## **Room Temperature Ambient Pressure (RTAP)-Hydroformylation** in Water Using a Self-Assembling Ligand

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Abstract: We herein demonstrate a hydroformylation at room temperature and ambient pressure (RTAP) using our Rh/6-DPPon (1) system in aqueous media. The hydrogen bonding network of the ligand backbone stays intact, exemplified by the excellent regioselectivity for the linear aldehyde. Various substrates with different functional groups (with some prone to hydrolysis) are stable under the applied conditions and can undergo hydroformylation resulting in good vields.

Keywords: aldehydes; hydroformylation; phosphane ligands; regioselectivity; rhodium; self-assembly; surfactants; sustainable chemistry; water chemistry

The ligand 6-DPPon (1) is able to form complementary hydrogen bonds and, in the presence of

a metal, acts as a bidentate ligand. This system shows

a very high reactivity and selectivity, which enables

a hydroformylation reaction even at room temperature and atmospheric pressure (RTAP).<sup>[4]</sup> These

unique properties can be ascribed to the flexibility

and simultaneous structural integrity of the hydrogen

bonding network within the ligand backbone accommodating different coordination geometries without

significant energy penalties.<sup>[5]</sup> On the other hand,

water as a reaction medium has a lot of beneficial

properties. It is preferred as a solvent because it is in-

expensive, non-toxic, non-explosive, non-flammable

and allows for easy temperature control.<sup>[6]</sup> However, there are some intricacies when using it as a medium for organic reactions; the often poor solubility of both substrates and catalysts being major issues. In the Ruhrchemie/Rhône-Poulenc process,<sup>[7]</sup> hydroformyla-

tion of propene is achieved in a biphasic system using

Rh(I) in combination with tris(3-sulfophenyl)phosphine trisodium salt [TPPTS (2), Figure 1] as catalyst. This allows for easy separation of the catalyst and

the product. However, higher olefins  $(>C_4)$ , which

are poorly soluble in water, suffer from a low reaction

rate. To overcome this issue several solutions have

been developed.<sup>[8]</sup> Recently, the group of Lipschutz published several transition metal-catalyzed reactions in aqueous media with use of a surfactant and without the need for specially designed substrates or cata-

### Introduction

Hydroformylation is one of the most important industrially applied homogeneous catalytic processes with more than 9 million tons of oxo products produced annually.<sup>[1]</sup> Unfortunately, laboratory applications of hydroformylation have remained underdeveloped, most likely because for most catalyst systems high pressure and high temperatures are necessary. That requires special pressure equipment, not available in every synthetic laboratory. To overcome this problem, our group has developed the Rh/6-DPPon (1) hydroformylation system (Scheme 1).<sup>[2]</sup> Other catalyst systems developed so far suffer from lacking selectivity and/or reactivity.<sup>[3]</sup>



Scheme 1. Rh/6-DPPon (1) system.

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lysts.<sup>[9,10,11]</sup> We wondered if it is possible to perform an 🛞 WILEY 順 © 2013 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

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Figure 1. Structure of tris(3-sulfophenyl)phosphine trisodium salt (TPPTS, 2).

RTAP hydroformylation under these conditions, thus giving access to all the advantages that water as a reaction medium can offer without the necessity to develop a new catalyst system.

## **Results and Discussion**

We commenced our investigations by optimizing the reaction conditions for 1-octene (6) as a substrate (Table 1). Our major interest was to see whether the hydrogen bonding system within the ligand backbone would remain intact and operative in the presence of water.<sup>[12]</sup>

First we applied the previously reported conditions for the RTAP hydroformlyation in THF, just exchanging the organic solvent with water (entry 1).<sup>[13]</sup> In this case, no conversion could be observed. This is proba-

Table 1. Optimization of the reaction conditions.<sup>[a]</sup>

bly due to the low solubility of the catalyst in 1octene. Next we added sodium dodecyl sulfate (SDS, 3) and Triton X-100  $(4)^{[14]}$  as two common surfactants (Figure 2). Of these two, 4 gave the better results, giving high conversion at low surfactant concentrations (Table 1, entry 4 and 6). While both surfactants (3 and 4) produced nearly perfect chemo- and regioselectivity, the surfactant loading was still too high (6 wt%). Conversely, by applying the tocopherol derivative polyoxyethanyl  $\alpha$ -tocopheryl sebacate (PTS, 5)<sup>[15]</sup> we could lower the surfactant loading to 1.5 wt%



SDS (3)

Triton™ X-100 (4)



PTS (5)

Figure 2. Investigated surfactants.

