



Triphenylphosphine modified rhodium catalyst for hydroformylation in supercritical carbon dioxide

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ABSTRACT

The kinetics of 1-octene hydroformylation catalyzed by triphenylphosphine modified rhodium in carbon dioxide have been explored at 90 °C and pressures up to 48 MPa. The apparent catalyst solubility was determined by evaluating the reaction rate for different rhodium amounts. The kinetics follow a first order in 1-octene, a negative order of -1.2 in carbon monoxide, an order of 0.25 in hydrogen, and a negative order of -0.2 in triphenylphosphine, which is to a great extent in agreement with studies on the hydroformylation of linear 1-alkenes in organic solvents. The observed apparent turnover frequencies range from 1900 to 7000 $\text{mol}_{\text{aldehyde}} \text{mol}_{\text{Rh}}^{-1} \text{h}^{-1}$. These turnover frequencies are of the same order of magnitude as observed for hydroformylations in organic solvents, indicating that rhodium modified with triphenylphosphine can be used with high efficiency in supercritical carbon dioxide rich mixtures.

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1. Introduction

Aldehydes mainly serve as intermediates for the production of solvents, plasticizers and detergents. Their synthesis via hydroformylation of alkenes is an important example of homogeneous catalysis on an industrial scale [1–6]. In this respect, substantial academic and industrial research is devoted to the improvement of homogeneous hydroformylation catalysts based on rhodium [7].

Research focus is on modification of the catalyst and tuning of the reaction environment to improve the hydroformylation rate and selectivity, as well as facilitating a convenient separation of catalyst from the reaction products. Perfluorinated solvents [8–10], ionic liquids [11], water in combination with phase-transfer agents [12], PEGs [13], supercritical fluids and in particular supercritical carbon dioxide (scCO₂) [14–17], and CO₂ expanded solvents [18,19] are regarded as promising alternative solvents [20–22]. Using polymeric or inorganic catalyst supports in conventional organic solvents or in combination with the above mentioned alternative solvents also receives much attention [23–28].

The particular advantages of using carbon dioxide as a solvent over traditional liquid (organic) solvents include improved mass transfer rates, nonflammability, environmentally benign character, convenient separation from reaction products by changing the pressure, and the possibility to create a single phase reaction system [14–17]. In particular for relatively fast reactions, the use of a single phase carbon dioxide rich reaction medium will allow for a reliable estimation of hydroformylation kinetics, because mass transfer limitations will be less pronounced when all reactants reside in a single phase [29,30].

In general, many well-known hydroformylation catalysts have a poor solubility in carbon dioxide rich reaction mixtures [15,16]. Strategies to deal with this poor solubility include the use of cosolvents [31] and other agents [32], and in particular the attachment of perfluoroalkyl substituents [33–42] or other functional groups [43–47] on the phosphorus ligands of the catalyst. An advantage of using perfluoroalkylated phosphorus ligands is that supercritical reaction mixtures at relatively moderate pressures (<30 MPa) can be used; a disadvantage is the additional effort involved in the synthesis of the modified ligands.

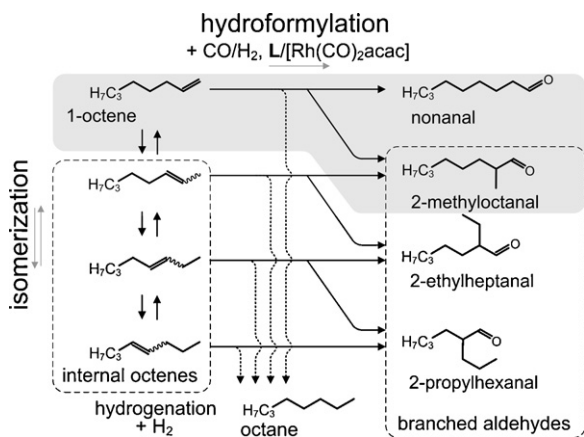
Another approach to improve the efficiency of common hydroformylation catalysts in supercritical carbon dioxide rich media is to adapt the reaction medium density and temperature [48]. An advantage of this approach is that no additional effort has to be put in ligand modification; drawbacks are associated with the required higher initial pressures, typically exceeding 30 MPa. Recently, it has been demonstrated that initial turnover frequencies (TOF) higher than 1000 $\text{mol}_{\text{aldehyde}} \text{mol}_{\text{Rh}}^{-1} \text{h}^{-1}$ can be achieved at temperatures of 70 and 90 °C at initial pressures higher than 40 MPa for the hydroformylation of 1-octene with the well-known triphenylphosphine

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Scheme 1. Reaction scheme for the hydroformylation of 1-octene (**1a**), with the two main products nonanal (**2a**) and 2-methyloctanal (**2b**). The side products are (E,Z)-2-octene (**1b**, **1c**), (E,Z)-3-octene (**1d**, **1e**), (E,Z)-4-octene (**1f**, **1g**), 2-ethylheptanal (**2c**), 2-propylhexanal (**2d**), and *n*-octane (**3**). **L** is the phosphorus ligand.

modified rhodium catalyst in a supercritical carbon dioxide rich reaction mixture [48].

Little is known about the kinetics of the hydroformylation with Rh/PPH₃ in a supercritical medium. The only kinetic effect established for triphenylphosphine modified rhodium catalyzed hydroformylation in carbon dioxide is that an increase in PPH₃ concentration reduces the reaction rate and increases the selectivity for the linear product [47–49].

There are several reports about the reaction kinetics of hydroformylation of 1-alkenes with the Rh/PPH₃ catalyst in organic solvents. Among the earliest and more extensive examples are contributions of Wilkinson and co-workers [50,51] and Andreetta and co-workers [52–54]. Generally, the reaction conditions chosen in the various studies, like reactant concentration, catalyst concentration, and temperature differ widely. As a result, kinetic expressions vary widely with respect to reaction orders in reactant concentration and, if taken into account, triphenylphosphine concentration.

In this paper an explorative study is presented of reaction kinetics of hydroformylation of 1-octene (Scheme 1) in a supercritical medium rich in carbon dioxide, catalyzed by rhodium modified with triphenylphosphine.

