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Kinetics of hydroformylation of 1-decene using homogeneous $HRh(CO)(PPh_3)_3$ catalyst: a molecular level approach ☆

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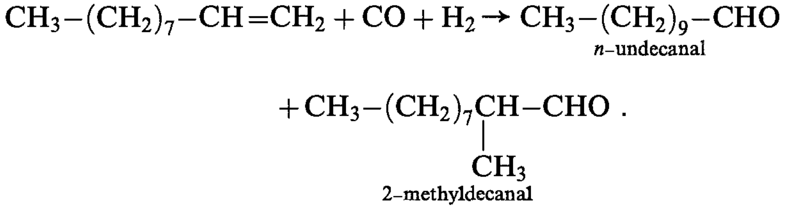
The kinetics of hydroformylation of 1-decene using homogenous $HRh(CO)(PPh_3)_3$ catalyst has been reported in the temperature range of 50–70°C. The effect of catalyst, P_{H_2}, P_{CO}, and 1-decene concentration on the rate of hydroformylation has been studied. Based on the analysis of initial rate data, a rate equation has been proposed and kinetic parameters evaluated. The activation energy was found to be 11.76 kcal/mol. A molecular level approach to kinetic modelling has also been illustrated. The rate equation derived assuming oxidative addition of H_2 as a rate determining step, has been found to represent the data satisfactorily. The rate parameters for the mechanistic model have been evaluated for the data at 60°C.

Keywords: Hydroformylation; rhodium complexes; alkene functionalization

1. Introduction

Hydroformylation of olefins (Oxo process) is important in the manufacture of a wide range of aldehydes and alcohols and is an example of one of the largest scale applications of homogeneous catalysis. In this reaction, an olefin reacts with CO and H_2 in the presence of a homogeneous catalyst to produce a linear or branched aldehyde product. The stoichiometric reaction is given below:



$$CH_3-(CH_2)_7-CH=CH_2 + CO + H_2 \rightarrow \underset{n\text{-undecanal}}{CH_3-(CH_2)_9-CHO} + \underset{\text{2-methyldecanal}}{CH_3-(CH_2)_7\underset{\displaystyle CH_3}{\underset{|}{CH}}-CHO} . \tag{I}$$

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The hydroformylation products have important applications in plasticizers, perfumes, surfactants and solvents.

Previous work on the type of catalysts, promoters, product distribution and selectivity behavior in hydroformylation, has been reviewed by several investigators [1,2]. This reaction system is very complex due to the simultaneous dissolution of two or more gases followed by a catalytic reaction and hence understanding of the reaction mechanism, catalytic cycle and kinetics of the reaction is very important. There are only a few reports in the literature on the kinetics of hydroformylation [3–6]. These studies have considered mainly empirical rate forms to represent the kinetic data. The aim of this paper is to present experimental data on hydroformylation of 1-decene and illustrate the molecular level approach to kinetic modelling.

Hydroformylation of 1-decene in the presence of $HRh(CO)(PPh_3)_3$ catalyst gives undecanal and 2-methyldecanal as the main products. These products have important applications as perfumery chemicals [7]. Wender et al. [8] reported initial rates using $Co_2(CO)_8$ catalyst at 110°C and 233 atm pressure, while Heil and Marko [9] suggested the use of $Rh_4(CO)_{12}$ complex catalyst. There are no published reports on the kinetics of this reaction. In this paper, the effect of catalyst ($HRh(CO)(PPh_3)_3$) concentration, H_2 and CO partial pressures and 1-decene concentration on the rate of reaction has been studied in a high pressure stirred reactor. Based on these data, a rate equation has been proposed and a molecular level approach in the interpretation of the kinetic data discussed.

