



High-pressure effects in the homogeneously catalyzed hydroformylation of olefins

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Abstract

The homogeneously catalyzed hydroformylation of linear olefins was investigated at pressures ranging from 7 to 550 MPa. A change in the selectivity was observed, which was reflected by a change of the product distribution. At high-pressures, increased yields of aldehydes were also obtained from the hydroformylation of sterically hindered olefins.

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1. Introduction

Homogeneous catalysis offers an efficient access to high-value products that require high product purity and, hence, high synthesis selectivity. During the last decades, many efforts were made to enhance selectivities and productivities by the utilization of non-classical conditions in homogeneous catalysis, e.g. through multi-phase catalysis [1] with novel reaction media [2,3] or through ultrasonic or microwave activation [4].

Although high-pressure reaction technology was industrially introduced in heterogeneous catalysis nearly 90 years ago, most homogeneously catalyzed processes are operated with pressures lower than 30 MPa. According to the Le-Chatelier principle, reactions with a negative entropy should preferably be carried out at high-pressures, if gases are involved. With a process economy being high enough, which has to be expected in particular for high-value products, also cost-intensive high-pressure technologies could be economically efficient.

Surprisingly, systematic approaches to studying high-pressure effects in homogeneous catalysis are very rare.

The present study focuses on the investigation of rhodium-catalyzed hydroformylation of olefins in order to understand the effect of high-pressure on the conversion rate, aldehyde selectivity and olefin isomerization.

2. Experimental

All experiments were performed in a newly constructed equipment (Fig. 1). It allows for the experiments being carried out under inert conditions in two different batch reactors at pressures of up to 15 MPa (reactor A, Fig. 2a) and 700 MPa (reactor B, Fig. 2b), respectively, and at temperatures of up to 200 °C [5]. Reactor A was made by the mechanical workshop of the Forschungszentrum Karlsruhe. High-pressure reactor B, high-pressure valves, tubings and fittings were delivered by Sitec Sieber Engineering AG, Switzerland. Other valves, tubings, and fittings were purchased from Swagelok, USA.

All manipulations of substances were carried out under an atmosphere of dry argon using standard Schlenk techniques. Hydroformylation reactions were carried out either in the stainless steel reactor A equipped with an electronic manometer, a thermocouple, and a magnetic stirrer, or in the high-pressure reactor B that was equipped with an electronic manometer and a thermocouple, but not with a stirrer. Temperature and pressure data were collected and stored by

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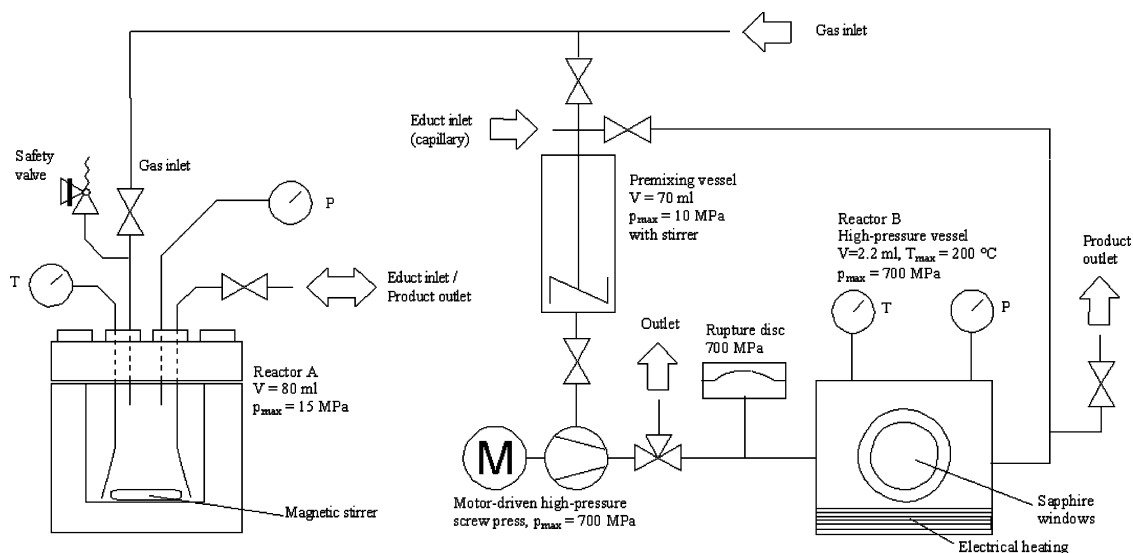


