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HYDROFORMYLATION OF ALLYL ALCOHOL CATALYZED BY WATER-SOLUBLE Ru(III)–EDTA COMPLEX

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Summary

Hydroformylation of allyl alcohol was studied in aqueous medium using [Ru(III)–EDTA] complex as catalyst and (1:1) $CO + H_2$ gas in a high pressure autoclave at pressures up to 50 atm and in the temperature range 90 - 130 °C. The hydroformylation of allyl alcohol gives γ-hydroxybutyraldehyde as the primary product, along with the side products γ-butyrolactone, dihydrofuran and 1,4-butanediol. The hydroformylation of allyl alcohol is first order with respect to allyl alcohol and catalyst concentrations, and has a linear dependence on $CO + H_2$ (1:1) pressure of the syngas. The activation energy of the reaction is found to be 23.13 kcal mol^{-1}.

Introduction

The oxo reaction [1 - 3] is an important process which is industrially exploited for the conversion of olefins and functionalized olefins [4] to aldehydes, ketones or alcohols. The reaction uses the conventional cobalt hydridotricarbonyl catalyst [2, 3] at 200 - 300 atm pressure of synthesis gas at 150 - 200 °C. Presently, the use of water-soluble rhodium catalysts [5 - 7] enables the hydroformylation reaction to be conducted at 80 °C and 8 atm of synthesis gas. Recently, we have reported [8] the use of [Ru(EDTA)(Cl)] as a catalyst for the carbonylation of benzyl chloride to phenylacetic acid and its ester. The hydroformylation of allyl alcohol to γ-hydroxybutyraldehyde catalyzed mostly by $HRhCO(PPh_3)_{2-4}$ is an important reaction [9 - 12] which has been described primarily in patent literature [9] and has not been studied thoroughly, especially from the viewpoint of reaction kinetics and mechanism. In the present paper we have studied the kinetics of the hydroformylation of allyl alcohol catalyzed by [Ru(EDTA)(Cl)]. The products of the reaction are γ-hydroxybutyraldehyde, along with γ-butyrolactone, dihydrofuran, formaldehyde and 1,4-butanediol. The various

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kinetic parameters of the reaction and the activation energy parameters are reported.

Experimental

The catalyst K[Ru(EDTA—H)Cl]·$2H_2O$ (EDTA = ethylenediaminetetraacetic acid) was prepared according to the procedure described elsewhere [13, 14]. Other chemicals used were of AR grade and distilled before use. Synthesis gas 1:1 ($CO + H_2$) composition was obtained from IOL, Bangalore.

Apparatus and procedure

The hydroformylation reaction was carried out in a 300 cm^3 pressure reactor (Parr Instruments Co.) with provisions for temperature control, pressure recording, stirrer speed control, gas inlet and sampling.

Known quantities of the catalyst, solvent and allyl alcohol were charged to the reactor and flushed with the (1:1) $CO + H_2$ gas twice. After the desired temperature was obtained, the reaction was started by adjusting the reactor to the desired pressure and the stirrer speed to 600 rpm. The kinetics of the reaction were followed by withdrawing samples at different time intervals from the reactor and analyzing them for conversion of allyl alcohol to products. The products of hydroformylation were identified by GLC (Shimadzu) using a TCD detector. The column used for the analysis was 3 ft long Porapak-Q with carrier gas (H_2). The flow rate was 30 cm^3 min^{-1} and temperature programming was done in the range 150 - 200 °C. The kinetics of the reaction were analyzed from the observed number of the moles of allyl alcohol reacted per unit time from the disappearance of the GLC peak of allyl alcohol.

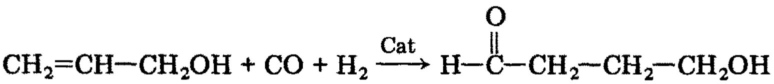
The mixture of the products removed from the reaction vessel was extracted with diethyl ether, and the separate organic and aqueous layers were analyzed for product distribution. The aqueous layer was distilled and the fraction boiling in the range 100 - 120 °C was collected and identified as formaldehyde (2%). To the mother liquor ethanol was added to precipitate the catalyst. The filtrate after removal of ethanol yielded γ-hydroxybutyraldehyde (35%), confirmed by preparation of the 2,4-dinitrophenylhydrazine derivative [15] m.p. 119 - 120 °C. The other product was 1,4-butanediol (1%) characterized by IR and NMR data.

