Kinetics assessment of the homogeneously catalyzed

hydroformylation of ethylene on a Rh-catalyst

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Abstract

The homogeneously catalyzed hydroformylation of ethylene to propanal using a $Rh(H)(PPh_3)_3(CO)$ catalyst has been assessed experimentally in a gas-liquid batch reactor and via microkinetic modeling, based on Wilkinson's dissociative mechanism. A higher reaction rate was observed with increasing temperature, up to 100 °C. Even higher temperatures resulted in catalyst deactivation, which was also attributed to lower total pressures and PPh₃/rhodium molar ratios. The model and its parameters were statistically significant and could be used to simulate the trends observed in the experimental data. Activation energies for the insertion of ethylene and the oxidative addition of H₂ of 42 kJ mol⁻¹ and 48 kJ mol⁻¹, respectively, were obtained. Ethylene insertion and oxidative addition of H₂ were identified as the most kinetically relevant steps in the reaction mechanism.

Topical category: Kinetics, Catalysis, and Reaction Engineering

Keywords: Hydroformylation, ethylene, homogeneous catalysis, rhodium, kinetics, microkinetic model

1. Introduction

Hydroformylation is a chemical reaction in which olefins and syngas, i.e., a mixture of CO and H₂, are converted to aldehydes, containing one more carbon atom than the reactant olefin [1]. It was discovered in 1938 by Otto Roelen under the name "oxo process" [2] and has since then become one of the largest applications of homogeneous catalysis in the chemical industry [3]. With ethylene as reacting olefin, the propanal obtained via hydroformylation can be further converted to other chemicals such as propanol and propylene [4, 5]. Propylene is the chemical with the 4th largest global production volume (around 80 Mt in 2010) and is currently mostly produced through steam cracking [6]. Its production is responsible for the 4th largest greenhouse gas emissions of all bulk chemicals, emitting around 1 ton CO₂-eq/ton propylene [6].

Industrially, ligand-modified homogeneous rhodium and cobalt catalysts are predominantly used to catalyze the hydroformylation [7]. The ligands have an important effect on the performance of the catalyst and a wide range of ligands can be used, including phosphines [8, 9] and phosphites [10] as common choices. One of the most extensively investigated catalysts is the triphenylphosphine (PPh₃)modified Rh catalyst Rh(H)(PPh₃)₃(CO), which is also used in the industry [8], although ligands leading to faster reaction rates have been found, such as certain hydrocarbyl phosphine ligands [4] and pyrrolyl-based phosphorus ligands [11]. The widely-used homogeneous catalysts are highly active and selective, with an ethylene conversion exceeding 98% and an aldehyde selectivity close to 100% for the hydroformylation of ethylene [8]. For olefins containing at least three carbon atoms, the olefin conversion and the aldehyde selectivity are close to 100% as well, but there is formation of both linear and branched aldehydes [12, 13]. However, as a homogeneously catalyzed process, hydroformylation suffers from disadvantages such as difficult catalyst separation/recycling and product stream contamination [3]. Despite major efforts to overcome these drawbacks, it remains a challenge to design heterogeneous catalysts with similar olefin conversions and aldehyde yields as the homogeneous variants which are currently employed industrially [3]. This has led to an increase in the popularity of heterogeneously catalyzed hydroformylation and hydroformylation in general as a research topic, with a particular focus on the reaction mechanism and corresponding kinetics. Recently, an elegant combination of hydroformylation with OCoM (Oxidative Conversion of Methane), which produces ethylene and syngas, has been proposed [14], which further increases the interest in hydroformylation. A strategy for the design of a heterogeneous catalyst which is currently extensively investigated in the literature is the "heterogenization" of the homogeneous catalyst [15], aiming at the immobilization of the ligand-modified homogeneous catalyst, in order to maintain its catalytic performance. Some promising approaches are the immobilization of the ligand-modified rhodium catalyst, such as on a solid support [16], on a polymer [17] or on a polymer grafted on silica [18], and the use of SILP catalysts [19], i.e. porous materials with a thin film of ionic liquid containing the homogeneous catalyst. Other approaches which do not involve immobilization include the separation of the homogeneous catalysts from the products using nanofiltration [20, 21], the use of supercritical CO₂ as a solvent to facilitate catalyst recovery through precipitation [22], the use of a two solvent system to transport the catalyst between the two phases by varying the temperature [23] and the use of a catalyst which can get immobilized through coordination to a metal-organic framework under certain experimental conditions [24].

To design optimal catalysts for olefin hydroformylation, a thorough understanding of the mechanism and the kinetics of the reaction is essential. It is widely accepted in the literature that the most likely mechanism for olefin hydroformylation is Wilkinson's dissociative mechanism [9, 25-27]. The mechanism is illustrated in Figure 1, which represents the current scientific consensus on the mechanism. It consists of a cycle of 6 reaction steps: ethylene coordination $(1 \rightarrow 2)$, ethylene insertion (2 \rightarrow 3), CO coordination (3 \rightarrow 4), CO insertion (4 \rightarrow 5), H₂ oxidative addition (5 \rightarrow 6) and propanal reductive elimination (6 \rightarrow 1). Despite the consensus on the mechanism, there are still many uncertainties on the exact composition of the catalyst during reaction, i.e., which ligands are present on the catalyst, and which reaction steps are kinetically relevant [28]. The original consensus was that the oxidative addition of H_2 was rate determining [28, 29], but it is now understood that the kinetic relevance of the reaction steps depends on the reactant olefin(s), the reaction conditions and the catalyst composition [30, 31]. Numerous density functional theory (DFT) studies have been conducted to investigate the kinetics and thermodynamics of the various reaction steps in the hydroformylation mechanism [28, 32-37]. Correspondingly, kinetic models have been constructed as well [8, 38-40], including a microkinetic one for the hydroformylation of styrene on a homogeneous Rh(BDP) catalyst [41] and the hydroformylation of ethylene on a heterogeneous Rh catalyst [42].



Figure 1: Wilkinson's dissociative mechanism for the hydroformylation of ethylene. L_1 represents a ligand which catalyzes the hydroformylation such as a phosphine or a phosphite ligands, while L_2 represents the same ligand as L_1 or CO. Reworked from [9, 32].

In this work, a microkinetic model is constructed for the hydroformylation of ethylene catalyzed by a homogeneous Rh(H)(PPh₃)₃(CO) catalyst. To the best of our knowledge, no description including such molecular detail exists for the homogeneously catalyzed hydroformylation of ethylene on this catalyst. The current work includes an experimental investigation of the hydroformylation in a gas-liquid batch reactor, which serves as a basis for the proposal of a reaction mechanism and the mathematical description of the kinetics of the elementary steps. A gas-liquid batch reactor was selected as it relatively simple to model and, as the kinetics of the hydroformylation do not depend on the chosen reactor type, any type of reactor could have been used for a kinetic investigation in theory. By describing the kinetics and the thermodynamics of all reaction steps in such a detailed matter, a physico-chemical understanding of the homogeneous hydroformylation catalysts, explaining their superior performance, will be acquired [43], aiming to aid future catalyst design. The construction of kinetic models for heterogenized catalysts could be facilitated if the reaction mechanism can be assumed to exhibit similarities to the homogeneously catalyzed hydroformylation. This allows for a potential decoupling of the effect of the ligand-modified rhodium catalyst and its solid support.

2. Methodology

2.1 Experimental

The homogeneously catalyzed hydroformylation of ethylene was investigated experimentally in a 50 ml fed-batch pressure reactor from Asynt, modified by the addition of a sampling tube and charged with a glass liner, reducing the volume to 48 ml. The homogeneous catalyst Rh(H)(PPh₃)₃(CO) was synthesized from a literature procedure [44] and was dissolved in toluene along with the internal standard hexane and the additive triphenylphosphine (PPh₃). Toluene and hexane were purchased from VWR and were dried and degassed prior to use, while PPh₃ was purchased from Sigma-Aldrich/Merck and used without purification. The reactants ethylene, CO and H₂ were purchased from Linde (AGA) as premixes with molar ratios of 1:1:1 and 1:1:2 and were diluted with argon as inert during the feeding to the reactor, until the partial pressures of argon and the feed gas containing the reactants were 70% and 30% of the total pressure, respectively, as measured by a manometer. During the reaction, part of the reactants dissolved in the liquid phase, where the reaction takes place, leading to partitioning of the reactants and the products in the gas and the liquid phases. The operating conditions considered during the experimental investigation are summarized in Table 1.

property	symbol	value	units
catalyst amount	n _{cat}	0.0001-0.001	mmol
temperature	Т	353-473	К
total pressure	p _{tot}	30–50	bar
H ₂ /ethylene molar ratio	$n_{H_2}/n_{C_2H_4}$	1-2	mol mol⁻¹
CO/ethylene molar ratio	$n_{CO}/n_{C_2H_4}$	1	mol mol ⁻¹
additive/rhodium molar ratio	n_{PPh_3}/n_{cat}	3–50	mol mol ⁻¹

Table 1: Summary of the ranges of operating conditions used during the ethylene hydroformylation experiments in a 48 ml gas-liquid batch reactor

Prior to an experiment, a catalyst solution was prepared by dissolving the catalyst and the additive PPh₃ separately in toluene with 5 vol% hexane as internal standard for the analysis. In a typical

experiment, 1 ml of catalyst solution and 1 ml of additive solution were added to the glass liner inside the reactor and diluted with the toluene/hexane mixture until a total liquid volume of 20 ml was reached. The reactor was closed and pressurized to 10 bar with argon at room temperature before heating to the reaction temperature, which takes approximately 30 min. Once the desired temperature was reached, the mixture of ethylene and synthesis gas was fed, immediately followed by argon until the desired total pressure was reached. The total pressure was maintained during the process by cofeeding only argon, which means that no reactants were added after the start of the reaction. Eight 0.1 ml samples were taken from the reaction solution at 2, 5, 10, 15, 30, 60, 90 and 120 min after the desired total pressure was reached. After 120 min, the reaction was stopped by cooling the reactor in an ice bath. To ensure that no sample was contaminated by the previous sample, the sampling tube was first rinsed three times, i.e., 0.3 ml of liquid was removed from the reactor prior to collection of the new sample. Thus, at the end of the reaction, a total of 3.2 ml of liquid had been removed from the reactor. All samples were analyzed using a GC with a headspace sampler, see Section 2.2.