Reaction conditions have been chosen based on results obtained previously [48]. The ligand concentration (0.01–0.03 mol L⁻¹) and temperature (90 °C) used in this study approach industrial conditions [3]. To the best of our knowledge no detailed studies have been reported on hydroformylation kinetics with triphenylphosphine modified rhodium catalyst in a supercritical medium. Furthermore, knowing the conditions where Rh/PPH₃ is applicable in CO₂ is valuable information when one wants to use CO₂ as an antisolvent to precipitate the catalyst from the product aldehyde phase. Understanding of the hydroformylation kinetics with Rh/PPH₃ in supercritical carbon dioxide will allow for a meaningful comparison with the performance of Rh/PPH₃ in organic solvents and may shed light on the mechanism of hydroformylation in supercritical carbon dioxide.

2. Experimental

2.1. Materials

Carbon dioxide, carbon monoxide, and hydrogen, grade 5.0, 4.7, and 5.0, respectively, were obtained from Hoekloos (The Netherlands). Prior to use CO₂ was passed over a Messer Oxisorb filter to remove oxygen and moisture. 1-Octene, **1a**, obtained from Aldrich, was passed over activated alumina, dried with pre-

treated molsieves 3 Å (Aldrich, 4–8 mesh), and stored under argon. The rhodium precursor, dicarbonyl rhodium(1)-2,4-pentanedione ([Rh(CO)₂(acac)]), was obtained in the form of dark green crystals from Fluka. Triphenylphosphine (white to off-white powder, reagent plus, 99% purity) was obtained from Aldrich. The catalyst precursors were stored under argon. The solvent toluene (Merck, analytical grade), *n*-heptane (Merck, analytical grade), the internal standard *n*-decane (Aldrich, >99% purity) and the substances involved in the reaction, *n*-octane (Aldrich, >99%), 2-octene (ABCR, mixture of E and Z, 98%) and nonanal (Fluka, >95%) used for the GC-analysis (gas chromatography with flame ionization detection) were used as received.

2.2. Hydroformylation in CO₂

Details on the setup, the general procedures applied during the hydroformylation experiments and the analysis have been reported in detail in references [49,55]. **Important note:** The risks of using the very toxic flammable carbon monoxide gas and the highly flammable hydrogen gas in combination with the use of high pressure were extensively assessed. A variety of safety measures were taken including using detection for carbon monoxide and hydrogen, working in a fume hood, using pressure relief devices, and using equipment with a pressure rating 10–40 MPa above the maximum allowable working pressure of the reactor. Blank reaction runs were performed regularly. In the **Supplementary Information the pressure and temperature profiles are given for the experiments 1–12 in Table 1**, and for a blank reaction run. The procedure for sampling the reactor contents started with rinsing the contents of the tubing connecting the sample volume and reactor with a small volume high-pressure syringe pump. After taking the high pressure sample the content of the sample volume (0.192 mL) was carefully bubbled through a vial with a solution of *n*-decane in toluene and afterwards rinsed with additional toluene solution to collect 1-octene and its reaction products quantitatively. The amount of the toluene solution used, containing 0.01 mol L⁻¹ of *n*-decane as a standard, was determined. By means of GC analysis the concentration of 1-octene and the reaction products in the toluene solution could be determined. Subsequently, the concentrations of 1-octene and reaction products present in the sample volume could be calculated.

2.3. Reaction parameters

To obtain normalized concentration profiles for **1a** and its reaction products, each concentration obtained by GC analysis, C_{GC,i}, was divided by the sum of all obtained concentrations (**1a** and all products) and multiplied by the concentration based on the total amount of **1a**, n_{1a} in mol, injected and the reactor volume, V_{reactor} in L:

$$C_i = \frac{C_{GC,i}}{\sum_i C_{GC,i}} \times \frac{n_{1a}}{V_{reactor}} \quad (1)$$

for *i* = **1a–1g**, **2a–2d** and **3**. The outcome of the hydroformylation was expressed in one of the following parameters. The definitions used were based on Westerterp et al. [56]. The conversion, X, was given by:

$$X = \frac{C_{1a,0} - C_{1a}}{C_{1a,0}} \times 100 \quad (\%) \quad (2)$$

The subscript 0 indicates the normalized concentration at *t* = 0 h. The overall selectivity, S_{*i*}, towards a product *i* was defined as:

$$S_i = \frac{C_i}{C_{1a,0} - C_{1a}} \times 100 \quad (\%) \quad (3)$$

where C_i is the normalized concentration of a product i , with $i = \mathbf{1b-1g, 2a-2d}$ or $\mathbf{3}$. The overall yield, Y_i , for a product i was then:

$$Y_i = \frac{C_i}{C_{\mathbf{1a},0}} \times 100 \quad (\%) \quad (4)$$

The initial overall rate of reaction R_0 (units mol s^{-1}), were estimated by multiplying the initial amount of $\mathbf{1a}$ in mol, $n_{\mathbf{1a},0}$, with the slope of a line fitted through the first four conversion or yield data points. A distinction is made between the linear aldehyde product, $\mathbf{2a}$, and total amount of aldehydes, $\mathbf{2a-2d}$, abbreviated as 'ald'. So, $R_{\mathbf{1a},0}$, $R_{\text{ald},0}$, and $R_{\mathbf{2a},0}$, are the rate of conversion of $\mathbf{1a}$, the rate of formation of aldehydes, and the rate of formation of $\mathbf{2a}$, respectively. The turnover frequency based on the formation rate of aldehydes was calculated as follows:

$$\text{TOF}_{\text{ald}} = \frac{R_{\text{ald},0}}{n_{\text{Rh}}} \times \frac{3600 \text{ s}}{1 \text{ h}} \quad (5)$$

where n_{Rh} is the overall amount of Rh used in mol. The (cumulative) $l:b$ ratio was obtained by dividing the concentration of linear aldehyde product by the sum of the concentrations of the branched aldehyde products:

$$l : b = \frac{C_{\mathbf{2a}}}{C_{\mathbf{2b}} + C_{\mathbf{2c}} + C_{\mathbf{2d}}} \quad (6)$$