2. Experimental

2.1. MATERIALS

Rhodium trichloride ($RhCl_3 \cdot 3H_2O$), obtained from Arora Mathey Ltd. was used. The catalyst $HRh(CO)(PPh_3)_3$, was prepared by a procedure described by Evans et al. [10]. 1-decene (Aldrich) and freshly distilled benzene (solvent) were used in all the experiments. Hydrogen (Indian Oxygen Ltd., Bombay) and carbon monoxide ($>99.9\%$ pure) gases were used directly from cylinders.

2.2. APPARATUS

All the hydroformylation experiments were carried out in a 300 ml, SS-316 stirred autoclave reactor similar to that discussed earlier [5]. The autoclave supplied by Parr Instruments Co. Ltd., USA, was provided with arrangements for sampling of liquid and gaseous contents, automatic temperature control, and variable stirrer speeds. A safety rupture disk was also fitted to the reactor. The reactor was designed for a working pressure of 2000 psig and temperatures upto 250°C. In order to monitor the consumption of CO and H_2 at a constant pressure, a gas reservoir was used along with a constant pressure regulator. The pressure in the reservoir was recorded using a pressure transducer and a recorder system.

2.3. EXPERIMENTAL PROCEDURE

The experimental procedure for kinetic study was similar to that described in our earlier work [5]. In each of the kinetic runs, initial and final samples were analyzed for reactants and products in order to check the material balance. It was generally observed that in the low conversion range (<10–20%) the rates of hydroformylation were constant. 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_2 and CO, and temperature on the initial rate of hydroformylation was studied. The analysis of the reactants and products was carried out using a Varian 3600 gas chromatograph using 5% PEG 20M on a Chromosorb W-AW column (2 m length). The two aldehyde products were identified by comparison with the standard samples.

3. Results and discussion

The aim of this work was to investigate the kinetics of hydroformylation of 1-decene using $HRh(CO)(PPh_3)_3$ complex catalyst. A few experiments were carried out in which the amount of 1-decene consumed, products formed, and syngas consumed were compared. It was observed that the quantities of CO or H_2 and 1-decene consumed were consistent with the amount of total aldehyde products formed as per the stoichiometry. The material balance in all these reactions was found to be $\geqslant 95\%$. Also, in the range of conditions covered in this work, the only products formed were undecanal and 2-methyldecanal. No hydrogenation or isomerization products were observed. Thus, the overall hydroformylation kinetics could be followed by observing the consumption of syngas, in a 1 : 1 ratio of CO and H_2. For the purpose of detailed kinetic modelling, several experiments were carried out to understand the influence of catalyst and olefin concentrations, hydrogen and carbon monoxide partial pressures and temperature on the rate of reaction. The results are discussed below. Here the initial rate data evaluated from H_2 or CO consumed versus time plots were used.

3.1. EFFECT OF PARTIAL PRESSURE OF CO (P_{CO})

The effect of P_{CO} on the rate of hydroformylation of 1-decene was studied at a constant partial pressure of $H_2 = 13.6$ atm, 1-decene concentration of 5.28×10^{-4} mol/cm^3, and catalyst concentration of 1.00×10^{-6} mol/cm^3. The results are shown in fig. 1 for all the temperatures studied. The rate was found to decrease with increase in P_{CO}. It is a general observation that the hydroformylation rates are

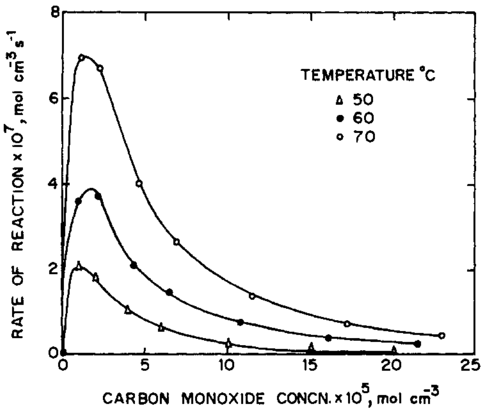

Fig. 1. A plot of rate versus carbon monoxide concentration in liquid phase. 1-decene $= 5.28 \times 10^{-4}$ mol cm^{-3}, catalyst$= 1.00 \times 10^{-6}$ mol cm^{-3}, $P_{H_2} = 13.6$ atm.

inversely proportional to the partial pressure of CO [4,5,11], however, an important observation made here is that the rate is very sensitive to slight changes in the partial pressures of CO. The sensitivity was found to be more pronounced with increase in temperature. This observation can be explained on the basis of the mechanism proposed earlier [12,13] (see fig. 2).