The experiments are performed in the intrinsic kinetics regime, meaning that the effects of mass and heat transfer limitations on the reaction rates can be neglected. The verification of the intrinsic kinetics regime was performed using correlations at the most extreme experimental conditions to ensure that the entire range of experimental conditions satisfies the requirements. To mix the gas and liquid phases in the reactor, a sufficiently high stirring rate of 12 s⁻¹ is used. This stirring rate is well above 2 s⁻¹, which is the rate required to achieve better mass transfer than simply bubbling gas from the bottom of the reactor according to Van Dierendonck et al. [45]. The correlation for surface aeration by Joshi et al. [46] states that surface aeration becomes significant at stirring rates above 1.2 s^{-1} , which means that the gas-liquid interfacial area is increased and gas-liquid transfer is facilitated. To overcome gas-liquid mass transfer limitations, the Carberry number [47] needs to be lower than 0.05/n for all three gas phase reactants, with n being the (absolute value of the) estimated reaction order of the reactant. Although the criterium is easily fulfilled for all components, it is the hardest to fulfill for CO, as it has a low solubility in toluene and a potentially high absolute reaction order, leading to a Carberry number of around 0.003. The reaction order of CO varies quite significantly, within the range of operating conditions, from positive to negative values [8]. Hence, a high, conservative, value of -1 is chosen and the maximally allowed value for the Carberry number then becomes as low as 0.05, which is well above the calculated Carberry number for CO. As the reactor content is well mixed, it can be readily assumed that the extent of potential heat transfer limitations is negligible as well since the reactor temperature is well controlled.

2.2 Analysis

The liquid phase composition in the reaction mixture at a certain reaction time is determined by headspace GC analysis of the extracted samples. In addition to the solvents, i.e., toluene with 5 vol% hexane, only volatile components present in the liquid samples are analyzed. Hence, the only analyzed component is the product propanal. The gaseous components H₂, CO and ethylene, and the heavy, non-volatile components, such as the catalyst species and the additive (PPh₃) are not analyzed. The other potential and volatile product, propanol, was not observed during the experiments. An analysis of the gas phase of a reference experiment (T = 100 °C, $p_{tot} = 50$ bar, $C_2H_4/CO/H_2$ molar ratio = 1:1:2, $n_{cat} = 1 \ \mu mol$ and PPh₃/Rh = 49 mol mol⁻¹) showed that ethane was only formed in trace amounts. This is in agreement with literature as the propanal selectivity using a Rh(H)(PPh₃)₃(CO) catalyst is known to be very close to 100% [8], as mentioned in Section 1. It was therefore assumed that the selectivity towards propanal amounts to 100% in all experiments. The parameters used during the GC analysis are given in Table 2.

Headspace sampler	Teledyne Tekmar HT3, Headspace Autosampler
Sample temperature	373 К
Sample equilibrium time	5 min
Flow rate	5 ml/min
Valve / transfer line temperature	473 K
GC type	GC 6890N (G1540N), serial no US10407058
Analytical Column	190091P-U04, HP-PLOT U
Carrier gas	He, 2 ml/min
Oven temperature	403 K (25 min) – 20 K/min – 443 K (16 min)
Detector	FID, 533 K

Table 2: Method parameters for the headspace GC analyses

2.3 Definitions

The extent of reaction is quantified in terms of the ethylene conversion:

$$X = \frac{n_{\text{ethylene}}^{\circ} - n_{\text{ethylene}}}{n_{\text{ethylene}}^{\circ}} \cdot 100\% \,[\text{mol mol}^{-1}]$$
(1)

The ethylene conversion is equivalent to the amount of formed propanal divided by the initial amount of ethylene, as one mole of propanal is formed for each mole of ethylene in case of 100% selectivity (see Section 2.2). To determine the initial amount of ethylene, the amount of gas needed to reach the target total pressure is calculated, taking into account that some of the feed gas dissolves into the liquid.

2.4 Reactor model

The amount of each component A in the reactor can be determined by solving the differential Equation (2), representing the mass balance of the considered component A. The reactor model equations describe the change in the number of moles of each component A as a function of the reaction time by equating it to the net rate of formation of that component through the reactions occurring in the liquid phase.

$$\frac{\mathrm{dn}_{\mathrm{A}}}{\mathrm{dt}} = \mathrm{R}_{\mathrm{A}} \, [\mathrm{mol} \, \mathrm{s}^{-1}] \tag{2}$$

The reactor equations are used for the reactants and the products, as well as the intermediate catalyst species. The rate of formation of a certain component can be calculated using the expressions for the reaction rates in Equations (15) to (22). To simulate the reactor composition, the differential equations are integrated from the starting time t = 0 s, when the reactor has reached the desired temperature, to the reaction time t = 7200 s. The equations are integrated starting from the initial condition where the amount of reactants equals the amount of reactant gas fed to the reactor and all of the catalyst species are in their initial state. The integration is briefly halted at reaction times where samples are taken, to take the loss in liquid volume resulting from the sample extraction into account, and the integration is resumed afterwards. The integration is done numerically using the open-source differential-algebraic equation solver DASPK [48].

As can be seen in the reactor model equations, there is no contribution for the exchange of reactants and products between the gas and liquid phases, as the gas and liquid are considered in equilibrium, see the assessment of the intrinsic kinetics regime in Section 2.1. Nevertheless, the gas-liquid equilibrium still needs to be calculated, as the liquid phase concentrations are required to calculate the reaction rates. The gas-liquid equilibrium is recalculated at each time step of the integration, as the (liquid) concentration of the reactants and the product during hydroformylation are timedependent. The gas-liquid equilibrium is achieved when the Gibbs free energy of both phases is equal, which is equivalent to the fugacities of both phases being equal, as shown in Equation (3) for a component i [49].

$$f_i^{G} = f_i^{L}$$
(3)

This equation can be expressed in terms of fugacity coefficients as follows:

$$y_i \phi_i^{\ G} = x_i \phi_i^{\ L} \tag{4}$$

Thus, the composition of the gas and liquid phase can be determined by calculating an equilibrium coefficient for each component based on the fugacity coefficients, as in Equation (5).

$$K_{i} = \frac{y_{i}}{x_{i}} = \frac{\varphi_{i}^{L}}{\varphi_{i}^{G}}$$
(5)

The fugacity coefficients were calculated using the PSRK (Predictive Soave-Redlich-Kwong) equation of state [50]. This method makes use of the activity coefficients of the components, which were calculated by applying the UNIFAC group-contribution method [51]. As the mole fraction z_i of a component over the entire reactor is known, its mole fraction in the liquid phase and in the gas phase can be calculated using a mass balance, as in Equation (6), which can be rewritten to Equation (7) and Equation (8) [52, 53].

$$z_i = \Phi y_i + (1 - \Phi) x_i \tag{6}$$

$$x_{i} = \frac{z_{i}}{1 + K_{i} (\Phi - 1)}$$
(7)

$$y_{i} = \frac{K_{i} z_{i}}{1 + K_{i} (\Phi - 1)}$$
(8)

In Equations (6)-(8), Φ is the molar vapor fraction. The set of equations is solved in an iterative manner for a physically realistic solution with a molar vapor fraction between 0 and 1.

2.5 Parameter estimation

To calculate the reaction rates of all the elementary steps in the reaction mechanism, the law of mass action is applied to each of the reaction steps, i.e., the reaction rate is proportional to the concentrations of the reactants of the corresponding reaction step, with the rate coefficient k_i as the proportionality factor. The forward rate coefficients of the reactions are calculated using the reparametrized Arrhenius equation, as in Equation (9). The equilibrium coefficients of all reaction steps are calculated using the reparametrized van 't Hoff equation, as in Equation (10), and are equal to the ratio of the rate coefficients of the forward and backward reaction step. The equations have been reparametrized to reduce the correlation between the pre-exponential factor and the reaction enthalpy or the activation energy [54]. The pre-exponential factor is then equal to the rate coefficient at the average temperature T_{av} .

$$\mathbf{k}_{i} = \mathbf{k}_{i,T,av} \exp\left(-\frac{\mathbf{E}_{a}}{\mathbf{R}}\left(\frac{1}{\mathbf{T}} - \frac{1}{\mathbf{T}_{av}}\right)\right)$$
(9)

$$K_i = K_{i,T,av} \exp\left(-\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_{av}}\right)\right) = \frac{k_{i,+}}{k_{i,-}}$$
(10)

All rate and equilibrium coefficients, reaction free energies and reaction entropies in this work are expressed relative to the standard state of 1 mol m⁻³ in toluene for all liquid phase components (see Section S1 in the Supporting Information). The pre-exponential factors, activation energies and reaction enthalpies necessary to determine the kinetics and the thermodynamics of the reaction steps are calculated to the extent possible via theoretical calculations to reduce the number of parameters to be estimated. Nevertheless, some of these values need to be estimated by regression to the experimental data, leading to 11 parameters to be estimated, see Section 4.2. The equilibrium coefficients at the average temperature are calculated based on the reaction enthalpy and entropy as in Equation (11) if they are not determined through regression. Likewise, the Eyring-Polanyi equation [55], shown in Equation (12), can be used to relate the rate coefficient at the average temperature to the activation entropy between the reactants and the transition state.

