

Hydrogenation of crotonaldehyde and cinnamaldehyde catalyzed by water-soluble palladium complex

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Abstract

The selective hydrogenations of crotonaldehyde and cinnamaldehyde in the aqueous-benzene biphasic system were investigated using water-soluble palladium complex PdCl₂(TPPTS)₂ as catalyst. The hydrogenation rate of crotonaldehyde was higher than that of cinnamaldehyde under similar reaction conditions. The palladium complex selectively catalyzed the hydrogenation of C=C bond in crotonaldehyde to form butanal (100%). On the contrary, hydrogenation of both C=C and C=O bonds in cinnamaldehyde occurred simultaneously, with the amount of phenylpropanal only slightly higher than that of phenylpropanol. However, the reduction of C=O bond of cinnamaldehyde could be inhibited by the addition of Na₂CO₃ solution. Therefore, high selectivity to form phenylpropanal (91%) could be obtained by using Na₂CO₃ solution at pH 12.2. Other factors affecting the hydrogenation conversion and selectivity of crotonaldehyde and cinnamaldehyde were also discussed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The hydrogenation of α,β -unsaturated aldehydes to give saturated aldehydes could be easily carried out using either homogeneous or heterogeneous catalysts [1–10]. It has been demonstrated that highly selective reduction of unsaturated aldehydes to specific products such as saturated aldehyde and alcohol, as well as unsaturated alcohol, could be achieved by choosing the suitable metal complexes as the catalysts. The application of water-soluble tran-

sition metal complexes as catalysts in the biphasic hydrogenation have been extensively studied in recent years [11–27]. Water-soluble ruthenium complexes containing ligand TPPTS [trisodium tris(*m*-sulfonatophenyl)phosphine] could selectively reduce carbonyl group of α,β -unsaturated aldehydes [13,20,21], whereas water-soluble rhodium and palladium complexes could selectively catalyze the hydrogenation of carbon-carbon double bond to form saturated aldehydes [11,28,29]. The special effect of Na₂CO₃ solution on the catalytic behaviors of PdCl₂(TPPTS)₂ has also been observed in citral hydrogenation [30,31]. In this paper, we would like to

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Table 1
Effect of reaction temperature

Temperature(°C)	Crotonaldehyde ^a		Cinnamaldehyde ^b	
	Conversion (%)	Selectivity (%) butanal	Conversion (%)	Selectivity (%) phenylpropanal
10	21.7	100	—	—
20	51.4	100	—	—
30	68.1	100	53.7	58.0
40	80.1	100	64.6	59.2
50	94.4	100	72.8	53.8
60	98.3	100	99.5	58.2

Reaction conditions: substrate: 5 ml, water: 30 ml, benzene: 5 ml, [PdCl₂(TPPTS)₂]: 5.3 × 10⁻⁴ mol dm⁻³.

^aH₂ pressure: 20 kg cm⁻², reaction time: 1 h.

^bH₂ pressure: 40 kg cm⁻², reaction time: 2 h.

report the catalytic hydrogenation of crotonaldehyde and cinnamaldehyde by the water-soluble PdCl₂(TPPTS)₂ in the water–benzene biphasic system. The effects of a variety of reaction parameters and pH values on the conversion and selectivity were also discussed.

2. Experimental

Reagent grade crotonaldehyde (> 99%, RDH), cinnamaldehyde (> 98%, RDH), benzene (A.R., A.T.A.), hydrogen (99.995%, H.K. Oxygen) were obtained commercially and were used directly. TPPTS and PdCl₂(TPPTS)₂ were prepared by the methods reported in our previous papers [28,29,32,33].

Appropriate amount of PdCl₂(TPPTS)₂, aqueous solution and substrate solution in benzene were introduced into a Teflon-lined stainless steel autoclave equipped with stirrer (Parr 4561 minireactor). The autoclave was evacuated and flushed with high purity hydrogen consecu-

tively for three times. The autoclave was then filled with hydrogen to desired pressure. The reaction mixture was stirred at 600 rpm at the desired temperature and at the end of the hydrogenation, the reaction was quenched by putting the reactor in an ice-water bath. The pH measurements of Tables 4 and 5 were performed prior to the hydrogenation reactions.

