

solvent mixture. However, the process was not very attractive for synthesis of higher aldehydes.² This limitation led to the development of a novel solvent system – the TMS system or temperature dependent multicomponent solvent system. The TMS-system provides easy separation of the expensive catalyst from the products on cooling of the reaction mixture.^{3,4,5} The isomerizing hydroformylation of trans-4-octene in the TMS-system of propylene carbonate (PC)/dodecane/*p*-xylene has been carried out producing a very high conversion (about 99%) of the trans-4-octene and offering very attractive selectivities of *n*-nonanal ranging from 79 to 90%⁶ but a strong rhodium leaching as high as 47% was reported. On the other hand, Tijani et al.⁶ has developed a thermomorphic biphasic rhodium system using an inexpensive and conventional ligand such as P(OPh)₃ to catalyze the hydroformylation of higher olefins (>C6). However, neither experimental data nor any empirical model on the kinetics of the hydroformylation of higher alkenes in the TMS-system are available in the literature.

Here we report the kinetics of hydroformylation of 1-octene and 1-dodecene in the TMS-systems consisting of PC, dodecane and 1,4-dioxane. In the above context, the specific objectives of this work are to: (1) study the kinetics of the hydroformylation of 1-octene and 1-dodecene with the above catalyst and reaction medium, (2) develop a mechanistic rate model of the reaction and evaluate the rate parameters by fitting experimental data, and (3) assess the validity and quality of the developed rate model by fitting experimental hydroformylation data.

Experimental

Materials

1-Octene, 1-dodecene, triphenylphosphite, propylene carbonate, dodecane and 1,4-dioxane, purchased from Merck, were 97-99 % pure. The chemicals were used without further purification. No impurity could be detected by GC analysis. Nitrogen and syngas (1:1 CO/H₂) were supplied by MOX, with purity of 99.99 %.

Experimental setup and procedure

The catalyst was prepared in situ by mixing a rhodium catalyst precursor, HRh(CO)(PPh₃)₃ (ABCR, Germany) and triphenylphosphite, P(OPh)₃ in molar ratio of 1:12. Experimental runs were conducted at different temperatures, partial pressure of H₂ and CO and catalyst concentrations varying from 1.8×10^{-4} to 8.3×10^{-4} kmolm⁻³ (0.17 to 0.76 g L⁻¹). Hydroformylation of 1-octene was carried out in a stirred high pressure reactor (model: Parr 4843) equipped with a stirrer and temperature control system. The feed (240 mL) mixed with the catalyst was added to the preheated reactor. The reactor was purged with nitrogen and syngas successively, and then adjusted to the desired temperature. It was pressurized with an equimolar mixture of CO and H₂ to a desired total pressure which was maintained constant during the whole run. The stirrer speed was set at 450 rpm while the reaction continued. Liquid samples (each less than 1 mL) were withdrawn at regular time intervals to follow the progress of the reaction. The reaction was stopped quickly by cooling down the mixture to the room temperature. The gas was vented out and the biphasic mixture was separated. The analysis of reactants and products was carried out by a gas chromatographic method using 5 % phenylmethyl siloxane capillary column. Each type of experiment was repeated three times to check for reproducibility. Measurements are, in general, reproducible within a maximum of 10 % but often within a few per cent.

Solubility measurement

The solubilities of pure H₂ and CO in TMS-systems of PC/dodecene/1,4-dioxane were measured by the absorption method at different pressures (1-25 bar) and temperatures (353-373 K). Requisite volume of the solvent only was taken in the reactor which was then quickly pressurized. The contents were stirred at 450 rpm for about 1 hr to equilibrate the liquid phase with the gas. A few preliminary experiments showed that this time was sufficient for equilibration. The total pressure change due to absorption was recorded on-line as a function of time till it attained a steady and constant value, indicating saturation of the liquid phase. From the initial and final pressure readings, the solubility was calculated in kmolm⁻³ as:

$$C_L = \frac{[P_i - (P_f - p^v)]V_g}{RTV_L} \quad (2)$$

where C_L represents the concentration of the solute gas in the liquid phase, P_i and P_f are the initial and final pressure readings in the reactor; p^v is the vapour pressure of the solvent; V_g and V_L are the volumes of the gas and liquid phases, respectively. Within the temperature range of this study, PC and dodecane have negligible vapour pressure. The vapour pressure of pure 1,4-dioxane was calculated with the Antoine equation.⁷ In order to ensure the applicability of the ideal gas law in Eq. 2, the H₂ and CO fugacity coefficients, were calculated using the Peng-Robinson equation of state (PR EoS). The fugacity coefficients are very close to unity, and the vapour phase could be considered as an ideal gas.⁸ Measurements are reproducible within 2-3 %.