Fig. 1. High-pressure set-up for homogeneously catalyzed reactions.

a PC. Yields of aldehydes were determined by GC/FID and GC/MS analysis. Commercially available reagents and purified solvents were used as received or freshly degassed.

2.1. Synthesis of the Rh precatalyst $\text{Rh}(\text{cod})(\text{PPh}_3)_2\text{BF}_4$ (**1**)

Starting from RhCl_3 , $[\text{Rh}(\text{cod})\text{Cl}]_2$ (**2**) was synthesized as described in literature [6–8]. In a second step, (**2**) was converted into $\text{Rh}(\text{cod})_2\text{BF}_4$ (**3**) [9].

A solution of (**3**) (272.5 mg, 0.67 mmol) in 200 ml of dry toluene with a three-fold excess of triphenylphosphine

(534.9 mg, 2.04 mmol) was stirred for 48 h at 25 °C. After the color had changed from orange to yellow, precipitation of a yellow solid, $\text{Rh}(\text{cod})(\text{PPh}_3)_2\text{BF}_4$ (**1**), was observed. The solid was filtered and washed three times with 10 ml of pentane, then dried in a vacuum. The yield of (**1**) amounted to: 506.6 mg (93.0%), mp: 192 °C.

^1H NMR data (CDCl_3 , 250 MHz): 2.1–2.5 (m, 8H, COD: CH_2); 4.5 (s, 4H, COD: CH); 7.2–7.3 (m, 30H, PPh_3). ^{13}C ^1H NMR data (CDCl_3 , 63 MHz): 31.0 (COD: CH_2); 99.5 (d, $|^1J_{\text{Rh,C}}| = 4.6$ Hz, COD: CH); 129.1 (PPh_3 - C_{meta}); 130.7 (PPh_3 - C_{para}); 131.4 (PPh_3 - C_{ortho}); 134.5 (PPh_3 - C_{ipso}). ^{31}P

