

# Stereoselective hydrogenation of *p*-*tert*-butylphenol over supported rhodium catalyst

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## Abstract

*p*-*tert*-Butylcyclohexanol is used as an intermediate for manufacturing esters with lower carboxylic acids, which are important in perfumery, soap and detergents manufacturing. Stereoselective hydrogenation of *p*-*tert*-butylphenol (PTBP) to *cis* and *trans*-*p*-*tert*-butylcyclohexanol (PTBCH) has been carried out by using supported metal catalysts such as rhodium supported on carbon (2% Rh/C), Raney nickel, nickel supported on silica (20% Ni/SiO<sub>2</sub>), and palladium supported on carbon (5% Pd/C). Among the variety of catalysts used 2% Rh/C exhibited 100% conversion of PTBP and 100% selectivity of the *cis*-isomer of PTBCH when methanesulphonic acid was used as the co-catalyst. The reaction was 100% selective towards the product. The effects of various parameters on the rates of reaction were studied systematically and a kinetic model was built. The reaction was found to be kinetically controlled. The formation of *cis*-isomer was explained theoretically. © 2002 Published by Elsevier Science B.V.

**Keywords:** *p*-*tert*-Butylcyclohexanol; *trans*-*p*-*tert*-Butylcyclohexanol; *cis/trans* ratio; Hydrogenation; Stereo-selectivity; Stereo-isomers; Supported rhodium

## 1. Introduction

Stereoselective hydrogenation of aromatic compounds is a problem of great importance in the production of fine chemicals. The stereochemistry of different heterogeneous catalytic reactions has remained a subject of considerable interest throughout the years [1]. In such catalytic systems, the activity and stereoselectivity has been seen to depend on the nature of the catalyst and of the compound to be hydrogenated, reaction conditions, solvents, etc. Several studies have focused on the liquid-phase catalytic hydrogenation of monoalkylphenols. In this case,

industrial interests attaches only to the *cis*-form of the corresponding monoalkylcyclohexanols as they serve as important intermediates for the fragrance industry [2].

4-*tert*-Butylcyclohexanol (PTBCH), a chemical of wide industrial importance, is conventionally prepared by catalytic hydrogenation of 4-*tert*-butylphenol (PTBP). It is used as an intermediate for manufacturing esters with lower carboxylic acids, which are important in perfumery, soap and detergent manufacturing [3]. There are various reports in literature on hydrogenation of 4-*tert*-butylphenol using supported and unsupported metal catalysts. Konuspaev et al. [4] synthesized PTBCH with a *cis/trans* ratio of 1:2 by hydrogenation of PTBP over unsupported rhodium catalyst. Sekiguchi and Tanaka [5] have claimed 93.4% PTBCH with a *cis/trans* ratio of 89.9:10.1

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in the presence of Rh/C and HCl. In another claim, Sekiguchi and Tanaka [6] have reported 93.1% PTBCH with a *cis/trans* ratio of 91.1:8.9 over Rh/C and HBr. Vogtman et al. [7] hydrogenated PTBP to give 99.3% PTBCH containing 28% *cis*-isomer in the presence of nickel supported on alumina. Furumoto et al. [8] synthesized 99.2% PTBCH at 150 °C and 3 MPa in the presence of modified nickel catalyst. Morikawa [9] has obtained 97% PTBCH containing 58% *cis* in presence of Raney Ru catalyst. In another claim, 95.5% PTBCH containing 82.1% *cis*-isomer was obtained over Rh/C and HClO<sub>4</sub> [10].

This work is concerned with experimental data on *cis* selectivity and the corresponding kinetic modeling for 4-*tert*-butylphenol hydrogenation over a supported rhodium catalyst.