Results and Discussions

Solubility of CO and H₂

For the kinetic study, knowledge on the solubility of gaseous reactants in the reaction medium is essential. The solubility of H₂ and CO in the TMS system is linearly dependent on the pressure in the pressure range of 0.1 to 2.5 MPa. Henry's law constants for solubilities of CO and H₂ in TMS system of PC/dodecane/1,4-dioxane with composition of 0.30/0.10/0.60 are presented in Table 1. These values were used in the calculation of the concentrations of dissolved CO and H₂ in the reaction medium. The effect of temperature (353 to 373 K) and pressure (0.1-2.5 MPa) on the solubility was also determined.

Kinetics

The reaction proceeds via catalytic addition of H and formyl (CHO) groups across the double bond of the olefin to give aldehydes. The main steps in the catalytic cycle follow the Heck and Breslow mechanism developed for the cobalt-catalyzed oxo reaction.⁹ The initial rates of hydroformylation were determined under the range of conditions as shown in Table 2.

Table 1: Solubility of H₂ and CO in TMS-system of PC/dodecane/1,4-dioxane (0.30/0.10/0.60).

Temperature (K)	Henry's law constant (m ³ MPa kmol ⁻¹)	
	H ₂	CO
353	10.13	8.05
363	9.98	7.88
373	9.79	7.56

To ensure the reaction is in the chemical reaction controlling region, preliminary experiments were carried out at temperature of 363 K with different stirring speeds. It was observed that the reaction rate was enhanced greatly with the increase of the stirring speed at first and then approached to a constant, above 400 rpm. Therefore, all the subsequent experimental runs were conducted at the fixed agitation speed of 450 rpm. This conclusion is further supported upon comparing the rates with the maximum rates of mass transfer ($\frac{R_0}{k_L a C_{H_2}^*}, \frac{R_0}{k_L a C_{CO}^*}$) of CO and

H₂ at the respective conditions. Here, R_0 represents the initial rate of hydroformylation, in $\text{kmolm}^{-3}\text{s}^{-1}$; $k_L a$ is the volumetric mass transfer coefficient, in s^{-1} ; and $C_{H_2}^*$ and C_{CO}^* are the solubilities of H₂ and CO at the gas-liquid interphase, in kmolm^{-3} , respectively. The calculated ratio of initial reaction rate to the maximum mass transfer rate of gas-to-liquid was found to be less than 0.10 at 450 rpm. This clearly shows that the rates observed in the entire range of conditions studied are much smaller than the mass transfer rates that would prevail under these conditions, and hence the rate data are in the kinetic regime.

The kinetics of the reaction has been investigated at three temperatures - 353, 363 and 373 K. The rate was found to decrease with higher P_{CO} (or liquid phase concentration of CO) in the pressure range of 1.0 to 11.5 atm (Fig. 1). The rate was found to be first order with respect to the concentrations of catalyst for both the substrates, the substrate concentration as well as the partial pressure of hydrogen gas. In fact, the parametric effects were found to be similar to that of kinetics in homogeneous system under the industrial operating conditions.⁹ The aldehyde concentration versus time data for each experiment were fitted by a polynomial equation which was then differentiated to determine the slope (experimental reaction rate in $\text{kmolm}^{-3}\text{s}^{-1}$) at the initial time. This rate versus concentration data were then used to determine the parameters by fitting the experimental rate.

