

# Transfer hydrogenation of citral to citronellol with Ru complexes in the mixed solvent of water and polyethylene glycol

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The transfer hydrogenation of citral to citronellol was studied with  $[\text{RuCl}_2(\textit{benzene})]_2$  catalyst in a mixed solvent of water and polyethylene glycol ( $\text{H}_2\text{O}$ –PEG). The influence of several important factors including hydrogen source, solvent, temperature and active species is discussed. Under the present conditions, citronellol was produced with an extremely high selectivity above 90%. The Ru complexes could be immobilized in the  $\text{H}_2\text{O}$ –PEG phase well and separated from organic products successfully. Moreover, a stable catalytic activity was obtained after the first run, although the decomposition of Ru complexes occurred during the recycling processes. The selectivity to citronellol decreased but kept a stable level about 60% in the recycling runs. Copyright © 2010 John Wiley & Sons, Ltd.

**Keywords:** transfer hydrogenation; citral; citronellol; polyethylene glycol; ruthenium complex

## Introduction

Transfer hydrogenation has attracted much attention because the operating process is easier and safer compared with the hydrogenation at high pressure of molecular hydrogen. In catalytic transfer hydrogenation, organic hydrogen sources such as  $\text{HCOOH}$ – $\text{NEt}_3$  azeotropic mixture and  $\text{HCOONa}$  are usually used to replace the molecular hydrogen.<sup>[1–4]</sup> The transfer hydrogenation of aldehyde with high chemoselectivity is still challenging.<sup>[5–7]</sup> Xiao and co-workers reported that  $[\text{Cp}^*\text{IrCl}(\mu\text{-Cl})_2]$  combined with monotosylated ethylenediamine was an efficient catalyst for chemoselective transfer hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to  $\alpha,\beta$ -unsaturated alcohols in the presence of sodium formate in aqueous phase.<sup>[8]</sup> Recently, Baratta and co-workers showed that  $\alpha,\beta$ -unsaturated aldehydes could be reduced quickly to primary alcohols with terdentate CNN ruthenium complex  $\text{RuCl}(\text{CNN})(\text{dppb})$  in the presence of potassium carbonate in *i*-propanol.<sup>[9]</sup>

Organometallic catalysts have attracted continuous interest due to their high activity and selectivity but they are usually expensive and difficult to separate and recover. It is proposed to resolve this difficulty through immobilizing the homogeneous metal complexes in polyethylene glycol (PEG)<sup>[10]</sup> or ionic liquid.<sup>[11]</sup> PEG, one of the green reaction media, has been paid more attention since it is inexpensive, non-toxic, non-volatile, recyclable and has stable properties.<sup>[12]</sup> In addition, in most cases PEG can dissolve many organometallic complex catalysts without any modification. Therefore, PEG was used to immobilize organometallic complexes in reactions such as polymerization,<sup>[13]</sup> Heck reaction,<sup>[14]</sup> oxidation,<sup>[15,16]</sup> hydrogenation<sup>[10,17–20]</sup> and aldol reaction.<sup>[21]</sup>

The transfer hydrogenation of citral was studied with  $[\text{RuCl}_2(\textit{benzene})]_2$  catalyst in a mixture of water and PEG in this work. In the hydrogenation of citral, the conjugated  $\text{C}=\text{C}$  and  $\text{C}=\text{O}$  bonds of citral was hydrogenated forming citronellal and two isomers of unsaturated alcohols, geraniol and nerol, respectively.

