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Activity and selectivity of Rh-complex catalysts in hydroformylation of 1,4-diacetoxy-butene to Vitamin A intermediate

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Abstract

Hydroformylation of 1,4-diacetoxy-butene using homogeneous $HRh(CO)(PPh_3)_3$ catalyst was investigated with the aim to understand product distribution, selectivity and intrinsic kinetics. The effect of $HRh(CO)(PPh_3)_3$ and 1,4-diacetoxy-2-butene (DAB) concentrations, and CO and H_2 partial pressures on the concentration versus time profiles was studied over a temperature range of 338–358 K. The activity and selectivity of a tethered Rh-complex catalyst on Na-Y zeolite support and a water-soluble Rh-TPPTS catalyst in a two-phase system were also studied and the performance was compared with the homogeneous catalyst. It was observed that both the tethered and biphasic catalysts were highly stable during recycle, though the activity of these catalysts was lower than the homogeneous catalyst. Rate equations have been proposed for both the hydroformylation and deacetoxylation steps. The activation energies were found to be 75.24 and 108.9 kJ/mol, respectively.

Keywords: Homogeneous catalysis; Kinetics; Rate equation; Hydroformylation; 1,4-Diacetoxy-2-butene

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1. Introduction

Hydroformylation of substituted olefins is gaining considerable attention in catalytic synthesis of several complex organic intermediates with applications in fine chemicals, pharmaceuticals and specialty chemicals [1,2]. The application of hydroformylation in organic synthesis is highly promising as it provides a clean catalytic route with high atom efficiency to substitute the conventional reagent based synthesis [3]. An important example of this class is the hydroformylation of 1,4-diacetoxy-2-butene (DAB) to obtain 1,4-diacetoxy-2-formyl butane (DAFB), which is an intermediate in synthesis of Vitamin A acetate [4]. BASF and Hoffmann–La Roche have developed processes for Vitamin A based on hydroformylation using rhodium complex catalyst as the key step [5,6]. In the BASF process [5], 1,4-diacetoxy-2-butene is first isomerised to 1,2-diacetoxy-3-butene and hydroformylated using unmodified rhodium catalyst, to give high yield of the desired branched aldehyde product at 150 atm and 348 K. In the Hoffmann–La Roche process [6], 1,4-diacetoxy-2-butene is directly hydroformylated using the phosphine modified rhodium catalyst to form 77% of 1,4-diacetoxy-2-formyl butane. In none of the previous reports, detailed investigations on the product distribution, selectivity and intrinsic kinetics of the reaction have been reported. The products

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Nomenclature

[CO]	concentration of dissolved CO in the liquid phase (kmol/m^3)
C_0	catalyst concentration (kmol/m^3)
C_1	DAB concentration (kmol/m^3)
C_{10}	DAB concentration at $t = 0$ kmol/m^3
C_2	DAFB concentration (kmol/m^3)
C_3	FAB concentration (kmol/m^3)
[H]	concentration of dissolved H_2 in the liquid phase (kmol/m^3)
k_1	rate constant for hydroformylation (kmol/(m^3 s))
k_2	rate constant for deacetoxylation (kmol/(m^3 s))
K_1, K_2, K_3, K_4	equilibrium constants for reactions (7), (8), (10), and (11)
T	temperature (K)

being non-volatile and unstable, their separation also poses a serious challenge. Therefore, investigations of homogeneous as well as heterogenized homogeneous catalysts would be worthwhile. The aim of this paper is to report a systematic study on the product identification, selectivity behavior and intrinsic kinetics of hydroformylation of 1,4-diacetoxy-2-butene using homogeneous $HRh(CO)(PPh_3)_3$ catalyst. The knowledge of kinetics and development of rate equations is important in understanding the mechanistic features of such complex reactions and hence rate equations have been proposed and kinetic parameters estimated.