The pathways of the hydroformylation reaction based on the Heck and Breslow mechanism are shown in Figure 3 and mechanistic rate equations were developed on this basis using the conventional quasi-steady state formalism. Qualitative reasoning and some available experimental observations form the basis of the scheme.^{9,10,11,12,13} In developing the rate equation, it is assumed that (i) all but one of the reaction steps are in equilibrium, (ii) the starting intermediate species at the reaction interface is the complex $\text{HRh}(\text{CO})_2(\text{L})_2$, and (iii) the total rhodium concentration remains constant. Three rate equations have been developed corresponding to the three possible transition states reported in open literature.¹⁰ These are

Table 2: Range of variables studied in the present work

	1-octene	1-dodecene
Conc. of catalyst (kmolm^{-3})	$8.66 \times 10^{-5} - 6.78 \times 10^{-4}$	$8.66 \times 10^{-5} - 3.46 \times 10^{-4}$
Conc. of 1-olefins (kmolm^{-3})	0.21-4.2	0.20-3.0
P_H (MPa)	0.3-1.5	0.3-1.5
P_{CO} (MPa)	0.3-1.5	0.1-1.5
T (K)	353-373	353-373
Reaction volume (mL)	240	220
Solvent	PC/dodecane/1,4-dioxane (0.30/0.10/0.60)	PC/dodecane/1,4-dioxane (0.30/0.10/0.60)

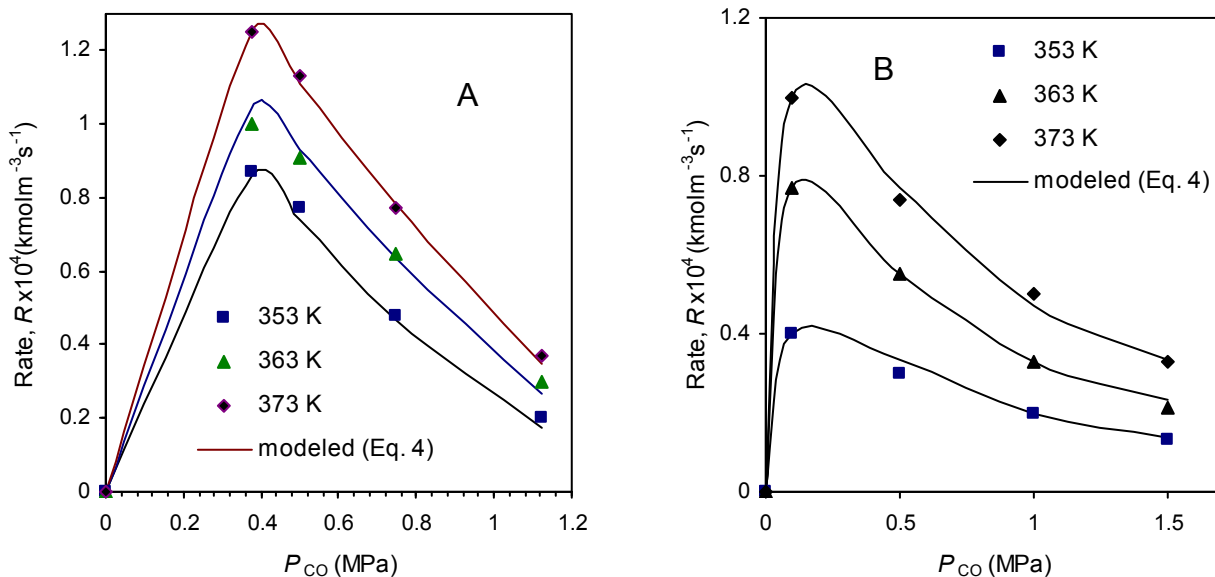


Figure 1. Effect of partial pressure of CO on the rate of hydroformylation of 1-octene (A) and 1-dodecene (B). Reaction conditions: $P = 1.5$ MPa, 1-olefins = 1.9 kmol m^{-3} , $\text{HRh}(\text{CO})(\text{PPh}_3)_3 = 1.73 \times 10^{-4} \text{ kmol m}^{-3}$, $\text{P}(\text{OPh})_3/\text{HRh}(\text{CO})(\text{PPh}_3)_3 = 12$, $\text{PC}/\text{dodecane}/1,4\text{-dioxane} = 0.30/0.10/0.60$.