The organic layer was dried over anhydrous sodium sulphate and ether was evaporated. The extract on TLC showed three spots (2% acetone in benzene). The three components were separated over silica gel (60 - 120 mesh) column. Of the three components, two were present in almost equal quantity and were identified as γ-butyrolactone (25%) and dihydrofuran (25%), on the basis of their well known physicochemical properties. The third component, a viscous mass probably a polymeric product (10 - 15%) could not be identified. The percentage yield of the various products agrees very well with the overall yield, taking into account both aqueous and organic layers.

For the kinetic study, initial rates were calculated using moles of allyl alcohol reacted and the dependence of the rate on allyl alcohol and catalyst concentrations and on the pressure of 1:1 ($CO + H_2$) obtained. The effect of temperature was studied in the range 90 - 130 °C; the activation energy was obtained from the Arrhenius plot.

Results and discussion

The hydroformylation of allyl alcohol was catalyzed by the water-soluble catalyst [Ru(EDTA)Cl] to give γ-hydroxybutyraldehyde as the major product 2 and other products of cyclization of 2, *viz.* γ-butyrolactone 3 and dihydrofuran 4. The reaction was conducted at comparatively mild conditions of 90 - 130 °C and a pressure of 50 atm of synthesis gas (1:1) $CO + H_2$. The stoichiometry of the reaction, based on the product analysis of the major product γ-hydroxybutyraldehyde 2 and its cyclization products 3 and 4, is:



$$CH_2{=}CH{-}CH_2OH + CO + H_2 \xrightarrow{Cat} H{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_2{-}CH_2OH$$

2

The reaction between a mole of allyl alcohol, carbon monoxide and hydrogen gives the primary product γ-hydroxybutyraldehyde. The decrease in selectivity for γ-hydroxybutyraldehyde (35%) is attributed to the side reactions resulting in the cyclization of γ-hydroxybutyraldehyde to give γ-butyrolactone 3 and dihydrofuran 4, whereas the hydrogenation of 2 under oxo conditions gives 1,4-butanediol 5 as a minor product. A small quantity of formaldehyde (2%) is obtained by the catalytic hydrogenation of CO.

Effects of process parameters

To optimise the conditions for a process, the effect of different parameters such as catalyst concentration, substrate concentration and pressure of ($CO + H_2$) gas on the activity and selectivity of the products is important. The effect of the above parameters was therefore studied, and the range of variables is presented in Table 1.

TABLE 1

Variables and their ranges studied

Variable	Range
Ru(III)–EDTA concentration	0.5 to 3 mmol
1:1 ($CO + H_2$) pressure	360 to 960 psig
allyl alcohol concentration	0.735 to 4.411 M
temperature	90 to 130 °C

Effect of Ru(III)–EDTA catalyst concentration

In order to study the rate of hydroformylation of allyl alcohol, experiments were carried out in the catalyst concentration range from 0.5 to 3 mmol, keeping all other conditions constant. The results are shown in Fig. 1 as a plot of percent conversion of allyl alcohol *vs.* time. At higher catalyst concentration and constant time, the percent conversion of allyl alcohol increases but the formation of side products 3 and 4 predominates, whereas at lower conversions of allyl alcohol, the selectivity for γ-hydroxybutyraldehyde is highest.

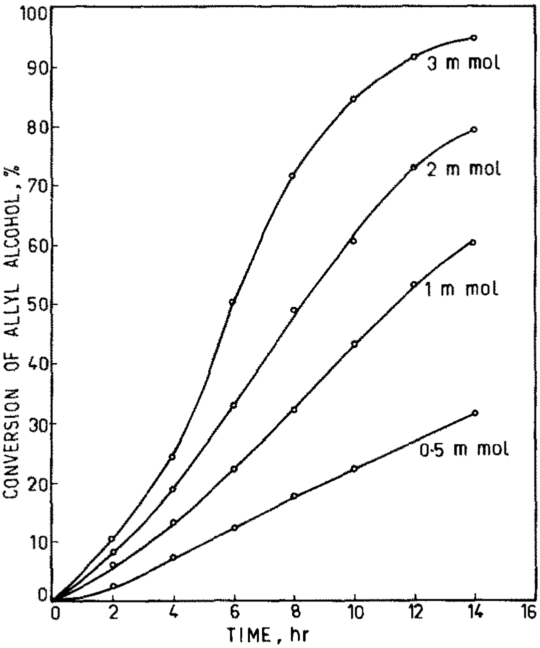


Fig. 1. Conversion *vs.* time plot for different Ru(III)–EDTA catalyst concentrations. Conditions: allyl alcohol = 2.94 M; temperature = 130 °C; pressure = 1:1 $(CO + H_2)$ = 760 psig; solvent = water; total volume = 100 cm^3; agitation = 600 rpm; pH = 3.0.

