

## Polystyrene anchored rhodium (I) bidentate ligand complexes as catalysts for hydrogenation

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**Abstract.** Polystyrene supported Rh(I) AA' (AA' = anthranilic acid, 2,2'-bipyridine or 1,10-phenanthroline) complexes catalyse the hydrogenation of monoolefins (terminal, cyclic and internal) and dienes. Ethyl sorbate undergoes saturation via the monoene intermediate. This *cis* olefin reacts faster than the *trans* isomer. The rate law for the reaction is: Rate  $\propto$  [catalyst] [substrate] [H<sub>2</sub>].

**Keywords.** Polymer-anchored Rh(I) catalyst; bidentate ligand; rate law.

### 1. Introduction

Polymer-supported rhodium species have been shown to be effective catalysts for the hydrogenation of a variety of substrates (Grubbs 1977; Pittman 1982). A number of studies have been carried out with phosphine-linked complexes anchored to polystyrene (Grubbs and Kroll 1971; Moreto *et al* 1975; Pittman *et al* 1975) probably due to the preponderance of phosphine complexes in homogeneous catalysis.

To overcome some of the inherent disadvantages of phosphine ligands like their sensitivity towards air and moisture (Holy 1980; Garrou and Ford 1986; Moberg and Rakos 1987) bidentate ligands like anthranilic acid, 2,2'-bipyridine and 1,10-phenanthroline were used for preparing rhodium complexes and were supported on poly [styrene-co-divinylbenzene (2%)]. We have earlier reported (Parameswaran and Vancheesan 1990) catalytic hydrogenation using polymer-supported Rh(I)-bipyridine and the meta-sulphonated phosphine complex of Rh(I) soluble in water.

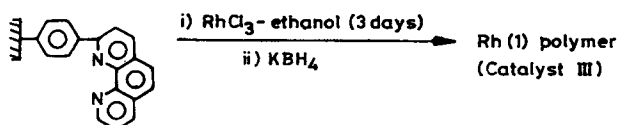
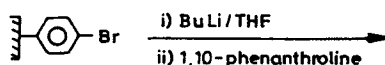
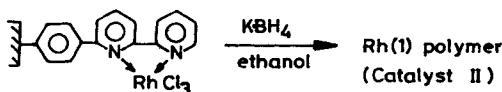
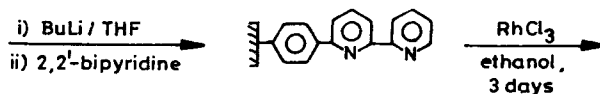
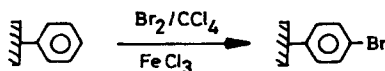
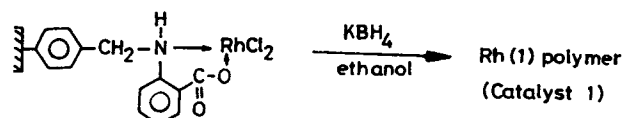
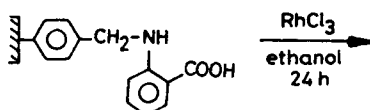
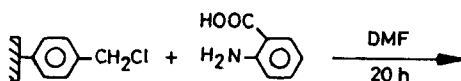
### 2. Experimental

Commercial samples of polystyrene (200–400 mesh) and chloromethylated polystyrene (4–5% of Cl) were used. The catalysts were prepared as shown in the scheme (Card and Neckers 1978; Holy 1979). Anchoring the ligands to the support followed by complexation with RhCl<sub>3</sub>·3H<sub>2</sub>O and subsequent reduction with KBH<sub>4</sub> resulted in active catalysts.

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## Preparation of catalysts



The rhodium content in the catalysts was determined spectrophotometrically (Sandell 1959) after leaching out the metal with conc.  $\text{H}_2\text{SO}_4$ . The amount of nitrogen was estimated by elemental analysis (table 1). The Rh  $3d_{5/2}$  signals in the X-ray photoelectron spectra are summarised in table 2. The XPS values suggest that the oxidation state of rhodium in the active catalysts is +1 (Hamer *et al* 1973). The catalysts were stable up to  $320^\circ\text{C}$  as determined by TGA. IR spectra of the catalysts (table 3) exhibited bands characteristic of the ligands. FT-IR was recorded on a PE model 983-G and XPS on model VG ESCA Lab Mark II using  $\text{MgK}\alpha$  X-radiation.