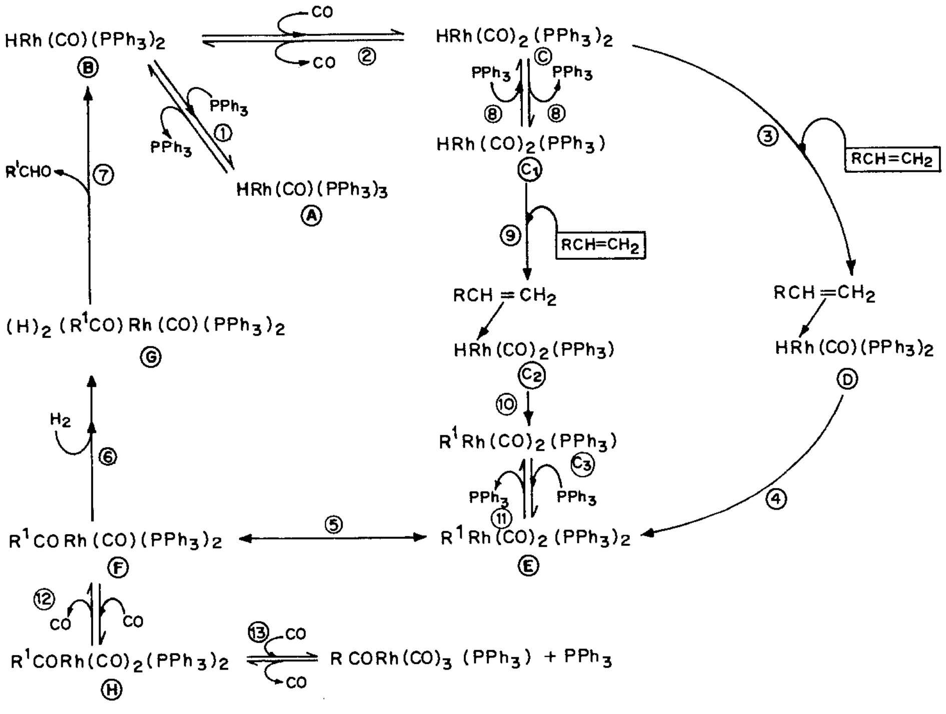

Fig. 2. Mechanism of hydroformylation using HRh(CO)(PPh$_3$)$_3$.

Inhibition of the rate of hydroformylation with increase in partial pressure of CO is due to the side reactions (steps 12 and 13 in fig. 2) leading to the formation of the inactive species $(RCO)Rh(CO)_2(PPh_3)_2$ and $(RCO)Rh(CO)_3PPh_3$ (fig. 2). The formation of these species reduces the effective concentration of the active catalytic species and hence the rate of the reaction is reduced. The equilibrium reaction (step 13) leading to the formation of $(RCO)Rh(CO)_3(PPh_3)$ will be more pronounced at higher partial pressures of CO causing a sharp decrease in the rate of reaction, as observed in this work.

