

# Kinetics of hydroformylation of 1-dodecene using homogeneous $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ catalyst

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## Abstract

The kinetics of the  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  catalyzed hydroformylation of 1-dodecene has been investigated in a temperature range of 323–343, K. The effect of 1-dodecene and catalyst concentration,  $P_{\text{H}}$  and  $P_{\text{CO}}$ , on the rate of reaction has been studied. The rate was found to be first order with respect to catalyst concentration and partial pressure of hydrogen. The rate vs.  $P_{\text{CO}}$  shows a typical case of substrate inhibited kinetics. The rate was found to be first order with respect to 1-dodecene in the lower concentration range while at higher concentrations a zero order dependence was observed. A rate equation has been proposed and kinetic parameters evaluated. The activation energy was found to be 57.12 kJ/mol. A batch reactor model has been used to predict the concentration-time profiles which were found to agree well with the experimental data at different temperatures. This indicates the applicability of the rate model over a wide range of conditions.

*Keywords:* Kinetics; Hydroformylation; 1-Dodecene

## 1. Introduction

Hydroformylation of a wide range of olefins ( $\text{C}_2$ – $\text{C}_{40}$ ) is practised industrially to obtain aldehydes and alcohols with applications as intermediates for surfactants, detergents, plasticizers and perfumery chemicals [1,2]. Extensive work has been done on the role of different types of metal complex catalysts, ligands and solvents on the activity and the selectivity in hydroformylation. One of the most established catalyst system consists of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$

complex which is also used commercially in the low pressure oxo process for propylene to n-butylaldehyde. A knowledge of the kinetics of such a complex catalytic reaction and the development of a rate equation is also important in understanding the mechanistic features of such reactions. In this paper, a detailed study on the kinetics of hydroformylation of 1-dodecene has been presented.

Hydroformylation of 1-dodecene is important in the synthesis of n-tridecanal, which has a wide range of applications in perfumes, fragrances, surfactants, etc. [3–5]. Activity and selectivity in hydroformylation of 1-dodecene and its isomers using unmodified cobalt as well as rhodium carbonyl catalysts have been studied

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by [6]. It is reported that the terminal dodecene gives higher selectivity to n-aldehydes in a temperature range of 373 to 433 K and at 10–14, MPa. Carlock [7] has studied the effect of the triphenyl group V family ligands on the selectivity of the rhodium catalysed hydroformylation of 1-dodecene. It is observed that the regioselectivity varies inversely with ligand basicity. Kohl et al. [8] reported the kinetics of hydroformylation of  $C_{11}$  to  $C_{14}$  olefin mixtures using a modified cobalt catalyst. A knowledge of intrinsic kinetics is useful in understanding the reaction mechanism as well as reactor design. There is no previous report on the kinetics of hydroformylation of 1-dodecene and hence the aim of the present work was to study the kinetics of this reaction using  $HRh(CO)(PPh_3)_3$  as a catalyst. For this purpose, the effect of catalyst and 1-dodecene concentration and partial pressures of CO and  $H_2$  on the rate of hydroformylation has been studied in a temperature range 323–343 K. A rate equation has been proposed based on the experimental rate data and the kinetic parameters evaluated. Based on the kinetic model, the performance of a batch reactor was evaluated using a mathematical model and the results on the concentration time profile were found to agree well with the experimental data.

## 2. Experimental

### 2.1. Materials

Rhodium trichloride ( $RhCl_3 \cdot 3H_2O$ ), obtained from Arora-Mathey was used as-received without further purification. Triphenyl phosphine ( $PPh_3$ ) was procured from Fluka, Switzerland. 1-dodecene (> 99% pure) was obtained from Aldrich, USA. The solvents, toluene, benzene, ethanol, etc. were freshly distilled and dried prior to use. Hydrogen gas supplied by Indian Oxygen, Bombay and carbon monoxide (> 99.8% pure, Matheson Gas, USA) were used directly from the cylinders. The syngas mixture ( $H_2 + CO$ ) with 1:1 ratio was prepared by mixing  $H_2$  and CO in a reservoir vessel. The catalyst,  $HRh(CO)(PPh_3)_3$ , was prepared by the procedure given by Evans et al. [9].

### 2.2. Experimental set up

All the hydroformylation experiments were carried out in a 50 ml microclave reactor. The microclave supplied by Autoclave Engineers, USA, was provided with arrangements for sam-

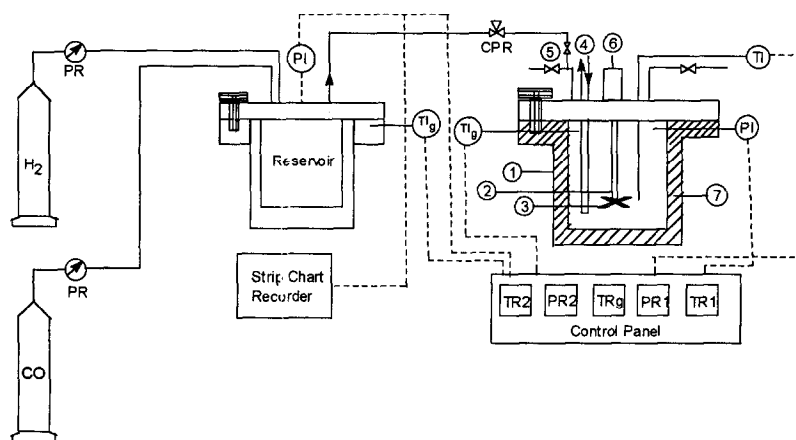


Fig. 1. Schematic representation of reaction set up. Legend: (1) reactor; (2) stirrer shaft, (3) impeller; (4) cooling water (5) sampling valve; (6) magnetic stirrer; (7) furnace; TI: thermocouple; PI: pressure transducer; CPR: constant pressure regulator; PR: pressure regulator; TR1: reactor temperature indicator; TRg: gas temperature indicator; PR1: reactor pressure indicator; PR2: reservoir pressure indicator; TR2: reservoir temperature indicator.