## 2. Experimental

### 2.1. Chemicals and catalysts

*p*-*tert*-Butylphenol, methanesulphonic acid and iso-propanol were obtained from M/s S.D. Fine Chemicals, Mumbai. *p*-*tert*-Butylcyclohexanol was obtained from M/s Hindustan Polyamides and Fibres, Mumbai, as a gift sample. Rhodium supported on carbon (2% Rh/C) was procured from M/s S.K. Agarwal, Mumbai. Raney nickel was obtained from Kalin Industries, Mumbai. Supported Ni catalyst (20% Ni/SiO<sub>2</sub>) was procured from M/s Monarch Chemicals, Mumbai. All chemicals were analytical grade reagents and used without further purification. Hydrogen gas cylinder was obtained from Industrial Oxygen, Mumbai.

### 2.2. Reaction procedure

All experiments were carried out in a 100 ml stainless steel autoclave manufactured by Parr Instruments Company, USA. A four bladed-pitched turbine impeller was used for agitation. Hydrogen gas was supplied from a cylinder. Predetermined quantities of reactants and the catalyst were charged into the autoclave which was repeatedly purged with hydrogen. The autoclave temperature was raised and maintained at  $\pm 1$  °C of the desired value with the help of an in-built proportional-integral-derivative (PID)

controller. Once the temperature had reached the set point, the autoclave was pressurized with hydrogen to the desired pressure level and agitation started. A constant pressure was maintained throughout the reaction period by opening the hydrogen inlet valve intermittently.

In a typical experiment, 0.02 mol of PTBP and *iso*-propanol were added to make-up a total volume to 50 cm<sup>3</sup>. A typical catalyst loading of 0.2 g was used which corresponds to 0.004 g/cm<sup>3</sup> liquid volume. 0.001 mol of methanesulphonic acid (MSA) was added as co-catalyst to get the desired selectivity towards *cis*-isomer. The reaction mixture was then allowed to reach a temperature of 80 °C and the initial/zero time sample was collected. Agitation was then commenced at a particular speed. Samples were withdrawn periodically for analysis.

### 2.3. Analysis

Analysis of the reaction mixture was done using G.C. (Chemito 8510) using 10% Carbowax neutral (2 m × 3.2 mm) column on Chromosorb WHP with FID. The injector and detector were kept at 250 °C and the oven temperature was programmed from 130 °C (0.5 min) up to 215 °C with a ramp rate of 20 °C min<sup>-1</sup>. Nitrogen was used as the carrier gas at 30 ml min<sup>-1</sup>. Calibrations were done with authentic samples for quantification of data. Identification of products was done by GC MS and by matching the retention time of reaction products to the authentic compounds in all cases.

## 3. Results and discussion

### 3.1. Effect of different catalysts

The published information suggested that an acid should be used as a co-catalyst to improve the selectivity of the *cis*-isomer and acids such as H<sub>2</sub>SO<sub>4</sub>, HCl, HBr and HClO<sub>4</sub> were employed. It was thus thought prudent to employ an organic acid such as carboxylic acids or sulphonic acids. The preliminary experiments indicated that MSA was a good co-catalyst which was used to evaluate the efficacy of all catalysts. A further discussion on the role of MSA will be provided later.



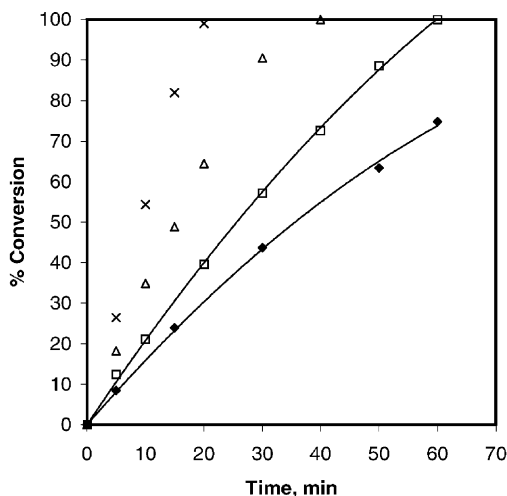


Fig. 2. Effect of catalyst loading on conversion of PTBP. PTBP:  $4 \times 10^{-4}$  gmol/cm<sup>3</sup>; MSA:  $2 \times 10^{-5}$  gmol/cm<sup>3</sup>; temperature: 80 °C; hydrogenation pressure: 0.5 MPa; solvent: *iso*-propanol; time: 60 min; speed of agitation: 800 rpm. (◆) 0.002 g/cm<sup>3</sup>; (□) 0.004 g/cm<sup>3</sup>; (△) 0.006 g/cm<sup>3</sup>; (×) 0.008 g/cm<sup>3</sup>.