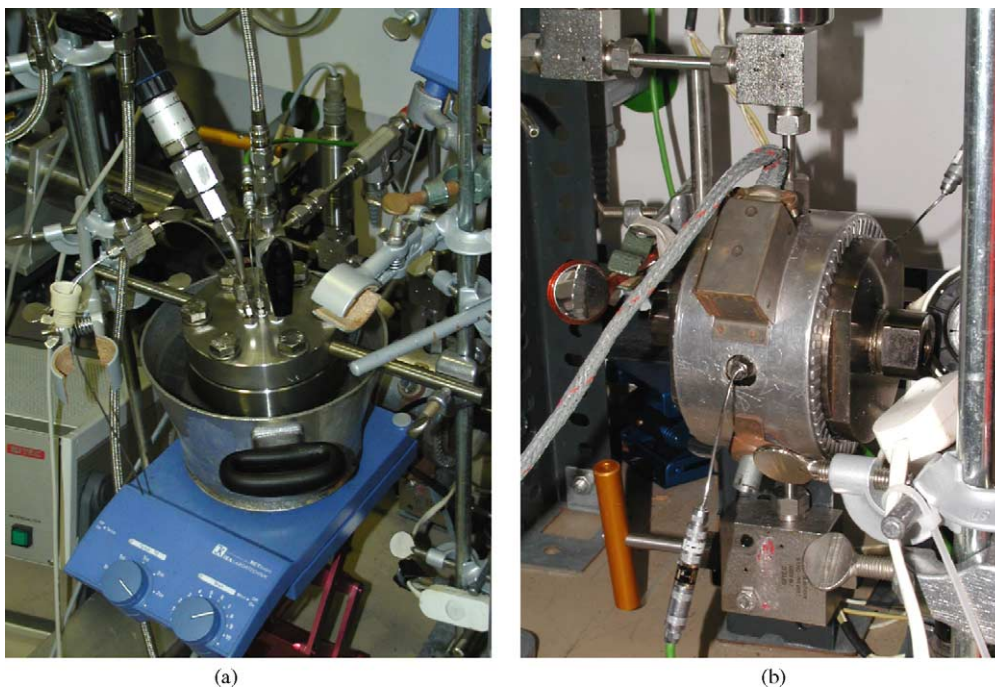


Fig. 2. (a) Reactor A ($p_{\text{max}} = 15$ MPa), (b) reactor B ($p_{\text{max}} = 700$ MPa).

^1H NMR data: (CDCl_3 , 101 MHz): $\delta = 27.4$ (d, $|^1J_{\text{Rh,P}}| = 145.2$ Hz, PPh_3). Anal. calculated (%) for $\text{C}_{44}\text{H}_{42}\text{RhP}_2$ ($M = 822.4$): C 64.26; H 5.15. Found: C 63.43; H 5.10. IR (KBr): 521(s), 696(s), 749(m), 1056(s), 1086(s), 1306(w), 1436(s), 1480(m), 2830(w), 2875(w), 2921(w), 3046(w) cm^{-1} .

2.2. X-ray crystallographic analysis of (1)

Yellow crystalline needles of $\text{Rh}(\text{cod})(\text{PPh}_3)_2\text{BF}_4$ (1) were grown from a toluene solution. The intensity data of (1) were collected by a Siemens Smart 5000 CCD diffractometer using graphite-monochromatic $\text{Mo K}\alpha$ radiation. The data were corrected for Lorentz, polarization, and absorption effects. The structure was resolved by direct methods and refined for F^2 by full-matrix least squares techniques. Fig. 3 illustrates the structure of (1), crystallographic data are given in Table 1, selected bond lengths and angles are presented in Table 2.

2.3. Catalysis

The catalyst ((1), 20 μmol) and substrate (1-octene, 1.7 up to 4.0 mmol) are dissolved in 50 ml of CH_2Cl_2 , if not stated otherwise (substrate/catalyst ratio: 85 up to 200). The substrate solution is saturated with synthesis gas (7 MPa, H_2/CO ratio = 1:1). In reactor A (inner volume: 80 ml), a gas reservoir remains above the liquid phase, from which more gas enters the solution during the reaction. In reactor B, only liquids compressed with a screw press are used. Thus, the solution is saturated with synthesis gas in a pre-mixing vessel prior to compression (see Fig. 1). Afterwards, one part of the liquid phase is used for complete filling of reactor B (inner volume: 2.2 ml). The reactors are heated

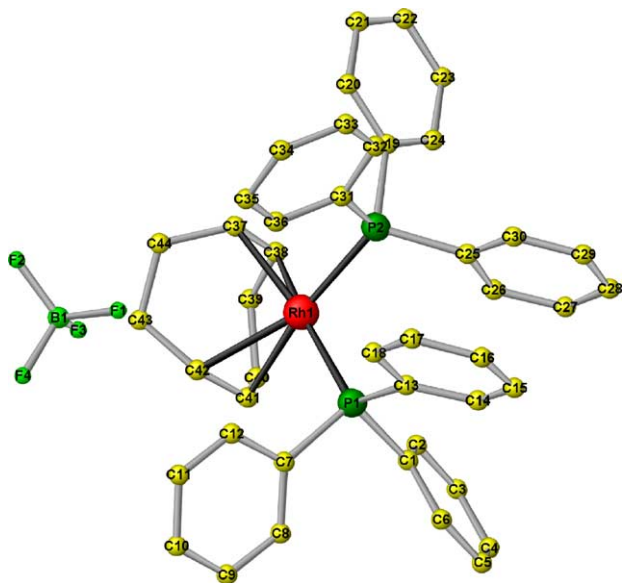


Fig. 3. Molecular structure of (1) in the crystal.