2. Experimental

2.1. Materials

Rhodium trichloride, $RhCl_3{\cdot}3H_2O$ (Arora Matthey, India), triphenyl phosphine (Merck) was used as received without further purification. The substrate, 1,4-diacetoxy-2-butene [7], and the catalysts, $HRh(CO)(PPh_3)_3$ [8], $[Rh(COD)Cl]_2$ [9] and tethered $HRh(CO)(PPh_3)_3$ on Na-Y zeolite [10] were prepared by the literature procedures. Hydrogen (Indian Oxygen, Bombay) and carbon monoxide (>99.8% pure, Matheson Gas, USA) were used directly from cylinders. The syn-gas mixture (($H_2 + CO$) with 1:1 ratio) was prepared by mixing H_2 and CO in a reservoir vessel. The solvent, toluene was obtained from Merck and was freshly distilled and dried prior to use.

2.2. Experimental setup and procedure

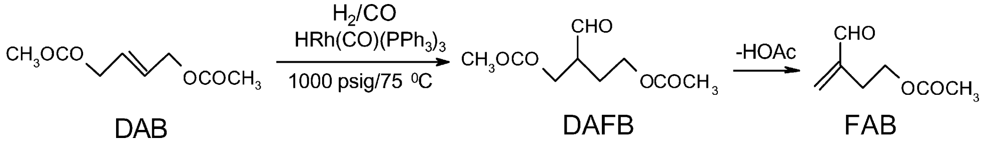
All the hydroformylation experiments were carried out in a 50 ml capacity stirred pressure reactor, supplied by Parr Instrument, USA, the details of which alongwith procedure for hydroformylation experiments was similar to that described previously [11]. The analysis of reactants and products was carried out by a gas chromatographic method on a 5% phenylmethyl siloxane capillary column. For this purpose, HP 6890 gas chromatograph was used. The aldehyde products, DAFB and FAB were identified by ^{1}H NMR (Hitachi Perkin-Elmer 200 and 300 MHz NMR spectrometers) and FT-IR (Bio-Rad Spectrometer). The compounds were further confirmed by GC–MS.

3. Results and discussion

3.1. Product distribution and selectivity

Scheme 1 presents the stoichiometric reactions involved in hydroformylation of DAB.

It is well known that the functional groups in substrates influence the hydroformylation reaction through changes in the double bond polarization and facilitate secondary organic reactions such as aldol-condensations and decomposition of primary hydroformylation products [12]. Therefore, in a few preliminary experiments, the product identification and material balance was examined first using a homogeneous $HRh(CO)(PPh_3)_3$ catalyst. The major products formed were DAFB and FAB, the latter being due to elimination of acetic acid from DAFB. Similar observations have been reported during hydroformylation of vinyl acetate [12]. The two products, DAFB and FAB are very high boiling oils and are difficult to separate, as they are prone to decompose during distillation. These products were separated by column chromatography to obtain pure fractions and characterized by ^{1}H NMR, IR and GC–MS. Typical concentration–time profiles are shown in Figs. 1–3,



Scheme 1. Stoichiometric reactions involved in hydroformylation of DAB.

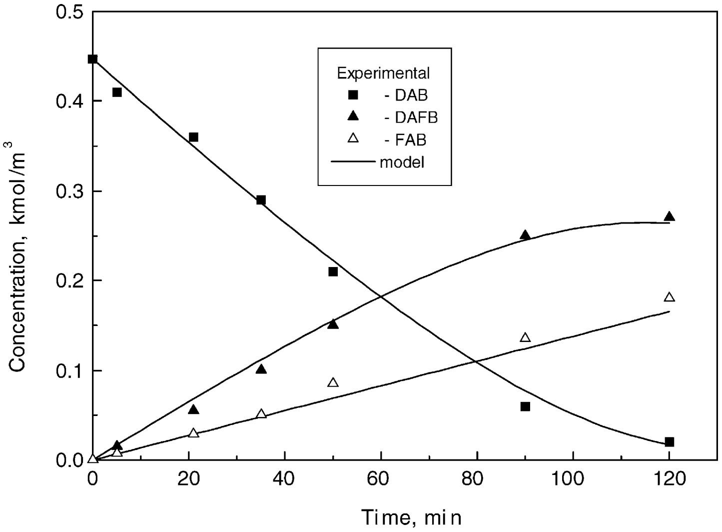


Fig. 1. Concentration–time profiles at 338 K. Reaction conditions: DAB, 0.447 kmol/m^3; catalyst, 1.25 kmol/m^3; P_{CO}, 3.40 MPa; P_{H2}, 3.40 MPa.