The organic products of the organic phase were analyzed by GC (HP 5890 SERIES II) with FID and a capillary column (HP-FFAP, 25 m × 0.2 mm × 0.33 μm) and GC graphs were handled with HP 3396 INTEGRATOR. The components were identified by GC and GC-MS (HP 5890 GC with Series Mass Selective Detector) techniques with authentic samples.

3. Results and discussion

3.1. Effect of reaction temperature

The effect of the reaction temperature on the conversion and selectivity of the two aldehydes

Table 2
Effect of hydrogen pressure

H ₂ pressure (kg cm ⁻²)	Crotonaldehyde		Cinnamaldehyde	
	Conversion (%)	Selectivity (%) butanal	Conversion (%)	Selectivity (%) phenylpropanal
1	37.7	100	—	—
10	76.9	100	—	—
20	80.1	100	32.5	60.4
30	100	100	62.3	64.8
50	—	—	98.5	60.2

Reaction conditions: same as in Table 1 except the temperature is at 40°C.

Table 3
Effect of catalyst concentration and water volume

PdCl ₂ (TPPTS) ₂ (mg)	H ₂ O (ml)	Pd (10 ⁻⁴ mol dm ⁻³)	Crotonaldehyde		Cinnamaldehyde	
			Conversion (%)	Selectivity (%) butanal	Conversion (%)	Selectivity (%) phenylpropanal
10.5	30	2.66	46.3	100	56.2	67.1
21.0	30	5.32	80.1	100	62.3	64.8
30.7	30	7.79	100	100	97.3	64.4
21.0	20	7.99	100	100	98.6	64.2
21.0	10	16.0	100	100	86.0	61.9

Reaction conditions: same as in Table 1, except the temperature is at 40°C.

were summarized in Table 1. The results indicated that the conversions of crotonaldehyde and cinnamaldehyde increased with increasing temperature, but the selectivity, which was defined as the percentage of saturated aldehyde in the hydrogenation products, was not influenced by temperature. The reactivity of cinnamaldehyde was lower than crotonaldehyde. The conversion of crotonaldehyde was 94.4% after 1 h at 50°C and 20 kg cm⁻² hydrogen pressure, while the conversion of cinnamaldehyde was only 72.8% at 50°C, despite higher hydrogen pressure (40 kg cm⁻²) and longer reaction time (2 h). The hydrogenation selectivity of the two substrates were quite different. Crotonaldehyde hydrogenation occurred exclusively on C=C bond and gave butanal as the only product. On the contrary, cinnamaldehyde hydrogenation could occur either only on C=C bond to form phenylpropanal or simultaneously on both C=C and C=O bonds to produce phenylpropanol. Both phenylpropanal and phenylpropanol were detected at the beginning of the reaction when

the conversion was only about 2%. The amount of phenylpropanal was slightly higher than that of phenylpropanol and their ratio did not change much with prolonged reaction time.

3.2. Effect of hydrogen pressure

The data in Table 2 showed that the conversion of the two aldehydes increased with increasing hydrogen pressure. The conversion of crotonaldehyde to butanal was completed (100%) in 1 h under 30 kg cm⁻² hydrogen pressure. The conversion of cinnamaldehyde was slower and had only reached 98.5% after 2 h under 50 kg cm⁻² hydrogen pressure. On the contrary, selectivity of the two aldehydes did not appear to be affected by the changing of hydrogen pressure.

3.3. Effect of catalyst concentration and water volume

The effects of different concentrations of catalyst and volumes of water on the conversion

Table 4
Effect of pH on crotonaldehyde hydrogenation

pH	Aqueous phase	Conversion (%)	Selectivity (%) butanal
1.1	HCl solution ^a	50.7	100
2.9	HCl solution ^a	59.5	100
6.3	H ₂ O	63.8	100
11.6	Na ₂ CO ₃ solution (1.00%, w/v)	84.8	100
11.9	Na ₂ CO ₃ solution (1.50%, w/v)	96.2	100
12.0	Na ₂ CO ₃ solution (2.00%, w/v)	97.2	100

Reaction conditions: same as in Table 1 except reaction time: 1.5 h, temperature: 40°C, benzene: 10 ml.