The initial differential $l:b$ ratio, $l:b_0$, was estimated with the following equation:

$$l : b_0 = \frac{R_{\mathbf{2a},0}}{R_{\text{ald},0} - R_{\mathbf{2a},0}} \quad (7)$$

The differential selectivity $\Sigma_{q,k}$ for product q was determined by:

$$\Sigma_{q,k} = \frac{Y_{q,\text{sample}_{k+1}} - Y_{q,\text{sample}_k}}{X_{\text{sample}_{k+1}} - X_{\text{sample}_k}} \quad (8)$$

with $q = \mathbf{1b-1g, 2a-2d}$ and $\mathbf{3}$. k runs from 1 to the total number of samples taken during an experiment minus 1. $\Sigma_{q,k}$ was only evaluated for total amount of aldehydes and for $\mathbf{2a}$. The differential $l:b$ ratio was calculated as follows:

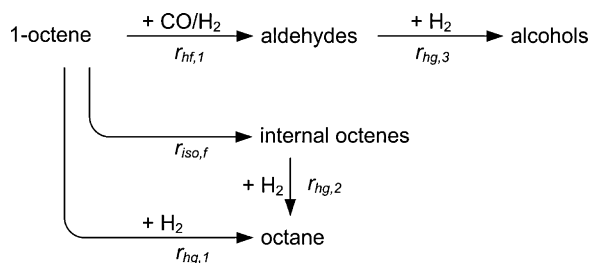
$$\text{differential } l : b_k = \frac{\Sigma_{\mathbf{2a},k}}{\Sigma_{\mathbf{2b},k} + \Sigma_{\mathbf{2c},k} + \Sigma_{\mathbf{2d},k}} \quad (9)$$

The differential parameters were evaluated as a function of aldehydes yield. The yield values corresponding to differential parameter values were calculated as follows:

$$Y_k = \frac{(Y_{\text{sample}_{k+1}} + Y_{\text{sample}_k})}{2} \quad (10)$$

2.4. Kinetic model

The kinetic model was based on the reaction network given in Scheme 2. According to this scheme the mass balances for a fixed volume batch reactor were set up (Eqs. (11)–(19)). The rate equations ($r_{\text{hf},1}$, $r_{\text{iso},f}$, $r_{\text{hg},1}$, $r_{\text{hg},2}$, $r_{\text{hg},3}$) for the various reaction steps are



Scheme 2. The reaction scheme used to derive the mass balances.

given as Eqs. (20)–(24) (below). The kinetic parameters $k_{\text{hf},1}$, $k_{\text{iso},f}$, $k_{\text{hg},1}$, $k_{\text{hg},2}$, and $k_{\text{hg},3}$ are the reaction rate constants for $r_{\text{hf},1}$, $r_{\text{iso},f}$, $r_{\text{hg},1}$, $r_{\text{hg},2}$, and $r_{\text{hg},3}$, respectively. p_1 – p_4 are the orders in reactant and catalyst precursor in $r_{\text{hf},1}$. The formation of internal octenes, octane, and alcohols are taken into account in this model. However, as the concentrations of these components were so low in the initial stage of the reaction, the calculated values of the kinetic parameters $k_{\text{iso},f}$, $k_{\text{hg},1}$, $k_{\text{hg},2}$, and $k_{\text{hg},3}$ were of minor significance. The hydroformylation of internal octenes to form branched aldehydes was neglected. It is known that the Rh/PPh₃ catalyst has a relatively low activity in the hydroformylation of secondary alkenes [51]. All the obtained values are given in the Supplementary Information.

$$\frac{dC_{\text{CO}}}{dt} = -r_{\text{hf},1} \quad (11)$$

$$\frac{dC_{\text{H}_2}}{dt} = -r_{\text{hf},1} - r_{\text{hg},1} - r_{\text{hg},2} - r_{\text{hg},3} \quad (12)$$

$$\frac{dC_{\text{1-octene}}}{dt} = -r_{\text{hf},1} - r_{\text{hg},1} - r_{\text{iso},f} \quad (13)$$

$$\frac{dC_{\text{internal octenes}}}{dt} = r_{\text{iso},f} - r_{\text{hg},2} \quad (14)$$

$$\frac{dC_{\text{octane}}}{dt} = r_{\text{hg},1} + r_{\text{hg},2} \quad (15)$$

$$\frac{dC_{\text{aldehydes}}}{dt} = r_{\text{hf},1} - r_{\text{hg},3} \quad (16)$$

$$\frac{dC_{\text{alcohols}}}{dt} = r_{\text{hg},3} \quad (17)$$

$$\frac{dC_{\text{Rh}}}{dt} = 0 \quad (18)$$

$$\frac{dC_{\text{PPh}_3}}{dt} = 0 \quad (19)$$

$$r_{\text{hf},1} = k_{\text{hf},1} C_{\text{CO}}^{p_1} C_{\text{H}_2}^{p_2} C_{\text{1-octene}}^{p_3} C_{\text{PPh}_3}^{p_4} C_{\text{Rh}} \quad (20)$$

$$r_{\text{iso},f} = k_{\text{iso},f} C_{\text{1-octene}} C_{\text{Rh}} \quad (21)$$

$$r_{\text{hg},1} = k_{\text{hg},1} C_{\text{H}_2} C_{\text{1-octene}} C_{\text{Rh}} \quad (22)$$

$$r_{\text{hg},2} = k_{\text{hg},2} C_{\text{H}_2} C_{\text{internal octenes}} C_{\text{Rh}} \quad (23)$$

$$r_{\text{hg},3} = k_{\text{hg},3} C_{\text{H}_2} C_{\text{aldehydes}} C_{\text{Rh}} \quad (24)$$