Effect of $(CO + H_2)$ pressure

The effect of 1:1 $(CO + H_2)$ pressure on the conversion of allyl alcohol to γ-hydroxybutyraldehyde 2 was studied in a batch reactor. In these experiments, the pressure of $(CO + H_2)$ was maintained constant throughout the reaction by recharging the autoclave with fresh gas.

Figure 2 shows a plot of percent conversion of allyl alcohol *vs.* time. At lower pressures (up to 760 psig), the conversion of allyl alcohol is a linear function of pressure, while at higher pressure (at 960 psig) saturation kinetics are observed and the reaction becomes independent of the pressure of syn-gas. A possible explanation for this is the saturation of the reaction

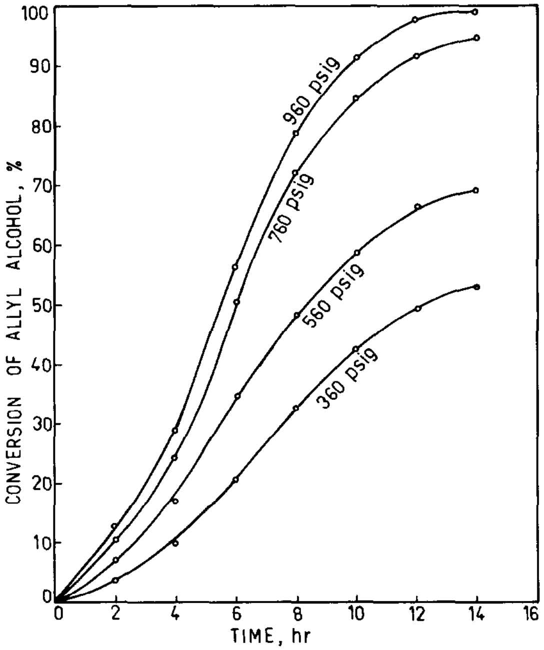


Fig. 2. Conversion *vs.* time plot for different pressures of 1:1 (CO + H_2) gas. Conditions: Ru(III)–EDTA catalyst = 3.0 mmol; allyl alcohol = 2.94 M; temperature = 130 °C; total volume = 100 cm^3; solvent = water; agitation = 600 rpm; pH = 3.0.

mixture with the gas, at which point conversion does not increase further with increasing pressure of CO + H_2.

Effect of allyl alcohol concentration

The effect of allyl alcohol concentration was studied at a catalyst concentration of 3 mmol, (CO + H_2) pressure 760 psig and temperature 130 °C. Figure 3 illustrates the plot of conversion *vs.* time. It may be seen from Fig. 3 that the conversion of allyl alcohol is a function of the initial concentration and the contact time. In a particular case, at 6 h contact time for 0.735 M allyl alcohol, the conversion is 100% whereas for 4.412 M the conversion is 29%.

Effect of temperature

The effect of temperature was studied in the range 90 - 130 °C at 3.0 mmol catalyst concentration, 2.94 M allyl alcohol concentration and 760 psig (CO + H_2) total pressure. The effect of temperature is shown in Fig. 4. It can be seen that the conversion of allyl alcohol is dependent on temperature, and conversions are fairly good between 110 - 130 °C. The optimum reaction temperature is 130 °C.