$$K_{T,av,i} = \exp(\frac{\Delta S_i}{R}) \exp(-\frac{\Delta H_i}{R T_{av}})$$
(11)

$$k_{T,av,i} = \frac{k_B T_{av}}{h} \exp(\frac{\Delta S^{\#}_{i}}{R}) \exp(-\frac{E_{a,i}}{R T_{av}})$$
(12)

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The regression of the model to the experimental data is done by minimizing the sum of squares of the residuals between the model-simulated and the experimentally observed amount of propanal. The sum of squares of the residuals is minimized by varying the values of the model parameters β :

$$SSQ(\beta) = \sum_{i}^{n_{exp}} \left(n_{propanal,i} - \hat{n}_{propanal,i} \right)^2 \xrightarrow{\beta} Min$$
(13)

The minimization is done numerically using the Rosenbrock method and the Levenberg-Marquardt algorithm. The Rosenbrock method is first applied, using an in-house implementation of the method, to reach an approximate estimation for the parameters [56]. To obtain a more precise solution, the Levenberg-Marquardt method, as available in the ODRPACK package [57], is applied afterwards. Once a set of parameters has been estimated, a statistical analysis is performed on the model and the individual parameters in order to assess the performance of the model. For each model parameter, a 95% confidence interval is generated, which cannot include zero for the parameter to be significant. A correlation matrix also showcases the binary correlation between all model parameters with a value between -1 and 1. Two parameters are considered to be statistically uncorrelated if the absolute value of the corresponding binary correlation coefficient is lower than 0.95. The *F* value for the global significance of the model is calculated as well and must be higher than the tabulated value for the model [58]. A visual analysis of the model performance is also performed using the parity diagram for propanal to illustrate the discrepancy between the experimental and the simulated amounts, and a residual figure as a function of the temperature is used to determine if the residuals are normally distributed and whether they showcase realistic trends.

3. Experimental results

The effects of different reaction conditions on the product spectrum of the homogeneously catalyzed hydroformylation of ethylene were investigated by varying one reaction condition while keeping the others constant. In this way, the effect of the temperature, the total pressure, the amount of rhodium catalyst, the molar reactant ratio and the additive/Rh molar ratio on the ethylene conversion and the amount of formed propanal are assessed in a systematic manner. In addition to the experiments used for the model regression, validation experiments have been performed in which the effects of different reaction conditions have been combined. No significant amounts of hydrogenation products such as propanol and ethane were observed during the experimentation, see Section 2.2.

3.1 Temperature effect

The effect of the temperature on the formation of propanal is shown in Figure 2.a. It can be seen that at 80 °C, 90 °C and 100 °C, the amount of formed propanal increases approximately linearly as a function of the reaction time, indicating that chemical equilibrium has not been reached. The conversion reached after 120 min varies from around 14% at 80 °C to around 74% at 100 °C. At higher temperatures, the amount of propanal formed increases more quickly, indicating that the temperature has an positive effect on the reaction rate, which corresponds to the behavior expected from the Arrhenius law. These trends also do not show any clearly visible signs of catalyst deactivation at 80 °C - 100 °C, as that would stabilize the total amount of propanal formed as a function of time due to the decreasing reaction rate. However, evidence for catalyst decomposition was observed for the experiments performed at 120 °C and 200 °C, and these results are further discussed in Section 3.6.



▲ PPh₃/Rh = 3 mol mol⁻¹ ■ PPh₃/Rh = 50 mol mol⁻¹

Figure 2: Experimentally measured amount of formed propanal as a function of reaction time. a) Results at T = 80 °C, 90 °C, 100 °C, 120 °C and 200 °C ($n_{C2H4,0} = 4.39$ mmol, 4.24 mmol, 4.11 mmol, 3.81 mmol and 3.00 mmol, respectively). Reaction conditions: $n_{cat} = 0.0001$ mmol, $p_{tot} = 50$ bar, $n_{H2}/n_{C2H4} = 2$ mol mol⁻¹, $n_{C0}/n_{C2H4} = 1$ mol mol⁻¹ and $n_{PPh3}/n_{cat} = 10$ mol mol⁻¹. b) Results at $p_{tot} = 30$ bar, 40 bar and 50 bar ($n_{C2H4,0} = 2.47$ mmol, 3.29 mmol and 4.11 mmol, respectively). Reaction conditions: $n_{cat} = 0.0001$ mmol, T = 100 °C, $n_{H2}/n_{C2H4} = 2$ mol mol⁻¹, $n_{C0}/n_{C2H4} = 1$ mol mol⁻¹ and $n_{PPh3}/n_{cat} = 10$ mol mol⁻¹. c) Results at $n_{cat} = 0.0001$ mmol and 0.001 mmol ($n_{C2H4,0} = 4.11$ mmol). Reaction conditions: T = 100 °C, $p_{tot} = 50$ bar, $n_{H2}/n_{C2H4} = 2$ mol mol⁻¹. d) Results at $C_{2H4}/CO/H_2$ molar ratios = 1:1:1 and 1:1:2 mol ($n_{C2H4,0} = 5.82$ mmol and 4.11 mmol, respectively). Reaction conditions: $n_{cat} = 0.0001$ mmol, T = 100 °C, $p_{tot} = 3$ mol mol⁻¹, 10 mol mol⁻¹ and 49 mol mol⁻¹ ($n_{C2H4,0} = 4.11$ mmol). Reaction conditions: $n_{cat} = 0.0001$ mmol, T = 100 °C, $p_{tot} = 50$ bar and $n_{PPh3}/n_{cat} = 10$ mol mol⁻¹. How mol, $n_{cat} = 10$ mol mol⁻¹ and $n_{PPh3}/n_{cat} = 10$ mol mol⁻¹. Results at $C_{2H4,0}/CO/H_2$ molar ratios = 1:1:1 and 1:1:2 mol ($n_{C2H4,0} = 5.82$ mmol and 4.11 mmol, respectively). Reaction conditions: $n_{cat} = 0.0001$ mmol, T = 100 °C, $p_{tot} = 50$ bar and $n_{PPh3}/n_{cat} = 10$ mol mol⁻¹. e) Results at $n_{PPh3}/n_{cat} = 3$ mol mol⁻¹, 10 mol mol⁻¹ and 49 mol mol⁻¹ ($n_{C2H4,0} = 4.11$ mmol). Reaction conditions: $n_{cat} = 0.0001$ mmol, T = 100 °C, $p_{tot} = 50$ bar, $n_{H2}/n_{C2H4} = 2$ mol mol⁻¹ and $n_{C0}/n_{C2H4} = 1$ mol mol⁻¹.

3.2 Total pressure effect

The effect of the total pressure on the formation of propanal is shown in Figure 2.b at total pressures of 30 bar, 40 bar and 50 bar. The fraction of reactants fed to the reactor is kept at 30% of the total gas feed, and consequently the total pressure. Thus, the initial amount of ethylene varies in the three experiments, with 2.5 mmol, 3.3 mmol and 4.1 mmol of ethylene fed at a total pressure of 30 bar, 40 bar and 50 bar, respectively. At the first points in time, the amount of propanal formed seems to be very similar at all three total pressures, suggesting that the total pressure has little effect on the initial reaction rate, despite the different initial amount of ethylene. At 40 bar, the total amount of propanal formed starts to stabilize at longer reaction times, as the reaction approaches equilibrium. At 30 bar, this effect is even more pronounced and it appears that equilibrium is reached already after 1 h. The amount of propanal formed after 2 h corresponds to an ethylene conversion of approximately 27%, 47% and 74% at 30 bar, 40 bar and 50 bar, respectively. The final conversion at 30 bar of around 27% is lower than the final ethylene conversions obtained at the higher total pressures, which indicates that the total pressure has a positive effect on the equilibrium conversion. This effect reflects Le Chatelier's principle, which states that a higher pressure will favor the formation of products if the number of moles of components decreases during the reaction [59]. However, it is also possible that the decrease in equilibrium conversion at lower total pressures is a result of catalyst deactivation, as lower total pressures are known to lead to more catalyst deactivation [60], see also Section 3.6. For example, rhodium dimers, which can be cleaved by H_2 to form active catalyst species, are known to form at lower concentrations of H_2 , resulting from lower total partial pressures of H_2 (mostly below 1 bar) [9]. As the partial pressure of H_2 only makes up around 10% of the total pressure in the experiments conducted in this work, it is possible that catalyst deactivation through dimerization is occurring to a certain extent.

3.3 Catalyst amount effect

The effect of the amount of rhodium catalyst on the formation of propanal is shown in Figure 2.c for 0.1 μ mol and 1 μ mol of rhodium catalyst. At reaction times until 10 min, the amount of propanal formed is approximately ten times larger when a ten times larger amount of rhodium catalyst is used. This corresponds with the observation in the literature that the reaction is first order in the amount of rhodium catalyst [8]. At higher reaction times, the amount of formed propanal stabilizes at a catalyst amount of 1 μ mol, reaching a conversion around 87%, while it is still increasing at a catalyst amount

of 0.1 μ mol, reaching a conversion around 72% after 2 h. This indicates that equilibrium has already been reached in the experiments performed with 1 μ mol of rhodium catalyst, as the initial reaction rate is accelerated. Equilibrium calculations indicate that the final conversion should be around 99% at these conditions. The lower observed final conversion might indicate that there are some effects of catalyst deactivation or it might be a consequence of experimental error. Rhodium dimerization, which was discussed in Section 3.2 might be a possible explanation, as it is promoted at higher catalyst concentrations.