pling of liquid and gaseous contents, automatic temperature control, and variable stirrer speed. A safety rupture disk was also fitted to the reactor. The reactor was designed for a working pressure of 2000 psi and temperatures up to 250°C. The consumption of CO and H<sub>2</sub> at a constant pressure was monitored by observation of the pressure drop in the gas reservoir, from which CO/H<sub>2</sub> was supplied through a constant pressure regulator. The pressure in the reservoir was recorded using a pressure transducer and recorder system to follow the consumption of CO + H<sub>2</sub> as a function of time. A schematic diagram of the experimental set up is shown in Fig. 1.

### 2.3. Experimental procedure

In a typical experiment, known quantities of the catalyst and olefin, along with the solvent were charged into the autoclave and the contents were flushed with nitrogen. The contents were then flushed with a mixture of CO and H<sub>2</sub>, and heated to the desired temperature. A mixture of CO and H<sub>2</sub>, in the required ratio, was introduced into the autoclave, a sample of the liquid was withdrawn, and the reaction was started by switching the stirrer on. The reaction was then continued at constant pressure by supply of CO + H<sub>2</sub> (1:1) from the reservoir vessel. Since, the major products formed were isomeric aldehydes, supply of CO + H<sub>2</sub> at a ratio of 1:1 (as per stoichiometry) was adequate to maintain a constant composition of H<sub>2</sub> and CO in the autoclave, as introduced in the beginning. This was confirmed in a few cases by analysis of the CO content of the gas phase at the end of the reaction. All the reactions for kinetic studies were carried out for short durations such that the conversion in the liquid phase was minimum, to ensure differential conditions. In each kinetic run, initial and final samples were also analyzed for reactants and products in order to check the material balance. It was generally observed that in this low conversion range (< 15%) the rates of hydroformylation were con-

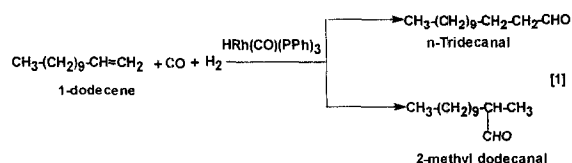
stant. The reproducibility of the experiments was found to be in a range of 5–7%. Following this procedure, the effect of the catalyst and olefin concentrations, partial pressures of H<sub>2</sub> and CO, and temperature on the rate of hydroformylation was studied.

### 2.4. Analytical methods

The quantitative analysis of the reactant and hydroformylation products was carried out by an external standard method using a gas chromatographic technique. For this purpose, Varian 3600 gas chromatograph was used. A 5% PEG 20M on a chromosorb W-AW column of 6 feet length was used. Authentic standards were prepared for calibration of the analysis.

## 3. Results and discussion

The main objective of this work was to investigate the kinetics of hydroformylation of 1-dodecene using HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> as a catalyst. The stoichiometric reaction is given in Scheme 1. Preliminary experiments were carried out to ensure the material balance and reproducibility of the experiments. In these experiments, the amount of 1-dodecene consumed, products formed, and syngas consumed were observed. A typical concentration-time profile is shown in Fig. 2. In general, it was observed that the material balance of (CO + H<sub>2</sub>) and 1-dodecene consumed were consistent with the amount of total aldehyde products formed. Also, in the range of conditions covered in this work, the only products formed were n-tridecanal and 2-methyl-dodecanal, which was confirmed by



Scheme 1.

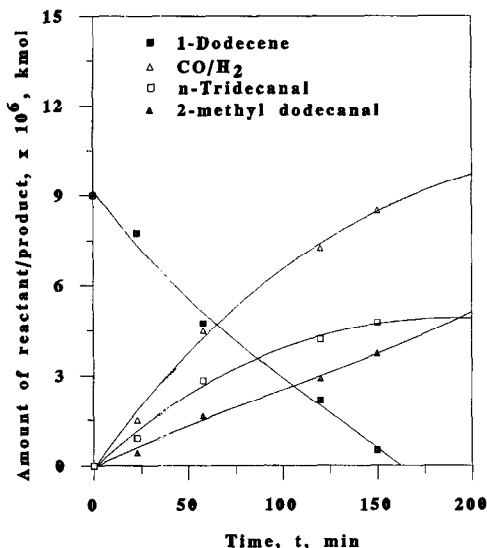


Fig. 2. A plot of amount of reactant/product vs. time. Reaction conditions:  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ :  $2 \times 10^{-3}$ ,  $\text{kmol}/\text{m}^3$ ; 1-dodecene:  $0.36 \text{ kmol}/\text{m}^3$ ;  $P_{\text{CO}} = P_{\text{H}_2}$ : 2.72 MPa; Agitation: 1000 rpm;  $T$ : 333 K; toluene:  $2.3 \times 10^{-5} \text{ m}^3$ .

comparison with GC of authentic standard samples. Thus, the overall hydroformylation kinetics could be followed by observing the consumption of syngas, (at a 1:1 ratio of CO and  $\text{H}_2$ ) as a function of time.