For all computations Matlab version 7.7.0.471 (R2008b) was used. Using the built-in function script 'lsqnonlin.m' the so-called objective function was minimized [57]. Vector F is the input for 'lsqnonlin.m' and is defined as follows:

$$F(\vec{p}) = \text{Data} - \text{Model}(\vec{p}) \quad (25)$$

The objective function is the sum of squares of F . 'Data' represents a matrix containing the concentration data of CO, H₂, 1-octene, octene isomers, octane, aldehydes, and alcohols obtained at the respective sample times for all the experiments. 'Model' is a matrix, which contains the calculated concentration values for the respective reaction components for experiments 3–12. Only the first 4 samples of each experiment were taken into account. The model concentration values were evaluated by solving the mass balances containing the rate equations at the respective experimental sample times. The mass balances were integrated numerically using the built-in ODE solver 'ode113.m' [57]. The rate equations contained the adjustable parameters ($k_{\text{hf},1}$, p_1 , p_2 , p_3 , p_4 , $k_{\text{iso},f}$, $k_{\text{hg},1}$, $k_{\text{hg},2}$, and $k_{\text{hg},3}$) represented by the vector \vec{p} for which the optimal values were to be calculated using 'lsqnonlin.m'. For the case presented here the built-in function 'lsqnonlin.m' uses a large scale trust-region reflective Newton method to calculate the optimal set of parameters associated with the minimum value of the sum of

Table 1
Summary of conditions and results.^a

Exp. nr.	n_{CO} (mol)	n_{H_2} (mol)	$n_{1\text{a}}$ (mol)	n_{Rh} (10^{-5} mol)	n_{PPh_3} (10^{-3} mol)	TOF ^b ($\text{mol}_{\text{ald}} \text{mol}_{\text{Rh}}^{-1} \text{h}^{-1}$)	R_{ald}^c ($10^{-3} \text{mol}_{\text{ald}} \text{L}^{-1} \text{s}^{-1}$)	$l:b^d$	t_r^e (h)	X^f (%)	S^f (%)	
											2a	2b
1	0.083	0.080	0.079	2.65	1.10	1990	0.135	3.1	0.71	49	75	24
2	0.083	0.080	0.079	2.16	1.09	2410	0.134	3.1	0.69	47	75	24
3	0.083	0.080	0.078	1.39	1.09	3730	0.133	3.1	0.68	46	75	24
4	0.082	0.081	0.078	0.74	1.11	4750	0.090	3.2	1.00	44	75	24
5	0.082	0.134	0.079	1.34	1.09	4480	0.155	3.2	0.73	56	75	24
6	0.136	0.081	0.079	1.37	1.11	1910	0.067	3.0	1.05	36	74	25
7	0.082	0.080	0.106	1.32	1.09	5550	0.187	3.1	0.63	44	75	24
8	0.082	0.135	0.106	1.37	1.11	7050	0.248	3.2	0.58	54	75	23
9	0.135	0.080	0.106	1.48	1.11	2760	0.105	3.0	0.96	38	74	25
10	0.109	0.109	0.102	1.36	1.09	3970	0.139	3.0	0.67	37	74	25
11	0.109	0.109	0.102	1.45	2.19	3570	0.132	3.1	0.97	49	75	24
12	0.109	0.109	0.102	1.36	3.25	3000	0.104	3.2	0.75	31	75	24

^a General applied conditions: $T=90^\circ\text{C}$, $V_{\text{reactor}}=0.108\text{L}$, $\rho_{\text{CO}_2}=0.56\text{--}0.59\text{kg L}^{-1}$, stirring rate = 700 rpm.

^b Turnover frequency, obtained by multiplying the substrate to catalyst ratio with the slope of a linear fit through the first four data points of the aldehyde yield as a function of time starting at the origin.

^c Calculated by multiplying the TOF with the rhodium amount divided by the reactor volume.

^d The $l:b$ ratio given in this table is determined by the ratio of the initial rate of nonanal formation over the initial rate of 2-methyloctanal formation. The amounts of other branched aldehydes were negligible at conversions reported after a time of reaction, t_r .

^e Reaction time at the time of taking the fourth sample.

^f Conversion, X , and selectivity S after time of reaction t_r , Eqs. (2) and (3) in Section 2.

squares of the function defined in Eq. (26) [57]. To obtain an estimate of the confidence intervals for the optimized values of \bar{p} the built-in Matlab function 'nlparci.m' was used.

3. Results and discussion

3.1. Hydroformylation experiment

Hydroformylation of 1-octene (**1a**) was carried out at 90°C and initial pressures ranging from 38 to 48 MPa. In Table 1 the applied conditions and main results are summarized. The main reaction, the direct formation of **2a** and **2b** from **1a**, CO, and H_2 (Scheme 1) proceeded smoothly with linear over branched aldehyde ratios ($l:b$) ranging between 3.0 and 3.2.

Fig. 1a gives the concentration–time profile of a hydroformylation in CO_2 . The reaction proceeded with a high chemoselectivity for the aldehydes when a near stoichiometric amount of reactants was used. After a reaction time of 0.68 h the selectivity for the linear aldehyde nonanal (**2a**) was 75% and the selectivity for 2-methyloctanal (**2b**) was 24%, see also entry 3 in Table 1. The combined selectivity towards octene isomers, n -octane, and other branched aldehydes was approximately 1%. An initial TOF of $3730 \text{mol}_{\text{aldehyde}} \text{mol}_{\text{Rh}}^{-1} \text{h}^{-1}$ was calculated (entry 3, Table 1).

In Fig. 1b the pressure and temperature during the experiment corresponding to Fig. 1a are depicted. Concentrations for CO, H_2 , and CO_2 of 0.76, 0.74, and 13mol L^{-1} , respectively, amounted to a pressure of 25.5 MPa at 70°C and 31.4 MPa at 90°C . These conditions were sufficient for the formation of the $\text{HRh}(\text{CO})_{4-n}(\text{PPh}_3)_n$ ($n=1, 2, 3$) species out of $[\text{Rh}(\text{CO})_2\text{acac}]$ and PPh_3 in the time interval of -1 to 0 h. This was confirmed by the fact that no apparent induction period was observed for this or any other of the experiments presented here. In other experiments catalyst formation was also performed using $13 \text{mol L}^{-1} \text{CO}_2$, but with the variable concentrations of CO and H_2 necessary to study the influence of CO and H_2 concentration on the hydroformylation. In this manner, the Rh species will be in equilibrium with the amounts of CO and H_2 present at the start of the hydroformylation. Furthermore, this procedure allows for a faster screening of reaction conditions, because the need for a depressurization of the reactor between catalyst preparation and hydroformylation is avoided. At time = 0 h **1a** was injected up to a pressure of