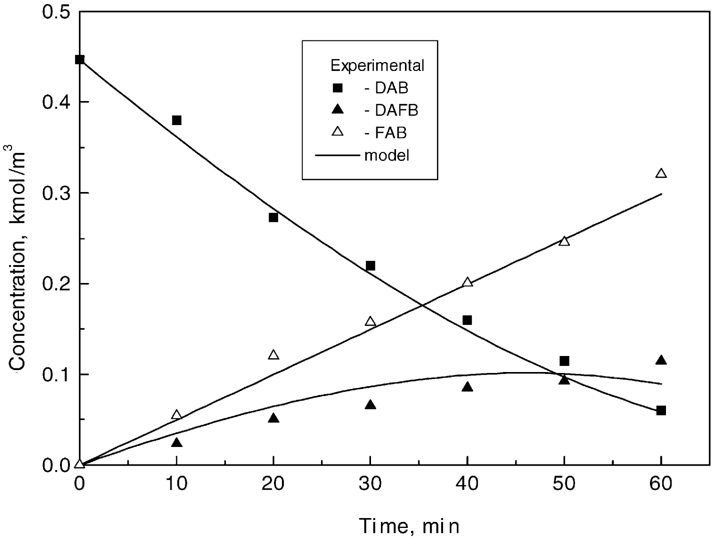


Fig. 2. Concentration–time profiles at 348 K. Reaction conditions: DAB, 0.447 kmol/m^3; catalyst, 1.25 kmol/m^3; P_{CO}, 3.40 MPa; P_{H2}, 3.40 MPa.

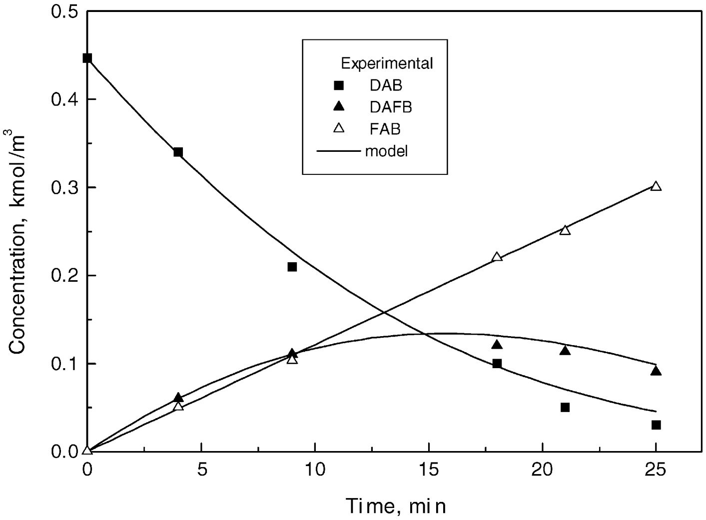


Fig. 3. Concentration–time profiles at 358 K. Reaction conditions: DAB, 0.447 kmol/m^3; catalyst, 1.25 kmol/m^3; P_{CO}, 3.40 MPa; P_{H2}, 3.40 MPa.

which indicate that the material balance of DAB consumed and products formed (DAFB + FAB) agreed to >95% as per stoichiometry. The acetic acid formed by deacetoxylation was also confirmed to be proportional to the amount of FAB formed. The effect of DAB and HRh(CO)(PPh$_3$)$_3$ catalyst, concentrations and CO and H_2 partial pressures on concentration–time profiles was investigated over a temperature range of 338–358 K. It was observed that the concentration of the deacetoxylated product, FAB increased upon increasing temperature but other parameters showed no significant effect on the rate of deacetoxylation. At 358 K, the selectivity of FAB was >90% for DAB conversion >95%.