3.4 Molar reactant ratio effect

Experiments have been performed using molar reactant ratios of 1:1:1 and 1:1:2 for ethylene, CO and H₂, see the results shown in Figure 2.d. As a total pressure of 50 bar is used in both cases, the amount of ethylene fed during the experiments is significantly different, varying between around 5.8 mmol at the molar reactant ratio of 1:1:1 and around 4.1 mmol at the molar reactant ratio of 1:1:2. Additionally, both the H_2 /ethylene molar ratio and the H_2 /CO molar ratio vary between the experiments, so the results are likely a combination of different effects. Despite the higher amount of ethylene fed to the reactor in the former case, the amount of propanal formed is significantly lower at the molar reactant ratio of 1:1:1. It can be expected that the reaction rate, and consequently the amount of propanal formed, will increase when higher H_2 /ethylene molar ratios are used, as the excess H_2 will favor the formation of propanal based on the principle of Le Chatelier [59]. As the CO/ethylene molar ratio is constant at 1 mol mol⁻¹ during the experiments, the absolute amount of CO is also higher in the experiment with the molar reactant ratio of 1:1:1. Since the coordination of CO is easier than the oxidative addition of H₂ and the coordination of ethylene [28], the larger amount of CO will also lead to a larger number of catalyst species which are reversibly deactivated by CO, resulting in a decrease in the reaction rate. It is also possible that the lower reaction rate is also affected by the lower concentrations of H_2 , leading to the formation of rhodium dimers, as was explained in Section 3.2.

3.5 Additive to rhodium molar ratio effect

To assess the effect of the molar ratio of the additive PPh₃ to the rhodium catalyst on the amount of propanal formed, experiments were performed at molar ratios of 3, 10 and 50 mol mol⁻¹, as shown in Figure 2.e. The amount of propanal formed as a function of the reaction time at an additive/rhodium

molar ratio of 10 mol mol⁻¹ is significantly higher than that at an additive/rhodium molar ratio of 3 mol mol⁻¹. Yet, a further increase to an additive/rhodium molar ratio of 50 mol mol⁻¹ only leads to minor differences, which are considered to be within the expected experimental error range. In the literature, a maximum is observed in the reaction rate as a function of the additive/rhodium molar ratio [7, 13], which means that there is an optimal molar ratio of 50 mol mol⁻¹, potentially even higher molar ratio is not visible yet at an additive/rhodium molar ratio of 50 mol mol⁻¹, potentially even higher molar ratios are required for this effect to become apparent. However, a decrease in the reaction rate at higher additive concentrations is expected, as the catalyst becomes saturated with ligands. At the additive/rhodium molar ratio of 3 mol mol⁻¹, the reaction rate starts to decrease as a function of the reactivation, which indicates that the lower formation of propanal stems from catalyst deactivation, which is a known effect of decreasing the additive/rhodium molar ratio [60].

3.6 Catalyst deactivation

Experiments performed at 120 °C exhibit a higher initial formation of propanal compared to the ones at 100 °C, but also a significant drop in the amount of propanal reached at a reaction time of 2 h. As the hydroformylation is an exothermic reaction, a lower equilibrium conversion is expected at higher temperatures, but the observed effect was significantly more pronounced than expected based on equilibrium calculations. These calculations indicate that an equilibrium conversion of over 99% is expected for the experiments at 120 °C, yet the conversion achieved after 2h is limited to approximately 41%. At even higher temperatures, the drop in the final conversion becomes progressively more pronounced, until no propanal is measured at all at 200 °C. At this temperature, a silverfish metallic layer was observed on the reactor walls after reaction. This observation, along with the mathematical indication that the effect does not solely result from thermodynamics, suggests that there might be significant catalyst deactivation at temperatures exceeding 100 °C.

In the literature, catalyst deactivation is indeed commonly associated with homogeneously catalyzed hydroformylation using phosphine-modified Rh catalysts [9]. Generally speaking, catalyst decomposition is the most common form of catalyst deactivation and it seems to play a significant role in this process as well according to scientific consensus [9]. Catalyst decomposition is known to be partly a result of the thermal degradation of the triphenylphosphine ligand [7]. This degradation results from the irreversible cleavage of the P-C bond in the ligand and leads to the formation of phosphide-bridged Rh clusters [61, 62]. Billig et al. [63] have observed the formation of a stable triangular Rh cluster from Rh(H)(PPh_3)_3(CO) at 120 °C in the absence of the reactants of the hydroformylation. The

clusters, which are catalytically inactive, are formed at temperatures starting from 80 °C in a wide variety of solvents. Deshpande et al. [60] reported similar experimental trends as observed in our work and attributed the catalyst deactivation to the formation of phosphide-bridged Rh clusters and inactive Rh dimers. It can be seen that in batch operation, the catalyst is initially active and slowly deactivates during reaction, which becomes more pronounced at higher temperatures. High temperatures and low total pressures are known to increase the rate of catalyst deactivation, while the addition of phosphine or phosphite ligands stabilizes the catalyst and partly slows down deactivation [60].

To avoid significant effects of catalyst decomposition or Rh cluster formation in the experimental dataset used for the kinetic model, only the temperature range of 80 °C to 100 °C was considered, which does not have clearly observable effects from catalyst deactivation. Furthermore, most experiments were performed using additive/catalyst molar ratios of 10 mol mol⁻¹ or 50 mol mol⁻¹ and at a total pressure exceeding 30 bar, which is expected to reduce the extent of catalyst decomposition and Rh cluster formation. It is likely that some extent of catalyst deactivation, Rh cluster formation in particular, is occurring at lower total pressures during the experimental investigation, as the final conversion reached is lower than would be expected based on equilibrium calculations and the discrepancy increases as the total pressure decreases. However, these experiments are still useful for the construction of the model as the data points at shorter reaction times likely contain less effects from catalyst deactivation and are necessary to take the effect of the total pressure into account in the model. The effects of catalyst decomposition and Rh cluster formation are not further investigated in this work and are not considered in the modeling effort. The addition of Rh dimerization to the model was investigated, but it was not included since its effect was not sufficiently pronounced, as will be explained in Section 4.1. The experimental conditions of the experiments which are selected for the model regression and validation are given in Section S2 of the Supporting Information.

4. Kinetic model development

4.1 Reaction network

As mentioned in the Introduction, Wilkinson's dissociative mechanism is widely-accepted for the hydroformylation of olefins and is therefore employed as the basis for the construction of the reaction mechanism in the microkinetic model developed as part of this work [9, 25]. No hydrogenation reactions are included in the reaction network, as no hydrogenation products were observed in

significant amounts during the experimental investigation. The reaction mechanism considered in the ethylene hydroformylation model is an extension of the widely-accepted mechanism in Figure 1 and is depicted in Figure 3 for a Rh(H)(L)₃(CO) catalyst, with 'L' representing a phosphine ligand. First, one of the phosphine ligands 'L' of the catalyst as synthesized undergoes a ligand exchange with a CO molecule from the feed gas (not shown), forming the Rh(H)(L)₂(CO)₂ species [33]. It has been observed that most of the catalyst species are in this form under a CO atmosphere [8, 64, 65], and that the replacement of the phosphine by a CO ligand is much faster than the hydroformylation reactions [33, 65, 66]. It is, thus, reasonable to assume that the catalytic cycle starts with this species, as the focus of the kinetic model is on the rates of the hydroformylation reaction steps converting ethylene and syngas to propanal.

The initially formed Rh(H)(L)₂(CO)₂ species cannot react with the liquid phase components yet and only becomes reactive once one of the ligands dissociates, to form a four-coordinate, 16-electron species. The two possibilities are the formation of a Rh(H)(L)(CO)₂ species through the dissociation of one of the phosphine ligands or the formation of a Rh(H)(L)₂(CO) species through the dissociation of a CO ligand, leading to two possible reaction pathways, with one or two phosphine ligand(s), respectively. In the literature, the former pathway is often considered to be the most likely one for ethylene hydroformylation [33]. Kinetic modelling has indeed indicated that the hydroformylation rate through the pathway involving two phosphine ligand, as long as the concentration of additional phosphine ligand is sufficiently low (well below 1 mol l^{-1}) [8, 38]. Hence, the formation of the Rh(H)(L)(CO)₂ species (r_L) is considered in the model, as the phosphine concentrations employed during the experimentation in this work are in the order of 0.1 mmol l^{-1} .

Once the catalyst has become active, the reactants ethylene, CO and H₂ can react at the catalyst center to form propanal. The formation of propanal can be described as a catalytic cycle comprising six reactions steps, see Figure 3. The first step is the coordination of ethylene to Rh (r_1), followed by the insertion of ethylene into the Rh-H bond to form a coordinated ethyl species (r_2). After coordination of another CO molecule (r_3), there is a migratory CO insertion into the Rh-C bond of the Rh-ethyl moiety (r_4). Next, H₂ coordinates and oxidatively adds to Rh (r_5), followed by the reductive elimination of propanal, which is the reverse of its oxidative addition (r_6). In addition to these reaction steps, it is also known that two of the catalytic intermediates can be reversibly deactivated by coordination of CO, as these deactivated species have been observed experimentally [9]. These reactions include the coordination of CO to the Rh(H)(L)(CO)₂ species (r_7) and the coordination of CO to the Rh(L)(COCH₂CH₃)(CO)₂ species (r_8).



Figure 3: Wilkinson's dissociative mechanism for the hydroformylation of ethylene. Coordination/dissociation and addition/elimination reactions (bimolecular) are indicated in blue and reactions steps on the catalyst (unimolecular) are indicated in orange. Reworked from [9].