### 3.1. Solubility data

For the purpose of kinetic study, a knowledge of the solubility of the gaseous reactants in the reaction medium is often essential. For the CO-toluene and  $\text{H}_2$ -toluene systems, the solubility data were obtained experimentally by a procedure described by Radhakrishnan et al. [10]. The data obtained are presented in Table 1. These data were used in the calculation of the concentrations of dissolved CO and  $\text{H}_2$  in the liquid medium.

Table 1  
Henri's law constants for  $\text{H}_2$  and CO in toluene

Serial number	Temperature (K)	CO ( $\text{m}^3 \text{ MPa}/\text{kmol}$ )	$\text{H}_2$ ( $\text{m}^3 \text{ MPa}/\text{kmol}$ )
1	323	16.88	55.26
2	333	18.75	61.69
3	343	20.26	76.74

Table 2

Range of conditions for kinetic study

Concentration of catalyst ( $\text{kmol}/\text{m}^3$ )	$1.0 \times 10^{-3}$ to $8.0 \times 10^{-3}$
Concentration of 1-dodecene, ( $\text{kmol}/\text{m}^3$ )	0.18 to 2.2
$P_{\text{H}_2}$ (MPa)	0.68 to 1.7
$P_{\text{CO}}$ (MPa)	0.17 to 2.04
Temperature (K)	323–343
Solvent	Toluene
Reaction volume ( $\text{m}^3$ )	$2.5 \times 10^{-5}$

In order to study the kinetics of the hydroformylation of 1-dodecene using  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  in toluene, several experiments were carried out in the range of conditions as shown in Table 2, by the procedure described earlier. The initial rates of hydroformylation were calculated from the observed data on the consumption of CO +  $\text{H}_2$  as a function of time. A sample plot showing absorption data is shown in Fig. 3. This shows the effect of catalyst concentration on the hydroformylation of 1-dodecene at 333 K. Under the conditions chosen for the kinetic study, no side reactions

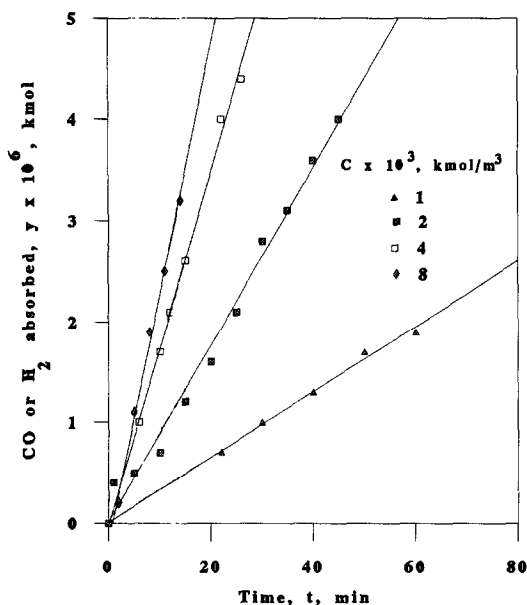


Fig. 3. A plot of CO or  $\text{H}_2$  consumed vs. time: Effect of catalyst concentration. Reaction Conditions: 1-dodecene:  $0.36 \text{ kmol}/\text{m}^3$ ;  $P_{\text{CO}} = P_{\text{H}_2}$ : 2.72 MPa; Agitation: 1000 rpm;  $T$ : 333 K; toluene:  $2.3 \times 10^{-5} \text{ m}^3$ .

were found to occur and hence, these data would be representative of the overall hydroformylation of 1-dodecene to the corresponding aldehydes. Since  $\text{CO} + \text{H}_2$  is consumed in a 1:1 ratio, the rate of reaction of either gas would be half of this overall absorption. The rate of hydroformylation was calculated as follows:

$$R = \frac{\text{slope of CO or H}_2 \text{ consumed vs. time plot}}{\text{Volume of liquid}} \quad (2)$$

These were essentially initial rates of reaction, observed under differential conditions. The results showing the dependence of the rates on different parameters and a kinetic model based on these data, are discussed in the following sections.

### 3.2. Effect of agitation speed

The effect of agitation speed on the rate of hydroformylation is shown in Fig. 4. The rate

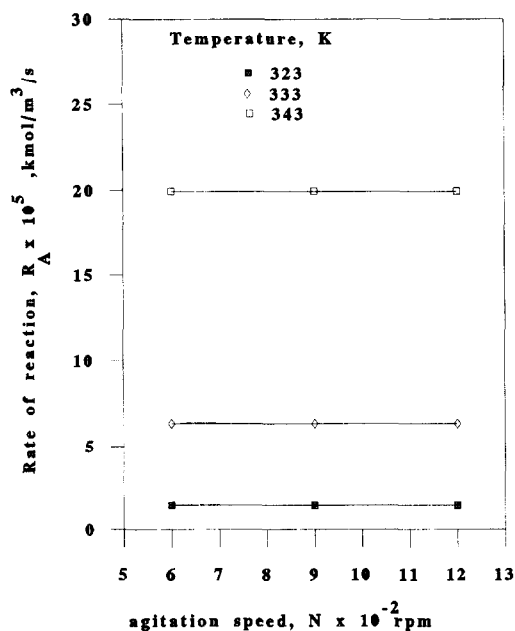


Fig. 4. Effect of agitation speed on the rate of reaction in hydroformylation of 1-dodecene reaction conditions:  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ :  $2 \times 10^{-3}$  kmol/m<sup>3</sup>; 1-dodecene: 0.36 kmol/m<sup>3</sup>;  $P_{\text{CO}} = P_{\text{H}_2}$ : 2.72 MPa;  $T$ : 333 K; toluene:  $2.3 \times 10^{-5}$  m<sup>3</sup>.