Experiments were also carried out using catalysts such as, tethered HRh(CO)(PPh$_3$)$_3$ on Na-Y zeolite and water-soluble Rh-TPPTS in two-phase system. A comparison of the performances of these catalysts is shown in Fig. 4, which indicates a clear advantage of the tethered and biphasic catalysts with respect to recyclability over the homogeneous catalyst (the recycle of homogeneous catalyst was studied by charging fresh amount of substrate after the first cycle was completed. This showed that in the recycle experiment, the average activity of hydroformylation decreased by about 15–18%). The selectivity of FAB was nearly 100% for the tethered catalyst on Na-Y zeolite, whereas selectivity for FAB was in the range of 70–80% for the biphasic catalyst. The heterogenized catalysts thus may prove to be better alternatives for the hydroformylation of DAB.

3.2. Kinetic study

In order to study the kinetics of the hydroformylation of DAB using HRh(CO)(PPh$_3$)$_3$ in toluene, the initial rates of hydroformylation were calculated from the observed concentration–time profiles. These were essentially initial rates of hydroformylation reaction calculated under low conversion of DAB (10% conditions). The experiments at different agitation speeds showed that the rate of the reaction was independent of the agitation speed beyond 600 rpm, indicating kinetic regime. All the reactions were therefore carried out at an agitation speed of 1000 rpm to ensure kinetic regime. The initial rate of hydroformylation of DAB was found to be linearly dependent on catalyst [HRh(CO)(PPh$_3$)$_3$] concentration (Fig. 5) and hydrogen partial pressure (Fig. 6). The effect of CO partial pressure (Fig. 7) shows typical substrate-inhibited kinetics for all the temperatures studied. As per the mechanism of hydroformylation proposed by Evans et al. [8], the inhibition of the rate with increase in partial pressure of CO is due to the side reactions leading to the formation of inactive dicarbonyl [(RCO)Rh(CO)$_2$(PPh$_3$)$_2$] and

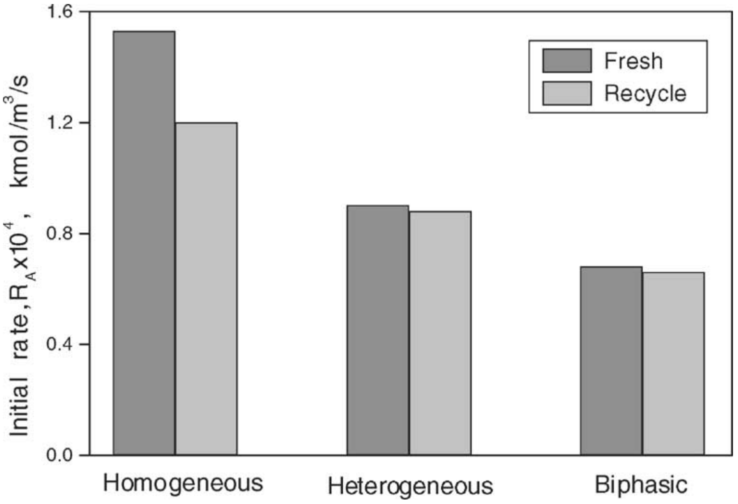


Fig. 4. Performance of homogeneous, tethered heterogeneous and biphasic catalysts. Reaction conditions: DAB, 0.447 kmol/m^3; Rh complex, 1.25 kmol/m^3; P_{CO}, 3.40 MPa; P_{H2}, 3.40 MPa, $T = 348$ K.

tricarbonyl rhodium species [(RCO)Rh(CO)$_3$(PPh$_3$)]. With increase in CO pressure, the concentration of these species is expected to increase, reducing the active species concentration and hence the rate of reaction. The observation of negative order dependence on CO partial pressure was also reported for other olefinic substrates [13–16]. The rate of hydroformylation was found to be zero order with respect to DAB (Fig. 8).