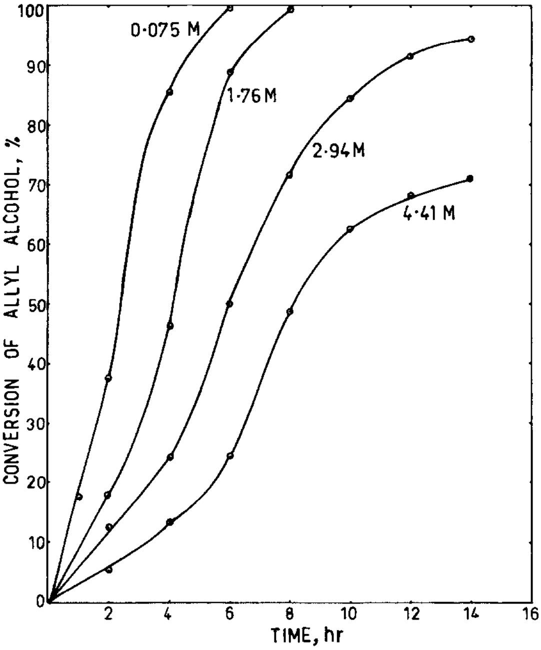


Fig. 3. Conversion *vs.* time plot for different concentrations of allyl alcohol. Conditions: Ru(III)–EDTA catalyst = 3 mmol; pressure of 1:1 (CO + H_2) = 760 psig; temperature = 130 °C; total volume = 100 cm^3; solvent = water; agitation = 600 rpm; pH = 3.0.

Kinetic study

The kinetics of Ru(III)–EDTA-catalyzed hydroformylation of allyl alcohol were studied by computing the initial rates up to 20% conversion of the reaction by measuring the amount of allyl alcohol converted into products. The effects of catalyst concentration, 1:1 (CO + H_2) gas pressure, allyl alcohol concentration and temperature were investigated.

The effect of Ru(III)–EDTA catalyst concentration on the rate of hydroformylation was studied at 130 °C, 2.94 M allyl alcohol concentration and 760 psig of 1:1 (CO + H_2). The results are presented in Fig. 5. It is found that the rate of hydroformylation is directly proportional to the catalyst concentration, showing a first order dependence.

Figure 6 shows the effect of allyl alcohol concentration on the rate of hydroformylation of allyl alcohol to give γ-hydroxybutyraldehyde. The effect of allyl alcohol concentration was studied at 130 °C, 3.0 mmol catalyst concentration and 760 psig (CO + H_2) pressure. It is found that the rate has a first order dependence on allyl alcohol concentration.

The effect of 1:1 (CO + H_2) pressure was also studied at 130 °C, 2.94 M allyl alcohol concentration and 3.0 mmol [Ru(III)–EDTA] catalyst concentration. The results are shown in Fig. 7. It can be seen that the rate of hydroformylation is directly proportional to (CO + H_2) concentration.

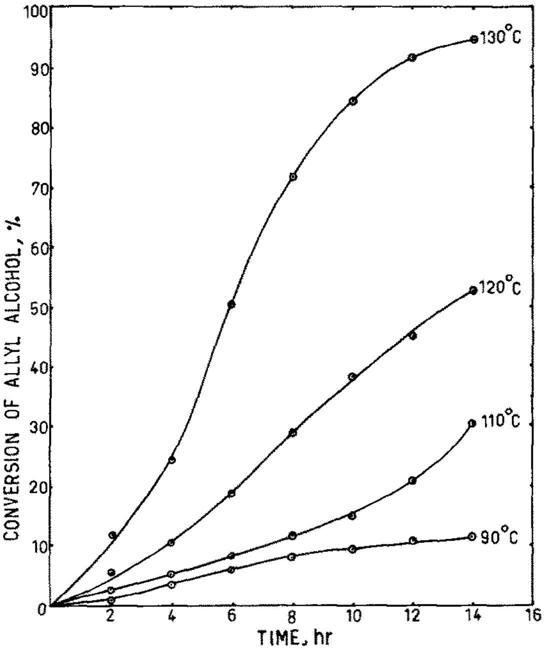
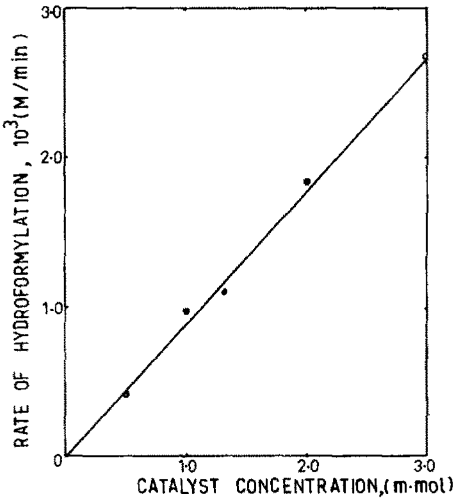


Fig. 4. Conversion *vs.* time plot for different temperatures. Conditions: Ru(III)–EDTA catalyst = 3.0 mmol; pressure 1:1 (CO + H_2) = 760 psig; allyl alcohol = 2.94 M; solvent = water; total volume = 100 cm^3; agitation = 600 rpm; pH = 3.0.