Table 1
Crystallographic data of $\text{Rh}(\text{cod})(\text{PPh}_3)_2\text{BF}_4$ (1)

Compound	$\text{Rh}(\text{cod})(\text{PPh}_3)_2\text{BF}_4$
Empirical formula	$\text{C}_{44}\text{H}_{42}\text{BF}_4\text{P}_2\text{Rh}$
Formula weight	822.475
Crystal size	0.4 mm \times 0.2 mm \times 0.25 mm
Crystal system	Monoclinic
Space group	Cc (no. 9)
Unit cell dimensions	$a = 2186.43(14)$ pm $b = 1083.66(7)$ pm $c = 1891.30(12)$ pm $\alpha = 90^\circ$ $\beta = 121.78900(10)^\circ$ $\gamma = 90^\circ$
Volume	3808.9×10^6 pm 3
Z	2
Density (calculated)	1.436 g/cm 3
Diffractometer	Siemens SMART 5000 CCD diffractometer
Wavelength	$\text{Mo K}\alpha$, graphite monochromator
Temperature	200(2) K
θ -Range	$2.18 \leq \theta \leq 28.30^\circ$
Scan	ω -Scan, $\Delta\omega = 0.3^\circ$
Index ranges	$-29 \leq h \leq 27$, $-14 \leq k \leq 14$, $-24 \leq l \leq 24$
Number of	
Reflections measured	19497
Independent reflexions	8705
Reflexions observed	8705
Parameters refined	479
Residual electron density	0.398×10^{-6} e/pm 3
Corrections	Lorentz and polarization, absorption correction (SADABS) [10]
Structure solution	Direct methods
Structure refinement	Full-matrix least square on F^2
Programs used	SHELX-97 [11], xpma, zortep [12]
R indices	
R_1	0.0487 ($I > 2\sigma$)
R_w	0.0811 (all data on F^2)

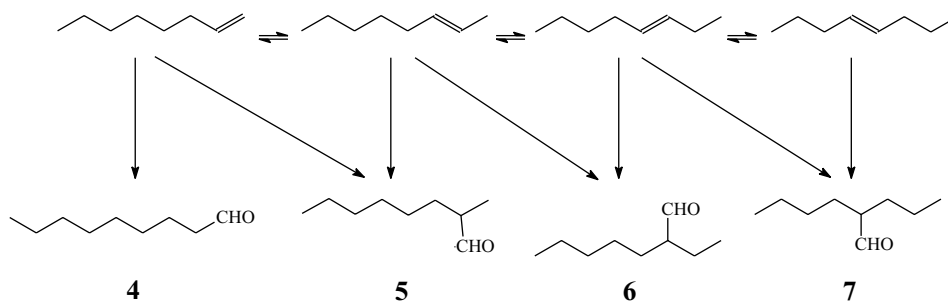
Standard deviations in parentheses.

up to 70 $^\circ\text{C}$ inner temperature. The reaction is monitored by pressure measurement. After the experiments (16 h), reactors A and B are cooled to 25 $^\circ\text{C}$ and the product solutions are collected under inert conditions. Yields and selectivities, based on the consumption of 1-octene, are determined by gas chromatographic analyses (GC/FID and GC/MS).

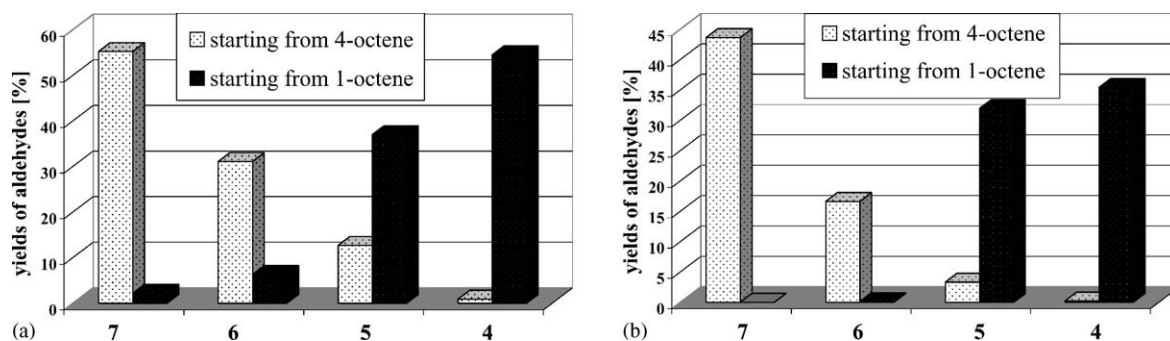
Table 2
Selected bond lengths (pm) and angles ($^\circ$) for $\text{Rh}(\text{cod})(\text{PPh}_3)_2\text{BF}_4$ (1)