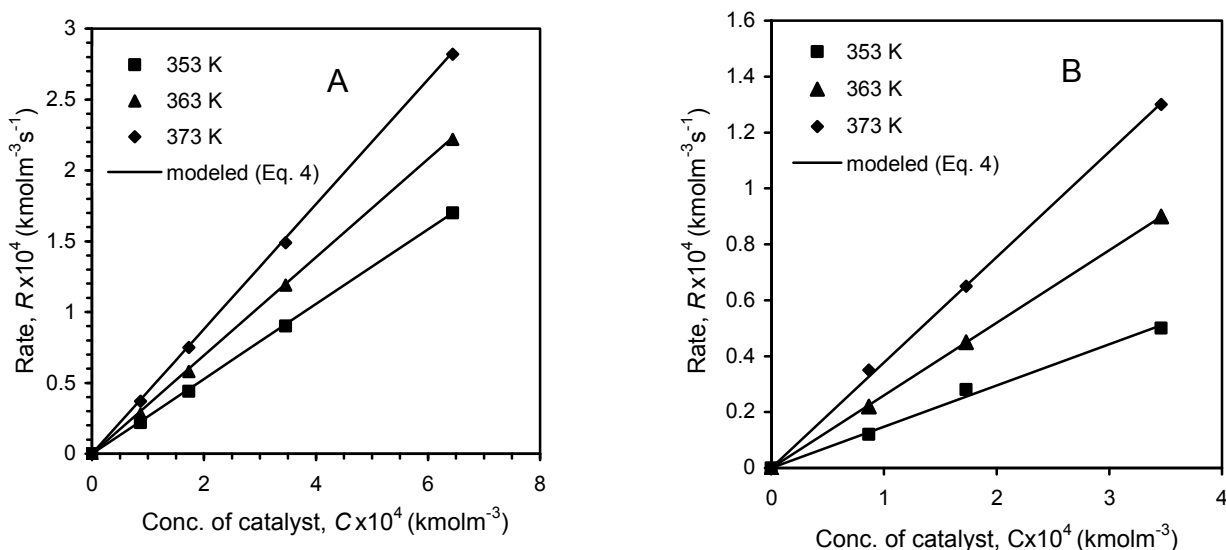


Figure 2. Effect of concentration of catalyst on the rate of reaction: 1-octene (A) and 1-dodecene (B). Reaction conditions: $P = 1.5$ MPa, 1-octene = 1.9 kmol m^{-3} , $\text{P}(\text{OPh})_3/\text{HRh}(\text{CO})(\text{PPh}_3)_3 = 12$, $\text{PC}/\text{dodecane}/1,4\text{-dioxane} = 0.30/0.10/0.60$.

Rate Model M1: Oxidative addition of H_2 is rate –controlling

$$\text{Rate} = \frac{k[\text{catalyst}][\text{CO}][\text{alkene}][\text{H}_2]}{1 + K_1^*[\text{CO}] + K_2^*[\text{CO}]^2 + K_3^*[\text{alkene}] + K_4^*[\text{CO}][\text{alkene}]} \quad (3)$$

where k is the reaction rate constant of the rate determining step and $K_1^* - K_5^*$ are ‘equilibrium constants’ of the other reaction steps in the pathways shown in Figure 3.