For the purpose of developing rate equations and estimation of kinetic parameters, the integral concentration–time data were used as the initial rates represent only the hydroformylation step. The change in concentrations of DAB (C_1), DAFB (C_2) and FAB

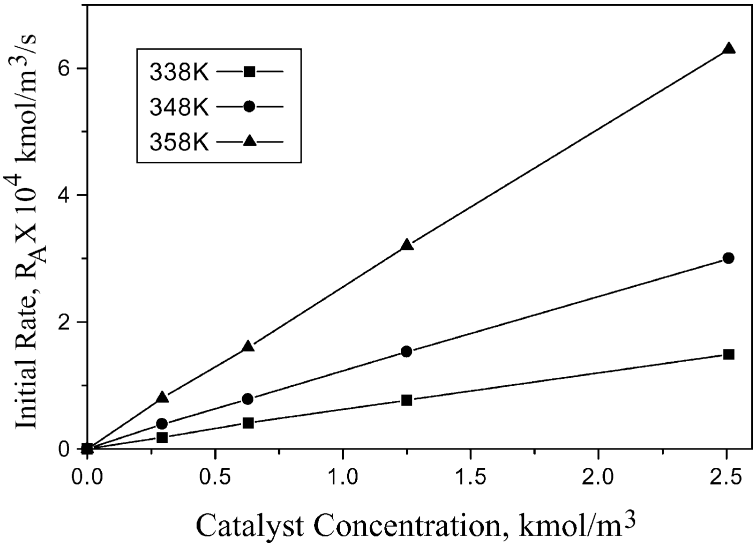


Fig. 5. Effect of catalyst concentration on rate of hydroformylation. Reaction conditions: DAB, 0.447 kmol/m^3; P_{CO}, 3.40 MPa; P_{H2}, 3.40 MPa.

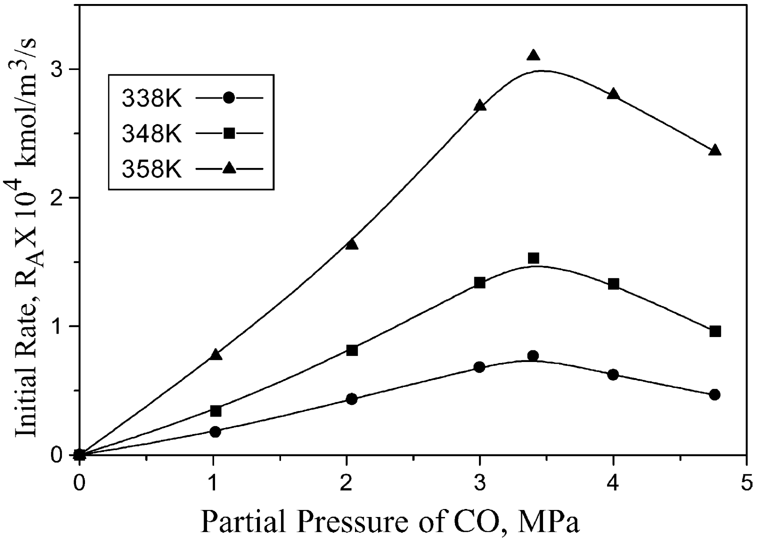


Fig. 6. Effect of hydrogen partial pressure on rate of hydroformylation. Reaction conditions: DAB, 0.447 kmol/m^3; catalyst, 1.25 kmol/m^3; P_{CO}, 3.40 MPa.