Rh1–P1	236.18(12)
Rh1–P2	232.20(10)
Rh1–C37	221.8(5)
Rh1–C38	221.3(4)
Rh1–C41	226.8(4)
Rh1–C42	228.7(3)
P1–Rh1–P2	93.26(4)
C38–Rh1–C41	80.05(15)
C37–Rh1–C42	78.81(15)
C41–Rh1–C42	35.13(14)
C37–Rh1–C38	36.21(16)

Standard deviations in parentheses.



Scheme 1. Isomerization and hydroformylation starting from 1- or 4-octene.

Fig. 4. (a) Hydroformylation at $p = 7$ Mpa, (b) hydroformylation at $p = 500$ MPa. (Reaction conditions and data are taken from Table 3.)Table 3
Hydroformylation of 1- and 4-octene (see also Fig. 4a and b)

Pressure (MPa)	Reactor	Starting material	Selectivities (%)				Octane (%)	Isomeric octenes (%)	<i>l/b</i> ratio	Yield (%)	Conversion (%)	Reaction time (h)
			(4)	(5)	(6)	(7)						
6.4	A	1-Octene	54.5	37.0	6.3	2.2	0.0	0.0	1.5	>99.9	>99.9	6.1
500	B	1-Octene	51.8	48.1	0.1	0.0	0.0	4.8	1.1	68.4	73.2	17.0
7	A	4-Octene	0.9	12.7	31.1	55.2	0.0	0.0	–	99.9	99.9	7.0
500	B	4-Octene	0.3	5.2	26.1	68.4	0.0	4.1	–	63.7	67.8	16.0

Catalyst: Rh(cod)(PPh₃)₂BF₄ (1), temperature: 70 °C, solvent: CH₂Cl₂, stirred in reactor A, not stirred in reactor B. Yields and selectivities based on GC analysis (for more details see Section 2).

3. Results and discussion

In the hydroformylation of linear octenes, competition of olefin isomerization and hydroformylation may lead to four different aldehydes (4)–(7) in principle, as is outlined in Scheme 1.

3.1. Hydroformylation of 1-octene

For hydroformylation starting from 1- or 4-octene, Rh(cod)(PPh₃)₂BF₄ (1) was used [13–15]. Preliminary experiments have shown that the catalyst is moderately stable, also with respect to traces of air and water.¹

¹ The solvent dichloromethane was chosen because of practical reasons (solubility of catalyst, educts, and products, different retention time in GC analysis). Experiments with other organic solvents (e.g. THF, toluene) did not reveal any dependency of the obtained selectivities on the solvent.

Results from the hydroformylation experiments at different pressures are presented in Table 3. The main products when starting from 1-octene are 1-nonanal (4) and 2-methyl-octanal (5) as expected. These products also represent the direct hydroformylation products. (6) and (7) are generated after the isomerization of 1-octene. At a pressure of 7 MPa, all products (4)–(7) are found in descending quantities, as expected. At a pressure of 500 MPa, however, product selectivity is changed significantly: the aldehydes (6) and (7) cannot be observed, which indicates that the isomerization of 1-octene is nearly completely suppressed under these conditions (Table 3, Fig. 4a and b).