Reactions were carried out in a static reactor in a toluene-methanol mixture (1:1 by volume) at  $35^\circ\text{C}$  and 1 atmosphere of  $\text{H}_2$ . The progress of the reaction was

**Table 1.** Amounts of rhodium and nitrogen in each catalyst.

	Rh (mg/g)	N (%)	N/Rh
Catalyst I	11.8	3.152	19.5
Catalyst II	6.2	1.048	12.4
Catalyst III	5.4	1.707	23.2

**Table 2.** Rh  $3d_{5/2}$  peak values in the XPS of the catalysts.

	Rh $3d_{5/2}$ (eV)	
	Before activation	After activation with $\text{KBH}_4$
Catalyst I	310.9	308.3
Catalyst II	—	308.5
Catalyst III	311.0	308.7

**Table 3.** IR spectra of catalysts.

Catalyst	Bands ( $\text{cm}^{-1}$ )	Assignment
Catalyst I	1720	O    —C—
	3400	N—H
	330	(Rh—Cl)
	550	out-of-plane deformation of benzene ring
Catalysts II & III	1580, 1440, 1020 820 and 790	(bipyridine anchored to polystyrene)
	1610	C=N→Rh
	330	Rh—Cl
	550	benzene ring deformation

monitored by measuring the uptake of hydrogen using a gas burette. Uniform rate of stirring was maintained to minimise diffusion effects.

### 3. Product analysis

Product analysis for the hydrogenation of ethyl sorbate was carried out by gas chromatography using SE-30 column at  $190^\circ\text{C}$  (2m packed column of 10% SE-30 on chromosorb W).

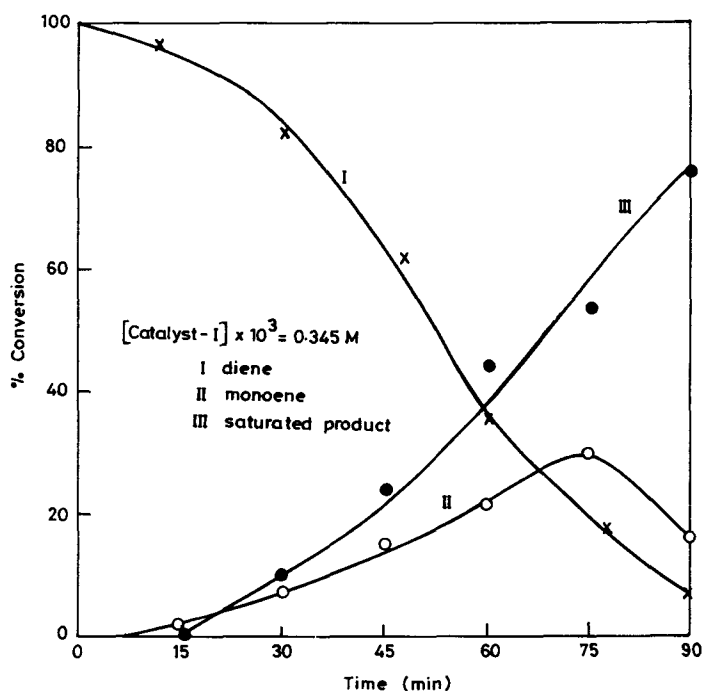


Figure 1. Hydrogenation of ethyl sorbate.

The substrate undergoes complete saturation to the extent of 70% in 90 minutes. The concentration of various constituents were determined assuming that the concentration of the saturated product at the end of the reaction is equal to that of the diene taken. A plot of the concentration of various species present as a function of time is given in figure 1.

#### 4. Result and discussion

A variety of terminal, internal and cyclic monoenes and dienes (cyclic and conjugated) were used as substrates. To study the *cis-trans* isomeric effect on the rate of hydrogenation, maleic and fumaric acid esters were also used. The results are presented in table 4.

