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Studies on catalytic hydrogenation of citral by water-soluble palladium complex

Kam-Chung Tin [a,*], Ning-Bew Wong [a], Rui-Xiang Li [a], Yao-Zhong Li [b], Xian-Jun Li [b]

[a] *Department of Biology and Chemistry, City University of Hong Kong, Kowloon, Hong Kong, China*
[b] *Department of Chemistry, Sichuan University, Chengdu, Sichuan 610064, China*

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Abstract

The hydrogenation of citral has been studied in biphasic system using water-soluble $PdCl_2(TPPTS)_2$ as catalyst. The selectivity to form citronellal increased with increasing pH values of the aqueous phase. At the same pH value, the selectivity was higher when the hydrogenation was carried out in the presence of Na_2CO_3 than in the presence of NaOH. The main product was citronellal and a maximum yield of 93% had been obtained using Na_2CO_3 solution at pH 11.6. The C=C bond in citronellal could be further hydrogenated to form dihydrocitronellal when the hydrogenation was carried out in distilled water at pH 6.0. The yield of dihydrocitronellal could reach 93% with prolonged reaction time to 6 h. Therefore, high yields of either citronellal or dihydrocitronellal could be obtained from citral by selecting the corresponding reaction conditions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Biphasic catalysis; Water-soluble palladium complex; Citral; Hydrogenation

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1. Introduction

The chemistry of water-soluble transition metal complexes has been developing rapidly in recent years [1]. These metal complexes have been successfully used as catalysts in the biphasic reaction system [2]. They have exhibited excellent activity and selectivity, as well as the advantages of simple separation of aqueous phase containing the catalyst from the product in organic phase after the reaction [3,4]. The water-soluble complexes of rhodium and ruthenium with TPPTS [trisodium tris(*m*-sulfonatophenyl)phosphine] have been used in the hydrogenation of α,β-unsaturated aldehydes and ketones [5–10]. The major products in citral hydrogenation were nerol and citronellal when using ruthenium complexes and rhodium complexes, respectively. The selective hydrogenation of the C=C bond conjugated with C=O in citral had been studied with Raney Ni, Ni/Cr_2O_3 and Pd/C as catalysts, but the activities and/or selectivity to form citronellal were not considered satisfactory

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[*] Corresponding author.

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[11–14]. Water-soluble palladium–TPPTS complex has the potential to become a useful catalyst for the hydrogenation of unsaturated compounds [15]. Although its catalytic behaviors were not completely understood, our investigation has demonstrated that water-soluble $PdCl_2(TPPTS)_2$ was an active catalyst in citral hydrogenation and exhibited high selectivity to form either citronellal or dihydrocitronellal under different reaction conditions. Its catalytic properties in aqueous/organic biphasic system and the important effect of Na_2CO_3 solution on its activity and selectivity in citral hydrogenation will be reported in this article.

2. Experimental

2.1. Preparation and characterization of catalyst

Ligand TPPTS was prepared according to the method reported in the literature [16,17]. $PdCl_2(TPPTS)_2$ was synthesized by reacting $PdCl_2$ with TPPTS in aqueous solution under argon atmosphere. They were characterized by ICP, XPS (X-ray photoelectron spectroscopy), NMR (nuclear magnetic resonance) and FT-IR (Fourier transform infrared spectroscopy). The results had indicated that there were no impurities in the TPPTS sample. The components of the palladium complex were found to be Pd:P:S = 1:2.1:6.1 (mole ratio). The binding energies of palladium, phosphorus and chlorine in the complex were 337.8 eV ($3d_{5/2}$ of Pd), 131.6 eV (2p of P) and 198.3 eV (2p of Cl), respectively. $^{31}P-$NMR spectrum had a single peak at $\delta = 35.1$ ppm. IR (infrared spectroscopy) spectrum was the same as reported [18]. These results have indicated that the complex was in agreement with the formula of $PdCl_2(TPPTS)_2$.

