhodium) the initial reaction rate increased significantly from TOF = 2362 h^{-1} to 3984 h^{-1} at 70°C and 50 bar (Tables 2 and 3). Further addition of the ligand, up to 100 equiv. per rhodium, did not further increase the reaction rate. Neither the pressure, the temperature, nor the tppts concentration had an influence on the regioselectivity (l/b = 1.2–1.5), which is considerably lower than in the Rh/tppts catalyzed hydroformylation of propene (l/b = 25) [7]. Apparently, the amide substituent has a directing effect in the hydroformylation reaction.

Previous studies on cationic Rh(diphosphine) complexes in the solid state have shown that the oxygen atoms of the amide substituents in 2-acetamido-*cis*-cinnamic acid methyl ester [8] and 2-acetamido-*cis*-2-hexenoic acid methyl ester [9] are coordinated to the rhodium simultaneously with the C=C bond. Similar observations were made, by means of NMR, in numerous other cationic Rh(diphosphine) complexes in organic [10], as well as in aqueous media [11]. In methanol, a cationic Rh(III)(H)(diphosphine)–alkyl complex, in which an acetamide substituent on the alkyl ligand is coordinated to the rhodium, has also been characterised by NMR [12]. Such a coordination might also occur in the Rh/tppts catalysed hydroformylation of *N*-allylacetamide prior to the migratory insertion of the C=C bond into the Rh–hydride (Scheme 2). The formation of a 6-membered chelate ring (the Markovnikov addition product), that eventually will lead to the branched aldehyde, will then be favoured over the anti-Markovnikov addition product.

In all experiments, the reaction follows a zero order profile until a conversion of ca. 80% is reached. Apparently, in the first stage of the reaction the concentration

Table 2
The effect of the H_2/CO pressure and temperature

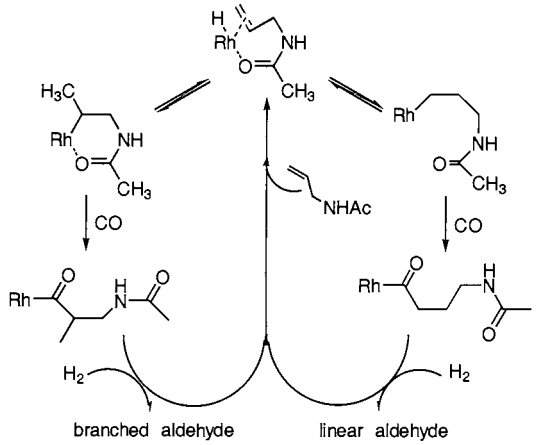
Exp. [a]	Pressure (bar)	Temp. (°C)	Time (min)	Yield (%)	l/b ratio	TOF (h^{-1})
2/1	50	70	90	98.2	1.5	2362
2/2	30	70	75	92.7	1.4	2607
2/3	10	70	75	94.8	1.5	2638
2/4	50	50	480	89.2	1.4	312
2/5 [b]	50	90	60	94.2	1.4	10714

[a] Reaction conditions: see Table 1, solvent: water, 0.10 mmol tppts.
[b] 50 mmol substrate, 0.0050 mmol $[Rh(acac)(CO)_2]$, 0.10 mmol tppts.

Table 3
The effect of ligand concentration

Exp. [a]	Tppts/Rh	Time (min)	Yield (%)	l/b ratio	TOF (h^{-1})
3/1	10	90	98.2	1.5	2362
3/2	25	60	98.6	1.2	3336
3/3	50	60	91.3	1.5	3984
3/4	100	60	85.5	1.5	3862

[a] Reaction conditions: see Table 1, solvent: water, 50 bar H_2/CO (1:1).



Scheme 2. Proposed intermediates in the Rh/tppts catalysed hydroformylation of *N*-allylacetamide.

of *N*-allylacetamide, which decreases in time, has no influence on the rate of the reaction. Nevertheless, when we increased the initial substrate concentration to 0.80 mol l^{-1} (Table 4, Exp. 4/3), we did observe a slight decrease in catalyst activity. We suggest that this is due to the lower water content of the reaction medium, as we have demonstrated previously that the reaction rate decreases with the amount of water (Table 1).