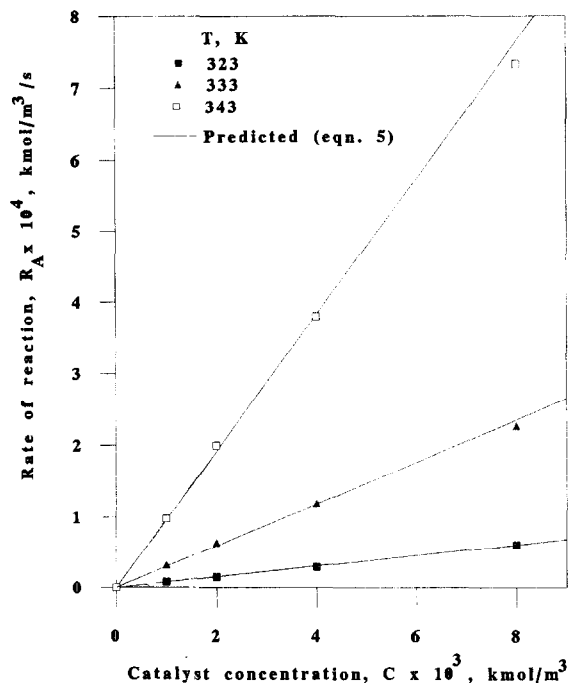


Fig. 5. A plot of rate vs catalyst concentration in hydroformylation of 1-dodecene reaction conditions: 1-dodecene: 0.36 kmol/m<sup>3</sup>;  $P_{\text{CO}} = P_{\text{H}_2}$ : 2.72 MPa; Agitation: 1000 rpm;  $T$ : 333 K; toluene:  $2.3 \times 10^{-5}$  m<sup>3</sup>.

was found to be independent of the agitation speed beyond 400 rpm, at all the temperatures studied, and therefore all the reactions were carried out at an agitation speed of 900 rpm to ensure that the reaction occurred in the kinetic regime.

### 3.3. Effect of catalyst concentration

The effect of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  concentration on the rate of hydroformylation of 1-dodecene was studied in a temperature range of 323–343 K, 1-dodecene concentration of 0.36 kmol/m<sup>3</sup> and a total pressure of  $\text{CO} + \text{H}_2 = 5.44$  MPa ( $\text{CO}/\text{H}_2 = 1$ ). The results are shown in Fig. 5. The rate was found to be linearly dependent on the catalyst concentration, indicating first order kinetics. A first order dependence is expected from the mechanism given in Fig. 6 [9], since increase in concentration of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  will cause an increase in active catalyst concentration, thus increasing the rate.

### 3.4. Effect of partial pressure of CO ( $P_{CO}$ )

The effect of  $P_{CO}$  on the rate of hydroformylation of 1-dodecene was studied at a  $H_2$  partial pressure of 2.72 MPa, 1-dodecene concentration of  $0.36 \text{ kmol/m}^3$  and a catalyst concentration of  $2 \times 10^{-3} \text{ kmol/m}^3$ . The results are shown in Fig. 7, for all the temperatures studied. The rate was found to be inversely dependent on the CO partial pressure.

From the mechanism of hydroformylation proposed by [9], the inhibition of the rate of hydroformylation at higher partial pressures of CO is due to the side reactions (see species, X, Y, Z, Fig. 6) leading to the formation of the inactive species  $(RCO)Rh(CO)_2(PPh_3)_2$  and  $(RCO)Rh(CO)_3(PPh_3)$ . The formation of these species reduce the effective concentration of the active catalytic species and hence, the rate of reaction is retarded. The equilibrium leading to the formation of  $(RCO)Rh(CO)_3(PPh_3)$  will be more pronounced at higher pressures of CO causing a sharp decrease in the rate of reaction as observed in this work.

### 3.5. Effect of partial pressure of hydrogen

The effect of partial pressure of  $H_2$  on the rate of hydroformylation of 1-dodecene was investigated at a constant partial pressure of  $CO = 2.72 \text{ MPa}$  and the results are shown in Fig. 8. The rate of reaction was found to be first order with  $P_{H_2}$ . Oxidative addition of  $H_2$  to the acyl Rh carbonyl species being a rate controlling step, a first order dependence in  $P_{H_2}$  is expected.