2.2. Hydrogenation of citral

Appropriate amount of $PdCl_2(TPPTS)_2$ was dissolved in distilled water. The aqueous solution of $PdCl_2(TPPTS)_2$, citral (RDH, $> 97\%$) and solvent were added into the stainless steel autoclave (Parr 4561 minireactor). The reactor was evacuated and filled with high-purity hydrogen (99.995%, Hong Kong Oxygen) alternatively for three times. The stirring was started at 10°C below the desired temperature. The reaction time was counted as zero at the desired temperature. The organic layer was analyzed by GC (HP 5890 SERIES II) equipped with FID (free induction decay) and a capillary column HP-FFAP 25 $m \times 0.12$ $mm \times 0.33$ μm. The products were identified by GC-MS (gas chromatography mass spectroscopy) (HP5890 Series Mass Selective Detector) techniques with primary standards.

3. Results and discussion

Citral has two C=C bonds and one carbonyl group in the molecule. These unsaturated groups could be hydrogenated separately under different reaction conditions. Seven possible types of reaction products from citral hydrogenation are listed below.

$$\begin{array}{rll}
 & (CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2CHO & (1) \\
 & (CH_3)_2CH(CH_2)_3CH(CH_3)CH_2CHO & (2) \\
 & (CH_3)_2CH(CH_2)_3C(CH_3){=}CHCHO & (3) \\
(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCHO + H_2 \rightarrow & (CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2CH_2OH & (4) \\
 & (CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCH_2OH & (5) \\
 & (CH_3)_2CH(CH_2)_3C(CH_3){=}CHCH_2OH & (6) \\
 & (CH_3)_2CH(CH_2)_3CH(CH_3)CH_2CH_2OH & (7)
\end{array}$$

The experimental results in our laboratory have shown that the main products of citral hydrogenation were citronellal (1) and dihydrocitronellal (2), depending on the reaction conditions. The selectivity was defined by the percentage of citronellal in the products. The effects of different reaction conditions on the conversion and selectivity of citral hydrogenation in biphasic system have been investigated in detail as follows.

3.1. Effect of temperature and H_2 pressure

The effects of temperature and H_2 pressure on the conversion and selectivity of the reaction were summarized in Table 1. With increasing temperature and pressure, the conversion increased significantly while the selectivity was not affected. However, the selectivity was much higher when the reaction was carried out by using 1.25% Na_2CO_3 solution as the aqueous phase than only using distilled water.

3.2. Effect of citral and catalyst concentrations

The effects of citral and the catalyst concentration were shown in Table 2. The conversion of citral decreased with increasing citral concentration in the benzene phase at the same catalyst concentration, but increased with increasing catalyst concentration. The selectivity was not affected by the change of citral or catalyst concentrations when using either distilled water or Na_2CO_3 solution as the aqueous phase. Substantial improvement of the selectivity has also been achieved by using 1.25% Na_2CO_3 solution as the aqueous phase.

Table 1
Effect of temperature and H_2 pressure

Temperature (°C)	H_2 pressure (kg cm^{-2})	Conversion[a] (%)	Selectivity[a] (%)
30	40	49.9 (51.0)	96.3 (74.5)
40	40	56.8 (54.2)	96.4 (73.8)
50	40	67.3 (58.1)	96.3 (72.3)
60	40	71.5 (63.0)	96.4 (72.4)
40	20	42.2 (36.4)	96.5 (66.2)
40	30	48.0 (44.5)	96.1 (70.0)
40	50	69.8 (64.8)	95.8 (71.6)

Reaction conditions: $PdCl_2(TPPTS)_2$: 0.016 mmol, citral: 60.9 mmol, benzene: 5 ml, Na_2CO_3: 1.25%, water: 30 ml, reaction time: 2 h.
[a] Figures in parentheses indicate the results of hydrogenation in distilled water.

