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HYDROFORMYLATION OF OLEFINS CATALYZED BY RHODIUM COMPLEX  
ANCHORED ON CLAY MATRICES

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Investigations on the catalytic activity of a transient Rh(I) triphenylphosphine complex 1 anchored on montmorillonite clay have been carried out with respect to hydroformylation of olefins at 70 °C and 60 atm of CO+H<sub>2</sub> (1:1). The analysis has shown that aldehydes and hydrocarbons of the corresponding olefins result under hydroformylation conditions. In limonene, reaction proceeds with double hydroformylation and hydrogenation to give the respective oxo products. The catalytic activities of 1 are compared with Wilkinson's Rh<sup>I</sup>(H)(CO)(PPh<sub>3</sub>)<sub>2</sub> (6) complex in solution under the same hydroformylation conditions.

INTRODUCTION

Hydroformylation of olefins catalyzed by rhodium phosphine complexes still ranks as one of the extensively investigated systems [1-6]. However, efficient use of the catalyst is not possible in homogeneous phase due to difficulties in separation of the catalyst from the reaction mixture; also selectivity problems may occur in homogeneous catalysis. To overcome this problem, recourse is taken to the use of supported catalysts in homogeneous catalytic processes [7-8] with a view

to achieving greater selectivity and ease of separation. In this communication we report our findings on the use of  $[\text{Rh}(\text{PPh}_3)_3]^+$  anchored on montmorillonite clay in the hydroformylation of olefins. The results are compared with those obtained using Wilkinson's  $\text{Rh}^{\text{I}}(\text{H})(\text{CO})(\text{PPh}_3)_2$  (6) in solution. The probable mechanism for the hydroformylation reaction catalyzed by 1 is also proposed.

#### EXPERIMENTAL

The complex  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  prepared by the literature method [6] was anchored on sodium form of the montmorillonite clay (Fluka A.G.) as described elsewhere [9]. The gravimetric estimation of  $\text{Cl}^-$  released from the reacted  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$  as  $\text{AgCl}$  indicated that 85 mg of complex was anchored per gram of clay. Magnetic resonance, XRD and XPS investigations have shown that the complex was intercalated in the form of the cationic species. The interlayer spacing increases to 18.8 Å from 9.5 Å after intercalation.

Hydroformylation reactions were carried out at 70 °C and 60 atm of  $\text{CO} + \text{H}_2$  (1:1) using a 300 ml pressure reactor (Parr Inst. Co., USA). Gas Chromatography (GC-9A, Shimadzu, Japan) as well as GC-Mass (Hewlett-Packard, IPCL, Baroda) were used to analyze reaction products after a reaction time of 1 h.

#### RESULTS AND DISCUSSION

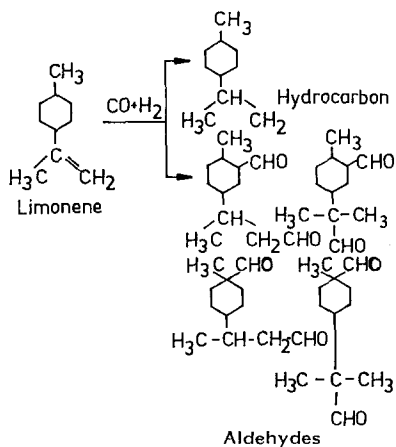
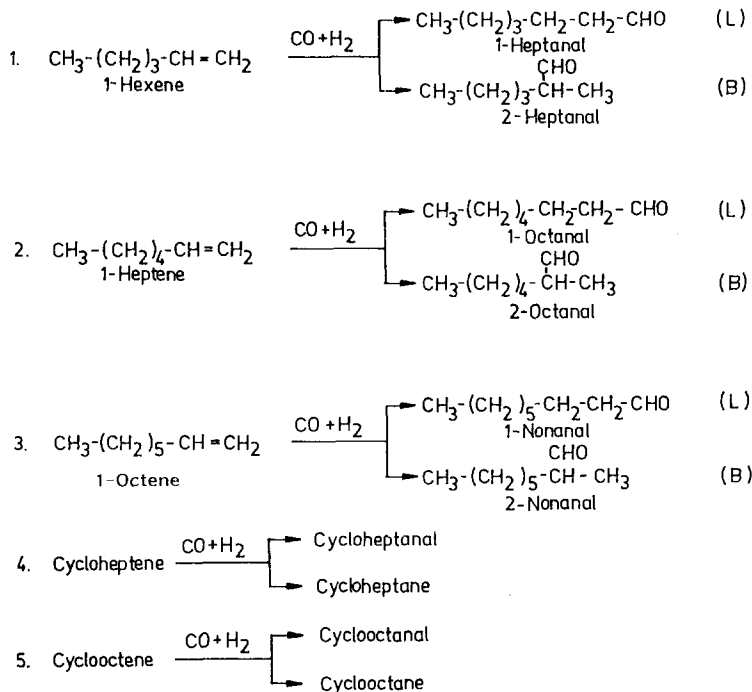
EPR studies indicated the formation of  $\text{Rh}^{\text{II}}(\text{H})(\text{CO})(\text{PPh}_3)_2$  (2) in the clay matrix. The broad spectrum obtained ( $g = 2.05$ ) was the same as that of transient  $\text{Ru}^{\text{II}}(\text{H})$  formed by the interaction of hydrogen with  $[\text{Rh}(\text{PPh}_3)_3]^+$  in montmorillonite [9]. Rh-H and Rh-CO stretchings were found at  $2004 \text{ cm}^{-1}$  and  $1926 \text{ cm}^{-1}$ , respectively in the IR spectrum.

