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# Hydroformylation of allyl alcohol catalysed by $(\text{Rh}(\text{PPh}_3)_3)^+$ / montmorillonite: a kinetic study

K.N. Bhatt, S.B. Halligudi\*

*Catalysis Group, Central Salt and Marine Chemicals Research Institute, Bhavnagar-364 002, India*

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## Abstract

$\text{Rh}(\text{PPh}_3)_3\text{Cl}$  complex exchanged with modified montmorillonite clay at room temperature gave a  $(\text{Rh}(\text{PPh}_3)_3)^+$  species, **1**, anchored in the hydration layers of the clay. Hydroformylation of allyl alcohol catalysed by **1** at 70°C and 60 atm of  $\text{CO} + \text{H}_2$  (1:1) gave *n*-hydroxybutyraldehyde (96%) and 2-methyl-3-hydroxypropionaldehyde (4%). The kinetics of hydroformylation of allyl alcohol catalysed by **1** was studied in the concentrations range of catalyst 0.1 to 0.75 mM, allyl alcohol 0.025 to 0.25 M,  $\text{CO} + \text{H}_2$  (1:1) pressure 5 to 30 atm and temperature between 70 to 90°C. The rates of hydroformylation of allyl alcohol catalysed by **1** showed a first order dependence with respect to catalyst, allyl alcohol (up to 0.1 M),  $\text{CO}$  and  $\text{H}_2$  concentrations respectively. Substrate inhibition effect was observed when the substrate/catalyst mole ratio exceeds 440. The insoluble catalyst residue formed during substrate inhibition runs showed an IR stretching at  $630\text{ cm}^{-1}$  which was attributed to the formation of  $\text{Rh}^{\text{II}}$ -allylic complex. Repeated use of the separated catalyst for 60 h showed no loss in catalytic activity in hydroformylation of allyl alcohol.

*Keywords:* hydroformylation; allyl alcohol; inhibition; intercalation; kinetics; leaching; montmorillonite; rhodium

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## 1. Introduction

Hydroformylation of olefins to give corresponding non-branched aldehydes is an industrially important reaction. Many efforts have been made to develop heterogenised homogeneous catalysts [1–10] to overcome the problems of conventional homogeneous catalyst systems, such as separation of catalyst from the reaction mixture and reusing the catalyst in further catalytic cycles. Rhodium phosphine complexes have been found to be potential catalysts systems for the hydroformylation of many olefinic substrates to their corresponding

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\*Corresponding author; fax. (+91-278)26970.

aldehydes [11–13]. The use of rhodium complexes immobilised on polymeric supports tested in hydroformylation of olefins also suffered a setback because of swelling and catalyst leaching problems associated with these under the hydroformylation conditions [14–16]. Therefore, in our attempts to develop a suitable heterogeneous catalyst system, we prepared a rhodium catalyst **1** by anchoring to inorganic support such as montmorillonite clay and reporting in the present paper the kinetic study of the hydroformylation of allyl alcohol catalysed by **1** to give *I*-hydroxybutyraldehyde (96%) and 2-methyl-3-hydroxypropion-aldehyde (4%) at 70°C and 60 atm of equimolar mixture of CO + H<sub>2</sub>.