Table 2
Effect of citral and catalyst concentrations

Citral (mol dm^{-3})	Catalyst (mmol dm^{-3})	Conversion[a] (%)	Selectivity[a] (%)
1.95	0.53	94.5 (97.0)	95.3 (75.4)
2.98	0.53	80.7 (78.6)	94.0 (75.4)
3.51	0.53	67.7 (65.4)	96.3 (74.5)
3.95	0.53	48.0 (44.5)	96.1 (70.0)
2.98	0.27	63.6 (60.8)	96.3 (73.8)
2.98	0.78	94.1 (93.8)	95.1 (77.5)

Reaction conditions: H_2 pressure: 30 kg cm^{-2}, benzene: 5 ml, water: 30 ml, Na_2CO_3: 1.25%, temperature: 40°C, stirring speed: 600 rpm, reaction time: 2 h.

[a] Figures in parentheses indicate the results of hydrogenation in distilled water.

3.3. Effect of pH of aqueous phase

The data in Table 3 showed that when the pH of aqueous phase varied from 1.0 to 11.6, the conversions of citral, which were all higher than 90%, did not change significantly. On the contrary, the effect of pH on the selectivity was quite obvious. When pH increased from 1.0 to 11.6, the citronellal content increased from 15.8% to 97%. Therefore, higher pH value would be more favorable for obtaining high yield of citronellal. At the same pH, the addition of Na_2CO_3 solution would give higher yield of citronellal than adding NaOH solution. Higher concentration of Na_2CO_3 also resulted in higher citronellal selectivity. When the concentration of Na_2CO_3 solution was increased to 1.5%, the selectivity of citronellal increased to 97% (Table 4). The results suggested that the carbonate group has played a special role in creating a favorable coordination environment for the formation of citronellal [19,20]. The promotion by Na_2CO_3 in citral hydrogenation catalyzed by Pd/C had also been observed [11–14]. Formation of dihydrocitronellal increased with decreasing pH values and became the major product at low pH values. At $pH < 3$, the combined amount of citronellal and dihydrocitronellal in the product became lower than 90% with the formation of other by-products.

Table 3
Effect of pH of aqueous phase

pH	Aqueous phase	Conversion (%)	Citronellal (%)	Dihydrocitronellal (%)
11.6	Na_2CO_3 solution	96.1	97.0	3.0
11.6	NaOH solution	95.4	89.4	10.6
11.1	Na_2CO_3 solution	94.2	91.9	6.9
11.1	NaOH solution	95.7	83.8	12.4
10.0	NaOH solution	96.9	71.7	22.8
8.09	NaOH solution	93.8	71.9	21.9
6.0	H_2O	96.8	62.3	27.2
3.0	HCl solution	96.4	60.1	32.0
2.0	HCl solution	96.1	36.1	53.2
1.0	HCl solution	97.5	15.8	66.7

Reaction conditions: $PdCl_2(TPPTS)_2$: 0.0228 mmol, citral: 14.6 mmol, benzene: 5 ml, water: 30 ml, H_2 pressure: 40 kg cm^{-2}, temperature: 40°C, stirring speed: 600 rpm, reaction time: 2 h.

Table 4
Effect of concentration of Na_2CO_3

Concentration of Na_2CO_3 (%)	Conversion (%)	Selectivity (%)
0	81.4	71.7
0.25	94.2	91.9
0.50	99.4	93.0
1.00	91.3	96.0
1.50	95.0	97.0

Reaction conditions: same as Table 2, citral: 14.6 mmol.

3.4. Effect of organic solvents

The effect of organic solvents on the conversion and selectivity of the citral hydrogenation were shown in Table 5. In the absence of Na_2CO_3, the addition of benzene led to an increase of the conversion. However, the addition of polar aprotic solvent, DMF, decreased the conversion. It was probably due to the interaction between the polar end of citral molecule and the dipole of DMF which had influenced the coordination of the substrate molecule to the palladium complex. Addition of Na_2CO_3 solution (0.25%) has significantly increased both the conversion and the selectivity. Moreover, the effect of different organic solvents has become almost negligible. These results suggested that the addition of Na_2CO_3 has caused an obvious change of the solution properties in the biphasic system. Therefore, high conversion and high selectivity of citronellal via citral hydrogenation could be achieved by incorporating a common organic solvent with Na_2CO_3 solution.