Fig. 2 shows the effect of catalyst loading on the conversion of PTBP. The conversion increases with increasing catalyst loading, which is obviously due to the proportional increase in the number of active sites. The reaction was too violent to control if the amount of catalyst was very large. All further experiments were carried out at 0.004 g/cm<sup>3</sup> of catalyst loading.

### 3.4. Effect of concentration of methanesulphonic acid

As stated earlier, a catalytic amount of methanesulphonic acid was added as a co-catalyst in the reaction to increase the *cis*-selectivity of the product. When no MSA was added, 100% conversion of PTBP could be achieved in 40 min but with only 80% selectivity towards the *cis*-isomer of PTBCH. When small quantity of MSA was added, selectivity towards the *cis*-isomer of PTBCH improves to 100% with 100% conversion of PTBP. The effect of concentration of MSA was studied at different concentrations from  $1.04 \times 10^{-5}$  to  $6.25 \times 10^{-5}$  gmol/cm<sup>3</sup> under otherwise similar conditions (Fig. 3). Marginal increase in conversion of PTBP was observed with increase in concentration of MSA. All further experiments were conducted with  $2.08 \times 10^{-5}$  gmol/cm<sup>3</sup> of MSA.

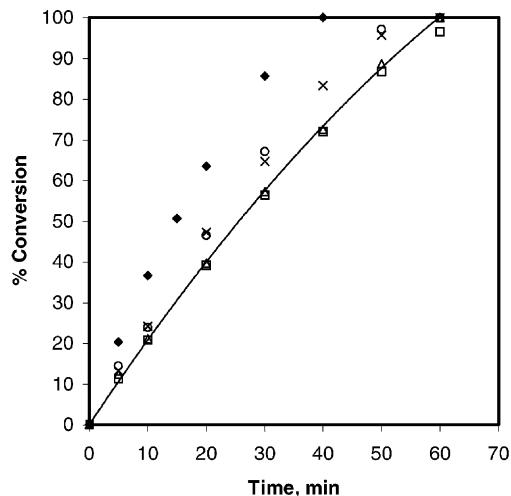


Fig. 3. Effect of concentration of MSA on conversion of PTBP. PTBP:  $4 \times 10^{-4}$  gmol/cm<sup>3</sup>; catalyst loading: 0.004 g/cm<sup>3</sup>; temperature: 80 °C; hydrogenation pressure: 0.5 MPa; solvent: *iso*-propanol; time: 60 min; speed of agitation: 800 rpm. (◆) Without MSA; (□)  $1.04 \times 10^{-5}$  gmol/cm<sup>3</sup>; (△)  $2.08 \times 10^{-5}$  gmol/cm<sup>3</sup>; (×)  $4.16 \times 10^{-5}$  gmol/cm<sup>3</sup>; (○)  $6.25 \times 10^{-5}$  gmol/cm<sup>3</sup>.

It was observed that the reaction rates were very high when no MSA was added in the reaction. With the addition of small amount of MSA reaction rates were slowed down. It means MSA is either selectively poisoning the catalyst surface or provide a new site environment for the formation of *cis*-PTBCH.

### 3.5. Effect of partial pressure of hydrogen

The effect of partial pressure of hydrogen was studied on the conversion of PTBP in the range 0.2–3 MPa (Fig. 4). With an increase in hydrogen pressure, the hydrogenation rate was found to increase markedly from 0.2 to 1.0 MPa but thereafter from 1.0 to 3.0 MPa the increase was moderate. All further reactions were carried out at the hydrogen partial pressure of 0.5 MPa.