### 3.6. Effect of 1-dodecene concentration

Fig. 9 shows the effect of 1-dodecene concentration on the rate of hydroformylation, at a total pressure of 5.44 MPa ( $CO/H_2 = 1$ ), and a catalyst concentration of  $2 \times 10^{-3} \text{ kmol/m}^3$ , in a temperature range of 323–343 K. The rate was found to be first order with 1-dodecene below  $0.36 \text{ kmol/m}^3$ . At higher concentration of 1-dodecene the rate was found to be independent of 1-dodecene concentration. As per the mechanism, the addition of olefin to form the olefin–Rh complex is an equilibrium reaction

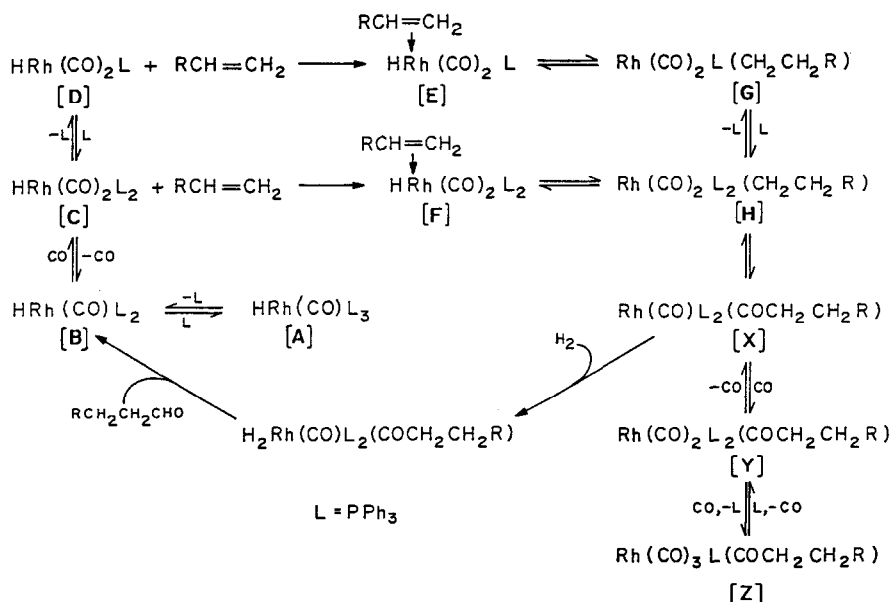


Fig. 6. Mechanism of hydroformylation of olefins [9].

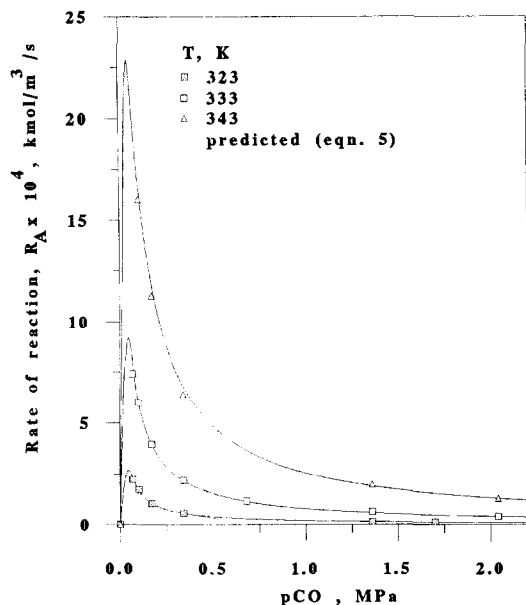


Fig. 7. A plot of the rate vs. partial pressure of carbon monoxide in hydroformylation of 1-dodecene reaction conditions:  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ ;  $2 \times 10^{-3}$  kmol/m<sup>3</sup>; 1-dodecene: 0.36 kmol/m<sup>3</sup>;  $P_{\text{H}_2}$ : 2.72 MPa; agitation: 1000 rpm;  $T$ : 333 K; toluene:  $2.3 \times 10^{-5}$  m<sup>3</sup>.

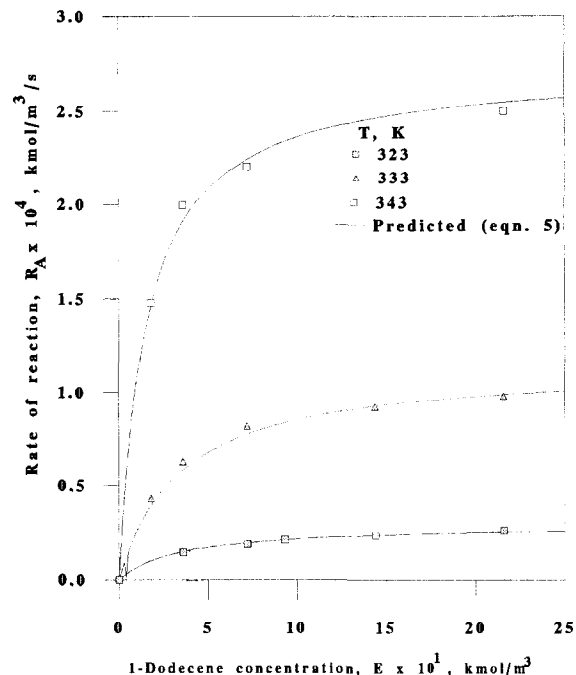


Fig. 9. A plot of the rate vs. 1-dodecene concentration in hydroformylation of 1-dodecene reaction conditions:  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ ;  $2 \times 10^{-3}$  kmol/m<sup>3</sup>;  $P_{\text{CO}} = P_{\text{H}_2}$ ; 2.72 MPa; agitation: 1000 rpm;  $T$ : 333 K; toluene:  $2.3 \times 10^{-5}$  m<sup>3</sup>.