Overall, nine reactions are considered in the reaction mechanism in Figure 3. This includes two unimolecular reaction steps on the catalyst, indicated in orange, and seven bimolecular coordination/dissociation or addition/elimination reactions, indicated in blue. Possible catalyst decomposition reactions, such as ligand decomposition, or the irreversible formation of deactivated rhodium complexes, are not taken into account in the model. The addition of rhodium dimerization in the reaction network through the addition of a reversible dimerization reaction has been investigated but did not lead to significant changes in the modelling results. The reversible Rh dimerization was therefore left out of the model as well in order to avoid overparametrization.

4.2 Rate equations

As shown in Equation (2), the net rates of formation of all the components, including the intermediates, need to be expressed to solve the mass balances. These net rates of formation, are determined from the forward and backward rates of all reaction steps of the mechanism in Figure 3. The first reaction in the mechanism, i.e., the dissociation of the phosphine ligand, is known to be fast in both directions compared to the actual hydroformylation [65, 66], so the $Rh(H)(L)_2(CO)_2$ species is assumed to be in equilibrium with the active $Rh(H)(L)(CO)_2$ species at all times in this model. In other words, only thermodynamics are considered using an equilibrium coefficient K_L for this specific reaction, as shown in Equation (14), as opposed to both kinetics and thermodynamics as for the other reaction steps. Another assumption is that a unique forward rate coefficient and a unique backward rate coefficient can be used for all CO coordination reactions (reactions 3, 7 and 8). In all of these reactions, the catalyst goes from a 16-electron species to an 18-electron species, the only difference being one of the ligands, which is either a hydrogen atom or a short carbon chain. As both the hydrogen atom and the alkyl chain are two-electron donors that form a covalent sigma-bond with Rh, it is assumed that the composition of this one ligand has little effect on the rate of the coordination of CO. The rates of all reaction steps are given in Equation (15) to (22) (see Section S1 in the Supporting Information for more information on the derivation of the equations and its units). In Equation (20), the oxidative addition of propanal was considered to be the forward reaction instead of the reductive elimination, to facilitate the comparison to the other coordination and addition reactions. The rate and equilibrium expressions show that in total six forward rate coefficients and seven equilibrium coefficients need to be determined.

$$K_{L} = \frac{n_{Rh(CO)_{2}(H)(L)_{2}}}{n_{Rh(CO)_{2}(H)(L)} C_{L}}$$
(14)

$$r_{1} = k_{1,+} \left(n_{Rh(CO)_{2}(H)(L)} \cdot C_{C_{2}H_{4}} - \frac{1}{K_{1}} \cdot n_{Rh(CO)_{2}(C_{2}H_{4})(H)(L)} \right) [mol \ s^{-1}]$$
(15)

$$r_{2} = k_{2,+} \left(n_{Rh(CO)_{2}(C_{2}H_{4})(H)(L)} - \frac{1}{K_{2}} \cdot n_{Rh(CO)_{2}(C_{2}H_{5})(L)} \right) [mol \, s^{-1}]$$
(16)

$$r_{3} = k_{3,+} \left(n_{Rh(CO)_{2}(C_{2}H_{5})(L)} \cdot C_{CO} - \frac{1}{K_{3}} \cdot n_{Rh(CO)_{3}(C_{2}H_{5})(L)} \right) [mol \ s^{-1}]$$
(17)

$$r_{4} = k_{4,+} \left(n_{Rh(CO)_{3}(C_{2}H_{5})(L)} - \frac{1}{K_{4}} \cdot n_{Rh(CO)_{2}(COC_{2}H_{5})(L)} \right) [mol \, s^{-1}]$$
(18)

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$$r_{5} = k_{5,+} \left(n_{Rh(CO)_{2}(COC_{2}H_{5})(L)} \cdot C_{H_{2}} - \frac{1}{K_{5}} \cdot n_{Rh(CO)_{2}(COC_{2}H_{5})(H)_{2}(L)} \right) [mol \, s^{-1}]$$
(19)

$$r_{6} = k_{6,+} \left(n_{Rh(CO)_{2}(H)(L)} \cdot C_{propanal} - \frac{1}{K_{6}} \cdot n_{Rh(CO)_{2}(COC_{2}H_{5})(H)_{2}(L)} \right) [mol \ s^{-1}]$$
(20)

$$\mathbf{r}_{7} = \mathbf{k}_{3,+} \left(\mathbf{n}_{Rh(CO)_{2}(H)(L)} \cdot \mathbf{C}_{CO} - \frac{1}{K_{3}} \cdot \mathbf{n}_{Rh(CO)_{3}(H)(L)} \right) [mol \, s^{-1}]$$
(21)

$$r_8 = k_{3,+} (n_{Rh(CO)_2(COC_2H_5)(L)} \cdot C_{CO} - \frac{1}{K_3} \cdot n_{Rh(CO)_3(COC_2H_5)(L)}) [mol \, s^{-1}]$$
(22)

As there are seven equilibrium coefficients, seven reaction enthalpies need to be determined. In order to do so, the reaction enthalpies are set as parameters of the model to be determined by regression. This is done for all reaction enthalpies, except for the one for ethylene insertion, which is calculated using the total enthalpy balance, thereby ensuring thermodynamic consistency. The total hydroformylation reaction enthalpy can easily be calculated based on the formation enthalpies of the reactants and the products in the gas phase at a standard pressure of 1 atm and the solvation enthalpies of the components in toluene, which were calculated using the Abraham method [67, 68] at a standard state of 1 atm for the gas and 1 mol m^{-3} for the liquid (see Section S3 in the Supporting Information). The equilibrium coefficients at the average temperature, on the other hand, are calculated using Equation (11) based on the reaction entropies and the aforementioned reaction enthalpies for all coordination and addition reactions. The reaction entropies of these reactions are calculated using the Sackur-Tetrode equation for the translational entropies [69] and the solvation entropies, assuming that during coordination, the components dissolved in toluene lose all three translational degrees of freedom (see Section S4 in the Supporting Information for a more detailed description). The reaction entropies of the two reaction steps on the catalyst (CO and ethylene insertion) cannot be calculated as easily based on the translational entropy as the ligands remain on the catalyst and there is no major change in the translational entropy. The equilibrium coefficient at the average temperature is therefore estimated through regression for the CO insertion, and in the same manner as the reaction enthalpy, the reaction entropy of the ethylene insertion is calculated from thermodynamic consistency, taking into account the solvation entropies [68, 70] (see Section S3). This means that in total, one equilibrium coefficient and six reaction enthalpies need to be determined through regression to describe the reaction thermodynamics.

The activation energies of the two oxidative additions and the two reaction steps on the catalyst are estimated *via* regression as well. The three coordination reactions are assumed to be nonactivated, i.e., the corresponding activation energies are set equal to zero. This is a reasonable assumption as a

real transition state with a much higher energy than the reactants is often improbable for coordination reactions. Moreover, such reactions are generally considered to be nonactivated [28, 32-34, 71]. Although a small activation energy is possible for ethylene coordination on certain catalysts [72], DFT calculations have indicated that the reaction is essentially nonactivated on a PPh₃-modified Rh catalyst [73]. Additionally, it is beneficial to assume the coordination reactions are nonactivated when the activation energy can be expected to be very small in order to reduce the total number of parameters and lead to a more accurate estimation of the other parameters. The rate coefficients at the average temperature are calculated using Equation (12), based on the activation entropy between the reactants and the transition state and the aforementioned activation energies. All activation entropies were determined using the Sackur-Tetrode equation [69] and the solvation entropies, assuming that the transition states have one translational degree of freedom (see Section S4 in the Supporting Information). In the end, this means that four activation energies are calculated through regression, which leads to eleven parameters in total to describe the kinetics and the thermodynamics of all reaction steps.

In addition to the microkinetic model, the experimental data is also regressed to a simple power law model in order to estimate the reaction orders of the reactants and the catalyst, and to facilitate comparisons with other kinetic studies. The rate equation of the power law model is given in Equation (23), with C° being the standard concentration of 1 mol m⁻³. The concentrations of ethylene, CO, H_2 and the rhodium catalyst are considered in the model with the reaction orders a, b, c and d, respectively. The four reaction orders, along with the rate coefficient at the average temperature and the activation energy lead to six parameters in the model.

$$r = k \left(\frac{C_{C_2H_4}}{C^{\circ}}\right)^a \left(\frac{C_{CO}}{C^{\circ}}\right)^b \left(\frac{C_{H_2}}{C^{\circ}}\right)^c \left(\frac{C_{Rh}}{C^{\circ}}\right)^d [mol \ m^{-3} \ s^{-1}]$$
(23)

4.3 Regression results

The obtained reaction enthalpies and equilibrium coefficients at the average temperature are shown in Table 3, while the obtained activation energies and rate coefficients at the average temperature are shown in Table 4. The corresponding reaction entropies and activation entropies can be found in Section S1 of the Supporting Information. A visual representation of the enthalpy profile is shown in Figure 4. It can be seen that the parameters estimated through regression (indicated in bold) have realistic values, not being extremely high nor low, and have narrow 95% confidence intervals which do not include 0. The parameters were also found to be statistically uncorrelated as the highest absolute value obtained for the binary correlation coefficients amounted to 0.86. The model has an *F* value of 140 for the global significance, which is higher than the tabulated value of 3, indicating that the model is globally significant. The parity diagram in Figure 5.a shows that the model performs well without pronounced deviations from the experimental amount of propanal. No clear trend which would indicate a major systematic deviation of the residuals as a function of the experimentally observed values for the amount of propanal formed can be distinguished. Figure 5.b also showcases that there is no major trend in the residuals as a function of the temperature. Indeed, any potential trend with temperature is situated within the spread observed at 100°C. Both figures also contain data points from a validation dataset that was not used during the model regression (indicated as orange triangles). These data points are generally well reproduced, although some points are slightly overestimated. These data points correspond to the experiments performed at a total pressure of 40 bar and the same overestimation is also present in the regression dataset for the experiments performed at total pressures below 50 bar.