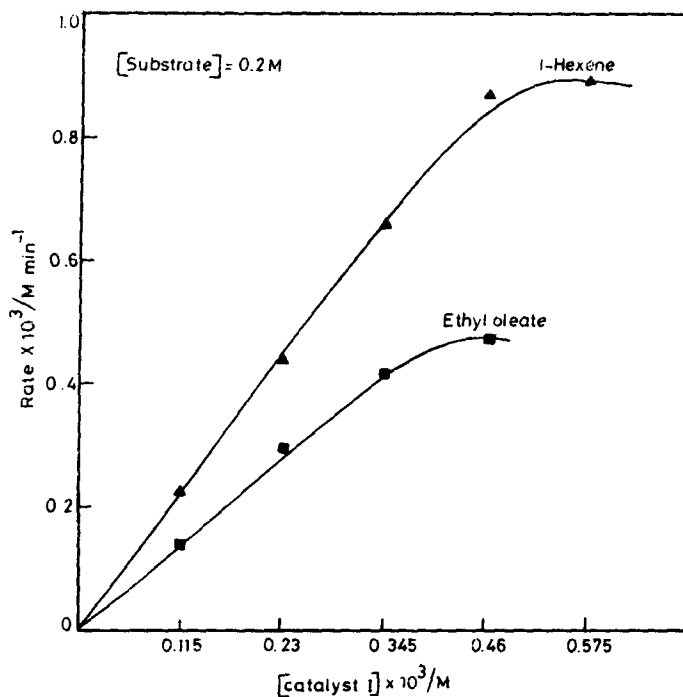
The present studies indicate that

- (i) rate of hydrogenation of terminal olefins is higher than that of internal and cyclic olefins;
- (ii) The *cis* olefin reacts faster than the *trans* olefin;
- (iii) the dienes react slower than monoenes;
- (iv) in the case of ethyl sorbate, a conjugated diene, the reaction proceeds to saturation via monoene intermediate.

For all the substrates studied the reaction is first order with respect to catalyst (figure 2). First order kinetics is observed for the substrates at a concentration range

**Table 4.** Rates and relative rates for various substrates.

Substrate 0.2 M	Initial rate ( $\times 10^3$ ) (M min <sup>-1</sup> )		
	[Cat I] $\times 10^3$ = 0.46 M	[Cat II] $\times 10^3$ = 0.06 M	[Cat III] $\times 10^3$ = 0.053 M
1-Hexene	0.87	0.53	0.39
Cyclohexene	0.73	0.40	0.22
Ethyl cinnamate	0.46	0.14	0.12
Diethyl maleate	0.78	0.28	0.36
Diethyl fumarate	0.62	0.08	0.14
Styrene	0.75	0.25	0.29
1,5-COD	0.53	0.17	0.19
Ethyl sorbate	0.42	0.12	—

**Figure 2.** Dependence of rate on catalyst concentration.

insufficient to saturate the catalyst (figure 3). At higher concentrations of the substrates hydrogen absorption is rate limiting.

The initial rate of hydrogen absorption increased linearly on increasing the partial pressure of hydrogen up to 1 atmosphere of H<sub>2</sub> (figure 4).