(C_3) as a function of time in a batch reactor is given by the following equations:

$$\frac{dC_1}{dt} = -r_1 \quad (1)$$

$$\frac{dC_2}{dt} = r_1 - r_2 \quad (2)$$

$$\frac{dC_3}{dt} = -r_2 \quad (3)$$

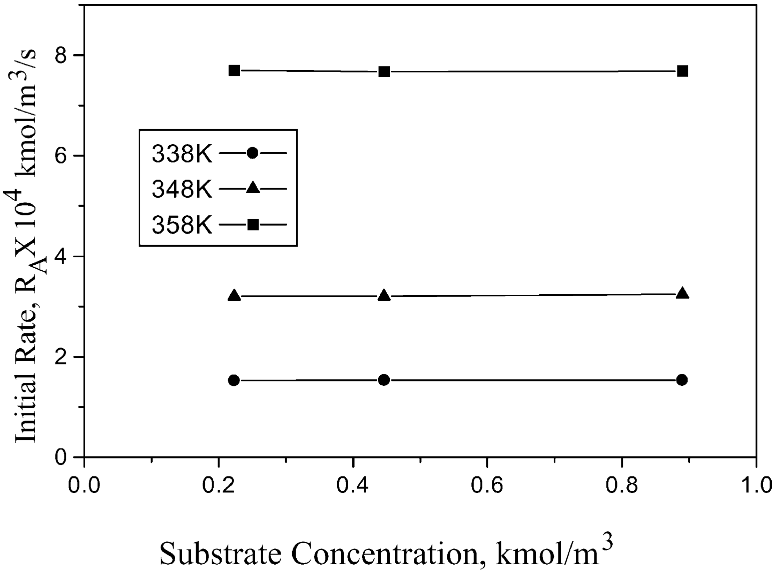


Fig. 7. Effect of carbon monoxide partial pressure on rate of hydroformylation. Reaction conditions: DAB, 0.447 kmol/m^3; catalyst, 1.25 kmol/m^3; P_{H2}, 3.40 MPa.

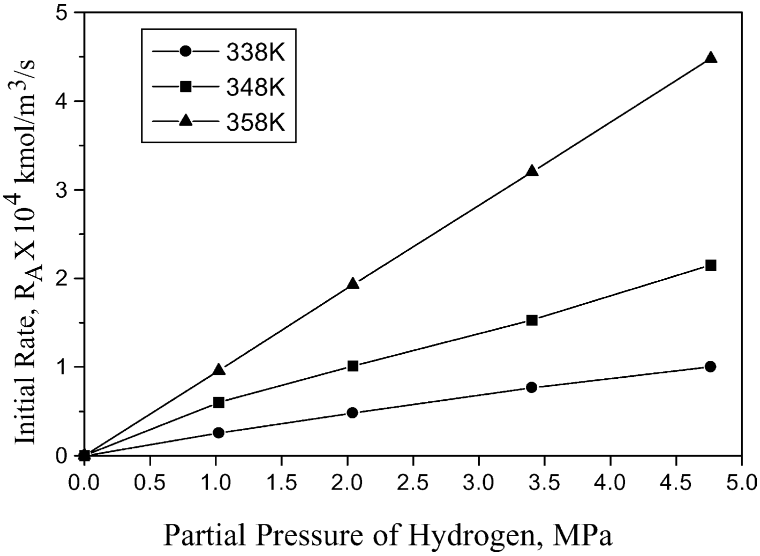


Fig. 8. Effect of DAB concentration on rate of hydroformylation. Reaction conditions: catalyst, 1.25 kmol/m^3; P_{CO}, 3.40 MPa; P_{H2}, 3.40 MPa.

with initial conditions:

$$t = 0,\ C_1 = C_{10},\ C_2 = 0,\ C_3 = 0 \tag{4}$$

Here, the rate terms, r_1 and r_2 represent the reaction rates for the hydroformylation and deacetoxylation steps, respectively. Various forms of rate equations were examined to fit the experimental concentration–time data by solving the above set of model equations in combination with an optimization programme [17]. The details of the procedure followed for model discrimination, statistical analysis and parameter estimation was the same as described earlier [17]. Based on the statistical criteria, the following rate equations were found to represent the concentration–time data obtained over a wide range of conditions as shown for a few typical cases in Figs. 1–3.