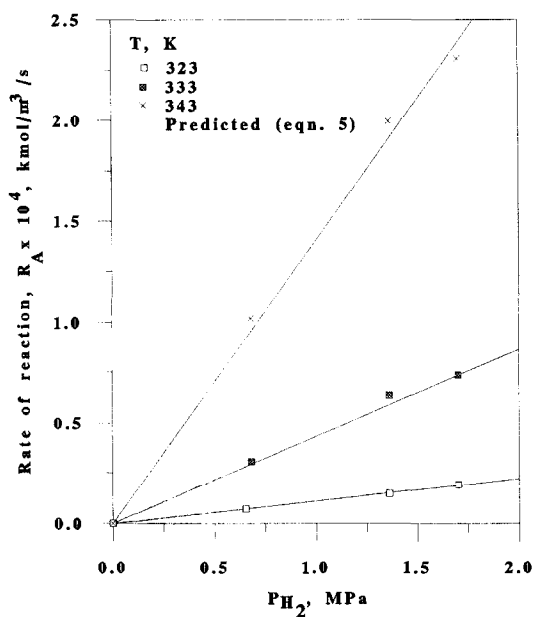


Fig. 8. A plot of rate vs partial pressure of hydrogen in hydroformylation of 1-dodecene reaction conditions:  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ ;  $2 \times 10^{-3}$  kmol/m<sup>3</sup>; 1-dodecene: 0.36 kmol/m<sup>3</sup>;  $P_{\text{CO}} = P_{\text{H}_2}$ ; 2.72 MPa; agitation: 1000 rpm; toluene:  $2.3 \times 10^{-5}$  m<sup>3</sup>.

(step E to G and F to H in Fig. 6). Thus, at higher olefin concentrations the rate of the reverse reaction is likely to be predominant leading to the observed zero order dependence.

### 3.7. Rate model

In order to develop a suitable rate equation representing the intrinsic kinetics of hydroformylation of 1-dodecene, it was first essential to ensure that the rate data obtained are in the kinetically controlled regime. The observation that agitation speed has no effect on the rate indicated the absence of mass transfer resistance. The observed dependency of the rate on different parameters indicates that the hydroformylation of 1-dodecene is first order with respect to catalyst and dissolved  $\text{H}_2$  concentrations, and a negative order with respect to  $P_{\text{CO}}$ .

The rate vs. 1-dodecene concentration also showed a first order kinetics tending to a zero order at higher concentrations. In order to fit the rate data, several rate equations were examined using a nonlinear regression analysis. The results on parameters estimated for different models are presented in Table 3. For this purpose, an optimization program based on Marquardt's method was used. The objective function was chosen as follows;

$$\Phi = \sum_{i=1}^n [R_{A_i} - R'_{A_i}]^2 \quad (3)$$

Where  $\phi$  is the objective function to be minimized ( $\phi_{\min}$ ), representing the sum of the squares of the difference between the observed and predicted rates,  $N$  is the number of experimental data,  $R_{A_i}$  and  $R'_{A_i}$  represent predicted

and experimental rates, respectively. The values of rate parameters and  $\phi_{\min}$  are presented in Table 3. Models 2 and 4 have parameters less than zero and hence were rejected. The rate models 3 and 5 are not consistent with the observed rate dependence. Also, the values of  $\phi_{\min}$  for these models were higher than model 1. Therefore, model 1 was considered the best model for representing the kinetics of hydroformylation of 1-dodecene using  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  complex catalysts.

$$R = \frac{kA^* B^* CE}{(1 + K_B B^*)^2 (1 + K_E E)} \quad (4)$$

where,  $k$  is the intrinsic rate constant ( $\text{m}^9/\text{kmol}^3 \text{s}$ ),  $A^*$ ,  $B^*$  are the concentrations of  $\text{H}_2$  and

Table 3  
Rate models examined to fit the data on 1-dodecene hydroformylation

Serial number	Rate model	$T$ (K)	$k$ ( $\text{cm}^9/\text{mol}^3/\text{s}$ )	$K_B$ ( $\text{cm}^3/\text{mol}$ )	$K_E$ ( $\text{cm}^3/\text{mol}$ )	$\phi_{\min}$
1	2	3	4	5	6	7
1	$\frac{kA^* B^* CE}{(1 + K_B B^*)^2 (1 + K_E E)}$	323	$3.43 \times 10^4$	$5.62 \times 10^2$	2.89	$9.18 \times 10^{-12}$
		333	$5.75 \times 10^4$	$3.73 \times 10^2$	2.93	$1.97 \times 10^{-11}$
		343	$9.93 \times 10^4$	$1.99 \times 10^2$	7.82	$1.26 \times 10^{-11}$
2	$\frac{kA^* B^* CE}{(1 + K_B B^*)^3 (1 + K_E E)}$	323	$2.16 \times 10^3$	78.5	$9.10 \times 10^{-2}$	$1.18 \times 10^{-10}$
		333	$1.06 \times 10^5$	$-1.25 \times 10^3$	-6.07	$1.18 \times 10^{-8}$
		343	$7.81 \times 10^3$	20.9	7.41	$3.89 \times 10^{-9}$
3	$\frac{kA^* B^* CE}{(1 + K_B B^*)^3 (1 + K_E E)^2}$	323	$2.16 \times 10^3$	79.2	$2.73 \times 10^{-2}$	$1.20 \times 10^{-10}$
		333	$1.46 \times 10^3$	25.1	0.553	$4.66 \times 10^{-10}$
		343	$3.59 \times 10^3$	21.0	0.818	$4.40 \times 10^{-9}$
4	$\frac{kA^* B^* CE}{(1 + K_B B^* + K_E E)^2}$	323	$5.05 \times 10^4$	$1.15 \times 10^3$	-3.48	$2.72 \times 10^{-10}$
		333	$4.07 \times 10^5$	$1.91 \times 10^3$	$-2.93 \times 10^1$	$3.53 \times 10^{-9}$
		343	$2.00 \times 10^5$	$7.78 \times 10^2$	$-1.21 \times 10^1$	$3.42 \times 10^{-8}$
5	$\frac{kA^* B^* CE}{(1 + K_B B^* + K_E E)^3}$	323	$1.07 \times 10^5$	295	7.42	$1.21 \times 10^{-10}$
		333	$6.70 \times 10^4$	127	6.21	$3.03 \times 10^{-9}$
		343	$1.59 \times 10^5$	115	6.30	$3.14 \times 10^{-9}$