### 3.6. Effect of initial concentration of PTBP

The effect of concentration of PTBP was studied at different initial concentrations from  $0.667 \times 10^{-4}$  to  $6.67 \times 10^{-4}$  gmol/cm<sup>3</sup> at a catalyst loading of 0.004 g/cm<sup>3</sup> under otherwise similar conditions (Fig. 5). The conversion was found to decrease

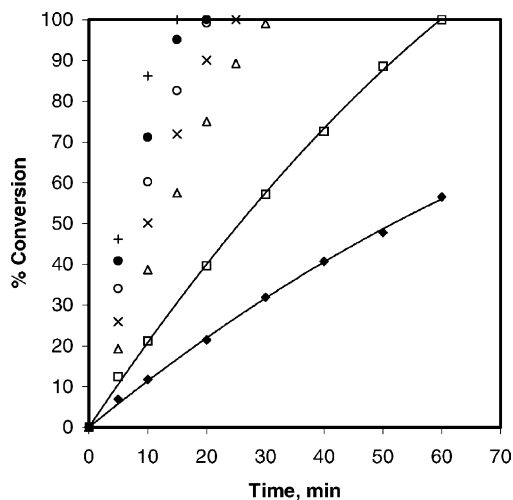


Fig. 4. Effect of partial pressure of hydrogen on conversion of PTBP. PTBP:  $4 \times 10^{-4}$  gmol/cm<sup>3</sup>; catalyst loading: 0.004 g/cm<sup>3</sup>; MSA:  $2 \times 10^{-5}$  gmol/cm<sup>3</sup>; temperature: 80 °C; solvent: *iso*-propanol; time: 60 min; speed of agitation: 800 rpm. (◆) 0.2 MPa; (□) 0.5 MPa; (△) 1.0 MPa; (×) 1.5 MPa; (○) 2.0 MPa; (●) 2.5 MPa; (+) 3.0 MPa.

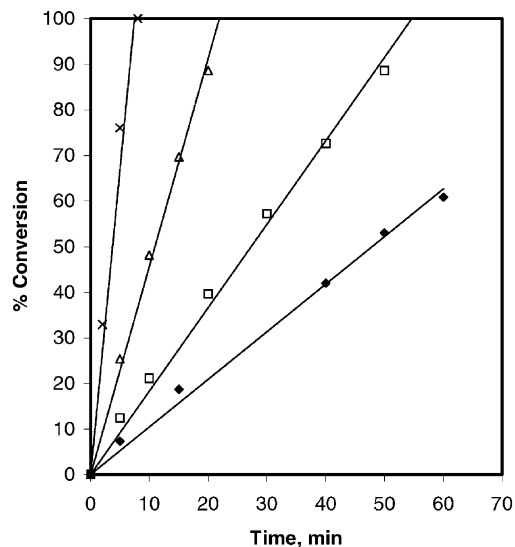


Fig. 5. Effect of initial concentration of PTBP. Catalyst loading: 0.004 g/cm<sup>3</sup>; MSA:  $2 \times 10^{-5}$  gmol/cm<sup>3</sup>; hydrogenation pressure: 0.5 MPa; temperature: 80 °C; solvent: *iso*-propanol; time: 60 min; speed of agitation: 800 rpm. (◆)  $6.67 \times 10^{-4}$  gmol/cm<sup>3</sup>; (□)  $4.0 \times 10^{-4}$  gmol/cm<sup>3</sup>; (△)  $2.0 \times 10^{-4}$  gmol/cm<sup>3</sup>; (×)  $0.667 \times 10^{-4}$  gmol/cm<sup>3</sup>.

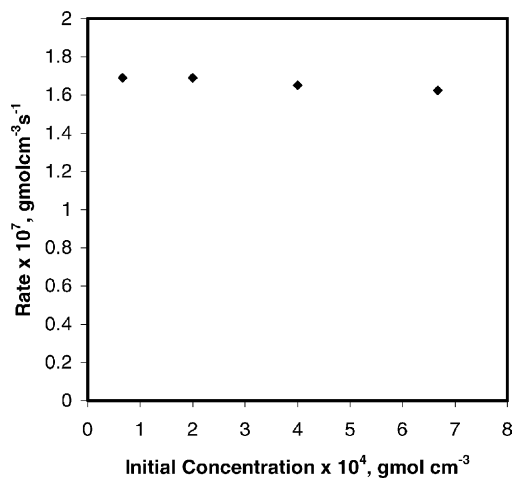


Fig. 6. Effect of initial concentrations of PTBP on rate of reaction.

due to higher quantity of PTBP present. The plot of initial rate against concentration was found to show the rate being independent of concentration (Fig. 6) and also the conversions are linear in time (Fig. 5) showing zero-order in the concentration of PTBP.