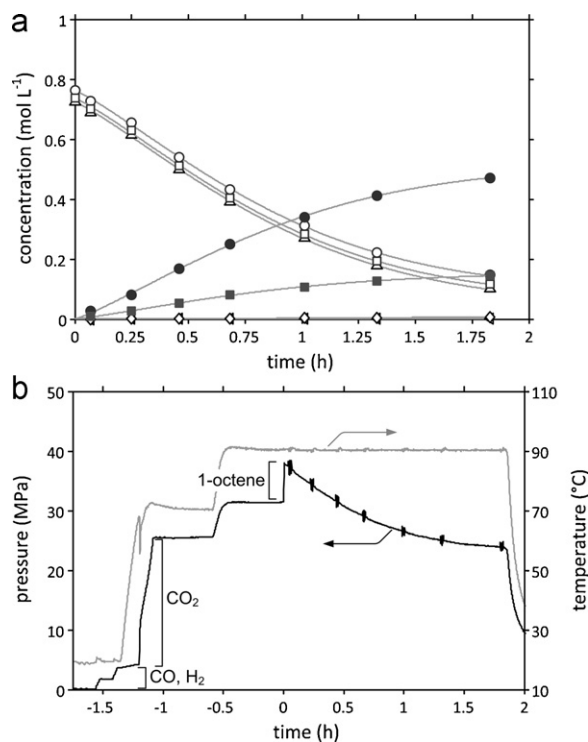


Fig. 1. (a) Concentration–time profile: carbon monoxide (\circ), hydrogen (\square), **1a** (\triangle), **1b+1c** (\diamond), **3** (∇), **2a** (\bullet), **2b** (\blacksquare); (b) pressure and temperature–time profile during a hydroformylation experiment. In both graphs $t=0\text{h}$ designates the start of the reaction.

38.1 MPa to initiate the hydroformylation reaction. Mainly as a result of the reaction and to some extent due to sampling the pressure decreased to 23.8 MPa at 1.8 h corresponding to a conversion of 86%.

3.2. Catalyst solubility

The reactor used in this study does not allow for a visual observation of the phase behavior of the reaction mixture. The maximum positive deviation of the total concentration (sum **1a** and reaction

products) found by GC analysis from the concentration present in the reactor based on the amount of **1a** injected and the reactor volume is about 35%. These deviation values were found in samples from experiments irrespective from the amount of **1a** used or whether the sampling was done from the top or bottom part of the reactor. Such a deviation is to be expected considering the difference in temperature of the reactor, 90 °C, and the sample volume, 20–40 °C [58]. Therefore, the reactants, products, and CO₂ appear to form a single phase in all the experiments discussed in this paper.

The concentrations of rhodium and triphenylphosphine cannot be conveniently determined by GC-analysis. The solubility of an Rh catalyst can be determined using *in situ* FT-IR or UV-vis spectroscopy [33,38,39,59,60]. However, in most cases catalyst solubility was determined using pure CO₂ as a solvent. In a reaction mixture catalyst solubility may be different.

In general, the initial rate of reaction increases proportionally with an increase in the amount of rhodium precursor [53,61]. An order lower than one in metal precursor is usually observed when a catalyst dissolves only partially or when metal dimers or clusters are formed. The low concentration of Rh and the presence of significant concentrations of carbon monoxide, hydrogen, and phosphine ligand make it unlikely that Rh dimers were formed at the initial conditions applied in this study [3,62]. In a kinetic study of [Rh(CO)₂acac]/P(C₆H₃-3,5-(CF₃)₂)₃ catalyzed hydroformylation in scCO₂ a clear first order in Rh was found under conditions approaching conditions used in this study [29,30]. Making use of this knowledge, the solubility of the catalytic species has been investigated by measuring the initial rate of reaction at varying rhodium precursor amounts while keeping the concentration of CO₂, reactants, and triphenylphosphine constant. Starting at 2.65×10^{-5} mol the rhodium amount was decreased to 0.74×10^{-5} mol. The corresponding initial reaction rates are given in Fig. 2 and in Table 1, experiments 1–4. It can be seen that the initial rates are constant at a value of about 0.135×10^{-3} mol_{aldehyde} L⁻¹ s⁻¹ in the range between 1.4×10^{-5} and 2.65×10^{-5} mol Rh. At a rhodium amount of 0.74×10^{-5} mol a lower initial reaction rate is found than at an Rh amount of 1.4×10^{-5} mol. Therefore, based on the assumption of a first order in Rh and taking into account the accuracy of the experiments, the catalyst solubility should be between 0.7×10^{-4} and 1.3×10^{-4} mol L⁻¹ at initial concentrations of 0.76 mol L⁻¹, 0.74 mol L⁻¹, 0.73 mol L⁻¹, and 0.01 mol L⁻¹ for CO, H₂, 1-octene, and triphenylphosphine, respectively. For experiments 1–4 the maximum pressure reached after injection of **1a** was 38–39 MPa with a CO₂ amount of about 62 g. The solubility using the method based on the initial rates at varying Rh amount is significantly higher than the value of about 1×10^{-6} mol L⁻¹ reported for

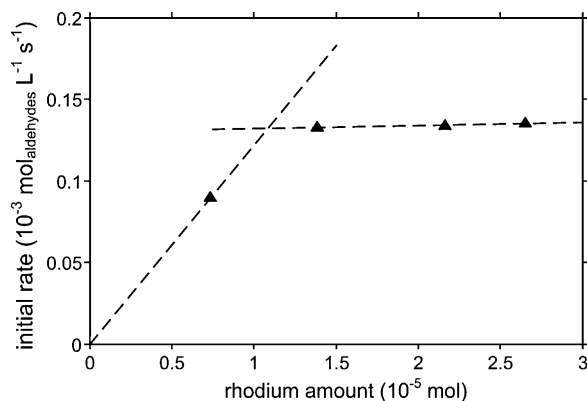


Fig. 2. The initial rate at varying amounts of rhodium precursor. Reaction conditions can be found in Table 1, experiments 1–4. The dashed lines are a guide to the eye.