The olefinic substrates used and their hydroformylation products are shown in Table 1.

It should be mentioned that in the case of limonene isomeric aldehydes were obtained along with the hydrocarbons. In

Table 1

Hydroformylation reactions



the case of open chain olefins both linear and branched chain aldehydes were the reaction products. In these cases we have found no evidence for the formation of hydrocarbons. Hydroformylation occurs without hydrogenation leading only to aldehydes in the reaction time (1 h). Hydrocarbons are formed along with aldehydes in the case of a closed system (cyclic olefins). It is also interesting to note that the isomeric aldehydes resulting from hydroformylation of the olefinic bonds both in the open and closed chain are the main products in the case of limonene.

Table 2

Hydroformylation of olefins catalyzed by  $[\text{Rh}(\text{PPh}_3)_3]^+$ /  
montmorillonite catalyst

	Substrate	Catalyst	Conversion (%)	TOF <sup>+</sup>		Selectivity (%)	
				L	B	L	B
1	1-Hexene	Rh-Clay	26	10.5	65	35	
		Complex <u>6</u>	85	34.0	70	30	
2	1-Heptene	Rh-Clay	30	11.9	60	40	
		Complex <u>6</u>	90	35.8	65	35	
3	1-Octene	Rh-Clay	35	13.1	50	50	
		Complex <u>6</u>	95	35.6	60	40	
4	Cycloheptene	Rh-Clay	24	9.8	50 (ald)	50 (hydrocarbon)	
		Complex <u>6</u>	40	16.5	75 (ald)	25 ( " )	
5	Cyclooctene	Rh-Clay	14	5.6	50 (ald)	50 ( " )	
		Complex <u>6</u>	35	13.9	75 (ald)	25 ( " )	
6	Limonene	Rh-Clay	25	10.0	50 (ald)	50 ( " )	
		Complex <u>6</u>	65	26.0	65 (ald)	35 ( " )	

Catalyst conc. = 0.250 g. Clay (0.25 mmol complex). Substrate = 0.01 mol; Substrate/catalyst = 40 (mole ratio). Solvent = Ethanol. Temp. = 70 °C. Total volume = 100 mL, Time = 1 h, Complex 6 =  $\text{Rh}^{\text{I}}(\text{H})(\text{Co})(\text{PPh}_3)_2$ . Conc. of complex 6 = 0.25 mmole  
<sup>+</sup>TOF = Turnover frequency (mole of product per mole catalyst per h)

Table 2 compares the catalytic activities of Wilkinson's complex 6 with that of the anchored catalyst 1. It is invariably found that the turnover frequencies are larger in the case of Wilkinson's complex. The activities of catalyst 1 are roughly three times lower than that of complex 6 in all the substrates. Presence of an open chain olefinic function, an initial product, which in turn could act as a promoter for the activation of the olefinic bond in the closed chain, may lead to the formation of all the four doubly hydroformylated isomeric products instead of the expected mono-aldehydes in hydroformylation of limonene, i.e. the reaction goes all the way. In the case of olefins, open chain hydroformylation predominates so much that no hydrogenation products are formed. The anchored catalyst 1 always gives more of branched chain aldehydes compared with those formed with Wilkinson's complex 6. In contrast to the behavior shown by open chain olefins, hydroformylation of cyclic olefins leads to considerable amounts of hydrogenated hydrocarbons. We surmise that this phenomenon is also a consequence of steric factors.

The proposed reaction mechanism shown in Scheme 1 is valid for both open chain and cyclic olefins. However, it has only been shown for open chain olefins. This scheme is similar to that proposed for the hydroformylation of olefins by Evans et al. [2] and involves an associate pathway for attack of olefin on  $\text{Rh}^{\text{II}}(\text{H})(\text{CO})(\text{PPh}_3)_2$  species 2 formed in anchored catalyst 1 under reaction conditions. The proposed participation of species 2 under the hydroformylation conditions is suggested based on spectroscopic evidence of its formation. The reaction proceeds through the formation of a  $\pi$ -bonded species 3 and is followed by a rate-determining transfer of hydride to give alkyl intermediate species 4. A fast insertion of CO into the M-C bond leads to acyl intermediate 5, which undergoes hydrogenolysis to give linear or branched chain aldehydes and regenerating the active catalytic species 2.

## CONCLUSION

The difference in the reactivities between complex 6 and anchored catalyst 1 can be attributed to different polarities of the Rh-H bond. Hydride insertion into the olefinic bond, which is the rate-determining step, requires the cleavage of Rh-H bond; this is more facile for the  $\text{Rh}^{\text{I}}$ -H bond (complex 6) than for the more covalent  $\text{Rh}^{\text{II}}$ -H bond (catalyst 2). Hence, reactions with complex 6 are faster than those involving anchored catalyst.

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