2.3. The effect of pH

In order to study the effect of the pH on the hydroformylation of *N*-allylacetamide, we carried out a series of hydroformylation experiments in different buffered reaction mixtures. We chose phosphate buffers since the phosphate anions are presumed to be only weakly coordinating to the intermediate rhodium complexes in aqueous solution and thus are expected not to alter the coordination sphere such that the hydroformylation rate is hampered. As shown in Table 5, the pH of the reaction mixture had a dramatic effect on the progress of the reaction. In the presence of a phosphate buffer at pH 4.7 the reaction proceeded slightly faster (TOF = 1156 h^{-1}, at 50°C, 10 bar H_2/CO) compared to the unbuffered reaction mixture. At pH 7.0 the reaction rate increased substantially to TOF = 2218 h^{-1} (50°C, 10 bar H_2/CO).

Analogous to the findings of Mortreux et al, in their studies of the biphasic hydroformylation of acrylic esters [6], we propose that the rate determining step involves the oxidative addition of H_2 to a Rh–acyl intermediate. In organic media, one might expect this step to be inhibited due to coordination of the amide substituent, which would result in the loss of a vacant coordination site. In the more polar aqueous media, the dissociation of the amide is facilitated due to solvophilic interactions. Dissociation might also be enhanced in phosphate buffered solutions, owing to the higher polarity and the presence of weakly coordinating phosphate or hydroxide anions, that might stabilise lower ligated intermediates.

The increase of the l/b ratio to 6.5 at pH 11.0, indicates that, under more basic conditions, the coordination of the amide was weaker indeed, although in this case the insertion of the olefin into the Rh bond is altered, rather than the oxidative addition reaction of H_2 to a Rh–acyl intermediate. Unfortunately, at high pH, the overall selectivity towards aldehydes decreased

Table 4
The effect of the initial *N*-allylacetamide concentration

Exp. [a]	Substrate/Rh	Time (min)	Yield (%)	l/b ratio	TOF (h^{-1})
4/1	2500	90	98.2	1.5	2362
4/2	5000	180	98.9	1.4	2351
4/3	10000	300	93.3	1.4	1986

[a] Reaction conditions: see Table 1, solvent: water, 0.10 mmol tppts, 70°C, 50 bar H_2/CO (1:1).

Table 5
The hydroformylation of *N*-allylacetamide in phosphate buffered solutions

Exp. [a]	pH	Time (min)	Conv. (%)	Yield (%)	l/b ratio	TOF (h^{-1})
5/1	4.7 [b]	300	99.4	99.4	1.3	844
5/2	4.7	300	99.9	99.8	1.4	1156
5/3	7.0	180	99.9	98.1	1.4	2218
5/4	11.0	90	83.1	34.1	6.5	2033
5/5	NaOH [c]	300	61.4	4.2	3.8	n.d.

[a] Reaction conditions: see Table 1, solvent: water, 0.25 mmol tppts, 10.0 mmol KH_2PO_4, pH adjusted with 10% aqueous NaOH, 50°C, 10 bar H_2/CO (1:1).
[b] No buffer.
[c] NaOH (10 mmol), no phosphate.

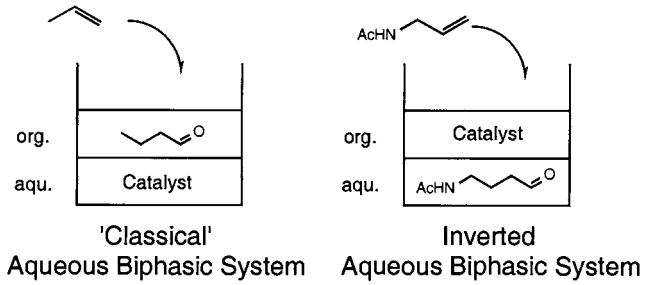


Fig. 2. 'Classical' and inverted aqueous biphasic catalytic systems.

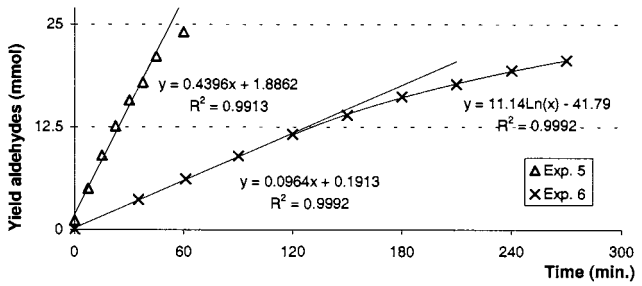


Fig. 3. Reaction profile of Exp. 6/1 and Exp. 6/2.

substantially, probably due to the hydrolysis of the amide substituents in both the substrate and the products. In the presence of NaOH the selectivity decreased even further to ca. 7% (Exp. 5/5). Consequently, variation in pH, as a tool to increase the selectivity towards the linear aldehyde, is rather ineffective.

