

# Homogeneous hydrogenation of maleic anhydride to succinic anhydride catalyzed by Rh complex catalyst

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## Abstract

Hydrogenation of maleic anhydride using various homogeneous transition metal complex catalyst system has been investigated. It was observed that  $\text{RhCl}(\text{PPh}_3)_3$  was the most active catalyst precursor for the hydrogenation of maleic anhydride to succinic anhydride. The optimum ligand and solvent were  $\text{PPh}_3$  and ethylene glycol dimethylether, respectively. The effects of  $\text{PPh}_3:\text{Rh}$  mole ratio, temperature and pressure of  $\text{H}_2$  have been studied. The typical experimental conditions are: temperature, 353–383 K; pressure of  $\text{H}_2$ , 0.5–2.5 MPa;  $\text{PPh}_3:\text{RhCl}(\text{PPh}_3)_3$ , 0–16;  $\text{RhCl}(\text{PPh}_3)_3$ , 0.03 mmol; maleic anhydride, 20 mmol; volume of liquid, 8 ml; reaction time, 30–360 min. Under these experimental conditions, succinic anhydride was the only product, and the highest yield (99.0%) was obtained. A reasonable reaction mechanism is proposed. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Homogeneous hydrogenation; Maleic anhydride; Rh complex; Succinic anhydride

## 1. Introduction

Succinic anhydride (SA) is an example of a small volume commodity chemical of considerable industrial interest, as indicated by both the actual market and the growth prospects. In particular, SA is required as intermediate for the chemical, pharmaceutical and food industries. There are basically two processes for the production of SA—dehydration of succinic acid and hydrogenation of maleic anhydride (MA) [1,2]. Because of MA's availability and lower price which become possible by the construction of large fluid bed plants, according to Alusuisse–

Lumnus and BP/UCB technologies, MA may be considered as a good feedstock nowadays [3–6]. The hydrogenation of MA is the most direct way to produce SA and economically favored compared with dehydration of succinic acid to SA. So far, the hydrogenation of MA to SA has been carried out over heterogeneous catalysts and most were reported in patent literature [7–11]. Only a few reports of the homogeneous hydrogenation of MA to SA have appeared in literature. Jardine et al. [12] studied the hydrogenation of MA using  $\text{RhCl}(\text{PPh}_3)_3$  as catalyst in the solvent benzene under 50 cm hydrogen partial pressure. The results show that the rate of hydrogenation is very much lower (less than 0.01 mmol/min) because MA reacts

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to form a stable complex with the transition metal ion. As homogeneous catalysis has a number of advantages such as high activity (all catalytic centers are identical), high selectivity and mild operating conditions, the aim of this study was to investigate the homogeneous hydrogenation of MA to SA. Under high pressure and in the solvent of ethylene glycol dimethylether (EGD), SA can be prepared by the hydrogenation of MA catalyzed by  $\text{RhCl}(\text{PPh}_3)_3$ . Here, we wish to present the results of the homogeneous hydrogenation of MA to SA.

## 2. Experimental

### 2.1. Materials

Catalyst precursors  $\text{PdCl}_2(\text{PPh}_3)_2$  [13],  $\text{NiCl}_2(\text{PPh}_3)_2$  [14],  $\text{RhCl}(\text{PPh}_3)_3$  [15],  $\text{RhH}(\text{CO})(\text{PPh}_3)_2$  [16],  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$  [17],  $\text{CoCl}_2(\text{PPh}_3)_2$  [18],  $\text{RuCl}_2(\text{PPh}_3)_3$  [19] were prepared by procedures described in the literature.

The results of elemental analysis for these complexes were consistent with the theoretical values. All solvents used were refluxed over sodium metal with diphenyl ketone until the appearance of blue color and distilled before use. All ligands were of A.R. grade.

### 2.2. Experimental procedure for the hydrogenation reaction

In the experiment, the appointed amount of catalyst precursor, ligand, MA and solvent were

placed into a 25 ml autoclave. The autoclave was flushed with  $\text{H}_2$  for five times, and then charged with  $\text{H}_2$  to the desired pressure. The mixture was stirred at constant temperature for a certain time. At the end of reaction, the autoclave was cooled to ambient temperature and slowly depressurized. The reaction mixture was analyzed by GC on a  $25 \text{ m} \times 0.25 \text{ mm}$  SE-52 capillary column with hydrogen flame. The injector and detector temperature were  $280^\circ\text{C}$ , the oven temperature was  $130^\circ\text{C}$ . The reactant and product were identified on the basis of the retention times of authentic compounds. The retention times were as follows: MA, 6.1 min; SA, 9.2 min.