^aHCl (1 N) was used to adjust pH to the corresponding values.

Table 5
Effect of pH on cinnamaldehyde hydrogenation

pH	Aqueous phase	Conversion (%)	Selectivity (%) phenylpropanal
4.5	HCl solution ^a	99.0	54.7
6.3	H ₂ O	99.6	61.4
10.8	Na ₂ CO ₃ solution (0.20%, w/v)	99.8	70.3
11.9	Na ₂ CO ₃ solution (1.50%, w/v)	97.1	80.4
12.2	Na ₂ CO ₃ solution (2.50%, w/v)	93.2	91.3
12.2	NaOH solution ^b	99.8	69.1

Reaction conditions: same as in Table 1, except benzene: 4 ml, PdCl₂(TPPTS)₂: 1.39×10^{-3} mol dm⁻³, H₂ pressure: 20 kg cm⁻², temperature: 90°C.

^aHCl (1 N) was used to adjust pH to 4.5.

^bNaOH (5%, w/v) was used to adjust pH to 12.2.

and selectivity of crotonaldehyde and cinnamaldehyde were listed in Table 3. As expected, the conversion of both substrates increased with increasing palladium complex PdCl₂(TPPTS)₂ concentration. When the amount of PdCl₂(TPPTS)₂ was kept constant (21 mg), the change of the volume of water had shown different influences on the cinnamaldehyde and crotonaldehyde conversion. When the volume of water increased from 10 ml to 20 ml, the conversion of cinnamaldehyde was raised from 86.0% to 98.6%, whereas the conversion of crotonaldehyde was not affected. Further increase of the volume of water to 30 ml had decreased the conversion of both aldehydes which suggested that there could be optimum catalyst concentrations in the hydrogenation of the unsaturated aldehydes. On the contrary, the change of PdCl₂(TPPTS)₂ concentration and water volume did not appear to have any influence on the selectivity of these two aldehydes.

3.4. Effect of pH value of aqueous solution

The effects of pH on the conversion and selectivity of crotonaldehyde and cinnamaldehyde were summarized in Tables 4 and 5, respectively. The hydrogenation conversion rates of crotonaldehyde increased with increasing pH and butanal was again the only product irrespective of the pH values.

In order to improve the selectivity to form phenylpropanal in cinnamaldehyde hydrogenation,

the reaction was attempted under higher PdCl₂(TPPTS)₂ concentration (1.39×10^{-3} mol dm⁻³) and higher temperature (90°C). The results in Table 5 indicated that the conversions were nearly completed under relatively low hydrogen pressure (20 kg cm⁻²) and were not influenced by the change of pH value of the aqueous phase. However, the selectivity has increased significantly with increasing pH by the addition of Na₂CO₃. High selectivity of 91.3% has been obtained at pH 12.2 with Na₂CO₃. If NaOH was used instead of Na₂CO₃, the selectivity would drop to 69.1% at the same pH value.

4. Conclusions

The work presented in this paper has demonstrated the potential application of water-soluble palladium complex for carbon-carbon double bond hydrogenation of α,β -unsaturated aldehydes. The high reactivity of C=C bond in crotonaldehyde hydrogenation could be related to its good solubility in water (18.1 g per 100 g of H₂O at 25°C) and the presence of C=O bond conjugated with C=C bond which was similar to that of the citral hydrogenation. The lower hydrogenation rate of C=C bond in cinnamaldehyde could be attributed to its poor solubility in water (0.14 g per 100 g of H₂O at 25°C) and the steric effect of the phenyl group. The stability of the large conjugated π system

of cinnamaldehyde has also influenced its hydrogenation reactivity. Probably, the electronic factor of the large conjugated π system has caused the decrease of the selectivity of C=C bond hydrogenation in cinnamaldehyde. This was very different from those observed in citral and crotonaldehyde hydrogenations in which the C=O bonds could not be hydrogenated easily. The addition of sodium carbonate has not only changed the pH values and the properties of aqueous solution but also could modify the coordination environment around the palladium atom. Therefore, high selectivity of C=C bond hydrogenation in cinnamaldehyde could also be achieved by choosing the suitable reaction conditions in the presence of Na_2CO_3 .

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