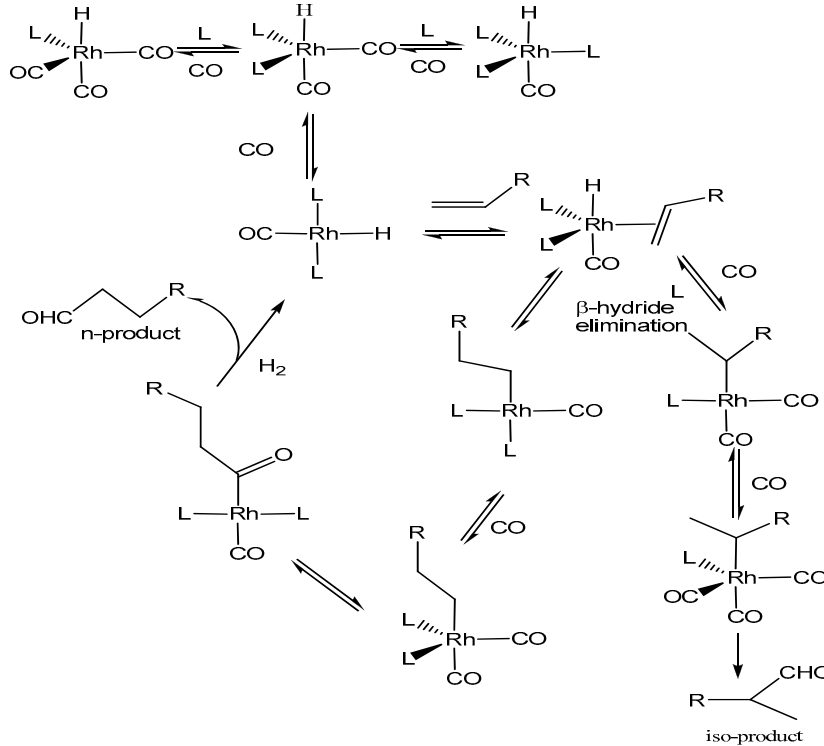


Figure 3: Plausible steps for rhodium catalyzed hydroformylation in the presence of excess concentration of $P(OPh)_3$ ligand.

Rate Model M2: The insertion of the alkene into Rh-complex is rate-controlling

$$\text{Rate} = \frac{k[\text{catalyst}][\text{CO}][\text{alkene}][\text{H}_2]}{(1 + K_1^*[\text{CO}]^2 + K_2^*[\text{alkene}] + K_3^*[\text{CO}][\text{alkene}][\text{H}_2] + K_4^*[\text{CO}][\text{alkene}])} \quad (4)$$

and

Rate Model M3: Formation of the acyl complex is rate-controlling:

$$\text{Rate} = \frac{k[\text{catalyst}][\text{CO}][\text{alkene}][\text{H}_2]}{(1 + K_1^*[\text{CO}] + K_2^*[\text{CO}]^2 + K_3^*[\text{alkene}] + K_4^*[\text{CO}][\text{alkene}][\text{H}_2] + K_5^*[\text{CO}][\text{alkene}])} \quad (5)$$

Non-linear least square regression based on the criterion of minimization of the mean residual sum of squares (MRSS) was performed to determine the kinetic parameters where N_{expt} is the number of experimental data, N_{param} is number of model parameters, R_{calc} and R_{expt} represent calculated and experimental rates, respectively.

$$\text{MRSS} = \frac{\sum_{i=1}^N (R_{\text{calc}} - R_{\text{expt}})^2}{N_{\text{expt}} - N_{\text{param}}} \quad (6)$$

The activation energy of the rate-controlling reaction step and the pre-exponential factor were obtained from the Arrhenius equation with 'temperature centering'.

$$k_i = A_i \exp\left[\frac{-E_i}{R} \left(\frac{1}{T} - \frac{1}{T_m}\right)\right] \quad (7)$$

Table 3: Estimated kinetic model parameters with 95% confidence limits

Substrate	T (K)	k	K_1^*	K_2^*	K_3^*	K_4^*	SEE	E_a (kJ mol ⁻¹)
1-octene	353	9.6×10^2	9.1×10^{-3}	4.4×10^2	9.3×10^{-3}	3.32	4.5	66.3
C ₈	363	1.6×10^3	20.3	3.5×10^2	1.2×10^{-1}	8.8×10^{-1}		
	373	3.1×10^3	55.6	3.3×10^2	8.5×10^{-1}	6.4×10^{-7}		
1-dodecene	353	7.1×10^2	0.37	2.6×10^3	0.86	54.1	3.6	76.1
C ₁₂	363	1.3×10^3	42.4	2.9×10^3	0.45	42.1		
	373	2.8×10^3	139.0	3.2×10^3	7.2×10^{-2}	23.9		

Here T_m is introduced for temperature centering. In the present study $T_m = 363$ K was used for temperature centering and parameter estimation. This scaling procedure admits of robust parameter estimation minimizing non-linear correlation effects.^{14,15,16} An ‘equilibrium constant’, K , was similarly determined as a function of temperature using the van’t Hoff equation also with temperature centering.

$$K_i^* = \exp \left[\frac{\Delta S_i}{R} - \frac{\Delta H_i}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] \quad (8)$$

The error estimate given by Eq. (6) together with thermodynamic consistency of the calculated activation energy or negative kinetic parameter, if any, were used as the criteria of discrimination among the three rate models.^{16,17,18} Model M2 was rejected because it displayed a non-linear Arrhenius plot. Model M3 showed high average standard error estimate ranging from 11% to 18% besides having negative kinetic parameters. The rate model M1 is able to describe the experimental data reasonably well over the whole range of pressure, concentrations of the olefins (1-octene and 1-dodecene) and temperature.