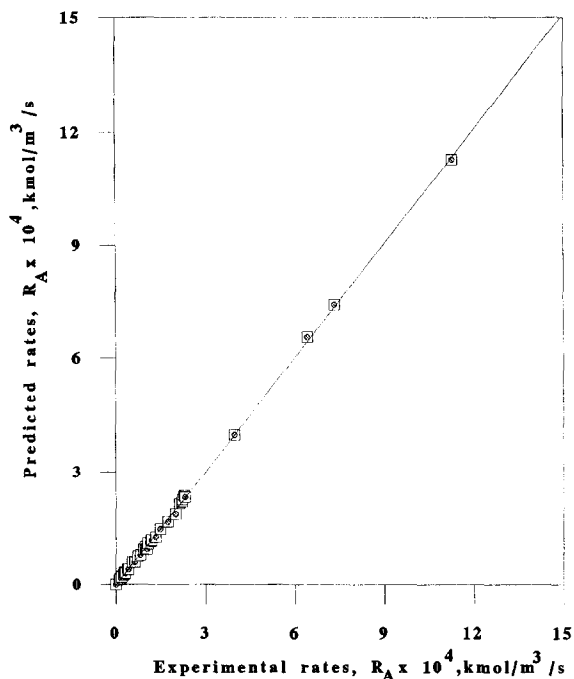


Fig. 10. A plot of predicted rate vs. experimental rate.

CO in toluene at the gas-liquid interface ( $\text{kmol}/\text{m}^3$ ), respectively, and  $C$  and  $E$  represent the concentrations of the catalyst and 1-dodecene ( $\text{kmol}/\text{m}^3$ ), respectively. The rate parameters in Eq. (4) are presented in Table 3 (item 3). The experimental rates were compared with those predicted by rate model (Eq. (4)) in Fig. 10, which shows reasonably good fit of the data. The average deviation in the predicted and observed rates was found to be in the range of  $\pm 8\%$ . The Arrhenius plot showing the effect of temperature on the rate parameters is shown in Fig. 11 and Fig. 12, from which the activation energy was evaluated as 57.12 kJ/mol. The dependence of the rate parameters  $K_B$  and  $K_E$  on temperature show opposite trends; however, it is important to note that these parameters may not be representative of a single equilibrium reaction step and are in fact lumped parameters describing observed overall trends.

### 3.8. Concentration-time profiles

In a semibatch reactor, the concentration of 1-dodecene varies as a function of time and

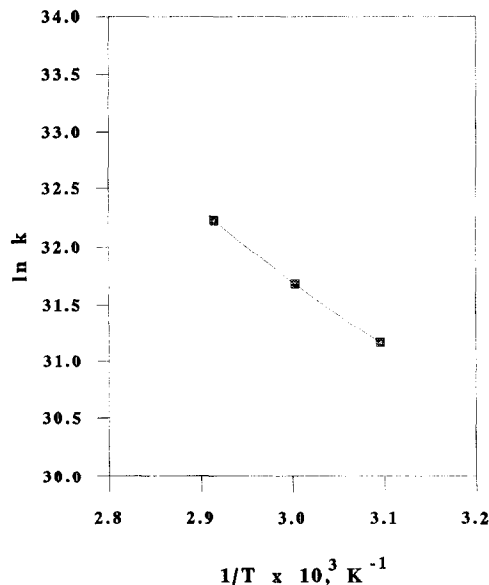


Fig. 11. Temperature dependence of rate constant,  $k$ .

hence, it was necessary to check the validity of the rate equation over the entire range of conditions involved in a semibatch reactor operated at higher conversions. The experiments were carried out at 323, 333 and 343 K to observe the

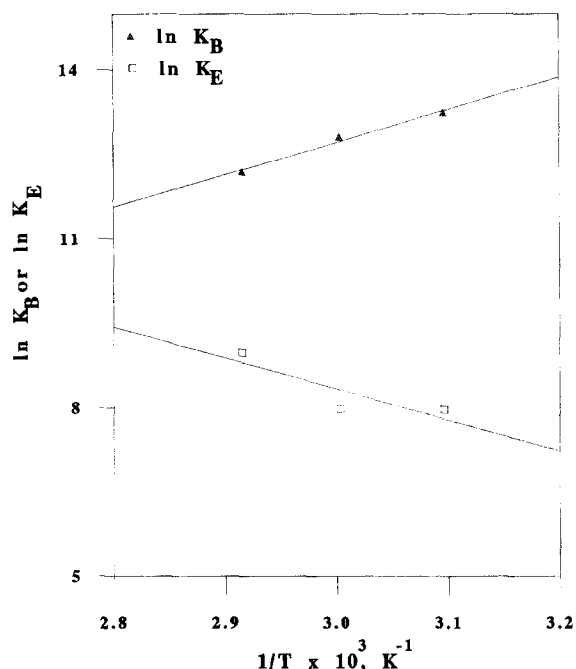


Fig. 12. Temperature dependence of  $K_B$  and  $K_E$ .