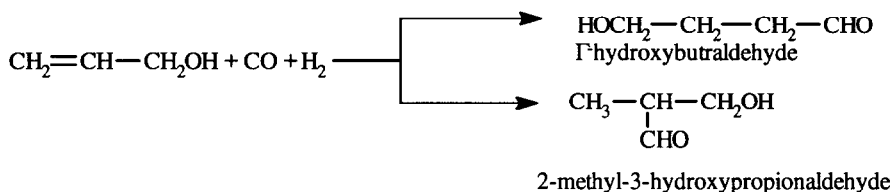
## 2. Experimental

RhCl<sub>3</sub> · 3H<sub>2</sub>O was procured from M/S Arora Matthey, Calcutta, and the Rh(PPh<sub>3</sub>)<sub>3</sub>Cl complex prepared by a known procedure [17]. Montmorillonite clay procured from M/S Fluka AG had the chemical composition (wt.%) SiO<sub>2</sub> (70%), Al<sub>2</sub>O<sub>3</sub> (15%), Fe<sub>2</sub>O<sub>3</sub> (1.5%), CaO (2.5%), MgO (3.0%), Na<sub>2</sub>O (5.0%), K<sub>2</sub>O (1.5%) and loss on ignition (6%). Rh(PPh<sub>3</sub>)<sub>3</sub>Cl dissolved in benzene–methanol (70:30) solvent was exchanged with a known amount of the sodium form of the montmorillonite clay [18] with constant agitation under argon atmosphere for 10–12 h. It was filtered and dried under vacuum. The gravimetric estimation of Cl<sup>-</sup> released from the reacted Rh(PPh<sub>3</sub>)<sub>3</sub>Cl as AgCl indicated that 85 mg of complex was anchored per gram of the clay. The complex anchored in the hydration layers of the clay as the cationic species (Rh(PPh<sub>3</sub>)<sub>3</sub>)<sup>+</sup>, **1**, showed peaks at 493 and 521 cm<sup>-3</sup> which were assigned to ν(Rh–P). The absence of a peak around the 300 cm<sup>-3</sup> region indicates the absence of coordinated chloride in the complex. The X-ray basal spacings of montmorillonite clay before and after intercalation of Rh complex were measured with a Philips X-ray diffractometer using a Ni filter and Cu K<sub>α</sub> radiation. X-ray diffraction pattern of the intercalated complex showed basal region expansion (001) from 9.5 to 17.65 Å of dehydrated montmorillonite clay. These results indicate the presence of the complex in the interlamellar region of the clay as cationic species (Rh(PPh<sub>3</sub>)<sub>3</sub>)<sup>+</sup>. The XPS data on binding energy of the different elements present in the intercalated complex as well as the solid state NMR data of the complex were all consistent with the earlier reported values [19,20].

The kinetics of the hydroformylation of allyl alcohol catalysed by **1** was studied in a 300 ml (S.S) pressure reactor (M/S Parr Instruments Co. USA), synthesis gas CO + H<sub>2</sub> (1:1) procured from M/S B.O.C., UK, had a purity of >99.9%. In a typical run, the reaction mixture prepared by adding known amounts of allyl alcohol in ethanol and catalyst **1** were placed in a bomb. Initially, the reaction mixture was purged with N<sub>2</sub> twice to remove any dissolved gases. The bomb was pressurized by CO + H<sub>2</sub> (1:1) to 60 atm when the desired temperature (70°C) was attained. The reaction was commenced by starting the agitation and at this stage a sample was withdrawn from the reactor through the sampling valve. The progress of the reaction was monitored by analysing the samples withdrawn at different time intervals. Reaction products were analysed by gas chromatograph (GC-9A, Shimadzu, Japan) using 10% SE-30 column and FID detector. The initial rates of hydroformylation of allyl alcohol were calculated from the plots of the amounts of allyl alcohol reacted vs. time.

### 3. Results and discussion

Hydroformylation of allyl alcohol catalysed by **1** at 70°C and 60 atm of CO + H<sub>2</sub> gave  $\Gamma$ -hydroxybutyraldehyde (96%) and 2-methyl-3-hydroxypropionaldehyde (4%). The reaction scheme is as shown below:



The data on the variation of concentrations of substrate, catalyst, CO and H<sub>2</sub> and the turnover frequencies (TOF) obtained in the hydroformylation of allyl alcohol catalysed by **1** are presented in Table 1 and 2.

#### 3.1. Kinetics

##### 3.1.1. Effect of catalyst concentration

The concentration of the catalyst varied in the range 0.25 to 0.75 mM (substrate/catalyst mole ratio between 133–400) by keeping other variables constant as allyl alcohol 0.11 M, CO + H<sub>2</sub> (1:1) 60 atm and 70°C. The results are presented in Table 1. The rate of hydroformylation showed a first-order dependence with respect to catalyst concentration.

Table 1

Effect of catalyst concentration on the rates of hydroformylation<sup>a</sup> of allyl alcohol catalysed by **1** at 70°C and 60 atm of (CO + H<sub>2</sub>)

Entry no.	Substrate/cat. (mole ratio)	Conversion (%)	TOF <sup>b</sup>
1	400	42	36.9
2	220	66	58.1
3	147	95	83.6

<sup>a</sup>Contact time = 5.0 h, total volume = 100 ml, solvent = ethanol allyl alcohol = 0.11 M.

<sup>b</sup>TOF = mol-products/mol-cat./h.