3.2. EFFECT OF PARTIAL PRESSURES OF H_2 (P_{H_2})

The effect of partial pressure of H_2 on the rate of hydroformylation of 1-decene was investigated at a constant partial pressure of CO = 13.6 atm, 1-decene concentration of 5.28×10^{-4} mol/cm^3, and a catalyst concentration of 1.00×10^{-6} mol/cm^3. The results are shown in fig. 3. The rate of reaction was found to vary with 1.5th order with P_{H_2}. No hydrogenation products were observed in the range of conditions studied. At lower P_{H_2}, formation of a dimeric species (T) is possible [13] as shown below:

$$2HRh(CO)_2(PPh_3)_2 \rightleftharpoons \underset{(T)}{[Rh(CO)_2(PPh_3)_2]_2} + H_2 . \qquad (II)$$

This will lead to a reduction in the concentration of the active catalytic species. With increase in P_{H_2}, the formation of the dimer (T) will be inhibited, thereby increasing the rate of hydroformylation. Besides this, the oxidative addition of H_2 to the acyl complex (step 6 in fig. 2) is also dependent on H_2 concentration. An overall order of reaction higher than unity can arise from a combined effect of these two steps.

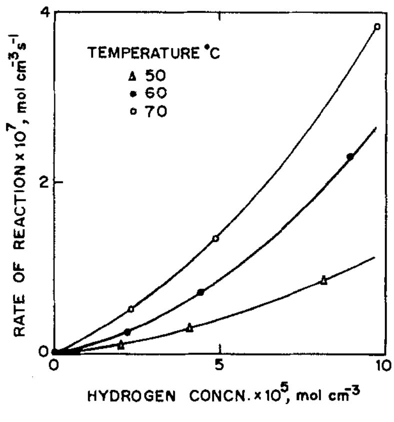

Fig. 3. A plot of rate versus hydrogen concentration in liquid phase. 1-decene = 5.28×10^{-4} mol cm^{-3}, catalyst = 1.00×10^{-6} mol cm^{-3}, P_{CO} = 13.6 atm.

3.3. EFFECT OF 1-DECENE AND CATALYST CONCENTRATION

Fig. 4 shows the effect of 1-decene concentration on the rate of hydroformylation, at a total pressure of 27.2 atm ($CO/H_2 = 1$), a catalyst concentration of 1.00×10^{-6} mol/cm^3, in a temperature range of 50–70°C. The rate was found to be directly proportional to the concentration of 1-decene showing a first order dependence but for higher concentrations, the effect was marginal. These observations are also consistent with the mechanism shown in fig. 2. The near zero order dependence observed at higher olefin concentrations is probably due to the equilibrium in the steps (4) and (10) in fig. 2. At higher olefin concentrations, the reverse equilibrium in steps (4) and (10) may become significant. These observations are however in contrast to the inhibition observed at higher olefin concentrations for other substrates [4,5].

The effect of catalyst ($HRh(CO)(PPh_3)_3$) concentration was studied in a temperature range of 50–70°C, 1-decene concentration of 5.28×10^{-4} mol/cm^3, and a total pressure of $CO + H_2 = 27.2$ atm ($CO/H_2 = 1$). The rate was found to vary with 1.2th order with respect to the catalyst concentration.

4. Kinetic modelling

In order to propose a suitable rate equation for the kinetics of hydroformylation of 1-decene, the initial rate data presented above were analyzed. For this purpose, both empirical rate equations as well as those based on a mechanistic model (molecular level approach) were considered. These results are discussed here.

Several empirical rate forms were evaluated for fitting the initial rate data. These were selected based on the trends observed on the dependence of the rates on

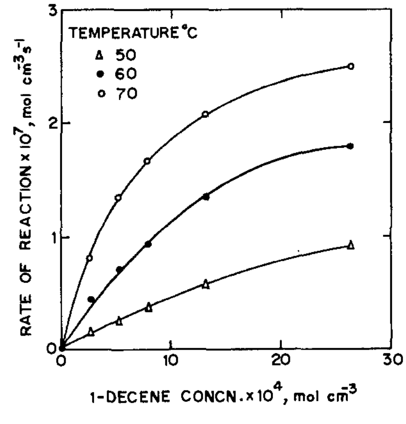

Fig. 4. A plot of rate versus 1-decene concentration. Catalyst $= 1.00 \times 10^{-6}$ mol cm^{-3}, $P_{CO} = P_{H_2} = 13.6$ atm.

