

Synthesis of linear aldehydes from internal olefins in water†

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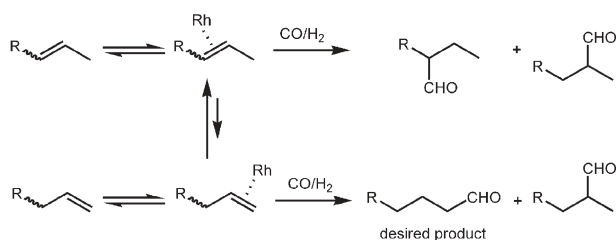
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We show here, for the first time, that the carbonylation of internal olefins in a biphasic water system is possible. It is shown that control of the pH and CO partial pressure are important factors for successful reactions. Interestingly, the water-soluble catalyst leads to significantly higher regioselectivity compared to similar catalysts soluble in organic solvents. The obtained *n/i*-selectivities exceed all known literature data and the catalyst can be easily reused several times.

A fundamental problem of homogeneous catalysis is the simple and efficient separation and recycling of the catalyst from starting materials and products. The application of a biphasic system of water and a non-miscible organic solvent constitutes probably the most elegant and practical solution to this problem.¹ Here, the catalyst should be water-soluble and easily isolated by simple phase separation. The industrial feasibility of this concept has been successfully proven by the large scale production of butyraldehyde (>300 000 t/a) via hydroformylation of propene (Ruh Chemie/Rhône-Poulenc process).² Unfortunately, most catalytic reactions have significantly reduced rates in water compared to standard organic solvents. For example, aliphatic olefins other than propene or 1-butene cannot be efficiently carbonylated in water so far.³

Therefore in recent years other solvents have become important as reaction media for two-phase-reactions.⁴ Examples are liquid CO₂,⁵ fluorinated phases⁶ and especially ionic liquids.⁷ Nevertheless, water is the ideal green solvent with regard to availability, price and toxicity. Hence, it is desirable to develop concepts which allow for a more general use of this type of biphasic catalysis.

One of the most important goals in current hydroformylation research is the selective conversion of internal olefins to linear aldehydes (Scheme 1).⁸ Such transformations offer the opportunity to use cheaper mixtures of internal and terminal olefins as feedstock and to save time and energy, which is needed for the additional purification steps.⁹ So far, known catalyst systems for



Scheme 1 Rhodium-catalysed isomerisation–hydroformylation of internal olefins.

† Dedicated to Prof. Dr Günther Wilke on the occasion of his 80th birthday.

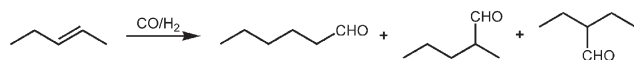
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the hydroformylation of internal olefins have been mainly developed by ligand design.¹⁰ Elegant examples include the diphosphite ligands of UCC¹¹ and Dupont/DSM,¹² the Xantphos ligands of van Leeuwen and co-workers,¹³ the acylphosphite ligands of Börner *et al.*¹⁴ and substituted NAPHOS ligands, that were introduced by us.¹⁵ However, to the best of our knowledge there exists no example for a selective hydroformylation of internal olefins to linear aldehydes in water.

Here, we describe for the first time such reactions, which proceed with hitherto unknown *n/i*-selectivity (>99:1), for the synthesis of linear aldehydes from internal olefins. In addition, we demonstrate that the control of pH in biphasic hydroformylations allows for faster and more selective transformations of terminal and internal olefins, which broadens the applicability of this method.

In the course of our investigations into the rhodium-catalysed hydroformylation and hydroaminomethylation of internal olefins, we reported that 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene (NAPHOS¹⁶) and similar phosphines allow for the conversion of internal olefins in homogeneous phase.¹⁵ Based on this work the question arose, whether water-soluble NAPHOS-ligands in presence of rhodium complexes are able to catalyse the reaction of internal olefins to linear aldehydes. Sulfonated NAPHOS (so-called BINAS¹⁷) was introduced by Herrmann *et al.* and shows high activity and *n/i*-selectivity in the rhodium-catalysed hydroformylation of propene.¹⁸ However, such ligands have never been successfully applied in hydroformylations of internal olefins. Thus, it was not surprising that initial tests on the hydroformylation of 2-pentene (Table 1), in the presence of 0.05 mol% Rh(CO)₂acac and 0.25 mol% BINAS, were disappointing.¹⁹ Applying conditions that are typical for the hydroformylation of propene ($T = 125\text{ }^{\circ}\text{C}$, $p = 30\text{ bar}$, $\text{CO:H}_2 = 1:1$), a mixture of aldehydes is obtained in only 12% yield (Table 1, entry 1). However, by lowering the synthesis gas pressure to 10 bar, olefin isomerization is faster and the yield of *n*-hexanal is significantly increased (Table 1, entry 2). The very high *n/i*-selectivity of 97:3 and the marginal hydrogenation of pentene (<0.3%) and aldehyde (0.7% hexanols) are noteworthy.