roac	tion	ΛЦ.		V	
over a nomogeneous intervals.	KN(H)(L)3(CO) catalyst to the ex	perimental data,	are written in bold	along with their 95%	confidence
				1	C 1
369 K for all reactions.	The values, which were obtained	d after regression (of the kinetic model	for the ethylene hydro	formylation

Table 3: Calculated values for the reaction enthalpies ΔH_i and the equilibrium coefficients $K_{T,av,i}$ at the average temperature of

reaction	Δ	Hi	K _{T,av,i}	
PPh ₃ coordination	-50.0 ± 2.0	kJ mol⁻¹	8.0 · 10 ³	m ³ mol ⁻¹
ethylene coordination	-40.1 ± 2.4	kJ mol⁻¹	1.3 · 10 ⁻³	m ³ mol ⁻¹
ethylene insertion	-38.1	kJ mol⁻¹	$1.1\cdot10^{6}$	
CO coordination	-61.9 ± 2.6	kJ mol⁻¹	0.3	m ³ mol ⁻¹
CO insertion	-43.3 ± 3.3	kJ mol⁻¹	(3.9 ± 0.5) · 10 ⁶	
H ₂ oxidative addition	9.4 ± 1.6	kJ mol⁻¹	$9.9 \cdot 10^{-10}$	m ³ mol ⁻¹
propanal oxidative addition	-17.5 ± 1.3	kJ mol⁻¹	1.1 · 10 ⁻⁵	m ³ mol ⁻¹

Table 4: Calculated values for the activation energies $E_{\alpha,i}$ and the rate coefficients $k_{T,av,i}$ at the average temperature of 369 K for all reactions. The values, which were obtained after regression of the kinetic model for the ethylene hydroformylation over a homogeneous $Rh(H)(L)_3(CO)$ catalyst to the experimental data, are written in bold along with their 95% confidence intervals.

reaction	Ea	ı,i	k _{t,}	av,i
ethylene coordination	0.0	kJ mol⁻¹	$7.2 \cdot 10^6$	m ³ mol ⁻¹ s ⁻¹
ethylene insertion	42.1 ± 2.0	kJ mol⁻¹	$8.4\cdot10^{6}$	S ⁻¹
CO coordination	0.0	kJ mol ^{−1}	$3.4\cdot10^{6}$	m ³ mol ⁻¹ s ⁻¹
CO insertion	43.9 ± 3.9	kJ mol⁻¹	4.8 · 10 ⁶	S ⁻¹
H ₂ oxidative addition	48.1 ± 5.5	kJ mol ^{−1}	5.8	m ³ mol ⁻¹ s ⁻¹
propanal oxidative addition	22.4 ± 2.6	kJ mol⁻¹	$1.5\cdot10^4$	m ³ mol ⁻¹ s ⁻¹



Figure 4: Energy profile of the hydroformylation reaction, starting from the dissociation of the phosphine ligand until the reductive elimination of propanal. Enthalpy values of the intermediate catalyst species are indicated by a green line, while transition states are indicated by a red line.

The performance curves of the model are given in Figure 6 and show that the model manages well to reproduce the trends retained in the experimental data. It can be seen that the positive effect of the temperature on the conversion is captured by the model in Figure 6.a. The nearly linear trend in the formed amount of propanal is present in the model-simulated results at 80 °C and 90 °C. The slightly decreasing reaction rate as a function of the reaction time at 100 °C is captured as well, leading to a slight curvature in the trend, although the formation of propanal is slightly overestimated at this temperature. In the performance curves for the total pressure variation, shown in Figure 6.b, the

increase in equilibrium conversion at higher total pressures is captured by the model as well, albeit less pronounced compared to what was experimentally observed. At short reaction times, i.e., until 900 s, the reaction rates are very similar regardless of the total pressure and this trend is captured by the model. However, equilibrium is achieved faster in the experiments compared to the modelsimulated results at a total pressure of 30 bar. This can potentially be attributed to an extent of catalyst deactivation through Rh cluster formation occurring at 30 bar, as lower total pressures enhance this form of catalyst deactivation [9, 60]. The partial pressure of the reactants is only 30% of the total pressure, which could indicate that the employed reactant partial pressure is not sufficient to avoid this effect of catalyst deactivation. The effect of the amount of catalyst on the amount of propanal formed is also captured by the model, as shown in Figure 6.c. Both the experimental and the simulated amounts of propanal appear to achieve equilibrium, yet the experimental values are a bit lower than would be expected based on theoretical equilibrium calculations, which might be a result of some catalyst deactivation or experimental error. In Figure 6.d, it can be seen that the negative effect of using a molar ethylene/CO/H₂ ratio of 1:1:1 instead of 1:1:2 at the same total pressure can be reproduced by the model. Although the experimentally observed shift was a bit more pronounced, the simulated amount of propanal is still within the error margin at a molar reactant ratio of 1:1:1 and just outside the error margin at the molar reactant ratio of 1:1:2 at reaction times exceeding 1h.



Figure 5: a) Parity diagram for the amount of formed propanal, and b) residuals as a function of temperature, in the kinetic model for the ethylene hydroformylation over a homogeneous $Rh(H)(L)_3(CO)$ catalyst using Equation (2) with the parameter values shown in Table 3 and Table 4 (curves). Experimental data points which were used during the model regression are indicated as green dots, while data points which were used for model validation are indicated as orange triangles.



Figure 6: Experimentally measured amount of formed propanal as a function of reaction time (data points) and modelsimulated results as a function of reaction time using Equation (2) with the parameter values shown in Table 3 and Table 4 (curves). a) Results at T = 80 °C, 90 °C and 100 °C ($n_{C2H4,0} = 6.27$ mmol, 6.04 mmol and 5.82 mmol, respectively). Reaction conditions: $n_{cat} = 0.0001$ mmol, $p_{tot} = 50$ bar, $n_{H2}/n_{C2H4} = 1$ mol mol⁻¹, $n_{C0}/n_{C2H4} = 1$ mol mol⁻¹ and $n_{PPh3}/n_{cat} = 50$ mol mol⁻¹. b) Results at $p_{tot} = 30$ bar, 40 bar and 50 bar ($n_{C2H4,0} = 2.47$ mmol, 3.29 mmol and 4.11 mmol, respectively). Reaction conditions: $n_{cat} = 0.0001$ mmol, T = 100 °C, $n_{H2}/n_{C2H4} = 2$ mol mol⁻¹, $n_{C0}/n_{C2H4} = 1$ mol mol⁻¹ and $n_{PPh3}/n_{cat} = 10$ mol mol⁻¹. c) Results at $n_{cat} = 0.0001$ mmol and 0.001 mmol ($n_{C2H4,0} = 4.11$ mmol). Reaction conditions: T = 100 °C, $p_{tot} = 50$ bar, $n_{H2}/n_{C2H4} = 2$ mol mol⁻¹, $n_{C0}/n_{C2H4} = 1$ mol mol⁻¹. d) Results at $C_2H_4/CO/H_2$ molar ratios = 1:1:1 and 1:1:2 ($n_{C2H4,0} = 5.82$ mmol and 4.11 mmol, respectively). Reaction conditions: $n_{cat} = 0.0001$ mmol, T = 100 °C, $p_{tot} = 50$ bar and $n_{PPh3}/n_{cat} = 10$ mol mol⁻¹.

The results of the parameter estimation of the power law model are shown in Table 5. The model is statistically significant with an *F*-value of 190 for the significance of the model, as compared to the tabulated value of 3. The parameters have realistic values and can be considered to be uncorrelated, as the highest value in the correlation matrix amounts to 0.84. The reaction orders a, b, c and d were estimated to be 1, -0.8, 1 and 1.1 for ethylene, CO, H_2 and Rh, respectively. Most studies find a first-order dependence of the reaction rate on the concentration of the alkene [8, 40, 41], which is in good

agreement with the value estimated in this work. Kiss et al. [8] found the reaction order of H₂ to be positive, the reaction order of CO to be usually negative and the reaction order of Rh to be 1 for the hydroformylation of ethylene, and Deshpande et al. [74] found the same trends in the hydroformylation of 1-hexene. Cavalieri d'Oro et al. [75] calculated reaction orders of 0.6, -0.1, 0 and 1 for propene, CO, H₂ and Rh, respectively, in propene hydroformylation at partial pressures of 1 to 25 bar for CO and 1 to 45 bar for H₂. The observations in the literature therefore show a good correspondence with the reaction orders estimated by regression to the power law model in this work. The positive reaction rate of H₂ which is measured under certain reaction conditions is believed to be a result of Rh dimerization [9]. The estimated value of 80 kJ mol⁻¹ for the activation energy of hydroformylation is also close to the 76 kJ mol⁻¹ estimated by Kiss et al. [8] for ethylene hydroformylation and the 84 kJ mol⁻¹ estimated by Cavalieri d'Oro et al. [75] for propene

Table 5: Calculated values for the activation energy E_a , the rate coefficient $k_{T,av}$ at the average temperature of 369 K and the reaction orders a, b, c and d obtained after regression of the power law model in Equation (23) for the ethylene hydroformylation over a homogeneous $Rh(H)(L)_3(CO)$ catalyst to the experimental data, with their 95% confidence intervals.

parameter		estimated value		
activation energy	Ea	79.6 ± 0.1	kJ mol⁻¹	
rate coefficient at T_{av}	k _{T,av}	(3.02 ± 0.01) · 10 ⁻²	mol m ⁻³ s ⁻¹	
reaction order ethylene	а	0.98 ± 0.01	-	
reaction order CO	b	-0.75 ± 0.01	-	
reaction order H ₂	с	0.95 ± 0.01	-	
reaction order Rh catalyst	d	1.13 ± 0.01	-	