Table 2

Effect of CO and H<sub>2</sub> pressures on the rates of hydroformylation<sup>a</sup> of allyl alcohol catalysed by **1** at 70°C

Entry no.	<i>p</i> (H <sub>2</sub> ) (atm)	<i>p</i> (CO) (atm)	Conversion (%)	TOF <sup>b</sup>
1	5	30	14	12.3
2	10	30	24	21.1
3	20	30	42	36.9
4	30	5	45	39.6
5	30	10	19	16.7
6	30	20	12	10.6

<sup>a</sup>Catalyst = 0.25 mM, allyl alcohol = 0.11 M, solvent = ethanol, total volume = 100 ml.

<sup>b</sup>TOF = mol-products/mol-cat./h.

### 3.1.2. Effect of allyl alcohol concentration

The rates of hydroformylation of allyl alcohol were measured by varying the allyl alcohol concentrations between 0.025 to 0.22 M having catalyst concentration 0.25 mM, CO + H<sub>2</sub> (1:1) 60 atm and 70°C. The plot of rate of hydroformylation vs. allyl alcohol concentration is as shown in Fig. 1. It is seen from the Fig. 1 that the rate of hydroformylation of allyl alcohol shows linear dependence with respect to allyl alcohol concentration up to 0.1 M (substrate/catalyst mole ratio = 440). Above 0.1 M allyl alcohol concentration, the rate of hydroformylation gradually drops and reached a saturation kinetics. This is a clear case of substrate inhibition due the strong interaction between catalyst and substrate molecule especially at higher concentrations of substrate. The catalyst residue separated showed an IR stretching band at 630 cm<sup>-3</sup> which is assigned to Rh-allylic bond.

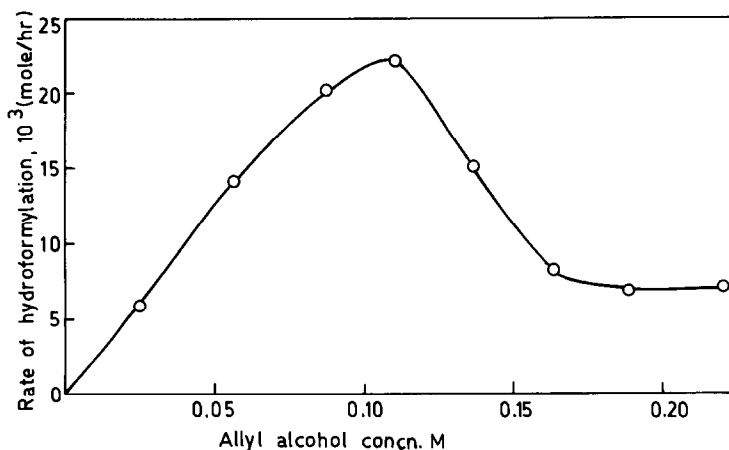


Fig. 1. Effect of allyl alcohol concentration on the rate of hydroformylation.

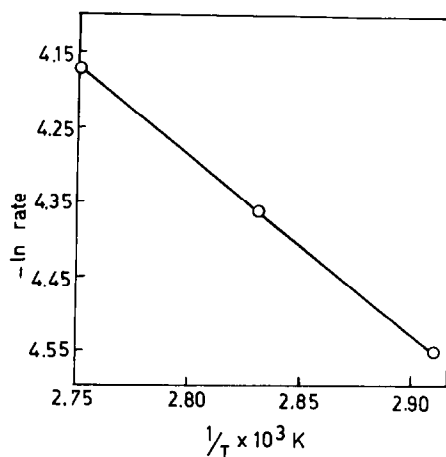
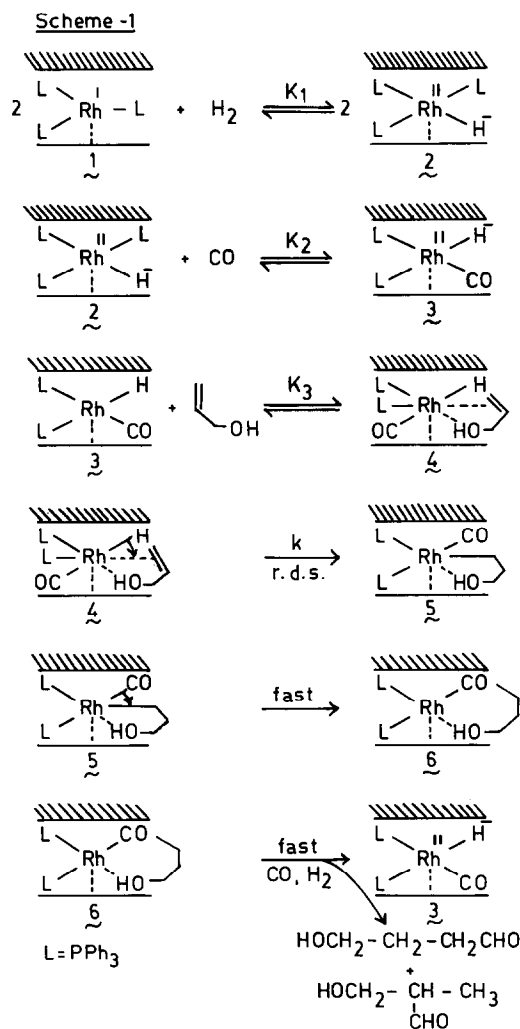