Next, the influence of the partial pressures of carbon monoxide and hydrogen were systematically studied. Selected results are shown in Table 1. It became clear that, by reduction of the carbon monoxide pressure down to 2 bar, an increase in both activity and *n/i*-selectivity can be achieved. A lower pressure of CO leads to increased hydrogenation side reactions. On the other hand, variations of the CO:H₂ ratio seem to have a negligible influence on the test reaction. Then the influence of the pH of the water phase on the hydroformylation was examined in more detail.²⁰ So far there is no such study for internal olefins known to the best of our knowledge. Surprisingly, the aldehyde yield in the buffered system (phosphate buffer pH 6–9) was in all cases higher, compared to the non-buffered reaction mixture (Table 1, entries 5–9).

Table 1 Biphasic hydroformylation of 2-pentene with Rh-BINAS catalyst^a

Entry	$p_0(\text{CO})$ (bar)	$p_0(\text{H}_2)$ (bar)	p_R^b (bar)	Additive	<i>n</i> -Hexanal (%)	<i>n</i> : <i>i</i>	Hexanols (%)
1	11	11	30	—	11	88:12	0.2
2	3	3	10	—	33	97:3	0.7
3	3	9	18	—	33	97:3	0.8
4	2	10	18	—	48	98:2	1
5	2	10	18	Buffer (pH: 6)	59	98:2	2
6	2	10	18	Buffer (pH: 7)	72	99:1	4
7	2	10	18	Buffer (pH: 8)	73	99:1	3
9	2	10	18	Buffer (pH: 9)	62	99:1	3
10	2	10	18	Triethanolamine (1 ml)	75	>99:1	4
11	2	10	18	TMEDA (0.5 ml)	69	99:1	3
12	2	10	18	Triethylamine (1 ml)	59	98:2	2
13	1.5	10.5	18	Triisooctylamine (1 ml)	42	98:2	1

^a Reaction conditions: 40 ml organic (anisole) and 40 ml aqueous phase; 73.0 mmol 2-pentene; 2-pentene:BINAS:Rh = 2000:5:1; 125 °C; 24 h.

^b Pressure at reaction temperature.

Especially at pH 7 and 8 a significant increase of the aldehyde yield (72–73%; TON = 1460, TOF = 61 h⁻¹) and an excellent regioselectivity (99:1) are observed. *This is the highest regioselectivity that has been described for a hydroformylation of any internal olefin to date.* Interestingly, this excellent regioselectivity is only achieved in water. When the tetra-*n*-butylammonium BINAS salt was used as the ligand, in a one-phase-system (anisole:NMP = 1:1) and under the same reaction conditions [$p_0(\text{CO}) = 2$ bar, $p_0(\text{H}_2) = 10$ bar, $p_R = 18$ bar, $T = 125$ °C, $t = 24$ h], the *n*/*i*-selectivity was only 85:15, and the yield of *n*-hexanal was only 52%. The possible reason for the higher *n*/*i*-selectivity in water is so far unclear, although one might speculate about the increased steric size of the ligand due to sulfonation and hydrogen bonding to water molecules.

We assume that the main reason for the higher reactivity under basic conditions is an easier preformation of the active catalyst species, as was described by Joó *et al.* for hydrogenations using chloride containing Rh-complexes.²¹ The lower yield in the non-buffered solvent system is explained by a sharp decrease of the pH in the aqueous catalyst solution (pH < 5) due to the acidity of the Rh-hydride complex, and the formation of CO₂ and HCO₂H by water-gas shift reaction. *This example clearly demonstrates the importance of pH control for transition metal-catalysed reactions in aqueous media.*²²

Excellent results for the hydroformylation of 2-pentene can be also obtained in the presence of amines (Table 1, entries 10–11). By applying triisooctylamine as an additive it became again apparent, that the increase in the reactivity is not due to the transfer of the catalyst (as ammonium BINAS salt) into the organic phase.