·	ŀ	Hex $\sim$ $\frac{[Rh(CC)]{6-DPP}}{CO/H_2}$ $H_2O, s$	D) <sub>2</sub> acac] (0.67 mol%) on (1) (3.33 mol%) (1:1) 1 atm	Hex $7$ $8$		
Entry	Surfactant	wt%	Time [h]	Conversion [%] <sup>[b]</sup>	CS <sup>[b,c]</sup>	rs <sup>[b,d]</sup>
1	_	_	20	0	n.d.	n.d.
2	3	1.5	15	9	n.d.	n.d.
3	3	3.0	15	3	n.d	n.d.
4	3	6.0	15	81	97:3	97:3
5	4	1.5	15	38	95:5	99:1
6	4	3.0	15	89	96:4	>99:1
7	4	6.0	15	40	93:7	>99:1
8	5	1.5	15	85	95:5	99:1
9	5	1.5	15	96	96:4	>99:1
10	5	0.75	15	71	85:15	>99:1
11 <sup>[e]</sup>	5	1.5	20	83	80:20	>99:1
12	5	1.0	24	100	93:7	99:1
13 <sup>[f]</sup>	5	1.0	24	0	n.d	n.d
14 <sup>[f]</sup>	5	1.0	24	0	n.d	n.d

<sup>[a]</sup> Entries 1–8  $c_0 = 0.97$  M, entries 9-11  $c_0 = 0.48$  M, entries 12-14  $c_0 = 0.33$  M.

[b] Determined via GC.

[c] *cs*=chemoselectivity towards aldehyde (by-products: *n*-octane and octene isomers).

[d] rs = regioselectivity 7:8.

[e] [Rh(CO)<sub>2</sub>acac] 0.33 mol%, 6-DPPon (1) 1.67 mol%.

[f] Reaction run with either PPh<sub>3</sub> or Xanthphos instead of 6-DPPon (1).

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	- ~	6-DPPon ( <b>1</b> ) (3.33 mol%) CO/H <sub>2</sub> (1:1) 1 atm		0		_0	
	R ≪ —	H <sub>2</sub> O (PTS 1	.0 wt%), r.t., 24 h	R <sup>///</sup> linear	+	R <sup>//</sup> branched	
Entry	Substrate		Main pro	oduct		Yield [%] <sup>[a]</sup>	<i>r</i> s I:b <sup>[b]</sup>
1	$\sim$	√ 6	$\sim$	~~ <sub>0</sub>	7	77 (80)	99:1
2	$\sim$	N 9	°	~~ <sub>0</sub>	23	65 (72)	99:1
3	0,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	<ul> <li>≈ 10<sup>°</sup></li> </ul>		~~ <sub>0</sub>	24	53 (54)	99:1
4		≈ 11 <sup>0</sup>	$\sim$	~~o	25	82 (92)	99:1
5		<b>12</b>		~~ <sub>0</sub>	26	76 (93)	99:1
6		▶ 13		~~ <sub>0</sub>	27	79 (95)	95:5
7		<ul><li>≈ 14 <sup>(</sup></li></ul>		~~ <sub>0</sub>	28	83 (98)	99:1
8		15		∽~ <sub>0</sub>	29	76 (93)	99:1
9		16	$\neq_{si}^{o}$	~~ <sup>0</sup>	30	87 (91)	99:1
10	Ph Ph Ph O	🔪 17	Ph + O	~~o	31	80 (98)	99:1
11	HO	n 18	но	∽~ <sub>0</sub>	32	n.d. (99) <sup>[c]</sup>	99:1
12	$\left( \right)_{12}$	↓ 19	() 13	~~o	33	83 (84) <sup>[d]</sup>	99:1
13	$\bigcirc$	≈ 20	$\bigcirc$	<b>↓</b> <sub>≠</sub> 0	34	49 (99)	28:72
14		/ 21		<u>∕</u> ≠0	35	91 (95)	93:7
15		22	v o ↓		36	n.d. (51) <sup>[e]</sup>	1:99