## 3. Results and discussion

### 3.1. Effect of catalyst precursor on the hydrogenation of MA

In order to optimize the catalyst precursor for the hydrogenation of MA, the nature of different catalyst precursors was investigated. The results are presented in Table 1. Comparing the conversion and turnover number, rhodium-containing catalyst systems,  $\text{RhCl}(\text{PPh}_3)_3/\text{PPh}_3$ ,  $\text{RhCl}(\text{CO})(\text{PPh}_3)_2/\text{PPh}_3$ ,  $\text{RhH}(\text{CO})(\text{PPh}_3)_2/\text{PPh}_3$  and  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}/\text{PPh}_3$  were found to give higher activities comparing with  $\text{PdCl}_2$ -

Table 1  
Screening of catalyst precursor for the hydrogenation of MA

Run no.	Catalyst precursor	Reaction time (min)	MA conversion (mol%)	Turnover number (mol/mol/h)
1	$\text{RhCl}(\text{PPh}_3)_3$	180	73.0	162.2
2	$\text{RhCl}(\text{CO})(\text{PPh}_3)_2$	180	71.1	158.0
3	$\text{RhH}(\text{CO})(\text{PPh}_3)_2$	180	50.5	112.2
4	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	180	47.0	104.5
5	$\text{PdCl}_2(\text{PPh}_3)_2$	300	64.2	85.6
6	$\text{RuCl}_2(\text{PPh}_3)_3$	300	40.4	53.9
7	$\text{NiCl}_2(\text{PPh}_3)_2$	300	33.6	44.8
8	$\text{CoCl}_2(\text{PPh}_3)_2$	300	25.0	33.4

Reaction conditions: catalyst precursor, 0.03 mmol;  $\text{PPh}_3$ , 0.3 mmol; MA, 20 mmol; pressure of  $\text{H}_2$ , 1.5 MPa; temperature, 373 K; EGD as solvent; volume of liquid, 8 ml.

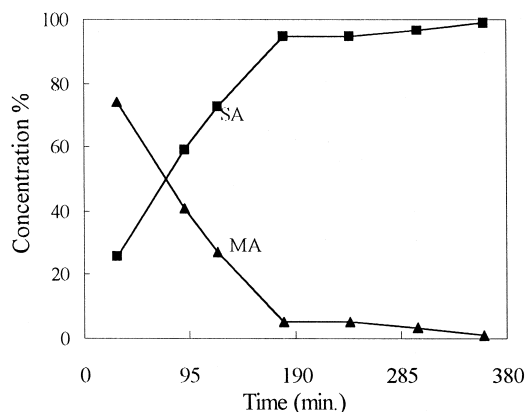


Fig. 1. Concentration–time plot for the hydrogenation of MA catalyzed by  $\text{RhCl}(\text{PPh}_3)_3/\text{PPh}_3$ . Reaction conditions:  $\text{RhCl}(\text{PPh}_3)_3$ , 0.03 mmol;  $\text{PPh}_3$ :Rh, 6; MA, 20 mmol; pressure of  $\text{H}_2$ , 2.0 MPa; temperature, 383 K; EGD as solvent; volume of liquid, 8 ml.

$(\text{PPh}_3)_2/\text{PPh}_3$ ,  $\text{NiCl}_2(\text{PPh}_3)_2/\text{PPh}_3$ ,  $\text{CoCl}_2(\text{PPh}_3)_2/\text{PPh}_3$  and  $\text{RuCl}_2(\text{PPh}_3)_3/\text{PPh}_3$ . Among the Rh complexes studied,  $\text{RhCl}(\text{PPh}_3)_3$  was the most active catalyst precursor. In the experiment no other products were observed except SA, and the selectivity for SA was 100%. A typical concentration–time profile for this reaction catalyzed by  $\text{RhCl}(\text{PPh}_3)_3/\text{PPh}_3$  is shown in Fig. 1.