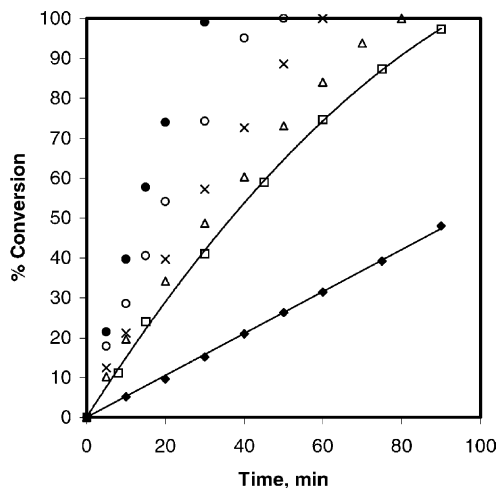


Fig. 7. Effect of temperature on conversion of PTBP. PTBP:  $4 \times 10^{-4}$  gmol/cm<sup>3</sup>; catalyst loading: 0.004 g/cm<sup>3</sup>; MSA:  $2 \times 10^{-5}$  gmol/cm<sup>3</sup>; hydrogenation pressure: 0.5 MPa; solvent: *iso*-propanol; time: 60 min; speed of agitation: 800 rpm. (◆) 50 °C; (□) 60 °C; (△) 70 °C; (×) 80 °C; (○) 90 °C; (●) 100 °C.

### 3.7. Effect of temperature

The effect of temperature on conversion under otherwise similar conditions was studied in the range 50–100 °C (Fig. 7). The conversion was found to increase substantially with increase in temperature.

## 4. Kinetics of the reaction

The addition of MSA on 2% Rh/C changes the *cis/trans* ratio and in fact, as the MSA concentration is increased, the *trans* content goes on reducing and finally only *cis*-isomer is found. Thus, the role of MSA is to alter the activity of the sites particularly for the adsorption of PTBP. There should be two different types of sites  $S_1$  and  $S_2$  on the catalyst surface; one the sites covered by MSA and other the metal sites.

### 4.1. Adsorption of MSA on $S_1$ site



$$K_{\text{MSA}} = \frac{C_{S_1^*}}{C_{\text{MSA}} C_{S_1}} \quad (2)$$

The site balance gives

$$C_{t_1} = C_{S_1} + C_{S_1^*} \quad (3)$$

where  $C_{t_1}$  is the total  $S_1$  site concentration;  $C_{S_1}$  the vacant  $S_1$  site concentration;  $C_{S_1^*}$  the MSA occupied site concentration.

$$\begin{aligned} C_{t_1} &= C_{S_1} + K_{\text{MSA}} C_{\text{MSA}} C_{S_1} \\ &= C_{S_1} (1 + K_{\text{MSA}} C_{\text{MSA}}) \end{aligned} \quad (4)$$

or

$$C_{S_1} = \frac{C_{t_1}}{(1 + K_{\text{MSA}} C_{\text{MSA}})} \quad (5)$$

Thus, the concentration of sites covered with MSA is

$$C_{S_1^*} = C_{t_1} - C_{S_1} = C_{t_1} - \frac{C_{t_1}}{(1 + K_{\text{MSA}} C_{\text{MSA}})} \quad (6)$$

$$C_{S_1^*} = \frac{C_{t_1} (K_{\text{MSA}} C_{\text{MSA}})}{1 + K_{\text{MSA}} C_{\text{MSA}}} \quad (7)$$

when  $K_{\text{MSA}} C_{\text{MSA}} \gg 1$ ,

$C_{S_1^*} = C_{t_1}$ , all  $S_1$  sites are occupied by MSA.