The  $\text{C}=\text{O}$  bond of citronellal and the  $\text{C}=\text{C}$  bond of geraniol or nerol were further hydrogenated, giving citronellol, which then changed to 3,7-dimethyl-1-octanol through hydrogenation of the remaining  $\text{C}=\text{C}$  bond. In previous literature, the geraniol and nerol were reported to be the main products in citral transfer hydrogenation with  $\text{Ir-CF}_3\text{Ts}(\text{en})$ <sup>[8]</sup> or  $\text{RuCl}_2(m\text{-TPPMS})_2$  (with excess  $m\text{-TPPMS}$ )<sup>[22,23]</sup> in the presence of  $\text{HCOONa}$  in aqueous phase, while citronellol could be produced directly from transfer hydrogenation of citronellal with  $[\text{RuCl}_2(m\text{-TPPMS})_2]$  (with excess  $m\text{-TPPMS}$ ) in the presence of sodium formate.<sup>[22,23]</sup> Citronellol<sup>[24]</sup> as one of the most important fragrances is difficult to obtain directly from citral hydrogenation due to its further transformation to 3,7-dimethyl-1-octanol. Interestingly, citronellol was formed directly with a high selectivity above 90% in the transfer hydrogenation of citral in the present work. The present reaction system has several advantages in terms of green synthesis: it uses environmentally benign solvents ( $\text{H}_2\text{O}$  and PEG were selected), separable and recyclable homogeneous catalysts (Ru complexes immobilized in PEG– $\text{H}_2\text{O}$  phase) and a safe hydrogen resource (organic hydrogen donors). Some important factors including transfer agent, solvent, temperature and active species are discussed.

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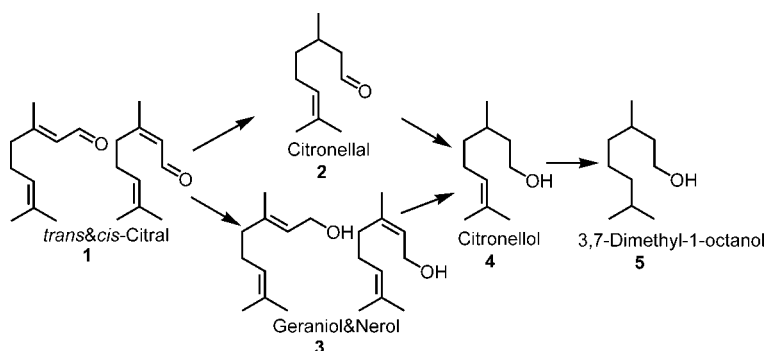
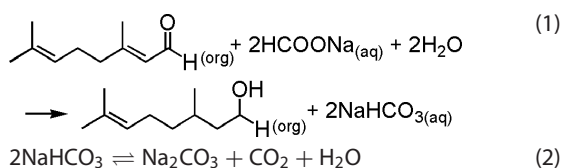
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## Experimental

[RuCl<sub>2</sub>(benzene)]<sub>2</sub> and citral were purchased from Aldrich and used as received. NaHCO<sub>3</sub>, HCOONa·2H<sub>2</sub>O, PEG400 (PEG with an average molecular weight of 400 g mol<sup>-1</sup>) and all the solvents from Beijing Chemical Reagent Plant were of analytical grade and used without further purification. In a typical transfer hydrogenation, [RuCl<sub>2</sub>(benzene)]<sub>2</sub> (2.5 mg 0.005 mmol) and HCOONa·2H<sub>2</sub>O (0.26 g 2.5 mmol) were loaded into a 10 ml glass reactor with a magnetic stirrer, 0.5 ml deionized water was added to dissolve HCOONa·2H<sub>2</sub>O and then 1.5 ml PEG400 and 0.5 mmol citral were placed into the reactor and sealed. The mixture was stirred at 90 °C for a certain period of time. The products were extracted with *n*-hexane and analyzed by GC. The conversion was calculated by moles of citral consumed divided by initial moles of citral used, and the selectivity of a certain product *i* was calculated by moles of product *i* divided by total moles of citral consumed. For recycling runs, after the extraction with *n*-hexane (3 × 2 ml), the residual H<sub>2</sub>O–PEG (1 : 3) phase was recharged with citral (85 μl, 0.5 mmol) and HCOOH (49 μl, 1.2 mmol) and the next reaction was started under the same reaction conditions. The products were analyzed and identified by gas chromatography (GC-Shimadzu-14C, FID, capillary column, Rtx-Wax 30 m × 0.25 mm × 0.25 μm) and gas chromatography–mass spectrometry (GC/MS, Agilent 5890). The extract was collected and analyzed by GFAAS (PE AA800) method for the leaching of Ru from the H<sub>2</sub>O–PEG phase. UV–vis absorption spectra were measured using a Cary 500 UV–vis–NIR spectrometer (Varian).