As Figure 4 displayed convincingly, the rate model M1 describes the experimental data of both substrates well. The estimated parameters as well as the activation energy and error

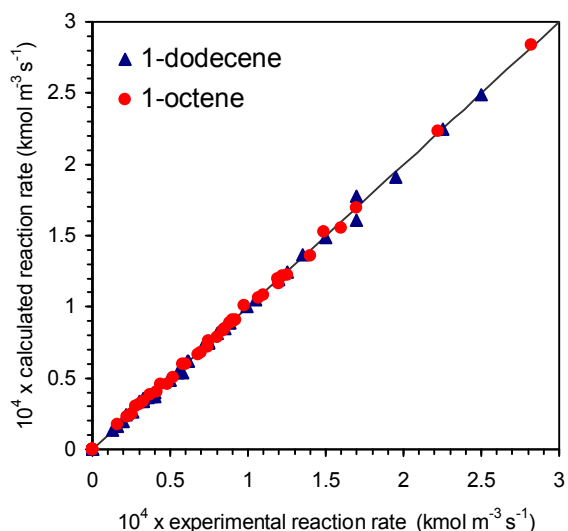


Figure 4. Parity plot of the model predictions of the rate of hydroformylation of 1-octene and 1-dodecene in TMS-systems of PC/dodecane/1,4-dioxane (0.30/0.10/0.60).

estimates are presented in Table 3. These results suggest that a mechanism of reaction featuring oxidative addition of H₂ to acylrhodium intermediate species as rate determining is fair to describe the hydroformylation of the two substrates – namely, 1-dodecene and 1-octene. The average deviation between experimental and calculated rate of reaction was found to be in the range of ± 4.0 % and the activation energy of 66.3 and 76.1 kJmol⁻¹ were determined for the hydroformylation of 1-octene and 1- dodecene, respectively. The results also support previous findings in demonstrating that under the experimental conditions listed in Table 1, the acylrhodium complex is the resting state and oxidative addition of H₂ is rate determining.¹⁹

Conclusion

The kinetics of hydroformylation of 1-octene and 1-dodecene a homogeneous catalyst consisting of HRh(PPh₃)₃(CO) and P(OPh)₃ in a TMS- system containing propylene carbonate (PC), dodecane and 1,4-dioxane has been investigated in a temperature range of 353-373 K. The rate versus P_{CO} shows a typical case of substrate inhibited kinetics. The rate was found to be first order with respect to concentrations of the catalyst, the olefins and hydrogen in the reaction mixture. A mechanistic rate equation has been proposed based on plausible mechanism steps. It was possible to fit reasonably well the experimental data considering oxidative addition of hydrogen as rate-determining. The validity and quality of the developed rate model was assessed with respect to C₁₂ substrate (1-dodecene). The rate model predicted the conversion of the 1-octene and 1-dodecene satisfactorily with maximum deviation of 4.5 %.

Notation

[catalyst]	concentration of catalyst HRh(CO)(PPh ₃) ₃ /P(OPh) ₃ in the reaction mixture, kmol m ⁻³
[CO]	concentration of carbon monoxide in the reaction mixture, kmol m ⁻³
[H ₂]	concentration of hydrogen in the reaction mixture, kmol m ⁻³
[alkene]	concentration of alkene in the reaction mixture, kmol m ⁻³
<i>E</i>	activation energy for rate constant, kJ mol ⁻¹
ΔH	heat of reaction, kJ mol ⁻¹
<i>k</i>	reaction rate constant, units will be specific to the form of the rate expression
<i>A</i>	pre-exponential factor, units will be identical to the rate constant
<i>R</i>	gas constant, 8.314 J mol ⁻¹ K ⁻¹
ΔS	entropy of reaction, J mol ⁻¹ K ⁻¹
<i>T</i>	temperature, K

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