### 4.2. Dissociative adsorption of hydrogen molecule on $S_2$ site



$$K_{\text{HS}_2} = \frac{C_{\text{HS}_2}^2}{p_{\text{H}_2} C_{S_2}^2} \quad (9)$$

$$C_{\text{HS}_2} = (K_{\text{HS}} p_{\text{H}_2})^{1/2} C_{S_2} \quad (10)$$

If the total sites are  $C_{t_2}$ , then

$$C_{t_2} = C_{S_2} + C_{\text{HS}_2} = C_{S_2} + C_{S_2} (K_{\text{HS}} p_{\text{H}_2})^{1/2} \quad (11)$$

Thus,

$$C_{S_2} = \frac{C_{t_2}}{1 + (K_{\text{H}_2} p_{\text{H}_2})^{1/2}} \quad (12)$$

$$C_{\text{HS}_2} = \frac{C_{t_2} (K_{\text{H}_2} p_{\text{H}_2})^{1/2}}{1 + (K_{\text{H}_2} p_{\text{H}_2})^{1/2}} \quad (13)$$

### 4.3. Adsorption of PTBP (A) on modified site ( $S_1^*$ ) for the formation of *cis*-isomer



### 4.4. Adsorption of PTBP (A) on $S_1$ site for the formation of *trans*-isomer



$$C_{S_1^*} = C_{S_1^*-v} + C_{\text{AS}_1^*} \quad (16)$$

$$\begin{aligned} C_{S_1^*} &= C_{S_1^*-v} + K_{\text{AS}_1^*} C_{\text{A}} C_{S_1^*-v} \\ &= C_{S_1^*-v} (1 + K_{\text{AS}_1^*} C_{\text{A}}) \end{aligned} \quad (17)$$

$$C_{S_1^*-v} = \frac{C_{S_1^*}}{(1 + K_{\text{AS}_1^*} C_{\text{A}})} \quad (\text{cis}) \quad (18)$$

$$C_{S_1-v} = \frac{C_{S_1}}{(1 + K_{\text{AS}_1} C_{\text{A}})} \quad (\text{trans}) \quad (19)$$

$$C_{\text{AS}_1^*} = K_{\text{AS}_1^*} C_{\text{A}} C_{S_1^*-v} \quad (20)$$

$$C_{\text{AS}_1^*} = \frac{C_{S_1^*} K_{\text{AS}_1^*} C_{\text{A}}}{(1 + K_{\text{AS}_1^*} C_{\text{A}})} \quad (21)$$

$$C_{AS_1^*} = \frac{C_{t_1} K_{AS_1^*} C_A K_{MSA} C_{MSA}}{(1 + K_{AS_1^*} C_A)(1 + K_{MSA} C_{MSA})} \quad (22)$$

Similarly,

$$C_{AS_1} = \frac{C_{S_1} K_{AS_1} C_A}{(1 + K_{AS_1} C_A)} \quad (23)$$

$$C_{AS_1} = \frac{C_{t_1} K_{AS_1} C_A K_{MSA} C_{MSA}}{(1 + K_{AS_1} C_A)(1 + K_{MSA} C_{MSA})} \quad (24)$$

If all the sites are occupied by MSA,  $C_{AS_1} = 0$  and there will be no *trans*-isomer.

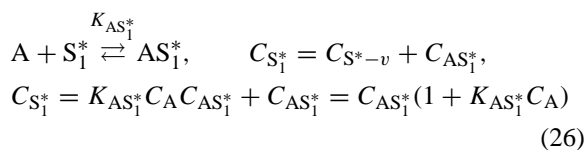
If  $K_{AS_1^*} C_A \gg 1$ , then

$$C_{AS_1^*} = \frac{C_{t_1} K_{MSA} C_{MSA}}{(1 + K_{MSA} C_{MSA})} \quad (25)$$

and it becomes independent of  $C_A$ .

When  $H_2$ , PTBP and MSA are present together, the following situation is envisaged.