Table 1
Solubility of H_2 and CO in benzene

Serial number	Temperature (°C)	Solubility × 10^6 (mol cm^{-3} atm^{-1})	
		H_2	CO
1	50	3.00	7.38
2	60	3.29	7.91
3	70	3.58	8.44

different parameters. The concentrations of dissolved H_2 and CO, required in kinetic modelling were evaluated from the solubility data obtained experimentally (see table 1). In order to fit the rate data, an optimization routine based on Marquardt's [14] method was used. The rate equations and the corresponding parameters evaluated are presented in table 2. Using the various criteria [15] in selection of a rate model, the following rate equation was proposed:

$$R = \frac{k(A^*)^{1.5}B^*C^{1.2}D}{(1+K_BB^*)^3(1+K_DD)}, \qquad (1)$$

where, R is the rate of reaction (mol/cm^3 s), k is the intrinsic reaction rate constant ($cm^{11.1}$/$mol^{3.7}$ s), $A^* = P_{H_2} \times H_A$ and $B^* = P_{CO} \times H_B$ are the concentrations of H_2 and CO in benzene at the gas–liquid interface (mol/cm^3), respectively, and C and D represent the concentrations of the catalyst and 1-decene (mol/cm^3) respectively. The rates predicted using eq. (1) were found to agree within 6–8% error with the experimental data.

For hydroformylation of olefins, a catalytic cycle has been proposed [12,13] based on well defined catalytic species. Hence, it is only appropriate to evaluate the molecular level approach to kinetic modelling in this case. Based on the mechanism shown in fig. 2, rate equations were derived assuming different steps as rate controlling. The rate data on hydroformylation of 1-decene was also fitted using these equations. For step 6 as rate controlling the following rate equation was derived:

$$R = \frac{k'K_1K_2A^*B^*CD}{1+K_2B^*+K_1K_2B^*D+K_1K_2K_3(B^*)^2D+K_1K_2K_3K_4(B^*)^3D}, \qquad (2)$$

where, K_1, K_2, K_3, K_4 are the equilibrium constants for the elementary reactions in the catalytic cycle, and k' is the reaction rate constant (cm^3/mol s).

Eq. (2) was found to be consistent with the general trends of dependence of the rates on P_{H_2}, P_{CO} and 1-decene concentration and particularly with the negative order dependence on P_{CO}. The results comparing the rates predicted by eq. (2) and the experimental data are shown in fig. 5, which indicate that eq. (2) also fits the

Table 2
Models examined to fit the data on 1-decene hydroformylation

Serial number	Rate model	Temp. (°C)	K_B	K_D	k	m	n	$\phi_{\min}$ [a]
1	$\frac{(A^*)^{1.5}B^*C^{1.2}D}{(1+K_B(B^*))^3(1+K_DD)}$	50	5.525×10^4	3.064×10^2	1.081×10^{16}	1.5	1.2	2.939×10^{-16}
		60	3.810×10^4	8.882×10^2	1.441×10^{16}	1.5	1.2	2.111×10^{-15}
		70	3.767×10^4	1.472×10^3	2.840×10^{16}	1.5	1.2	1.352×10^{-15}
2	$\frac{(A^*)B^*C^{1.2}D}{(1+K_B(B^*))^3(1+K_DD)}$	50	5.189×10^4	3.709×10^5	1.081×10^{16}	1	1.2	7.000×10^{-15}
		60	3.610×10^4	4.429×10^5	1.441×10^{16}	1	1.2	2.035×10^{-14}
		70	3.677×10^4	1.637×10^3	2.023×10^{16}	1	1.2	1.226×10^{-14}
3	$\frac{(A^*)^{1.5}B^*C^{1.2}D}{(1+\sqrt{K_B(B^*)})^4(1+K_DD)}$	50	5.503×10^4	1.257×10^3	1.081×10^{16}	1.5	1.2	2.234×10^{-15}
		60	4.024×10^4	1.814×10^3	1.441×10^{16}	1.5	1.2	6.893×10^{-14}
		70	3.891×10^4	2.406×10^3	2.911×10^{16}	1.5	1.2	1.079×10^{-14}
4	$\frac{(A^*)^{1.5}B^*C^{1.2}D}{(1+K_B(B^*))^2(1+K_DD)}$	50	1.418×10^5	3.019×10^2	1.081×10^{16}	1.5	1.2	1.4400×10^{-14}
		60	9.927×10^4	5.851×10^2	1.441×10^{16}	1.5	1.2	3.301×10^{-14}
		70	1.062×10^5	7.630×10^2	2.840×10^{16}	1.5	1.2	1.106×10^{-13}
5	$\frac{(A^*)^{1.5}B^*C^{1.2}D}{(1+K_B((B^*))^2)(1+K_DD)}$	50	5.546×10^4	1.257×10^3	1.081×10^{16}	1.5	1.2	4.559×10^{-9}
		60	3.919×10^4	8.337×10^2	1.441×10^{16}	1.5	1.2	7.064×10^{-9}
		70	3.766×10^5	1.471×10^3	2.840×10^{16}	1.5	1.2	2.541×10^{-8}