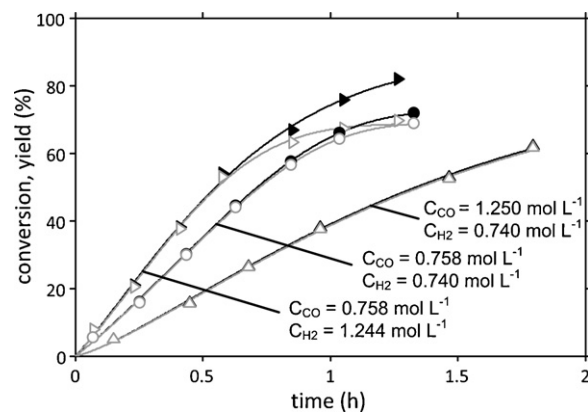


Fig. 3. Conversion and yield as a function of time. Conversion (●) and yield (○) experiment 7 ($C_{\text{CO}} = 0.758 \text{ mol L}^{-1}$, $C_{\text{H}_2} = 0.740 \text{ mol L}^{-1}$); conversion (▲) and yield (△) experiment 8 ($C_{\text{CO}} = 0.758 \text{ mol L}^{-1}$, $C_{\text{H}_2} = 1.244 \text{ mol L}^{-1}$); conversion (▲) and yield (△) experiment 9 ($C_{\text{CO}} = 1.250 \text{ mol L}^{-1}$, $C_{\text{H}_2} = 0.740 \text{ mol L}^{-1}$). The lines indicate the observed trends.

HRhCO(PPh₃)₃ by Shimoyama et al. at 17 MPa and 60 °C in pure CO₂ [39].

3.3. Selectivity

From the data in Table 1 it is clear that the selectivities for the aldehydes **2a** and **2b** are not particularly sensitive to variations in the initial reactant concentrations. After a certain time of reaction (t_r) the selectivities for the aldehydes **2a** and **2b** are 74–75% and 23–24%, respectively. During the course of the reaction the chemo- and regioselectivity only pronouncedly change when an excess of **1a** is used with respect to the amount of CO or H₂. This aspect is illustrated in Figs. 3–5. In Fig. 3 the conversion and aldehyde yield are given as a function of time for the experiments 7–9 in Table 1. For each of these experiments the maximum aldehyde yield is about 75% due to a limiting amount of CO or H₂. Fig. 3 shows that with respect to experiment 7 (0.76 mol L^{-1} CO and 0.73 mol L^{-1} H₂) an increase in initial H₂ concentration brings about a small increase in initial reaction rate. In contrast, an increase in initial CO concentration brings about a significant decrease in initial reaction rate. For each of the experiments the conversion and aldehyde yield practically have the same value as a function of time up to a con-

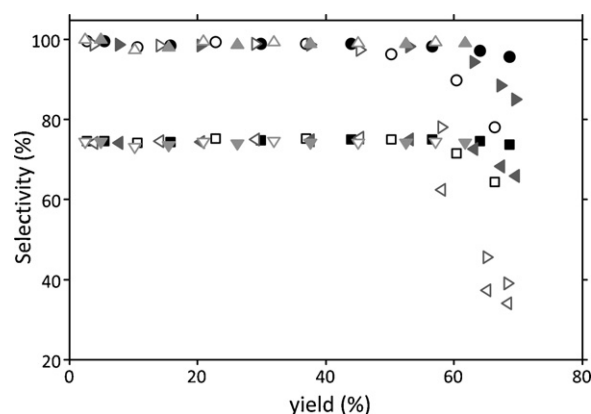


Fig. 4. The selectivity for aldehydes and **2a** as a function of aldehyde yield. Experiment 7 ($C_{\text{CO}} = 0.758 \text{ mol L}^{-1}$, $C_{\text{H}_2} = 0.740 \text{ mol L}^{-1}$): cumulative (●) and differential (○) aldehydes selectivity, cumulative (▲) and differential (△) **2a** selectivity. Experiment 8 ($C_{\text{CO}} = 0.758 \text{ mol L}^{-1}$, $C_{\text{H}_2} = 1.244 \text{ mol L}^{-1}$): cumulative (▲) and differential (△) aldehydes selectivity, cumulative (▼) and differential (▽) **2a** selectivity. Experiment 9 ($C_{\text{CO}} = 1.250 \text{ mol L}^{-1}$, $C_{\text{H}_2} = 0.740 \text{ mol L}^{-1}$): cumulative (▲) and differential (△) aldehyde selectivity, cumulative (▼) and differential (▽) **2a** selectivity.

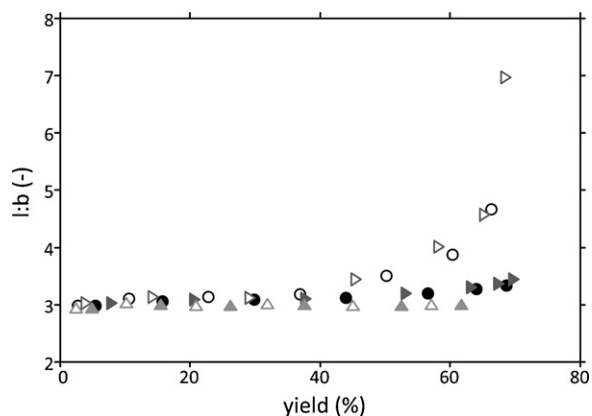


Fig. 5. The $l:b$ ratio as a function of yield. Cumulative (●) and differential (○) $l:b$ for experiment 7 ($C_{CO} = 0.758 \text{ mol L}^{-1}$, $C_{H_2} = 0.740 \text{ mol L}^{-1}$); cumulative (►) and differential (▷) $l:b$ ratio for experiment 8 ($C_{CO} = 0.758 \text{ mol L}^{-1}$, $C_{H_2} = 1.244 \text{ mol L}^{-1}$); cumulative (▲) and differential (△) $l:b$ ratio for experiment 9 ($C_{CO} = 1.250 \text{ mol L}^{-1}$, $C_{H_2} = 0.740 \text{ mol L}^{-1}$).

version of about 60%, which illustrates the high chemoselectivity for aldehydes.