For complete selectivity to *cis*-isomer, all  $S_1$  sites are covered with MSA. It should also be assumed that PTBP adsorbs on the sites where MSA is adsorbed. Thus,



$$C_{AS_1^*} = \frac{C_{S_1^*}}{(1 + K_{AS_1^*} C_A)} \quad (27)$$

Thus, the net rate of hydrogenation is given by

$$r_{H_2} = \left( \frac{k_{cis} C_{t_1} K_{MSA} C_{MSA}}{1 + K_{MSA} C_{MSA}} \right) \left( \frac{K_{AS_1^*} C_A}{1 + K_{AS_1^*} C_A} \right)$$

$$\times \left( \frac{C_{t_2} (K_{H_2} p_{H_2})^{1/2}}{1 + (K_{H_2} p_{H_2})^{1/2}} \right) + \left( \frac{k_{trans} C_{t_1}}{1 + K_{MSA} C_{MSA}} \right)$$

$$\times \left( \frac{K_{AS_1} C_A}{1 + K_{AS_1} C_A} \right) \left( \frac{C_{t_2} (K_{H_2} p_{H_2})^{1/2}}{1 + (K_{H_2} p_{H_2})^{1/2}} \right) \quad (28)$$

In the above equation, the first term accounts for the formation of *cis*-isomer and the second for the formation of the *trans*-isomer.

The inspection of data (Figs. 5 and 6) shows that the initial rates of hydrogenation are independent of  $C_A$  as well as the conversions are linear in time suggesting a

zero-order dependence of concentration of PTBP, i.e.  $K_{AS_1^*} C_A \gg 1$ . Thus,

$$r_{H_2} = \left( \frac{k_{cis} C_{t_1} K_{MSA} C_{MSA}}{1 + K_{MSA} C_{MSA}} \right) \left( \frac{C_{t_2} (K_{H_2} p_{H_2})^{1/2}}{1 + (K_{H_2} p_{H_2})^{1/2}} \right)$$

$$+ \left( \frac{k_{trans} C_{t_1}}{1 + K_{MSA} C_{MSA}} \right) \left( \frac{C_{t_2} (K_{H_2} p_{H_2})^{1/2}}{1 + (K_{H_2} p_{H_2})^{1/2}} \right) \quad (29)$$

The following plots could be made to test the above theory.

1) For a fixed hydrogen partial pressure when no *trans*-isomer is present.

$$r_{H_2} = \left( \frac{k_{cis} C_{t_1} K_{MSA} C_{MSA}}{1 + K_{MSA} C_{MSA}} \right) k,$$

$$k = \text{constant} = \left( \frac{C_{t_2} (K_{H_2} p_{H_2})^{1/2}}{1 + (K_{H_2} p_{H_2})^{1/2}} \right) \quad (30)$$

For initial rates,

$$\frac{1}{r_{H_2i}} = \left( \frac{1}{k_1 C_{t_1} K_{MSA} C_{MSA}} + \frac{1}{k_1 C_{t_1}} \right) \quad (31)$$

But  $C_{t_1} \propto w$ , the solid loading, and can be replaced without loss of generality by  $w$ .

$$\frac{w}{r_{H_2i}} = \left( \frac{1}{k_1 K_{MSA} C_{MSA}} + \frac{1}{k_1} \right) \quad (32)$$

A plot of  $w/r_{H_2i}$  vs.  $1/C_{MSA}$  was made to find that the above equation is valid (Fig. 8). From the slope and intercept, both  $k_1$  and  $K_{MSA}$  were calculated as  $30.5 \text{ gmol g}_{\text{cat}}^{-1} \text{ s}^{-1}$  and  $0.505 \text{ mol cm}^{-3}$ , respectively. This is the case for complete selectivity to *cis*-isomer.