The rate of reaction can be given as

$$\text{rate} \propto [\text{catalyst}] [\text{substrate}] [\text{H}_2].$$

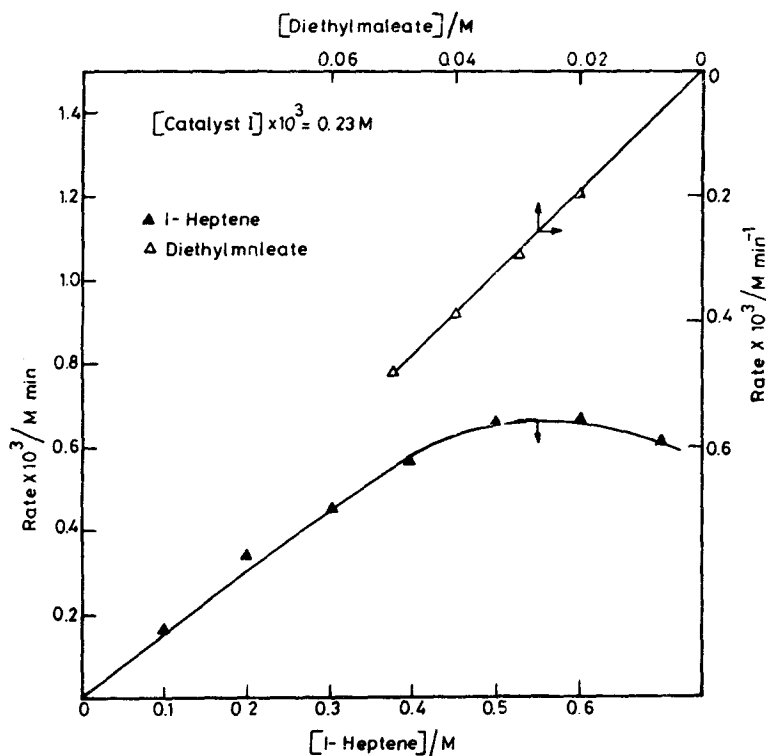


Figure 3. Dependence of rate on substrate concentration.

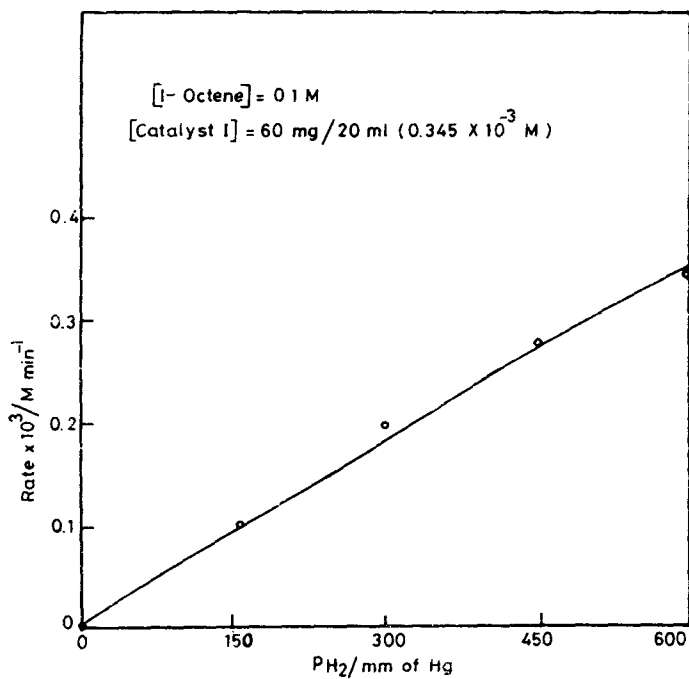


Figure 4. Dependence of rate on  $\text{H}_2$ -pressure.

**Table 5.** Turn over numbers.

Substrates	Catalyst I	Catalyst II	Catalyst III
1-Hexene	114	528	442
Cyclohexene	95	404	248
Ethyl cinnamate	60	140	142
Diethyl maleate	102	280	351
Diethyl fumarate	81	80	159
Styrene	98	249	336
1,5-COD	69	171	212
Ethyl sorbate	55	124	—

Turn over numbers (TON) of catalysts were calculated as moles of H<sub>2</sub> (g mol of Rh)<sup>-1</sup> (h)<sup>-1</sup> (table 5). Catalysts II and III exhibit higher values than catalyst I. The difference in the rate of hydrogenation may be attributed to the electronic factors of the ligands. In the case of 2,2'-bipyridine and 1,10-phenanthroline, the presence of two N-donor atoms increases the electron density on Rh(I) which in turn facilitates the oxidative addition of Rh(I) to Rh(III) and also the activation of substrate and H<sub>2</sub>. In the case of anthranilic acid, the electronic contribution to Rh(I) is less than to the other two ligands and has a slight deactivating effect due to the coordination of oxygen to metal (Collman and Rope 1968).

At least three variations of catalyst concentrations were studied in the saturation region. We did not observe any change in the rate of H<sub>2</sub> absorption in this region. In a purely homogeneous system a correlation of the rate of hydrogenation to steric factors of the ligand can be clearly drawn. In a polymer-supported system like the present study, the availability of the active metal centres is also governed by the porosity of the polymer. For the same catalyst under identical conditions there could be slight variation in the number of active sites. This problem does not arise under homogeneous conditions. Hence a meaningful correlation of the steric effect of the ligands on the rate is not possible.

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