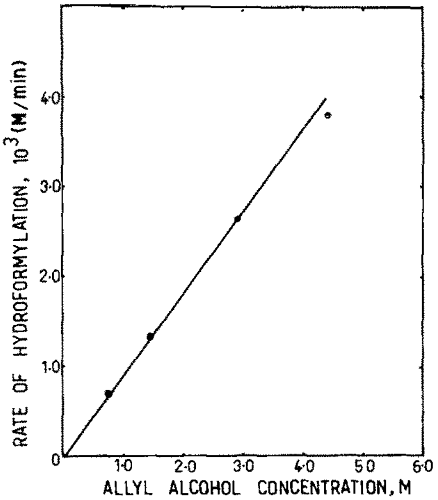
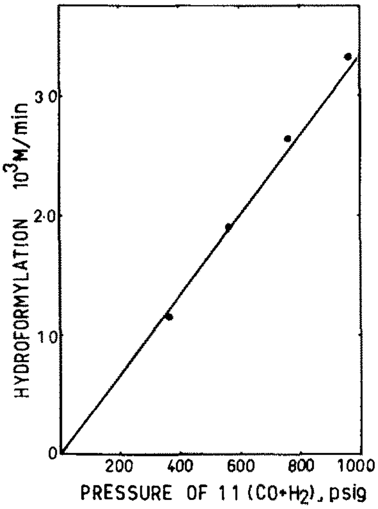


Fig. 5. Effect of Ru(III)–EDTA catalyst concentration on the rate of hydroformylation of allyl alcohol.

Fig. 6. Effect of allyl alcohol concentration on the rate of hydroformylation of allyl alcohol.



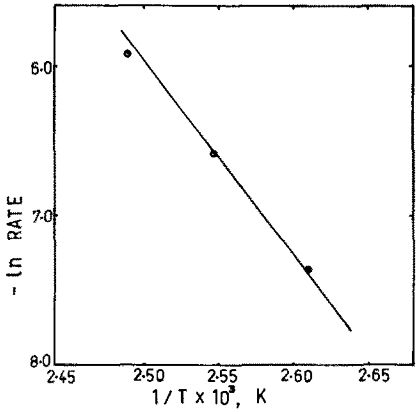


Fig. 7. Effect of (CO + H_2) pressure on the rate of hydroformylation of allyl alcohol.

Fig. 8. Arrhenius plot for hydroformylation of allyl alcohol catalysed by Ru(III)–EDTA catalyst.

The temperature dependence of the reaction is shown in Fig. 8 as a plot of $-\ln$ rate *vs.* $1/T$. From the slope of this plot, the activation energy of the reaction is found to be 23.13 kcal mol^{-1}.

Mechanism of hydroformylation of allyl alcohol

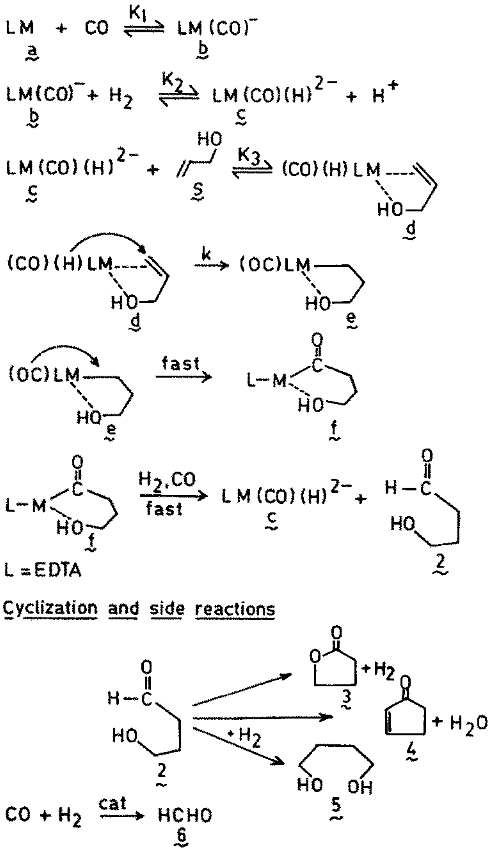
From the kinetic data a possible mechanism for the hydroformylation of allyl alcohol is proposed, as shown in Scheme 1.