variation in the concentrations of 1-dodecene as a function of time, at constant  $P_{\text{CO}}$  and  $P_{\text{H}_2}$ . The variation of the concentration of 1-dodecene can be expressed by the following balance equations for the kinetic regime

$$-\frac{dE_1}{dt} = \frac{kA^*B^*C}{(1 + K_B B^*)^2} \frac{E_1}{(1 + K_E E)} \quad (5)$$

with initial conditions that

$$t = 0 \text{ and } E = E_0 \quad (6)$$

For constant,  $\text{H}_2$  and  $\text{CO}$  pressure conditions, the following equation for the variation of 1-dodecene concentration with time can be derived,

$$\ln \frac{E_0}{E} + K_B [E_0 - E] = \frac{kA^*B^*C}{(1 + K_B B^*)^2} t \quad (7)$$

It was assumed here that the change in reactant and products concentration do not affect the solubility of  $\text{H}_2$  and  $\text{CO}$  significantly. Using Eq. (7), the concentration of 1-dodecene ( $E$ ), as

a function of time was predicted for different temperatures and compared with the experimental data. The results, shown in Fig. 13, indicate excellent agreement between the model predictions and experiments.

#### 4. Conclusions

The kinetics of the  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  catalysed hydroformylation of 1-dodecene has been investigated in a temperature range of 323–343, K. The rate versus  $P_{\text{CO}}$  shows a typical case of substrate inhibited kinetics. The rate was found to be first order with respect to catalyst concentration and partial pressure of hydrogen. The rate was found to be first order with respect to 1-dodecene in the lower concentration range while at higher concentrations a zero order dependence was observed. The following rate equation has been proposed based on the rate data.

$$R = \frac{kA^*B^*CE}{(1 + K_B B^*)^2(1 + K_E E)}$$

The rate parameters  $k$ ,  $K_B$ ,  $K_E$  were evaluated, and the activation energy was found to be 57.12 kJ/mol. A batch reactor model has been used to predict the concentration-time profiles which were found to agree well with the experimental data at different temperatures. This indicate applicability of the rate model over a wide range of conditions.

#### 5. Nomenclature

- $A^*$  Concentration of  $\text{H}_2$  in toluene in equilibrium with gas phase ( $\text{kmol}/\text{m}^3$ ).
- $B^*$  Concentration of  $\text{CO}$  in toluene in equilibrium with gas phase ( $\text{kmol}/\text{m}^3$ ).
- $C$  Concentration of the catalyst ( $\text{kmol}/\text{m}^3$ ).
- $E$  Concentration of the 1-dodecene ( $\text{kmol}/\text{m}^3$ ).
- $k$  Reaction rate constant ( $\text{m}^9/\text{kmol}^3/\text{s}$ ).

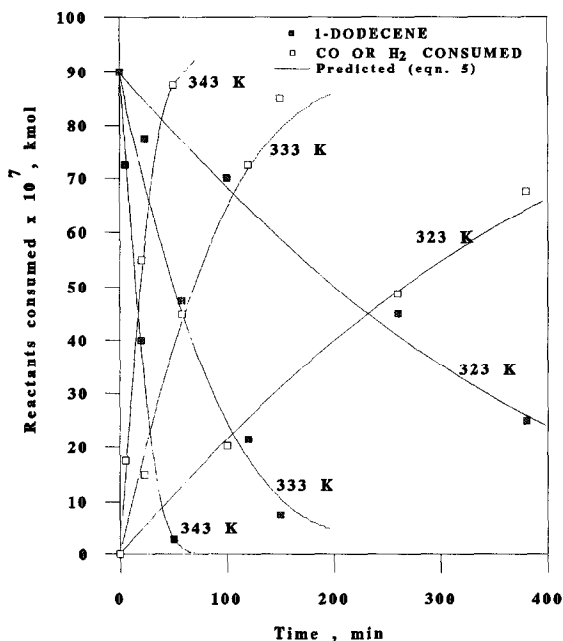


Fig. 13. Comparison of experimental concentration time data with model predictions reaction conditions:  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ :  $2 \times 10^{-3}$   $\text{kmol}/\text{m}^3$ ; 1-dodecene:  $0.36$   $\text{kmol}/\text{m}^3$ ;  $P_{\text{CO}} = P_{\text{H}_2}$ :  $2.72$  MPa; agitation:  $1000$  rpm; toluene:  $2.3 \times 10^{-3}$   $\text{m}^3$ .

$K_B$	Constant in Eq. (4) ( $\text{m}^3/\text{kmol}$ ).
$K_E$	Constant in Eq. (4) ( $\text{m}^3/\text{kmol}$ ).
$N$	Agitation speed (rpm)
$P_{\text{H}_2}$	Partial pressure of hydrogen (MPa).
$P_{\text{CO}}$	Partial pressure of carbon monoxide (MPa).
$R$	Rate of hydroformylation ( $\text{kmol}/\text{m}^3/\text{s}$ ).
$t$	Reaction time (min).

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