Table 2. Hydroformylation	of other terminal alkenes.
	[Rh(CO) <sub>2</sub> acac] (0.67 mol%)

<sup>[a]</sup> Isolated yield of both aldehyde products, in brackets crude NMR yield, determinded with 1,3,5-trimethoxybenzene as internal standard. If not differently noted, full conversion was observed in all cases.

<sup>[b]</sup> Regioselectivity, determinded *via* NMR from the crude reaction mixture.

- <sup>[c]</sup> Polymerizes upon concentration.
- <sup>[d]</sup> Conversion 88%.
- <sup>[e]</sup> Not isolated due to high volatility.

while getting similarly excellent chemo- and regioselectivity (Table 1, entry 8).

Lowering the overall concentration of the substrate resulted in nearly full conversion (entry 9). This is probably due to the increased reaction volume formed by the micelles, which is able to contain more substrate at the same time. By further varying the reaction conditions (entries 10–12), we found the optimal reaction conditions giving the best conversion (100%), very good chemoselectivity (93:7) and excellent regioselectivity (99:1, entry 12). We then checked whether our 6-DPPon (1) was still the best ligand under these conditions. Therefore we used triphenylphosphine and Xantphos instead of 1 (entries 13 and 14). With both ligands, no reaction at all was observed. It is apparent they do not form an active catalyst under these conditions.

With the optimized conditions in hand, we investigated the substrate scope (Table 2). Non-polar substrates such as 1-octene (6) and 1,7-octadiene (9) worked fine, as the latter selectively furnished the corresponding linear dialdehyde (Table 2, entry 2). Com-

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patible functional groups included aldehydes, acetals, esters, carbamates, a TBS ether of a primary alcohol, a free hydroxy group, and an acid-labile trityl ether. In every case, very clean reactions were observed, furnishing the linear aldehydes in excellent chemo- and regioselectivity. The lower yields observed for the more volatile substrates are due to a loss of product during the work-up. Lower regioselectivities (rs) were observed for styrene (entry 13, rs 28:72), allylbenzene (entry 14, rs 93:7) and the acetate (entry 6, rs 95:5). For styrene this can be explained by the formation of  $\pi$ -benzyl-complexes.<sup>[1b]</sup> For the acetate **13**, a chelation effect of the ester carbonyl could be the origin of the slightly reduced regioselectivity. It was even possible to convert the  $C_{16}$ -olefin **19** to the corresponding linear product with excellent regioselectivity. The lower conversion might be explained by the fact that the reaction mixture became increasingly heterogene-

ous because of precipitation of the solid aldehyde product. It was also possible to convert vinyl acetate (22) to the corresponding aldehyde product 35, which was branched, as expected. It should be noted that this was not possible in a previous work by a different group, where olefins with polar groups showed only poor reactivity.<sup>[8b]</sup>

Interestingly, the regioselectivities obtained in this water/surfactant medium are, in some cases, even higher than those observed previously using THF as the solvent.<sup>[4]</sup> This observation might be ascribed to the "hydrophobic effect", which can have a beneficial influence on reactions by bringing the actual reaction partners into close proximity.<sup>[6,11b]</sup> Since in an ideal process the catalyst should be recyclable, attempts have been made to reuse the water/catalyst phase.<sup>[16]</sup>

## Conclusions

In conclusion, we have demonstrated that it is possible to perform RTAP hydroformylation using self-assembly ligands in aqueous media. The ligands' hydrogen bonding system seems to stay intact, as excellent regioselectivity in favour of the linear aldehydes was obtained. Furthermore, we could show that these conditions are compatible with a wide range of functional groups. We think this extension of the already known RTAP hydroformylation offers interesting opportunities regarding the use of water as environmentally more benign and safer solvent.