$$r_1 = \frac{k_1 K_1 K_2 C_0 C_1 [\mathrm{CO}][\mathrm{H_2}]}{(1 + K_1[\mathrm{CO}] + K_1 K_2 [\mathrm{CO}] C_1 + K_1 K_2 K_3 [\mathrm{CO}]^2 C_1 + K_1 K_2 K_3 K_4 [\mathrm{CO}]^3 C_1} \tag{5}$$

$$r_2 = k_2 \tag{6}$$

The rate equation (Eq. (5)) is derived based on the well-known mechanism for hydroformylation of olefins [8] using HRh(CO)(PPh$_3$)$_3$ catalyst assuming the oxidative addition of H_2 to the acyl-Rh species as the rate determining step.

$$\mathrm{HRh(CO)L_2 + CO} \overset{K_1}{\rightleftarrows} \mathrm{HRH(CO)_2L_2} \tag{7}$$

$$\mathrm{HRh(CO)_2L_2 + RCH{=}CHR} \overset{K_2}{\rightleftarrows} \mathrm{Rh(CO)L_2(COCHRCH_2R)} \tag{8}$$

$$\mathrm{Rh(CO)L_2(COCHRCH_2R) + H_2} \xrightarrow{\kappa_1} \mathrm{HRH(CO)L_2 + RCH_2CHRCHO} \tag{9}$$

$$\mathrm{RH(CO)L_2(COCHRCH_2R) + CO} \overset{K_3}{\rightleftarrows} \mathrm{Rh(CO)_2L_2(COCHRCH_2R)} \tag{10}$$

$$\mathrm{Rh(CO)_2L_2(COCHRCH_2R) + CO} \overset{K_4}{\rightleftarrows} \mathrm{Rh(CO)_3L(COCHRCH_2R)} \tag{11}$$

Here, K_1, K_2, K_3 and K_4 are the equilibrium constants for reaction steps (7), (8), (10), and (11). A comparison of the results between experimental data and the model prediction (Figs. 1–3) was found to be excellent. The kinetic parameters estimated for 338–358 K are given in Table 1. The activation energies for the hydroformylation and acetoxylation steps were found to be 75.24 and 108.9 kJ/mol.

Table 1
Rate parameters

Temperature (K)	k_1 (kmol/(m^3 s))	k_2 ($\times 10^5$, kmol/(m^3 s))	K_1 ($\times 10^{-2}$, m^3/kmol)	K_2 (m^3/kmol)	K_3 (m^3/kmol)	K_4 ($\times 10^2$, m^3/kmol)
338	3.61	2.30	5.46	2.50	16.66	7.41
348	5.50	8.31	3.01	1.51	10.94	3.50
358	16.41	20.01	1.19	0.81	5.019	1.17

4. Conclusion

Kinetics of hydroformylation of 1,4-diacetoxy-2-butene using a homogeneous $HRh(CO)(PPh_3)_3$ was studied in a batch pressure reactor in a temperature range of 338–358 K. The reaction was found to be first order with respect to catalyst and H_2 partial pressure. The rate versus partial pressure of CO showed a substrate-inhibited kinetics at higher CO pressures, while the reaction was zero order with DAB. Rate equations have been proposed for the hydroformylation and deacetoxylation steps and kinetic parameters estimated. The activation energies of the hydroformylation and deacetoxylation steps were found to be 75.24 and 108.9 kJ/mol, respectively. A comparison of the performance of homogeneous, tethered heterogeneous and biphasic Rh-complex catalysts showed that the heterogeneous catalysts are more stable during recycle compared to the homogeneous catalyst in spite of lower rates of reaction. The heterogenized catalysts may have advantage in practical applications for high boiling and thermally unstable products.

Acknowledgements

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