2) For a fixed concentration of MSA, when no *trans*-isomer is present.

$$r_{H_2i} = k' \left( \frac{k_{cis} C_{t_2} (K_{H_2} p_{H_2})^{1/2}}{1 + (K_{H_2} p_{H_2})^{1/2}} \right),$$

$$k' = \text{constant} = \left( \frac{C_{t_1} K_{MSA} C_{MSA}}{1 + K_{MSA} C_{MSA}} \right) \quad (33)$$

But  $C_{t_2} \propto w$ , the solid loading

$$\frac{w}{r_{H_2i}} = \left[ \frac{1}{k_2 (K_{H_2} p_{H_2})^{1/2}} + \frac{1}{k_2} \right] \quad (34)$$

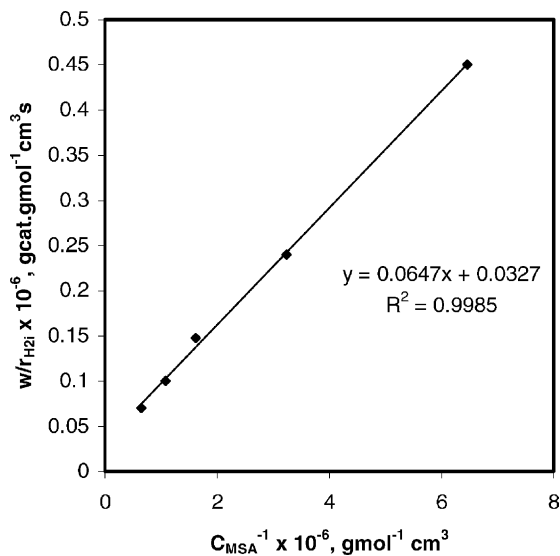


Fig. 8. Plot of  $w/r_{H_2i}$  vs.  $1/C_{MSA}$ .

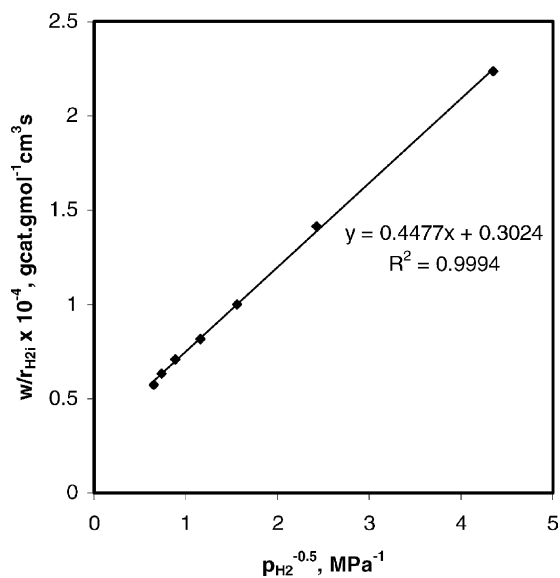


Fig. 9. Plot of  $w/r_{H_2i}$  vs.  $1/p_{H_2}^{0.5}$ .

Thus, again a plot of  $w/r_{H_2i}$  vs.  $1/p_{H_2}^{0.5}$  was made to get the slope as  $1/k_2 K_{H_2}^{0.5}$  and intercept as  $1/k_2$  (Fig. 9). The values of  $k_2$  and  $K_{H_2}$  were calculated as  $3.31 \times 10^{-4} \text{ gmol}_{\text{cat}}^{-1} \text{ s}^{-1}$  and  $54.5 \text{ MPa}^{-1}$ , respectively.

This suggests that the theory is valid for the formation of *cis*-isomer.

## 5. Conclusions

The kinetics of liquid-phase hydrogenation of 4-*tert*-butylphenol over metal catalysts was investigated and a kinetic model is built. In the hydrogenation of 4-*tert*-butylphenol with Rh/C only *cis*- and *trans*-4-*tert*-butylcyclohexanol were produced and the production of corresponding cyclohexanone was not observed. Among the variety of catalysts used 2% Rh/C exhibited 100% conversion of PTBP and 100% selectivity of the *cis*-isomer of PTBCH when methanesulphonic acid was used as the co-catalyst. The reaction was 100% selective towards the product. The effects of various parameters on the rates of reaction were studied systematically, and the reaction was found to be kinetically controlled. The formation of *cis*-isomer was explained theoretically.

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