Table 2  
Effect of ligands on the hydrogenation of MA

Run no.	Ligand	MA conversion (mol%)	Turnover number (mol/mol/h)
1	None	61.3	136.2
2	Triphenylphosphine	79.8	177.3
3	Tricyclohexylphosphine	74.0	164.4
4	RM-17 <sup>a</sup>	68.4	152.0
5	Benzyl cyanide	50.8	112.9
6	Tributyl phosphine	45.3	100.6
7	Tetramethylethylenediamine	43.2	96.0
8	Triethylamine	40.7	90.4
9	Quinoline	25.8	57.3
10	Pyridine	15.9	39.5

Reaction conditions:  $\text{RhCl}(\text{PPh}_3)_3$ , 0.03 mmol; ligand, 0.3 mmol; MA, 20 mmol; pressure of  $\text{H}_2$ , 2.0 MPa; temperature, 373 K; EGD as solvent; volume of liquid, 8 ml; reaction time, 180 min.  
<sup>a</sup>RM-17: 9-eicosyl-9-phosphadicyclo[3,3,1]nonane.

Table 3  
Effect of solvents on the hydrogenation of MA

Run no.	Solvent	MA conversion (mol%)	Turnover number (mol/mol/h)
1	EGD	79.8	177.3
2	1,4-dioxane	43.0	95.6
3	Toluene	37.4	83.2
4	<i>n</i> -hexane	10.1	22.4

Reaction conditions:  $\text{RhCl}(\text{PPh}_3)_3$ , 0.03 mmol;  $\text{PPh}_3$ , 0.3 mmol; MA, 20 mmol; pressure of  $\text{H}_2$ , 2.0 MPa; temperature, 373 K; volume of liquid, 8 ml; reaction time, 180 min.

### 3.2. Effect of ligands on the hydrogenation of MA

The effect of various N- or P-containing ligands on the conversion and turnover number in the hydrogenation of MA was studied. The results are given in Table 2. In the presence of triphenylphosphine, the conversion and turnover number of the catalyst system was the highest in all ligands. This ligand may play an important role in forming and stabilizing the active catalytic species  $\text{RhH}_2\text{Cl}(\text{PPh}_3)_2$  [15]. For triethylamine, tetramethylethylenediamine, quinoline, pyridine, tributylphosphine, a significantly lower activity was observed.

### 3.3. Effect of solvents on the hydrogenation of MA

The effect of solvents on the hydrogenation of MA was investigated using strong as well as

Table 4  
Effect of  $\text{PPh}_3$ :Rh mole ratio on the hydrogenation of MA

Run no.	$\text{PPh}_3$ :Rh ratio	MA conversion (mol%)	Turnover number (mol/mol/h)
1	0	61.3	136.2
2	2	73.6	163.6
3	6	85.8	190.6
4	10	79.8	177.3
5	16	67.7	150.4

Reaction conditions:  $\text{RhCl}(\text{PPh}_3)_3$ , 0.03 mmol; MA, 20 mmol; pressure of  $\text{H}_2$ , 2.0 MPa; temperature, 373 K; EGD as solvent; volume of liquid, 8 ml; reaction time, 180 min.

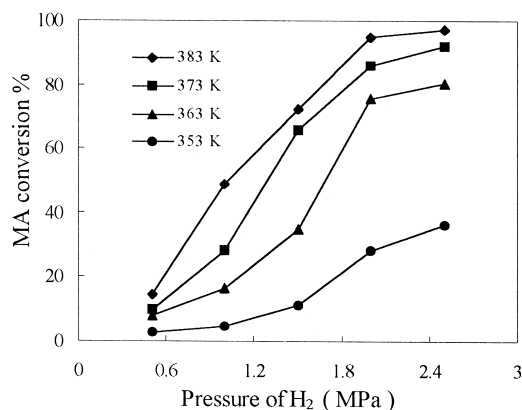


Fig. 2. Effect of temperature and pressure of H<sub>2</sub> on conversion of MA catalyzed by RhCl(PPh<sub>3</sub>)<sub>3</sub>/PPh<sub>3</sub>. Reaction conditions: RhCl(PPh<sub>3</sub>)<sub>3</sub>, 0.03 mmol; PPh<sub>3</sub>:Rh, 6; MA, 20 mol; EGD as solvent; volume of liquid, 8 ml; reaction time 180 min.