2.4. An inverted aqueous biphasic catalytic system

In our attempts to isolate the products from the aqueous reaction mixture by extraction with an organic solvent, only traces of both aldehydes could be recovered, obviously, due to their high water solubility. By means of HPLC, in a 1:1 (v/v) mixture of toluene and water, the fractions of *N*-allylacetamide, 4-acetamidobutanal and 3-acetamido-2-methylpropanal in the water layers were determined to be 95.2, 97.5 and 98.0%, respectively. In order to achieve product/catalyst separation, we turned to an 'inverted aqueous biphasic catalytic system' containing the hydrophobic Rh/PPh_3 catalyst in a toluene/water mixture. In such a system the catalyst remains dissolved in the organic phase, while the products will move to the aqueous layer, the opposite of standard aqueous biphasic catalysis (see Fig. 2).

In comparison with the water-soluble Rh/tppts in the same biphasic mixture, the hydrophobic Rh/PPh_3 is considerably less active in the hydroformylation of *N*-allylacetamide, which we attribute to the lower polarity of the organic solvent (see Table 1). In addition, after ca. 50% conversion, we observed a sudden decrease in the reaction rate. Since *N*-allylacetamide is predominantly dissolved in the aqueous phase we suggest that phase transfer limitations give rise to this decreased reactivity. In the case of Rh/tppts, which operates in the aqueous phase, a zero order reaction continued until ca. 80% conversion (see Fig. 3). Nevertheless, after the reaction the Rh/PPh_3 catalyst was conveniently separated from the aqueous product mixture by a simple phase separation.

An advantage of inverted biphasic systems is that, in principle, the full range of available (hydrophobic) phosphine ligands can be applied without the need to tailor their solubility in organic media. To increase the regioselectivity towards linear aldehydes, generally, bidentate diphosphine ligands with large bite angles are applied [13]. In this respect, Cuny and Buchwald previously reported that in THF, in the presence of a large bite angle diphosphite ligand, functionalised olefins, such as *N*-allylsuccinamide, were hydroformylated with high selectivities towards the linear aldehydes [14]. We selected the Rh/Xantphos combination (Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene) [15], and tested it in our inverted aqueous biphasic system. Although the reaction rate decreased dramatically to $TOF = 31\ h^{-1}$ at 70°C and 10 bar H_2/CO, the regioselectivity increased to $l/b = 20.0$. At 90°C, using 0.2% catalyst an almost quantitative conversion was obtained in 10 h of reaction time. The Rh/Xantphos catalyst solution was reused in five successive experiments, without loss in activity. Rh analysis of the water layers, by means of AAS spectrometry, confirmed the recovery of $>99\%$ of the catalyst (Table 6).

3. Conclusions

We have demonstrated that the Rh/tppts catalysed hydroformylation of *N*-allylacetamide proceeds expeditiously in aqueous media. The reaction rate increases with the temperature, while the pressure of the H_2/CO mixture had only little effect. Optimum results were obtained with a ligand concentration of 4.0 mmol l^{-1} (tppts/Rh = 50) and in a phosphate buffered solution at pH 7.0. Unfortunately the regioselectivity did not lend itself to optimisation and remained between $l/b = 1.1$ and $l/b = 1.5$.

Due to the high water solubility of the products, catalyst/product separation could be achieved in a two-phase protocol, using hydrophobic catalysts. By making use of Rh/Xantphos, a catalyst especially designed for the formation of linear aldehydes, in a toluene/water biphasic medium, 4-acetamidobutanal was obtained in high selectivity, while the catalyst was conveniently recycled.

Although the scope of the aqueous (biphasic) hydroformylation of functionalised olefins still needs to be explored, we propose that, in general, better results

might be expected compared to hydroformylation reactions in organic media. By making use of inverted aqueous biphasic catalytic systems, catalyst recycling can be achieved in an alternative manner, without the need to introduce solvophilic substituents into the ligands, to retain the catalytically active complexes in the organic phase.

4. Experimental details

The preparation of the catalyst precursor solutions were done under an inert nitrogen atmosphere. The solvents (p.a.) were used as received. Distilled water was saturated with nitrogen before use. Tppts [16], *N*-allylacetamide [17], and 4,5-bisdiphenylphosphino-9,9-dimethylxanthene (Xantphos) [15] were prepared according to literature procedures. All other chemicals were commercially available. Rh analyses were performed on a Perkin Elmer 5100Pc Atomic Absorption Spectrometer.