## Results and Discussion

Citral is a particularly attractive molecule, as it contains an isolated C=C bond and a pair of conjugated C=C–C=O bonds. Scheme 1 displays the reaction network of transfer hydrogenation of citral. Citral was reduced to the citronellol by hydrogen transfer with sodium formate in the presence of [RuCl<sub>2</sub>(benzene)]<sub>2</sub> catalyst through the following reactions:<sup>[25,26]</sup>



**Scheme 1.** Transfer hydrogenation of citral.

## Influence of Hydrogen Source

The influence of hydrogen donors was first checked and the results are listed in Table 1. The catalytic activity was lower (conversion <2%) when *i*-PrOH was used in both the absence and presence of base (entries 1 and 2). In the case of HCOOH–NEt<sub>3</sub> azeotropic mixture, the conversion was a little higher (8.7%) and it increased to 22% in the presence of water as co-solvent (entries 3 and 4). However, when HCOONa or HCOOH–NaHCO<sub>3</sub> was used (entries 5 and 6), nearly complete conversion was achieved and citronellol was produced as the main product with selectivity about 85%, which is much higher than that (16.9%) obtained with HCOOH–NEt<sub>3</sub>. In the literature, HCOONa was reported to be the most efficient hydrogen transfer agent<sup>[3,4,17]</sup> for the asymmetric transfer hydrogenation with Ru-TsDPEN complex in pure water and an unexpected high reaction rate was obtained.<sup>[3]</sup>

## Influence of Solvent

The effects of solvents are given in Table 2. The conversion was low when the reaction was performed in neat H<sub>2</sub>O or PEG400 (entries 1 and 2), but it was improved in the mixture of PEG and H<sub>2</sub>O and increased dramatically with the change of volume ratio of H<sub>2</sub>O–PEG. The conversion increased from 22.7 to 99.3% when the volume ratio of H<sub>2</sub>O–PEG was changed from 3 : 1 to 1 : 1, and it reached 100% at a volume ratio of 1 : 3 (entries 3–5). The present results could be explained by the phase behavior of

**Table 1.** Influence of hydrogen source on the transfer hydrogenation of citral<sup>a</sup>

Entry	Hydrogen source	Conversion (%)	Selectivity (%)			
			2	3	4	5
1 <sup>b</sup>	<i>i</i> -PrOH	1.3	38.4	61.6	–	–
2 <sup>c</sup>	<i>i</i> -PrOH	1.5	53.2	46.8	–	–
3 <sup>d</sup>	HCOOH–Et <sub>3</sub> N	8.7	46.0	38.7	15.3	–
4	HCOOH–Et <sub>3</sub> N	22.1	46.8	36.3	16.9	–
5	HCOONa	100	0.2	14.2	85.6	–
6	HCOOH–NaHCO <sub>3</sub>	96.2	–	13.5	84.7	0.8

<sup>a</sup> Reaction conditions: catalyst, [RuCl<sub>2</sub>(benzene)]<sub>2</sub> 0.01 mmol; citral, 1 mmol; hydrogen source, 5 equiv.; solvent, 2 ml; H<sub>2</sub>O–PEG, 1 : 3 (v/v); *T*, 80 °C; *t*, 3 h.

<sup>b</sup> Solvent, 2 ml; *i*-PrOH–PEG, 1 : 3; no base.

<sup>c</sup> Solvent, 2 ml; *i*-PrOH–PEG, 1 : 3; KOC(CH<sub>3</sub>)<sub>3</sub>–catalyst, 20 : 1.

<sup>d</sup> Solvent, PEG 2 ml.

**Table 2.** Influence of solvent on the transfer hydrogenation of citral

Entry	Solvent	Conversion (%)	Selectivity (%)			
			2	3	4	5
1	H <sub>2</sub> O	3.6	47.9	52.1	–	–
2	PEG	17.7	72.0	16.8	11.2	–
3	H <sub>2</sub> O–PEG (3 : 1)	22.7	42.1	31.1	26.8	–
4	H <sub>2</sub> O–PEG (1 : 1)	99.3	0.4	33.1	66.5	–
5	H <sub>2</sub> O–PEG (1 : 3)	100	0.1	8.5	90.3	1.1
6	H <sub>2</sub> O– <i>n</i> -PrOH (1 : 3)	53.9	19.3	40.5	40.2	–
7	H <sub>2</sub> O–DMF (1 : 3)	100	–	10.4	87.2	2.4