Obviously biphasic catalysis is advantageous compared to single phase catalysis, when it is possible to reuse the catalyst system several times. In order to demonstrate the reusability of the aqueous catalyst phase, six recycling experiments with a buffered solution (pH = 9) were carried out (Table 2). The initial increase in yield (Table 2, entries 2–3) is due to a drop of the pH to the optimal value (7–8). The following decrease in the yield can be mainly explained by the further descent of the pH. Indeed, pH-control of the catalyst phase after the seventh experiment showed a pH value of about 6. During the recycling experiments it was also

Table 2 Recycling of the catalyst^a

Entry	Hexanals (%)	<i>n</i> : <i>i</i>	Hexanols (%)
1 ^b	63	99:1	3
2	64	99:1	3
3	71	99:1	3
4	68	99:1	3
5	66	99:1	3
6	63	99:1	2
7	59	99:1	2

^a Reaction conditions: $p_0(\text{CO}) = 2$ bar, $p_0(\text{H}_2) = 10$ bar; $T = 125$ °C; $p(125$ °C) = 18 bar; 73.0 mmol 2-pentene, 2-pentene:Rh = 2000:1; $t = 24$ h. ^b BINAS:Rh = 5, after every reaction 1 equivalent (relating to Rh) of ligand was added.

shown, that the catalyst phase is stable over a reaction time of at least one week!

Finally, we tested other olefins under similar conditions (Table 3). Particularly interesting is the hydroformylation of 2-butene because of the industrial importance of inexpensive C₄-mixtures (>20M tons crack-C₄/a). With this olefin similar good results are obtained as with 2-pentene. The somewhat lower *n*/*i*-selectivity (98:2) can be explained by the higher vapour pressure of butenes, which causes an increase of the partial pressure of carbon monoxide during the reaction.

Also, 1-pentene yields hexanals in good yield (78%) and outstanding *n*/*i*-selectivity (>99:1). As stated in the introduction, a particular challenge is the hydroformylation of mixtures of olefins (Table 3, entries 4–6). Indeed, a mixture of octenes that contained only 3.6% 1-octene, gave 10% nonanals. In this case the reaction in a one-phase-system with the tetra-*n*-butylammonium BINAS salt under identical conditions, gave a higher yield of 20% but, as in case of 2-pentene, a significantly lower *n*/*i*-selectivity (77:23). Clearly, the use of water as solvent does not only allow for an easier catalyst recycling but also for higher selectivity towards the desired linear isomer. By using longer reaction times or a higher reaction temperature (140 °C) the aldehyde yield is increased to 33%. With pure 2-octene at 140 °C (entry 7) a somewhat higher yield (47%) and regioselectivity (99:1) are obtained due to its easier isomerization to 1-octene.

In addition styrene, which typically forms the branched aldehyde, is hydroformylated predominantly with the Rh-BINAS

Table 3 Hydroformylation of different olefins^a

Entry	Substrate	T (°C)	p ₀ (CO) (bar)	p ₀ (H ₂) (bar)	p _R ^b (bar)	t (h)	Aldehyde (%)	n:i	Alcohol (%)
1	2-Butene ^c	125	2	10	19	24	68	98:2	4
2	1-Pentene	110	4	8	18	16	78	99:1	1
3	2-Pentene	125	2	10	18	24	74	99:1	3
4	Octenes ^{d,e}	125	2	10	16	24	10	97:3	0.1
5	Octenes ^{d,e}	125	2	10	16	72	33	98:2	2
6	Octenes ^{d,e}	140	2	10	16	24	33	98:2	3
7	2-Octene ^d	140	2	10	16	24	47	99:1	3
8	Styrene ^f	125	1.5	10.5	15	6	87	84:16	1

^a Reaction conditions: aqueous phase: buffer (pH: 8), 73 mmol olefin, olefin:BINAS:Rh = 2000:5:1. ^b Pressure at reaction temperature. ^c 144 mmol 2-butene (E/Z-mixture), 2-butene:BINAS:Rh = 4000:5:1. ^d Aqueous phase: 19 ml H₂O + 1 ml triethanolamine + 20 ml PEG 300. ^e Octene mixture (1:2:3:4 = 4:46:34:13). ^f 36.5 mmol styrene, styrene:BINAS:Rh = 5000:10:1, addition of styrene at reaction temperature.

system to give phenylpropanals in 87% yield (TOF = 725 h⁻¹; n:i = 84:16). Due to the easier hydrogenation of styrene, a lower catalyst concentration is advantageous compared to the other experiments.

In conclusion, we have shown here for the first time that the carbonylation of internal olefins in a biphasic water system is possible. It is shown that control of the pH and CO partial pressure are important factors for successful reactions. Interestingly, the water-soluble catalyst leads to significantly higher regioselectivity compared to similar catalysts soluble in organic solvents. The obtained n/i-selectivities exceed all known literature data and the catalyst can be easily reused several times.

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