Fig. 2. Effect of temperature on the rate of hydroformylation of allyl alcohol.

### 3.1.3. Effect of the partial pressures of CO and H<sub>2</sub>

With both CO and H<sub>2</sub> partial pressures varied in the range 5 to 30 atm (Table 2), keeping catalyst at 0.25 mM, allyl alcohol at 0.11 M (substrate/catalyst mole ratio = 440) at 70°C, the rate of hydroformylation showed first-order dependence with respect to the partial pressures of CO and H<sub>2</sub>, respectively. However, above 60 atm of CO + H<sub>2</sub> (1:1), there was no change in the rates of hydroformylations indicating zero order or saturation kinetics with respect to CO and H<sub>2</sub> pressures.



Scheme 1.

### 3.1.4. Effect of temperature

Under constant conditions of catalyst 0.25 mM, allyl alcohol 0.11 M, CO + H<sub>2</sub> (1:1) 60 atm, the rates of hydroformylation of allyl alcohol were measured in the temperature range 70 to 90°C. From the plot of  $-\ln$  rate vs.  $1/T$  (Fig. 2), the activation energy evaluated was 4.25 kcal/mol.

### 3.2. Mechanism

Based on the kinetic study, the mechanism for the hydroformylation of allyl alcohol catalysed by **1** is as shown in Scheme 1.

The cationic  $(\text{Rh}(\text{PPh}_3)_3)^+$  /montmorillonite, **1**, reacts with hydrogen to give the hydride complex **2**. The complex **2** adds to a mole of CO in the second pre-equilibrium step resulting in the formation of an active intermediate species  $(\text{Rh}(\text{H})(\text{CO})(\text{PPh}_3)_2)^+$ , **3**, with the elimination of a ligand. The formation of this species, **3**, was confirmed by EPR and this was the same as reported in our earlier work [21]. In a third step, the hydridocarbonyl species **3** reacts with a mole of allyl alcohol to form a mixed-ligand intermediate complex, **4**. Species **4** is transient, and in the presence of higher concentrations of allyl alcohol, the Rh–allylic bond formed precipitates as an insoluble complex. Hence, we observed a substrate inhibition effect when the substrate/catalyst mole ratio exceeded 440 during hydroformylation of allyl alcohol (Fig. 1). The rate determining step will be the transfer of hydride to an olefinic bond forming an alkyl intermediate species, **5**. The insertion of CO followed by reductive elimination occurs in fast steps to give corresponding products and regenerating species **3** for the continuation of the catalytic cycle.

From the proposed mechanism for the hydroformylation of allyl alcohol catalysed by **1** and based on the kinetic results, by applying the steady state equilibrium conditions, the rate law derived is as follows:

$$\text{rate} = kK_1K_2K_3[\text{cat.}][\text{CO}][\text{H}_2][\text{S}] \quad (1)$$

where  $[\text{cat.}]$  = catalyst concentration,  $[\text{CO}]$  = carbon monoxide concentration,  $[\text{H}_2]$  = hydrogen concentration,  $[\text{S}]$  = allyl alcohol concentration,  $K_1$ ,  $K_2$  and  $K_3$  are the equilibrium constants for the formation of the intermediate species **2**, **3** and **4**, respectively.