Reaction conditions: catalyst, [RuCl<sub>2</sub>(benzene)]<sub>2</sub> 0.01 mmol; citral, 1 mmol; HCOONa, 5 equiv.; solvent, 2 ml; T, 80 °C; t, 5 h.

the reaction mixture: in neat PEG400, the reaction was sluggish due to the high viscosity of PEG and low solubility of HCOONa in PEG. However, in the mixture of PEG and H<sub>2</sub>O, the solubility of HCOONa was increased and the reaction mixture changed to a single phase at the volume ratio of H<sub>2</sub>O–PEG of 1 : 3 under the reaction conditions used, in which high conversion (100%) and high selectivity to citronellol (90.3%) were achieved. In neat H<sub>2</sub>O, the catalyst existed in citral organic phase and hydrogen donor HCOONa in water phase, for which the diffusion resistance lowered the reaction rate. The reaction was also examined in the mixed solvents of H<sub>2</sub>O–*n*-PrOH (entry 6) and H<sub>2</sub>O–DMF (entry 7). The latter is more effective, in which the selectivity to citronellol was 87.2% at complete conversion of citral, but it was still lower than that in H<sub>2</sub>O–PEG (entry 4). Therefore, H<sub>2</sub>O–PEG (v/v = 1 : 3) was the most effective solvent for the present citral transfer hydrogenation and it was selected for the following studies.

### Influence of Temperature and Reaction Time

Temperature has a prominent influence on the transfer hydrogenation of citral and the results are listed in Table 3. The conversion increased from 10.0 to 96.7% when the reaction temperature was raised from 60 to 70 °C (entries 1 and 2). The color of the reaction mixture changed faster at higher temperature, so that the transformation of the catalyst is easier at higher temperature, which may be one of the reason for the higher conversions. A maximum selectivity to citronellol of 92.4% appeared on complete conversion of citral at 90 °C (entry 4). With further increase in temperature, the selectivity to citronellol decreased slightly.

**Table 3.** Influence of temperature on the transfer hydrogenation of citral<sup>a</sup>

Entry	T (°C)	Conversion (%)	Selectivity (%)			
			2	3	4	5
1	60	10.0	41.6	44.0	14.4	–
2	70	96.7	12.9	12.4	74.7	–
3	80	100	0.2	14.2	85.6	–
4 <sup>b</sup>	90	100	0.2	4.5	92.4	2.9
5 <sup>b</sup>	100	100	0	3.9	90.1	6.0

<sup>a</sup> Reaction conditions: catalyst, [RuCl<sub>2</sub>(benzene)]<sub>2</sub> 0.01 mmol; citral, 1 mmol; HCOONa, 5 equiv.; solvent, 2 ml; H<sub>2</sub>O–PEG=1 : 3; t, 3 h.

<sup>b</sup> t, 1.5 h.

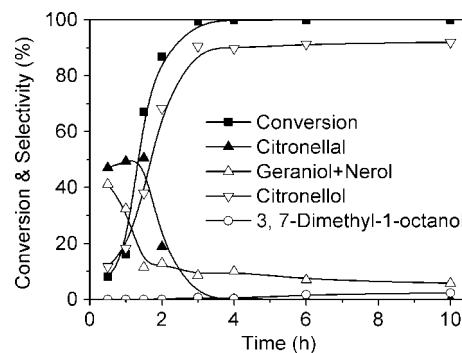
**Figure 1.** Variation of conversion and selectivity with time in the transfer hydrogenation of citral. Reaction conditions: catalyst, [RuCl<sub>2</sub>(benzene)]<sub>2</sub> 0.01 mmol; citral, 0.5 mmol; HCOONa, 5 equiv., solvent, 2 ml; H<sub>2</sub>O–PEG, 1 : 3; T, 80 °C.

Figure 1 presents the variation of conversion and selectivity with time in the transfer hydrogenation of citral. The conversion of citral was only 16.1% within the first 1 h, and then it increased to 86.8% after reaction for 2 h. During the reaction, citronellal was produced as an intermediate and then further hydrogenated to citronellol; the selectivity to citronellol first increased greatly (90%) and then increased slightly (92%) with extending the reaction time, due to the serial transformations of nerol–geraniol to citronellol.