5. Discussion

Numerous studies have focused on the investigation of the kinetics and thermodynamics of hydroformylation, with DFT calculations in particular being employed to obtain quantitative values. However, there are still uncertainties concerning which reaction steps are the most kinetically relevant. It used to be widely accepted that the rate-determining step in hydroformylation was the oxidative addition of H₂, but it has been shown that this is likely not the case at commercially relevant

conditions for phosphine-modified catalysts [28, 29]. It has been suggested that the ethylene coordination or insertion would be the most kinetically relevant reaction steps in this case [8, 31]. Many studies have concluded that the kinetic relevance of the reaction steps might strongly depend on the employed catalyst and the reaction conditions [30, 76], which means that no single reaction can be considered to be truly rate-determining. It has been reported that the most kinetically relevant step shifts from the oxidative addition of H_2 at high ethylene concentrations to the olefin coordination or the CO dissociation at low ethylene concentrations [77, 78]. Electron-withdrawing ligands, such as phosphites, are also more likely to render the oxidative addition of H_2 more kinetically relevant [79], while more electron-donating ligands, such as phosphines, are more likely to have the ethylene coordination or insertion as the most kinetically relevant step [28]. The coordination and the insertion of CO are unlikely to be the most kinetically relevant steps as a negative reaction order is usually observed for CO [8]. This is in agreement with the observation of intermediates deactivated by CO [9], indicating that CO coordination is easy. Furthermore, kinetic NMR studies have shown that the dissociation of PPh₃ is fast compared to the hydroformylation reactions [65], rendering this reaction unlikely to be very kinetically relevant as well. The uncertainty about the most kinetically relevant steps indicates that several of the reaction steps may have kinetic relevance [37, 78, 80, 81]. However, it can be concluded that the coordination of ethylene, the insertion of ethylene and possibly the oxidative addition of H₂ are the most likely steps to be kinetically relevant.

A comparison between the reaction enthalpies and activation energies obtained in this work and literature DFT values [28, 33] is given in Table 6. The model regression leads to an estimate of -50 kJ mol⁻¹ for the reaction enthalpy related to the coordination of the PPh₃ ligand. Along with the relatively low entropy loss of -56 J mol⁻¹ K⁻¹ of the PPh₃ coordination, this corresponds to the expectation that the coordination of the PPh₃ ligand is thermodynamically favored and stabilizes the catalyst, as the electronically saturated, 18-electron species $Rh(H)(PPh_3)_2(CO)_2$ has been observed experimentally, whereas the 16-electron $Rh(H)(PPh_3)(CO)_2$ species has not been observed [8, 64, 65]. Matsubara et al. [33] have determined reaction enthalpies of -78 kJ mol⁻¹ and 14 kJ mol⁻¹ for the coordination of the PPh₃ ligand coordination on the same catalyst without solvent and with ethylene as solvent, respectively, through DFT calculations. It is therefore expected that the actual reaction enthalpy would lie between these two extreme values as toluene is not a reactant in the homogeneously catalyzed hydroformylation, unlike ethylene. The coordination of the ethylene molecule is expected to be exothermic with a reaction enthalpy between $-92 \text{ kJ} \text{ mol}^{-1}$ and $0 \text{ kJ} \text{ mol}^{-1}$ according to Matsubara et al. [33], or -12 kJ mol⁻¹ according to DFT calculations by Sparta et al. [28], which is along the lines of the -40 kJ mol⁻¹, as obtained in this work. Sparta et al. [28] also considered a Rh(H)(PPh₃)₃(CO) catalyst and included estimations for the solvent effects of toluene in their

calculations. The ethylene coordination cannot be too exothermic as it is known that the reaction is not thermodynamically favored at room temperature [33]. The estimated reaction enthalpy along with the large entropy loss of -161 J mol⁻¹ K⁻¹ leads to a Gibbs free energy increase of 8 kJ mol⁻¹ at 25 °C and to an increase of 20 kJ mol⁻¹ at 100 °C, indicating that ethylene coordination is not thermodynamically favored. The coordination of CO, on the other hand, is thermodynamically favored with a reaction enthalpy of -62 kJ mol^{-1} as estimated by the model. The coordination of CO is known to be easy as the resulting catalyst species have been observed experimentally [9] and a large enthalpy decrease is necessary to make up for the pronounced entropy loss amounting to $-174 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$. The estimated reaction enthalpy is slightly lower than the reaction enthalpy of -45 kJ mol⁻¹ calculated by Sparta et al. [28] and inside of the interval of -17 kJ mol⁻¹ to -129 kJ mol⁻¹ calculated by Matsubara et al. [33]. Reaction enthalpies of -38 kJ mol⁻¹ and -43 kJ mol⁻¹ were determined for the insertion of ethylene and of CO, respectively. These are slightly lower than -23 kJ mol⁻¹ and -25 kJ mol⁻¹ as calculated by Sparta et al. [28], respectively, yet present the same small difference, and are on the lower side of the intervals of -95 kJ mol⁻¹ to 18 kJ mol⁻¹ and -42 kJ mol⁻¹ to 59 kJ mol⁻¹ calculated by Matsubara et al. [33], respectively. The insertion reactions are often considered to be irreversible [29, 32], so a significant decrease in the enthalpy can be expected. The reaction entropies determined in this work amount to 12 J mol⁻¹ K⁻¹ and 9 J mol⁻¹ K⁻¹ for the insertion of ethylene and the insertion of CO, respectively. Luo et al. [32] have also reported low reaction entropies of 7 J mol⁻¹ K⁻¹ and $3 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$, respectively, using DFT calculations for a rhodium catalyst with a different phosphine ligand (CHIRAPHOS-type ligand). The large obtained equilibrium coefficients of $1 \cdot 10^6$ and $4 \cdot 10^6$ are easy to interpret, as the reactions are unimolecular, and clearly show that the reactions are nearly irreversible. The obtained reaction enthalpy of the oxidative addition of H₂ amounts to 9 kJ mol⁻¹, which, combined with an entropy loss of $-144 \,\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}$, leads to a reaction which is not thermodynamically favored, in line with what is reported in the literature [28, 29, 32]. The determined reaction enthalpy is relatively close to -11 kJ mol⁻¹, as obtained by Sparta et al. [28], and inside of the interval of -36 kJ mol⁻¹ to 66 kJ mol⁻¹ reported by Matsubara et al. [33]. Even though the oxidative addition of H_2 is difficult, the reverse reaction is slow, as the product has a low concentration, resulting from the quick and favorable occurrence of the consecutive reaction, i.e., the reductive elimination of propanal. The reaction enthalpy obtained for the oxidative addition of propanal amounts to -18 kJ mol⁻¹, which corresponds to an endothermicity of 18 kJ mol⁻¹ for the reductive elimination of propanal. The limited endothermicity of the reductive elimination of propanal, combined with the relatively pronounced entropy gain of 138 J mol⁻¹ K⁻¹, leads to a thermodynamically favorable reaction and is along the lines of the consensus that the reductive elimination of propanal can be considered irreversible [9, 34]. Matsubara et al. [33] reported an reaction enthalpy between -65 kJ mol⁻¹ and 45 kJ mol⁻¹ for the reductive elimination of propanal, which includes the reaction enthalpy obtained in this work.

Activation energies amounting to 42 kJ mol⁻¹ and 44 kJ mol⁻¹ for the insertion of ethylene and of CO, respectively, were determined. Matsubara et al. [33] reported activation energies between 77 kJ mol⁻¹ and 83 kJ mol⁻¹, and between 95 kJ mol⁻¹ and 109 kJ mol⁻¹, respectively, while Sparta et al. [28] obtained 53 kJ mol⁻¹ for both reaction steps. The activation energies determined in this work are significantly lower than the first set of values but are quite close to the latter. The small difference in the activation energies between the insertion of ethylene and CO in this work and in the literature are similar, which can be expected as both are insertion reactions. Since CO and ethylene are inserted into a covalent bond, a quite high activation energy is expected. Both reactions have small reaction entropies, which means that both have a similar difficulty of taking place. However, it is important to take concentration differences in the catalyst species into account when comparing the kinetics of the reactions [43]. The kinetic relevance of ethylene insertion for the overall hydroformylation rate will be more pronounced, as the catalyst species consumed in the ethylene insertion is formed through the coordination of ethylene, which is a thermodynamically unfavored reaction. The insertion of CO, on the other hand, is preceded by the coordination of CO, which is thermodynamically favored and, consequently, will lead to a higher concentration of species to undergo the CO insertion. The oxidative addition of H₂ has an activation energy amounting to 48 kJ mol⁻¹, which is a bit higher than 21 kJ mol⁻¹, as obtained by Sparta et al. [28] and in the interval of 11 kJ mol⁻¹ to 101 kJ mol⁻¹ reported by Matsubara et al. [28]. This activation energy is a bit higher than that of the ethylene insertion, and the entropy loss between dissolved H₂ and the transition state will further decrease the rate coefficient, as its preexponential factor depends on the activation entropy. The reaction preceding the oxidative addition of H₂, i.e., the CO insertion, is more thermodynamically favored than the reaction preceding the ethylene insertion, i.e., the coordination of ethylene, so the effect of the oxidative addition of H₂ on the overall reaction rate will be reduced. Nonetheless, both ethylene insertion and H₂ oxidative addition are most likely kinetically relevant for the overall hydroformylation rate. An activation energy amounting to 22 kJ mol⁻¹ is determined for the oxidative addition of propanal, which corresponds to an activation energy of 40 kJ mol⁻¹ for its reductive elimination. This latter value is very close to the activation energy of 40 kJ mol⁻¹ and 37 to 47 kJ mol⁻¹ reported by Sparta et al. [28] and Matsubara et al. [33], respectively. The entropy gain between the added propanal and the transition state will speed up the reaction, making the reductive elimination of propanal fast. Additionally, the oxidative addition of propanal is very thermodynamically unfavored and the reductive elimination can be considered irreversible, thus, the reductive elimination of propanal is an unlikely candidate for the assumption of large kinetic relevance.