The mechanism suggested (Scheme 1) for the hydroformylation of allyl alcohol involves the initial formation of a mixed ligand carbonyl complex b in a pre-equilibrium step. Complex b forms a hydrido complex c which combines with allyl alcohol to form the mixed ligand complex d. The rate-determining step of the reaction is the transfer of hydride to the conducted olefinic bond of allyl alcohol, giving an intermediate alkyl complex e. The insertion of CO into the Ru—C bond, forming an intermediate complex f, takes place in a fast step. In the final step, rapid hydrogenolysis of f and addition of a mole of CO to the catalyst gives the active intermediate catalytic species c and the product 2, which cyclizes to 3 and 4 and is partly hydrogenated under oxo conditions to 5.

From the proposed mechanism for the [Ru(III)–EDTA]-catalyzed hydroformylation of allyl alcohol and the kinetic results, one can apply steady state and equilibrium conditions to derive the rate law as follows:

$$\text{rate} = kK_1K_2K_3[\text{ML}][\text{CO}][\text{H}_2][\text{S}] \qquad (1)$$

where [ML] = catalyst concentration, [CO] = carbon monoxide concentration, [H_2] = hydrogen concentration, [S] = allyl alcohol concentration, and K_1, K_2 and K_3 are the equilibrium constants for the formation of complexes



Scheme 1.

b, c and d respectively. Substituting [ML] in terms of its total concentration $[\mathrm{ML}]_{\mathrm{T}}$, the above equation can then be rearranged to the following rate laws:

$$\text{rate} = \frac{kK_1K_2K_3[\mathrm{ML}]_{\mathrm{T}}[\mathrm{CO}][\mathrm{H_2}][\mathrm{S}]}{1 + K_1[\mathrm{CO}] + K_1K_2[\mathrm{CO}][\mathrm{H_2}] + K_1K_2K_3[\mathrm{CO}][\mathrm{H_2}][\mathrm{S}]} \tag{2}$$

$$\frac{[\mathrm{ML}]_{\mathrm{T}}}{\text{rate}} = \left[\frac{1}{kK_1K_2K_3[\mathrm{CO}][\mathrm{H_2}]} + \frac{1}{kK_2K_3[\mathrm{H_2}]} + \frac{1}{kK_3}\right]\frac{1}{[\mathrm{S}]} + \frac{1}{k} \tag{3}$$

From eqn. (3), the plot of $[\mathrm{ML}]_{\mathrm{T}}$/rate *vs.* 1/[S] gave a straight line with a positive intercept, from which the value of k was calculated. The slope of the straight line of the above plot is written as:

$$\text{slope} = \frac{1}{kK_1K_2K_3[\mathrm{CO}][\mathrm{H_2}]} + \frac{1}{kK_2K_3[\mathrm{H_2}]} + \frac{1}{kK_3} \tag{4}$$

By substituting the values for concentrations [16] of carbon monoxide [CO] and hydrogen [H_2] and the equilibrium constants K_1 and K_2 obtained separately [17] in eqn. (4), the value of K_3 was obtained. Thus, the values of the constants k, K_1, K_2 and K_3 were found to be:

$k = 0.57\ \text{min}^{-1}$

$K_1 = 4.9\ \text{M}^{-1}$

$K_2 = 190.6\ \text{M}^{-1}$

$K_3 = 49.2\ \text{M}^{-1}$

where k is the rate constant of the slowest step, and K_1, K_2 and K_3 are the equilibrium constants of the steps shown in Scheme 1.

Conclusions

Hydroformylation of allyl alcohol using (1:1) CO + H_2 syngas catalyzed by a water-soluble Ru(III)–EDTA catalyst gave γ-hydroxybutyraldehyde as the major product. Side products such as γ-butyrolactone, dihydrofuran and 1,4-butanediol were obtained from the main hydroformylation product. Based on the products and kinetic observations, a probable mechanism has been proposed for the reaction.

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