### Recycling of Catalyst

The recyclability and reusability of the present Ru complex was examined for the citral transfer hydrogenation in the mixed solvent of H<sub>2</sub>O–PEG (v/v = 1 : 3). Upon completion of each reaction, the products were separated from the catalyst phase by extraction with *n*-hexane, and then the catalyst immobilized in H<sub>2</sub>O–PEG was used again for the next run. Formic acid was added to regenerate sodium formate in the recycling runs. As shown in Table 4, the catalyst could be reused seven times with high conversion levels of around 95%, but the selectivity of citronellol decreased from 91.2 to 62.2% in the second run (runs 1 and 2) and then remained

**Table 4.** Catalyst recycling test on the transfer hydrogenation of citral<sup>a</sup>

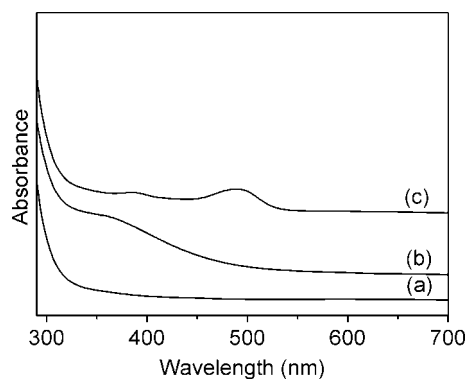
Run	Conversion (%)	Selectivity (%)			
		2	3	4	5
1	100	–	6.1	91.2	2.7
2	100	0.4	36.4	62.2	1.0
3	93.1	7.9	31.4	60.7	–
4 <sup>b</sup>	100	0.9	19.7	78.6	0.8
5	96.4	9.1	30.3	60.3	0.3
6	97.8	12.8	25.4	61.5	0.3
7	95.9	17.5	16.7	65.5	0.3
8 <sup>c</sup>	97.0	20.9	12.4	66.4	0.3
9 <sup>d</sup>	98.9	8.0	6.5	84.8	0.7

<sup>a</sup> Reaction conditions: catalyst, [RuCl<sub>2</sub>(benzene)]<sub>2</sub> 0.01 mmol; citral, 0.5 mmol; HCOONa, 5 equiv.; solvent 2 ml; H<sub>2</sub>O–PEG, 1 : 3; T, 90 °C; t, 1 h; HCOOH 1.2 mmol was added to regenerate sodium formate for the second and subsequent runs.

<sup>b</sup> t, 1.3 h.

<sup>c</sup> t, 1.5 h.

<sup>d</sup> t, 2 h.



**Figure 2.** UV-vis absorption spectra of the reaction mixture (a) before reaction, (b) after reaction for 20 min and (c) after reaction for 1 h. The reaction conditions were the same as in Table 4.

at around 60% in the following runs (runs 3 and 5–7). The decrease in the selectivity could be ascribed to the change of catalytic active species during the reaction as suggested from the color changes of the reaction mixture from orange (fresh) to deep red (after reaction), similar to the result reported in the literature.<sup>[26,27]</sup> In addition, the results of the UV-vis absorption spectra of the catalyst in H<sub>2</sub>O-PEG (Fig. 2) also revealed that the active species changed during the reaction. No absorbance peak was observed for the fresh catalyst mixture; however, a broad peak appeared between wavenumbers of 300 and 400 nm when the reaction was conducted for 20 min and it shifted to distinguish two peaks at the wavenumbers of 380 and 489 nm after the reaction for 1 h. Such a change in the Ru catalytic species during the reaction was also reported previously in the literature.<sup>[28–32]</sup> In the present reaction system, the Ru leached into the organic phase was less than 1% of original Ru in each recycling from ICP analysis, suggesting that the Ru complexes could be immobilized in the mixed solvent of H<sub>2</sub>O and PEG successfully.

## Conclusions

We have developed a practical and green method for the transfer hydrogenation of citral to citronellol using [RuCl<sub>2</sub>(benzene)]<sub>2</sub> catalyst immobilized in a mixture of H<sub>2</sub>O and PEG. The high selectivity to citronellol of 92.4% was achieved with HCOONa as hydrogen source. The Ru complexes could be immobilized in the H<sub>2</sub>O-PEG phase and separated from the organic products successfully, and the catalysts could keep the same catalytic activity after the first run, although transformation of active species occurred.

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