Table 6: Summary of the comparison of the reaction enthalpies and the activation energies obtained in this work to DFT values obtained by Matsubara et al. [33] and Sparta et al. [28]. * The activation energies of the coordination of ethylene and CO were assumed to be 0.

	ΔH _i [kJ mol ^{−1}]			E _{a,i} [kJ mol ⁻¹]		
reaction	current work	Matsubara et al. [33]	Sparta et al. [28]	current work	Matsubara et al. [33]	Sparta et al. [28]
PPh ₃ coordination	-50	-78 to 14	-	-	-	-
ethylene coordination	-40	-92 to 0	-12	0*	0*	0*
ethylene insertion	-38	-95 to 18	-23	42	77 to 83	53
CO coordination	-62	–129 to –17	-45	0*	0*	0*
CO insertion	-43	–42 to 59	-25	44	95 to 109	53
H ₂ oxidative addition	9	-36 to 66	-11	48	11 to 101	21
propanal reductive elimination	18	-65 to 45	-	40	37 to 47	40

As mentioned before, the most likely reactions steps to be kinetically relevant stated in the literature are ethylene coordination, ethylene insertion and H_2 oxidative addition, which is also reflected in the constructed microkinetic model. The activation energies for ethylene insertion, CO insertion, H₂ oxidative addition and propanal reductive elimination are all similar with activation energies of 42 kJ mol⁻¹, 44 kJ mol⁻¹, 48 kJ mol⁻¹ and 40 kJ mol⁻¹, respectively. This corresponds to the hypothesis in the literature which states that there are most likely several reactions steps with similar energy barriers [37, 78, 80, 81]. The effect of the activation energies of the different reactions on the overall reaction rate was assessed, by performing a sensitivity analysis where the activation energy of each reaction was increased by 1 kJ mol⁻¹ while keeping the other ones fixed, and evaluating the effect on the simulated amount of propanal formed, as shown in Table 7 at three sets of experimental conditions. The most pronounced effect was observed for the activation energy of the ethylene insertion, the reductive elimination of propanal, and the oxidative addition of H_2 . The increase in the activation energy of the CO insertion, the coordination of ethylene and the coordination of CO, on the other hand, had almost no effect. The pronounced reduction in reaction rate observed after the increase of the activation energy of the reductive elimination of propanal could result from the reaction directly influencing the concentrations of the product of H₂ oxidative addition and the reactant of ethylene coordination and deactivation through CO coordination, as can be seen in the reaction network. Taking a deeper look at the simulated amounts of intermediate species, an accumulation of $Rh(CO)_3(COC_2H_5)(L)$ and $Rh(CO)_2(H)(L)$ was observed, which precede the oxidative addition of H_2 and the coordination of ethylene, respectively. $Rh(CO)_2(COC_2H_5)(H)_2(L)$ has the lowest concentration of all species in all simulations, which indicates that the reductive elimination of propanal is likely fast, as some accumulation of the reactant would be expected if it were the slowest reaction step. Based on the obtained information, it can be concluded that the most kinetically relevant steps are the insertion of ethylene and the oxidative addition of H_2 However, it should be noted that the contribution of the oxidative addition of H_2 , and possibly the reductive elimination of propanal, to the overall reaction rate is likely overestimated in the model, as the positive reaction order of H_2 is often attributed to Rh dimerization which is promoted at lower H_2 concentrations [9].

Table 7: Change in the simulated amount of propanal formed in mmol when the activation energy of a reaction step is increased by 1 kJ mol⁻¹, using Equation (2) with the parameter values shown in Table 3 and Table 4 in bold (curves). Reaction conditions of sim. 1: 120 min, at T = 100 °C, $n_{cat} = 0.0001 \text{ mmol}$, $p_{tot} = 50 \text{ bar}$, $n_{H2}/n_{C2H4} = 2 \text{ mol mol}^{-1}$, $n_{C0}/n_{C2H4} = 1 \text{ mol mol}^{-1}$ and $n_{PPh3}/n_{cat} = 10 \text{ mol mol}^{-1}$. Reaction conditions of sim. 2: 120 min, at T = 80 °C, $n_{cat} = 0.0001 \text{ mmol}$, $p_{tot} = 50 \text{ bar}$, $n_{H2}/n_{C2H4} = 2 \text{ mol mol}^{-1}$, $n_{C0}/n_{C2H4} = 1 \text{ mol mol}^{-1}$ and $n_{PPh3}/n_{cat} = 10 \text{ mol mol}^{-1}$. Reaction conditions of sim. 3: 120 min, at T = 100 °C, $n_{cat} = 0.0001 \text{ mmol}$, $p_{tot} = 50 \text{ bar}$, $n_{H2}/n_{C2H4} = 1 \text{ mol mol}^{-1}$ and $n_{PPh3}/n_{cat} = 10 \text{ mol mol}^{-1}$. Reaction conditions of sim. 3: 120 min, at T = 100 °C, $n_{cat} = 0.0001 \text{ mmol}$, $p_{tot} = 50 \text{ bar}$, $n_{H2}/n_{C2H4} = 1 \text{ mol mol}^{-1}$.

	parameters used	$\Delta n_{propanal} / \Delta E_a$		
		sim. 1	sim. 2	sim. 3
a)	E_a (ethylene insertion) increased by 1 kJ mol ⁻¹	-0.217	-0.021	-0.089
b)	$E_a(H_2 \text{ oxidative addition})$ increased by 1 kJ mol ⁻¹	-0.053	-0.033	-0.056
c)	$E_{a}(propanal\ reductive\ elimination)$ increased by 1 kJ mol^-1	-0.224	-0.111	-0.223
d)	E_a (CO insertion) increased by 1 kJ mol ⁻¹	0.000	0.000	0.000
e)	E_a (ethylene coordination) increased by 1 kJ mol ⁻¹	-0.001	0.000	0.000
f)	E _a (CO coordination) increased by 1 kJ mol ⁻¹	0.000	0.000	0.000

6. Conclusions

A microkinetic model has been constructed for the hydroformylation of ethylene on a homogeneous $Rh(H)(PPh_3)_3(CO)$ catalyst in a gas-liquid batch reactor, based on Wilkinson's dissociative mechanism. During the experimental investigation, a negative effect on the reaction rate was observed when the partial pressures of ethylene and CO were increased and the partial pressure of H_2 was decreased, which was attributed to reversible deactivation of some of the intermediate catalyst species with CO. It was also found that a ratio of the phosphine additive to the rhodium catalyst of 10 mol mol⁻¹ is sufficient to significantly reduce the extent of catalyst deactivation which occurs at low additive/rhodium ratios. The temperature had an expected positive effect on the reaction rate

between 80 °C and 100 °C, however, at temperatures of 120 °C and higher, the temperature significantly decreased the conversion reached after 2 h until no propanal was observed at 200 °C, which is likely a result of thermal catalyst decomposition. A regression of the model to the experimentally observed formation of propanal led to a physically meaningful model, which is statistically significant and exhibits a good correspondence with the experimental data. The estimated kinetic and thermodynamic parameters were statistically significant without being correlated and were generally in good agreement with literature. The hydroformylation contains several reaction steps with a similar activation energy, i.e. the insertion of ethylene, the insertion of CO, the oxidative addition of H_2 and the reductive elimination of propanal, which were estimated at 42 kJ mol⁻¹, 44 kJ mol⁻¹, 48 kJ mol⁻¹ and 40 kJ mol⁻¹, respectively. The coordination of CO, with a reaction enthalpy amounting to -62 kJ mol⁻¹, was found to be significantly more thermodynamically favored than the coordination of ethylene, with a reaction enthalpy of -40 kJ mol⁻¹. It was concluded that this renders the ethylene reactivity, comprising ethylene coordination and insertion, much more kinetically relevant than the CO reactivity, comprising CO coordination and insertion. By performing a sensitivity analysis of the effect of the activation energies on the overall reaction rate and evaluating the simulated accumulation of intermediate species, it was concluded that the most kinetically relevant reaction steps are the insertion of ethylene and the oxidative addition of H₂. Although the influence of the oxidative addition of H₂ might be overestimated in the model due to the lack of Rh dimerization reactions, the model validates the hypothesis in the literature that the most kinetically relevant step likely involves the role of ethylene in the reaction mechanism, i.e., ethylene coordination or insertion. Additionally, it was found that the insertion of ethylene is more kinetically relevant than the coordination of ethylene. The detailed investigation of the kinetics of the homogeneously catalyzed hydroformylation may serve as a basis for kinetic models for new hydroformylation catalysts, including heterogenized catalysts with potentially similar reaction mechanisms.

Supporting information

Section S1 of the Supporting Information includes a brief description of the dependence of the rate and equilibrium coefficients on the selected standard state, the reaction entropies of the reaction steps are given at different standard states and the derivation of the rate equations is briefly explained. The experimental conditions of the datasets which were selected for the model regression and the model validation are given in Section S2. The calculation of the enthalpies and entropies of solvation is explained in more detail in Section S3 and the obtained values are shown. In Section S4, the calculation of the entropies of coordination are explained in detail and the resulting values are shown. This information is available free of charge via the Internet at <u>http://pubs.acs.org/</u>.

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Graphical Abstract