For experiments 7 and 8 at a conversion higher than 60% the conversion increases more rapidly than the aldehyde yield with time, which indicates a decrease in chemoselectivity for aldehydes (Fig. 3). At a conversion level above 60% isomerization of **1a** to the octenes **1b** and **1c**, and the hydrogenation of **1a** into **3** became significant, which is especially clear for the experiment where $1.25 \text{ mol L}^{-1} \text{ H}_2$ has been used (experiment 8 in Table 1). Apparently, at a yield of 60% the concentration of CO reaches a level that is too low to maintain a high chemoselectivity for aldehydes.

In several cases for hydroformylation in scCO_2 the chemo- and regioselectivity change during the course of reaction [35,49]. Therefore, we will evaluate the progress of selectivity through the course of the reaction in some detail here. In Fig. 4 the cumulative and differential selectivity (see Section 2, Eqs. (3) and (8), respectively) for aldehydes and the linear aldehyde **2a** as a function aldehyde yield are compared for different starting concentrations of CO and H_2 corresponding to entries 7–9 in Table 1. For all three cases the respective selectivities remain constant up to an aldehyde yield of about 55%. On average the selectivity for **2a** is slightly lower when a higher initial concentration of CO is used. For experiment 8 the differential selectivities for aldehydes and **2a** decrease significantly at an aldehyde yield above 55%. Furthermore, it appears that for experiment 8 the differential selectivity for aldehydes and **2a** are converging with increasing aldehyde yield, which implies that the hydroformylation is taking place with increasing regioselectivity as the concentration of CO approaches zero. For experiment 8 the chemoselectivity decreases more rapidly than for experiment 7. This is probably a result of the higher initial hydrogen concentration used in experiment 8. An increase in hydrogenation selectivity and a corresponding decrease in hydroformylation chemoselectivity is to be expected when the ratio of the hydrogen concentration over carbon monoxide concentration increases [61,63].

The increase in regioselectivity with an increase in aldehyde yield and a corresponding decrease in CO concentration is apparent in Fig. 5, which gives the cumulative and differential $l:b$ (see Section 2, Eqs. (6) and (9), respectively) for experiments 7–9 as a function of aldehyde yield. At aldehyde yields above 60% the differential $l:b$ ratio increase to values of 5–7 for experiments 7 and 8, respectively. The progress of the differential $l:b$ ratio as a function of aldehyde yield are similar for experiments 7 and 8, indicating that the decrease in CO concentration is the main factor responsible for the increase in regioselectivity and not the hydrogen concentration.

Table 2
Outcome of optimization results with 95% confidence intervals.^a

Parameter	Value
$k_{hf,1} \left[\text{L}^{p_1+p_2+p_3+p_4} \text{mol}^{p_1+p_2+p_3+p_4} \text{s}^{-1} \right]$	0.50 ± 0.05
p_1	-1.18 ± 0.03
p_2	0.25 ± 0.03
p_3	0.97 ± 0.05
p_4	-0.19 ± 0.03

^a Range of concentrations used as input for the calculations: C_{CO} : $0.24\text{--}1.25 \text{ mol L}^{-1}$; C_{H_2} : $0.30\text{--}1.24 \text{ mol L}^{-1}$; $C_{1\text{-octene}}$: $0.32\text{--}0.98 \text{ mol L}^{-1}$; C_{Rh} : $\{0.68\text{--}1.4\} \times 10^{-4} \text{ mol L}^{-1}$; C_{PPh_3} : $0.01\text{--}0.03 \text{ mol L}^{-1}$. For more details see Section 2 and the supplementary information.

3.4. Reaction kinetics

To obtain an estimation of the hydroformylation kinetics a general rate equation is assumed to describe the rate of formation of aldehydes, see Eq. (20). The reaction rate constant $k_{hf,1}$, and reaction orders $p_1\text{--}p_4$ were calculated by a minimization of the so-called objective function, see Section 2 and the Supplementary Information for more details. The concentration–time data (the first four samples) of experiments 3–12 were used as input for the calculations. It is assumed that the reaction is first order in Rh. It must be noted that a relatively small amount of input data are used for the calculations. Therefore, the outcome of the calculations given in Table 2 should be seen as starting point for a more elaborate evaluation of the kinetics. Fig. 6 shows a parity plot, which illustrates how well the experimental data are described by the kinetic model.

A clear negative order in carbon monoxide and triphenylphosphine has been calculated. A first order in **1a** has been calculated. The positive fractional order in hydrogen is closer to zero than to one. An increase in hydrogen does clearly enhance the reaction rate (cf. experiments 3, 5, 7, and 8 in Table 1).

In the range of concentrations studied here, carbon monoxide appears to have a larger effect on the reaction rate than triphenylphosphine. In the study of Cavalieri d'Oro et al. triphenylphosphine (an order of -0.7) had a greater inhibiting effect than carbon monoxide (an order of -0.1) [53]. The relatively small effect which PPh_3 concentration has on the reaction rate might originate from the limited solubility of PPh_3 in the reaction medium. Though, based on literature it is expected that PPh_3 was completely dissolved under conditions used in this study [38,39]. Cavalieri d'Oro observed saturation kinetics in the alkene concentration as indicated by the fractional positive order. It is likely that the differences in orders in alkene, carbon monoxide and triphenylphosphine between propene hydroformylation in toluene [53] and the hydroformylation of **1a** in CO_2 is mainly caused by the differences in the ranges of the respective concentrations of alkene,

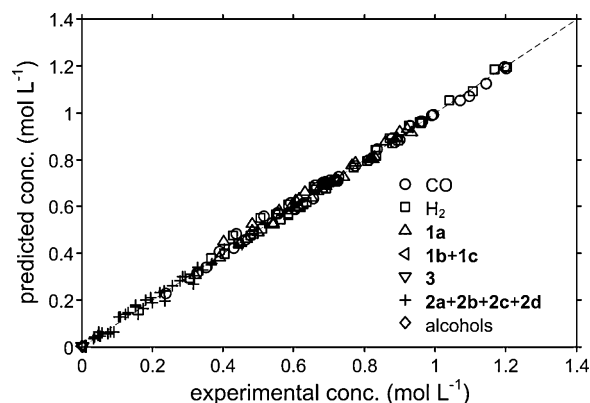


Fig. 6. The predicted concentrations in comparison with the experimentally determined concentrations.