## **Experimental Section**

#### **General Information**

All reactions were carried out in glassware that had been heated before use under vacuum using a heat gun and filled

with an atmosphere of argon. All solvents were dried and distilled by standard procedures. Water for hydroformylations was standard laboratory distilled water which had been degased before use. Chromatographic purification of products was accomplished using flash chromatography on Macherey-Nagel silica gel 60 (40-63 µm). Commercially available substrates for hydroformylation were distilled before use. Synthesis gas from Air Liquide (carbon monoxide 37, hydrogen 43, 1:1) was used. To maintain a constant pressure during hydroformylation, a balloon was used as gas reservoir. GC analysis was performed on a Agilent Technologies 6850 N apparatus equiped with HP-1 column (30.0 m  $\times$  $0.320 \text{ mm ID} \times 0.25 \text{ }\mu\text{m}$  film). Nuclear magnetic resonance spectra were acquired on a Bruker DRX 500 spectrometer, a Bruker Advance II 400 spectrometer and a Varian Mercury 300 spectrometer. NMR-spectra are referenced internally to residual solvent signals (CHCl<sub>3</sub>: <sup>1</sup>H 7.26 ppm, <sup>13</sup>C 77.10 ppm). Low resolution mass spectra were recorded on a Thermo TSQ 700 spectrometer (EI 70 eV, CI/NH<sub>3</sub> 110 eV). High-resolution mass spectra were obtained on a Thermo Exactive [pos.APCI(MeOH)]. Elemental analyses (CHN analyses) were performed on a VarioEL from Elementar Analysensysteme GmbH.

#### General Procedure for the Hydroformylation of 1-Octene (6); Optimization of the Reaction Conditions

A flat-bottom Schlenk tube equiped with a cross magnetic stirring bar was, under an argon atmosphere, charged with  $[Rh(CO)_2acac]$  and 6-DPPon (1). Then a PTS/H<sub>2</sub>O mixture was added and everything was stirred for 3 min at room temperature. After that, 1-octene (6) (0.156 mL, 0.112 g, 1.00 mmol, 1.0 equiv.) was added and the argon atmosphere replaced with CO/H<sub>2</sub> (1:1, 1 atm) by 3 cycles of vacuum/synthesis gas. The reaction mixture was then stirred at maximum speed at room temperature and under 1 atm of CO/H<sub>2</sub> (1:1) for the specified time. Afterwards the mixture was diluted with Et<sub>2</sub>O (5 mL), filtered through a short column of silica gel and the silica gel washed with Et<sub>2</sub>O (200 mL). The combined filtrates where evaporated under reduced pressure. Conversion and regioselectivity were determined via GC.

# General Procedure for the Hydroformylation of Substrates in Table 2

A flat-bottom Schlenk tube equiped with a cross magnetic stirring bar was, under an argon atmosphere, charged with substrate (1.00 mmol, 1.0 equiv.),  $[Rh(CO)_2acac]$  (1.73 mg, 6.70 µmol 0.67 mol%) and 6-DPPon (1) (9.30 mg, 33.3 µmol, 3.33 mol%). After that an  $H_2O/PTS$  mixture (1.0 wt%, 3.0 mL) was added and the argon atmosphere replaced with CO/H<sub>2</sub> (1:1, 1 atm) by 3 cycles of vacuum/synthesis gas. The reaction mixture was then stirred at maximum speed at room temperature and under 1 atm of  $CO/H_2$  (1:1) for 24 h. Afterwards the mixture was diluted with Et<sub>2</sub>O (5 mL), filtered through a short column of silica gel and the silica gel washed with Et<sub>2</sub>O (200 mL). The combined filtrates where evaporated under reduced pressure and the NMR-yield de-1,3,5-trimethoxybenzene termined with (16.8 mg. 0.100 mmol, 0.1 equiv.) as internal standard. Pure com-

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pounds where obtained after column chromatography on silica gel.

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- [13] Another situation one could imagine is that the reaction takes place in the substrate phase also without a surfactant.
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- [16] For details see the Supporting Information. The data shows that the water/catalyst phase is reusable once. The problem is the very slow phase separation.

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