[a] $\phi_{\min}$ is minimized sum of the squares of the difference between observed and predicted rates.

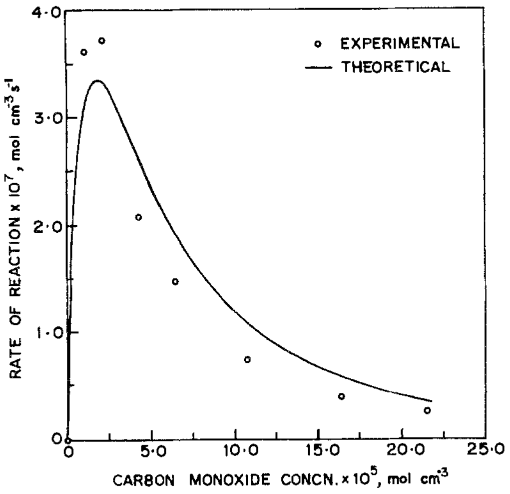

Fig. 5. A plot of rate versus carbon monoxide concentration in liquid phase. 1-decene = 5.28×10^{-4} mol cm^{-3}, catalyst = 1.00×10^{-6} mol cm^{-3}, P_{H_2} = 13.6 atm, temperature = 60°C.

data reasonably well. Though the predictions are not in precise agreement, there is a close analogy between the empirical rate equation (eq. (1)) and eq. (2) with respect to the general trends. However, eq. (2) is mechanistically more meaningful. There are obvious difficulties in fitting the rate data with these mechanistic models due to its complex form, and rigorous optimization procedure is necessary to evaluate these. The values of the rate parameters evaluated for eq. (2) at 60°C are $k' = 1.236 \times 10^6$ cm^3/mol s, $K_1 = 12.8$ cm^3/mol, $K_2 = 5.700 \times 10^9$ cm^3/mol, $K_3 = 1.302 \times 10^5$ cm^3/mol, $K_4 = 2.425 \times 10^5$ cm^3/mol.

5. Conclusions

The kinetics of hydroformylation of 1-decene using a homogeneous $HRh(CO)(PPh_3)_3$ catalyst has been studied. The reaction was found to be 1.2th order with catalyst concentration and 1.5th order with P_{H_2}. The rate of reaction varied linearly at lower concentrations of 1-decene but at higher concentrations the effect was marginal. With respect to P_{CO}, the rate decreased with increase in P_{CO}, indicating a negative order kinetics. Based on these data, a rate equation has been proposed, after examination of several empirical and mechanistic rate models and a rigorous model discrimination procedure. A molecular level approach to kinetic modelling has also been discussed. A rate equation derived from a reaction mechanism assuming oxidative addition of H_2 as rate determining was found to predict the observed trends. The kinetic parameters for this model have also been reported.

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