Due to the different conditions of the experiments in reactors A or B, the yield and conversion values shown in Table 1 are not completely comparable. As reactor B is not stirred, reaction times are probably longer. Furthermore, a gas reservoir is located above the reaction mixture in reactor A, from which additional gas is supplied during the

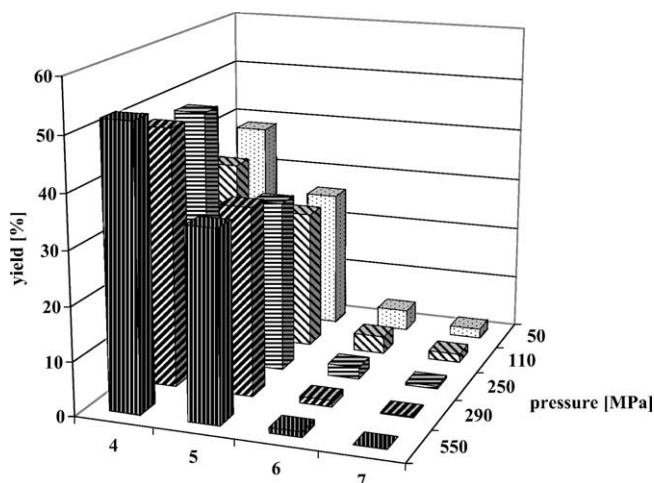


Fig. 5. Product distribution in the hydroformylation of 1-octene as a function of pressure.

conversion of 1-octene (at decreasing gas pressure). As reactor B has no gas reservoir, all gases have to be dissolved in the educt solution before the reaction is started.

3.2. Hydroformylation of 4-octene

Reaction of 4-octene as the substrate at 7 MPa yields all products (4) through (7). In this case, aldehyde (7) is the only direct hydroformylation product (Scheme 1). For the formation of aldehydes (4)–(6), isomerization of 4-octene has to take place prior to hydroformylation. At a pressure of 7 MPa, the product distribution here is similar to that observed for the hydroformylation of 1-octene at 7 MPa. Similar selectivities are obtained for each pair of (7) (starting from 4-octene) and (4) (starting from 1-octene), (6) and (5), and so on (Fig. 4a).

At 500 MPa (Fig. 4b), product distribution is different: (7) again is the main product, but quantities of (6) and (5) are lower than in the experiments at 7 MPa. The selectivity of (4) is less than 0.3%. Compared to the experiments starting from 1-octene, it is now interesting to note that the aldehydes (6) and (5) are generated in quite large quantities, although these products require the isomerization of 4-octene. Hence, in high-pressure reactions, starting from 4-octene, isomerization of olefin is also reduced, but not completely as it is in the case for 1-octene (Fig. 4a and b, data are taken from Table 3).

From the calculated heats of formation ($\Delta H_f^\circ(1\text{-octene}) = -82.7 \text{ kJ/mol}$, $\Delta H_f^\circ(4\text{-octene}) = -94.3 \text{ kJ/mol}$ [16,17]), an inverse product distribution is expected by thermodynamic control. As at 500 MPa, isomerization from the inner to the outer olefin (experiments starting from 4-octene) prevails over that from the outer to the inner olefin (experiments starting from 1-octene), pressure influence on isomerization is assumed to be a kinetic effect.

3.3. Yields and selectivities at high-pressure

In the hydroformylation of 1-octene under comparable reaction conditions, pressure increasing from 50 to 550 MPa leads to increased yields of (4) and (5). The aldehydes (6) and (7) (not generated directly from 1-octene) are found in descending quantities with increasing pressure (Fig. 5). Subsequent hydrogenation to octane does not take place in any experiment under these conditions.

Fig. 6 shows the linear/branched ratio as a function of pressure in 30 hydroformylation experiments. All experiments were carried out at a temperature of 70 °C over a reaction time of approximately 16 h. The variations of the values measured at the same pressure result from the difficult to reproduce reaction conditions, e.g. gas saturation.