3.5. Effect of CTAB concentration

The effect of the concentration of CTAB (cetyltrimethylammonium bromide) on the selectivity to form citronellal was shown in Table 6. The percentage of citronellal increased with increasing

Table 5
Effect of organic solvents

Organic solvent (5 ml)	Aqueous phase (distilled water)		Aqueous phase (0.25% Na_2CO_3 solution)	
	Conversion (%)	Citronellal (%)	Conversion (%)	Citronellal (%)
Nil	86.3	48.4	99.3	90.5
Benzene	96.8	62.3	96.1	95.4
n-Hexane	83.7	65.5	99.4	94.2
Ethanol	86.4	64.1	98.9	91.2
DMF	39.8	72.5	97.6	93.0

Reaction conditions: same as Table 3.

Table 6
Effect of concentrations of CTAB

Concentration of CTAB, (mmol dm^{-3})	Conversion (%)	Citronellal (%)
0	94.2	91.9
1	100	92.9
2	100	94.6
4	100	95.7
8	100	96.0

Reaction conditions: same as Table 2, except Na_2CO_3: 0.25%, citral: 14.6 mmol.

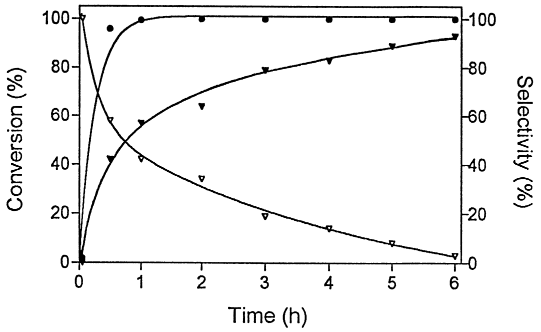

Fig. 1. Effect of reaction time on product distribution. ●, conversion; ▽, citronellal; ▼, dihydrocitronellal. Reaction conditions: same as in Table 1, except $PdCl_2(TPPTS)_2$ = 0.034 mmol, H_2 pressure = 40 kg cm^{-2}, temperature = 50°C.

concentration of CTAB in the presence of 0.25% Na_2CO_3 solution. It suggested that micelle could be formed in biphasic reaction system because the CTAB concentration in the reaction mixture was higher than its CMC (9.2×10^{-4} mol dm^{-3} at 25°C). The micelle structure in the two-phase system was more favorable for the isolated C=C bond at the hydrophobic end of citral to stretch into the organic phase and hindered its coordination with the palladium complex in the aqueous phase. Thus, the C=C bond at the hydrophobic end would become more difficult to be hydrogenated.

3.6. Analysis of citral hydrogenation process

Fig. 1 showed the change of product composition during the hydrogenation process in the absence of Na_2CO_3. It was quite obvious that the content of citronellal in the products decreased gradually with the increase of dihydrocitronellal in the reaction course. At the beginning of the reaction, only citronellal was detected. It suggested that the conjugated C=C bond in citral was preferentially hydrogenated to form citronellal, and then the C=C bond of citronellal was subsequently hydrogenated to form dihydrocitronellal. The content of dihydrocitronellal increased up to 93% and that of citronellal decreased to 3% when the reaction time was extended to 6 h. Only trace amount of 3,7-dimethyloctanol could be detected in these reactions. Therefore, we would like to conclude that it is possible to obtain high yields of either citronellal or dihydrocitronellal by selecting the suitable reaction conditions using water-soluble $PdCl_2(TPPTS)_2$ as catalyst in the biphasic system. Our results have also indicated that the citral hydrogenation proceeded via the sequential reaction as follows:

$$(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCHO \text{ (citral)}$$
$$\downarrow H_2$$
$$(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2CHO \text{ (citronellal)}$$
$$\downarrow H_2$$
$$(CH_3)_2CHCH_2(CH_2)_2CH(CH_3)CH_2CHO \text{ (dihydrocitronellal)}$$
$$\downarrow H_2$$
$$(CH_3)_2CHCH_2(CH_2)_2CH(CH_3)CH_2CH_2OH \text{ (3,7-dimethyloctanol)}$$

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