Substituting the value of  $[\text{cat.}]$  in terms of its total concentration  $[\text{cat.}]_T$ , the above equation can then be rearranged to the following rate law:

$$\text{rate} = \frac{kK_1K_2K_3[\text{cat.}]_T[\text{CO}][\text{H}_2][\text{S}]}{1 + K_1[\text{CO}] + K_1K_2[\text{CO}][\text{H}_2] + K_1K_2K_3[\text{CO}][\text{H}_2][\text{S}]} \quad (2)$$

$$\frac{[\text{cat.}]_T}{\text{rate}} = \left( \frac{1}{kK_1K_2K_3[\text{CO}][\text{H}_2]} + \frac{1}{kK_2K_3[\text{H}_2]} + \frac{1}{kK_3} \right) \frac{1}{[\text{S}]} + \frac{1}{k} \quad (3)$$

From Eq. 3, the plot of  $[\text{cat.}]_T/\text{rate}$  vs.  $1/[\text{S}]$  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:

$$\text{slope} = \frac{1}{kK_1K_2K_3[\text{CO}][\text{H}_2]} + \frac{1}{kK_2K_3[\text{H}_2]} + \frac{1}{kK_3} \quad (4)$$

By substituting the values of concentration of [CO] and [H<sub>2</sub>] determined earlier [22] and equilibrium constants  $K_1$  and  $K_2$  obtained separately [23] in Eq. 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:  $k = 286 \text{ h}^{-1}$ ,  $K_1 = 4.0 \text{ M}^{-1}$ ,  $K_2 = 150.0 \text{ M}^{-1}$ ,  $K_3 = 9.6 \text{ M}^{-1}$ , where  $k$  is the rate constant of the slowest step and  $K_1$ ,  $K_2$  and  $K_3$  are equilibrium constants of the steps shown in Scheme 1. The pre-equilibrium constants  $K_1$  and  $K_2$  were independently determined using the gas absorption method [23] and the values reported are within the experimental error limits (5%).

Hydroformylation of allyl alcohol was also studied in ethanol solvent using the soluble Wilkinson's complex, **7**, (H)Rh<sup>I</sup>(CO)(PPh<sub>3</sub>)<sub>2</sub> at 70°C and 60 atm of equimolar mixture of CO + H<sub>2</sub>. The products obtained were *l*-hydroxybutyraldehyde (65%) and 2-methyl-3-hydroxypropionaldehyde (35%). The turnover frequency at 98% conversion of allyl alcohol was 21 mole products per mole catalyst per hour with respect to the soluble complex **7**. The turnover frequency observed with anchored catalyst **1** in the hydroformylation of allyl alcohol at 70°C and 60 atm CO + H<sub>2</sub> (1:1) was 4.1 which is at least five times less than the activity of soluble complex **7** but had a higher selectivity for *l*-hydroxybutyraldehyde (70%).

It is interesting to compare the activity of Wilkinson's complex (H)Rh<sup>I</sup>(CO)(PPh<sub>3</sub>)<sub>2</sub>, **7**, with the intermediate species, **3**, [(H)Rh<sup>II</sup>(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, obtained from catalyst **1** (Scheme 1) as a hydroformylation catalyst. The basic steps of olefin activation, transfer of hydride to the olefin and CO insertion to form the  $\pi$ -bonded acyl complex are common to both the catalysts **7** and **3**. The difference in the reactivities of the two catalysts has to do with the difference in the polarities of the Rh<sup>II</sup>-H in **3** versus Rh<sup>I</sup>-H bond in **7**. The hydride insertion into the olefin requires cleavage of the rhodium hydride bond which is more facile for Rh<sup>I</sup>-H bond as compared to the more covalent Rh<sup>II</sup>-H bond. Since the hydride insertion is the rate determining step (Scheme 1) and hence the reactions are slower with Rh<sup>II</sup> complex **3** as compared to **7**. However, the covalent nature of the Rh<sup>II</sup>-H bond of catalyst **3** makes it more selective for the formation of linear rather than branched aldehydes which is evident in the hydroformylation of allyl alcohol.

The catalyst leaching studies were also conducted by reusing the spent catalyst for several batches of hydroformylation of allyl alcohol at 70°C and 60 atm of CO + H<sub>2</sub> (1:1) having 0.1 M as allyl alcohol concentration for each batch. The performance of the spent catalyst was reproducible up to 60 h (including all batches) without any loss in its activity and selectivity. Any characteristic absorption peaks of leached rhodium complex were not found when the reaction mixture after 60 h contact time was subjected to UV-Vis spectroscopy.

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