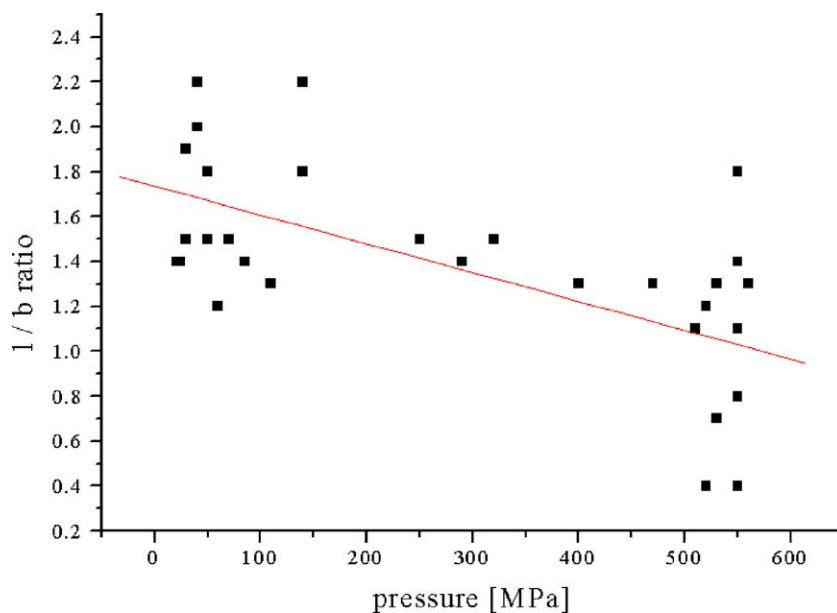
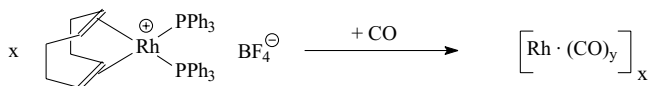
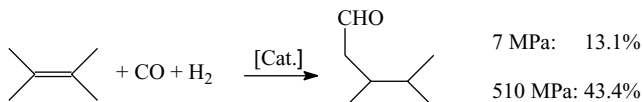


Fig. 6. *l/b* ratio as a function of pressure in the hydroformylation of 1-octene.



Scheme 2. Possible substitution of phosphines by carbon monoxide.



Scheme 3. Yields of the hydroformylation of 2,3-dimethyl-2-butene at different pressures.

In the hydroformylation of 1-octene, the selectivity to the linear aldehyde tends to decrease with increasing pressure (decreasing *l/b* ratios).

Under high-pressure conditions, the phosphine ligands in the active catalyst formed from (1) are assumed to be partially or completely substituted by carbon monoxide, yielding an unmodified rhodium catalyst system (Scheme 2) that is commonly known to produce low *l/b* ratios [18,19].

3.4. Hydroformylation of other olefins

Hydroformylation of sterically hindered, substituted butenes was found to produce increasing yields of aldehydes with increasing pressure in general. When testing 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene, 2-methyl-1-butene, 2-methyl-2-butene, and 3-methyl-1-butene, the corresponding aldehydes were obtained in all cases. Most interestingly, the yields of conversion of 2,3-dimethyl-2-butene into 3,4-dimethylpentanal rose from 13.1 to 43.4% when pressure was increased from 7 to 510 MPa (Scheme 3) under the same reaction conditions (temperature and reaction time). In this case, isomerization of the olefin prior to hydroformylation is necessary.

4. Conclusions

In a newly constructed experimental set-up for reactions of compressed liquids up to 700 MPa, pressure influence on the hydroformylation of octenes and substituted butenes was studied. At high-pressures, the yields of aldehydes generally increase. Lower *l/b* ratios at higher pressures are believed to result from the formation of an unmodified rhodium catalyst.

Furthermore, isomerization of the olefin prior to hydroformylation is completely suppressed in the conversion of 1-octene at high-pressures, whereas the isomerization of 4-octene finally leads to a mixture of all possible aldehydes: isomerization of 4-octene is less hindered at high-pressures

than is the isomerization of 1-octene. The pressure effect on the isomerization rates is assumed to be a kinetic effect.

Yields of hydroformylation of sterically hindered, substituted butenes were found to increase at high-pressures.

5. Supplementary material

Crystallographic data of the structure has been deposited at the Cambridge Crystallographic Database Centre, supplementary publication no. CCDC 234356 (1). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033, email: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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