4.1. Single phase hydroformylation of N-allylacetamide

A volume of 1.0 ml of a freshly prepared 0.010 M solution of $[Rh(acac)(CO)_2]$ (0.010 mmol) in MeOH was added to a solution of the ligand in the desired solvent (or solvent mixture). *N*-allylacetamide and standard (pentaerythritol for reactions in aqueous media, n-butanol for reactions in organic media) were added and the combined solution was transferred into a 300 ml Hasteloy C Parr autoclave. The nitrogen atmosphere was replaced by a mixture of H_2 and CO (1:1) and the autoclave was swiftly heated to reaction temperature (within 8 min). When the temperature was stabilised, the pressure was adjusted and a sample was taken ($t = 0$). Samples were taken at regular time intervals, and the pressure was maintained constant by adding the H_2/CO mixture. The samples were immediately analysed by HPLC (Phenomenex organic acid column, eluent: 0.01 M trifluoroacetic acid in water). The conversion, yield and selectivities were calculated relative to the standard. The products were identified by ^{1}H-NMR and LC/MS. The linear aldehyde, 4-acetamidobutanal, was also identified by HPLC by comparing the retention time with the compound prepared in situ by combining 4-aminobutyraldehyde diethylacetal with 1 equiv. of acetic anhydride.

4.2. Hydroformylation of N-allylacetamide in an inverted aqueous biphasic system

N-Allylacetamide (25 mmol) and pentaerythritol (4 mmol, internal standard) were dissolved in water in a 300 ml Hasteloy C Parr autoclave. A freshly prepared solution of $[Rh(acac)(CO)_2]$ in toluene and a solution of the ligand in toluene were combined and transferred into the autoclave. Further on, the same procedure was followed as described for the single phase hydroformylation reactions. Vigorous stirring (1000 rpm) afforded representative samples from the biphasic reaction mixture. The aqueous layers of the samples were analysed by HPLC. Since the concentrations of the substrate and the products in the organic layers were negligible, the organic layers were disregarded.

4.3. Partition coefficient determination in a toluene/water (1:1) mixture at room temperature (r.t.)

5 ml of an aqueous solution of *N*-allylacetamide (296.0 mM), 4-acetamidobutanal (155.2 mM) and 3-acetamido-2-methylpropanal (88.8 mM), was extracted with 5 ml toluene at r.t. The water layer was again analysed by HPLC and the following concentrations were measured: *N*-allylacetamide (281.8 mM), 4-acetamidobutanal (151.3 mM) and 3-acetamido-2-methyl-

Table 6
The hydroformylation of *N*-allylacetamide in toluene/water mixtures

Exp. [a]	Catalyst	Solvent	Time (min)	Yield (%)	l/b ratio	TOF (h^{-1})	[Rh] [e] (mg/l)
6/1	Rh/tppts	Toluene/H_2O	60	96.8	1.3	2946	n.d.
6/2	Rh/PPh_3	Toluene/H_2O	270	80.2	1.5	578	n.d.
6/3 [b]	Rh/xantphos	Toluene/H_2O	1320	24.4	20.0	31	n.d.
6/4 [c]	Rh/xantphos	Toluene/H_2O	600	96.4	15.3	177	n.d.
6/5 [c,d]	Rh/xantphos	Toluene/H_2O	1320	95.3	19.6	n.d.	0.10
	Recycle 6/5 1	Toluene/H_2O	1320	94.8	19.9	n.d.	0.06
	Recycle 6/5 2	Toluene/H_2O	1320	93.5	19.7	n.d.	0.07
	Recycle 6/5 3	Toluene/H_2O	1320	95.5	20.1	n.d.	0.03
	Recycle 6/5 4	Toluene/H_2O	1320	95.3	19.7	n.d.	0.14

[a] Reaction conditions: see Table 1, solvent: water (100 ml), toluene (100 ml), 70°C, 10 bar H_2/CO (1/1).
[b] 0.010 mmol $[Rh(acac)(CO)_2]$, 0.050 mmol Xantphos.
[c] 0.050 mmol $[Rh(acac)(CO)_2]$, 0.250 mmol Xantphos, 90°C.
[d] Solvent: water (50 ml), toluene (115 ml), 70°C.
[e] [Rh] in the aqueous layer, determined with AAS (detection limit 0.01 mg l^{-1}).

propanal (87.0 mM). Partition coefficients in the aqueous layer: *N*-allylacetamide: 0.952, 4-acetamidobutanal: 0.975 and 3-acetamido-2-methylpropanal: 0.980.

Acknowledgements

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