weak polar solvents, and the results are listed in Table 3. In all solvents studied, ethylene glycol dimethylether was found to be the best solvent in the presence of which 79.8% conversion of MA was obtained, but using *n*-hexane, toluene or 1,4-dioxane as solvent, low conversion and turnover number were obtained. RhCl(PPh<sub>3</sub>)<sub>3</sub> and MA have poor solubility in *n*-hexane and settled in the autoclave bottom forming a separate layer; MA has poor solubility in toluene and settled in the autoclave bottom forming a separate layer. The different solubility of MA and/or catalyst precursor in the solvent may lead to poor conversion and turnover number for the hydrogenation of MA.

### 3.4. Effect of PPh<sub>3</sub>:Rh mole ratio on the hydrogenation of MA

The effect of PPh<sub>3</sub>:Rh mole ratio on the conversion and turnover number was studied,

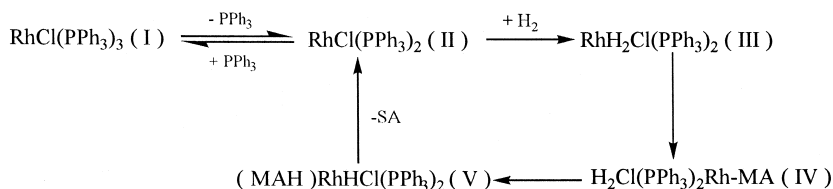
and the results are summarized in Table 4. The conversion of MA increased with the increase of PPh<sub>3</sub>:Rh mole ratio up to 6, beyond which it decreased with the increase of PPh<sub>3</sub>:Rh mole ratio up to 6, beyond which it was found to decrease. Therefore, optimum PPh<sub>3</sub>:Rh mole ratio was 6. In the following experiments, PPh<sub>3</sub>:Rh mole ratio was kept at 6.

### 3.5. Effect of temperature and pressure of H<sub>2</sub> on the hydrogenation of MA

The effect of temperature and pressure of H<sub>2</sub> on the hydrogenation of MA were studied. Under the experimental temperature and pressure of H<sub>2</sub>, the conversion of MA is presented in Fig. 2. Reaction temperature and pressure of H<sub>2</sub> affected the conversion of MA significantly. Keeping the constant temperature, the conversion of MA increased with the increase of H<sub>2</sub> pressure; keeping the constant pressure of H<sub>2</sub>, the conversion of MA increased with the increase of temperature.

Based on the above findings and previous work [12,20], a reasonable mechanism can be proposed. First, PPh<sub>3</sub> dissociates from RhCl(PPh<sub>3</sub>)<sub>3</sub> (I) to form RhCl(PPh<sub>3</sub>)<sub>2</sub> (II), then Rh activates molecular hydrogen, in the form of Rh–H<sub>2</sub> complex: RhH<sub>2</sub>Cl(PPh<sub>3</sub>)<sub>2</sub> (III), which reacts with MA to form intermediate (IV). This intermediate may then form an alkyl intermediate (V) by intramolecular hydrogen transfer reaction. Then it is subsequently decomposed to SA. The reaction pathway is described in Scheme 1.

Thus, the present study allows us to conclude that MA can be hydrogenated to SA directly by



Scheme 1. The catalytic cycle on the hydrogenation of MA to SA.

Rh, Ru, Pd, Ni, Co transition complex catalyst systems.  $\text{RhCl}(\text{PPh})_3/\text{PPh}_3/\text{EGD}$  is the most active catalyst system; the optimum P:Rh ratio is 6; reaction conditions—temperature, pressure of  $\text{H}_2$  and reaction time affect the conversion and turnover number of MA. Under the optimum conditions —  $\text{RhCl}(\text{PPh})_3$ , 0.03 mmol;  $\text{PPh}_3$ :Rh ratio, 6; pressure of  $\text{H}_2$ , 2.0 MPa; MA, 20 mmol; ethylene glycol dimethylether as solvent in volume of liquid, 8 ml at 383 K for 6 h, the conversion of MA is 99.0% and selectivity of SA is 100%. A reasonable mechanism can be proposed.

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