carbon monoxide, and triphenylphosphine, and by solvent effects. The substrate itself will also have an influence on the reaction kinetics. However, generally for linear aliphatic 1-alkenes the reaction orders in carbon monoxide, hydrogen, and alkene do not vary considerably. For Rh/PPH₃ catalyzed hydroformylation in benzene first order dependence of the initial reaction rate on concentration of various 1-alkenes was found [64]. For hydroformylation of ethene, 1-hexene, 1-decene, and 1-dodecene with HRhCO(PPh₃)₃ as catalyst precursor without added PPh₃, Chaudhari and co-workers generally found a positive order in H₂, a negative order in CO above a certain concentration, and first order in alkene up to a certain concentration [65–68].

Overall, it appears that the kinetics found for the hydroformylation of **1a** with the PPh₃ modified Rh in CO₂ shows a good resemblance with type I kinetics as discussed by van Leeuwen, see also Eq. (26) [3,69].

$$\text{rate}_I = \frac{a_1 C_{\text{alkene}} C_{\text{Rh}}}{a_2 + C_{\text{CO}}} \quad (26)$$

where a_1 and a_2 are the kinetic parameters, and C_{alkene} , C_{Rh} , and C_{CO} represent the concentration of alkene, Rh, and carbon monoxide, respectively.

The increase in reaction rate with an increase in hydrogen concentration was unlikely to be a result of a possible increase in solubility of the catalyst. The increase in hydrogen concentration did not result in a significant increase in supercritical reaction mixture density and the density can be regarded as the main parameter affecting catalyst solubility in combination with the temperature [38,70]. For PPh₃ modified Rh, with HRh(CO)(PPh₃)₂ species as the main contributor to the hydroformylation cycle, addition of hydrogen to Rh-acyl species is generally not considered to be the rate determining step in the catalytic cycle and consequently a zero order in hydrogen can be expected [3]. This is apparent from the work of Cavalieri d'Oro et al. [53], Kiss et al. [61], and Salmi et al. [71]. However, in those studies the PPh₃ concentration was often more than 5 times higher than 0.01 mol L⁻¹, the PPh₃ concentration mostly applied here for the hydroformylation in CO₂. In studies where either a small or no excess of triphenylphosphine with respect to rhodium was used an order close to one for the hydrogen concentration was reported [65,67,68]. In those cases the conversion of rhodium dimers into monometallic species can be seen as the cause of the positive effect of a higher hydrogen concentration on the reaction rate [69]. However, as mentioned earlier, formation of a significant concentration of dimers appears unlikely under the conditions applied for the reaction in CO₂. It might be that the small positive order in hydrogen is a result of using CO₂ as a solvent. However, very few studies discuss the effect of CO₂ as a solvent on hydroformylation kinetics and the concentration of intermediates in great detail [72,73]. Further studies have to be conducted to elucidate the small positive fractional order in hydrogen concentration.

The initial turnover frequencies obtained for the hydroformylation of **1a** in CO₂ is in the same range as can be derived from the study of Cavalieri d'Oro on the hydroformylation of propene in toluene (at 90 °C) [53] and in the same range of turnover frequencies reported by van Rooy et al. in the Rh/PPH₃ catalyzed hydroformylation of various 1-alkenes in benzene [64]. Accordingly, it can be stated that for Rh/PPH₃ catalyzed hydroformylation similar catalytic efficiencies, in terms of TOF [74], are possible in CO₂ as compared to organic solvents like toluene or benzene. Still, the initial rate expressed in mol per unit reactor volume per unit of time is lower in CO₂ in comparison with a solvent like toluene, which is a result of the relatively low solubility of Rh/PPH₃ in carbon dioxide rich hydroformylation mixtures. A concentration of 0.7 × 10⁻⁴ to 1.3 × 10⁻⁴ mol L⁻¹ of Rh applied here is about a factor of 10–20 lower than what has often been applied in studies on

hydroformylation of 1-alkenes with triphenylphosphine modified Rh at 90 °C [3,53,64].

4. Conclusion

An apparent solubility of PPh₃ modified rhodium species of 0.07 × 10⁻³ to 0.13 × 10⁻³ mol L⁻¹ has been derived in a reaction mixture with an initial composition comprising 13 mol L⁻¹, 0.76 mol L⁻¹, 0.74 mol L⁻¹, 0.73 mol L⁻¹, and 0.01 mol L⁻¹ for CO₂, CO, H₂, 1-octene, and triphenylphosphine. At a low carbon monoxide concentration, hydroformylation with a high regioselectivity was observed in combination with an increased isomerization and hydrogenation activity. This is in accordance with previous studies with toluene, tetraethylene glycol dimethyl ether, or de product aldehydes as solvents.

Based on an explorative kinetic study at a reaction temperature of 90 °C, a first order in 1-octene concentration, a negative order of -1.2 in carbon monoxide, a positive order of 0.25 in hydrogen, and negative order of -0.2 in PPh₃ was found assuming a first order in rhodium precursor concentration. These hydroformylation kinetics appear to resemble kinetics generally observed for the hydroformylation of aliphatic 1-alkenes where a PPh₃ concentration higher than 0.01 mol L⁻¹ and a rhodium concentration of about 1 × 10⁻³ mol L⁻¹ is applied.

Apparent turnover frequencies ranging from 1900 to 7000 mol_{aldehyde} mol_{Rh}⁻¹ h⁻¹ were observed, which are in a similar range as observed for hydroformylation of 1-alkenes in organic solvents. This study clearly indicates conditions in which the benchmark hydroformylation catalyst Rh/PPH₃ is applicable with high efficiency in supercritical reaction mixtures rich in carbon dioxide. Accordingly, the findings reported here can direct to novel prospects for the use of carbon dioxide rich reaction systems with ligands which are not especially modified for use in carbon dioxide.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.06.014.

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