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Reduction of citral in water under typical transfer hydrogenation conditions—Reaction mechanisms with evolution of and hydrogenation by molecular hydrogen

Ruixia Liu[a,b], Yu Wang[b], Haiyang Cheng[a], Yancun Yu[a], Fengyu Zhao[a,*], Masahiko Arai[b,**]

[a] State Key Laboratory of Electroanalytical Chemistry, Laboratory of Green Chemistry and Process, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China
[b] Division of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan

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ABSTRACT

The reduction of an α,β-unsaturated aldehyde, citral, was investigated over a 10 wt% Pd catalyst under transfer hydrogenation (TH) conditions in a closed system with microwave assistance. Surprisingly, it was found that hydrogen was produced quite fast under the microwave irradiation during the reaction, and the reduction of citral was proved to go mainly through consecutive pathways of hydrogen production – hydrogenation rather than those commonly considered for TH reactions. Similar reaction pathways were also observed with a homogeneous catalyst of $[RuCl_2(C_6H_6)]_2$ and other typical hydrogen donors like formate salts and isopropanol, which are usually used in the typical transfer hydrogenations.

1. Introduction

Reduction of organic compounds is significantly important for organic synthetic chemistry both in laboratory and in industry [1–4]. Among all the methods of reduction of organic functional groups, hydrogenation is the most commonly used one. It is a process including the addition of hydrogen or replacement of a functional group by hydrogen. Hydrogenation with molecular hydrogen has gained a great success in understanding the reaction mechanisms and has been widely used in industry. It is generally regarded that many catalytic hydrogenations with molecular hydrogen actually involve the action of atomic hydrogen over the surface of catalysts. For transfer hydrogenation (TH), a great deal of progress has been achieved [5–11], since the report on reduction of ketones and aldehydes to secondary alcohols with aluminum isopropylate catalysis in isopropanol in 1925 [7,12]. However, TH mechanisms are still not understood well, in particular for the heterogeneous catalytic TH [13–21]. Heterogeneous catalytic TH is not a simple reaction in which hydrogen is generated from a hydrogen donor and then an acceptor is reduced by hydrogen formed. In the TH reactions with hydrogen donors, it is still not clear how does the hydrogen transfer. For example, formic acid was proposed as a hydrogen donor to give a proton and a hydride or two hydrogen atoms [3]. Until now, the mechanisms are still contradictory. Earlier, Wieland suggested that the donor reacted initially with palladium catalyst to form a palladium hydride intermediate, which was added to the acceptor, and then decomposed [22]. Later researchers preferred a mechanism in which both hydrogen donor and acceptor were co-adsorbed onto the palladium surface followed by direct transfer of hydrogen without formation of a hydride [23]. According to the results of deuterium labeling experiments, hydrogen can be transferred directly from a donor to an acceptor [24]. However, some authors pointed out that the transfer of hydrogen as a hydride species was not unreasonable [2]. Certainly, some evidence was presented for the formation of a hydride species in the decomposition of formic acid over Pd [25]. More recently, it was proposed that transfer of hydrogen between adsorbed species was more available than transfer of hydrogen from metal to alkene [26]. The adsorption of alkene should give an intermediate that could transfer hydrogen directly to an adjacent adsorbed species.

In the present work, the reduction of C=C bonds in an α,β-unsaturated aldehyde (citral) was investigated over a commercial 10 wt% Pd catalyst under TH conditions with HCOONa as hydrogen donor in a closed system with microwave assistance. Although the reactions were carried out under typical TH conditions, these were

* Corresponding author. Tel.: +86 0431 85262410; fax: +86 0431 85262410.
** Corresponding author. Tel.: +81 011 7066594; fax: +81 011 7066594.
E-mail addresses: zhaofy@ciac.jl.cn (F. Zhao), marai@eng.hokudai.ac.jp (M. Arai).

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indicated to mainly go through the formation of molecular hydrogen. That is, the reduction of citral occurs through the formation of molecular hydrogen followed by hydrogenation of the substrate with hydrogen formed. The influence of other hydrogen donors and solvents on the reaction outcome and mechanisms has also been investigated.

2. Experimental

2.1. Materials

All microwave experiments were performed using a Biotage Initiator 2.0 microwave synthesizer (Uppasla, Sweden). A commercial 10 wt% Pd/C (Shanghai Reagent Ltd.) and $[RuCl_2(C_6H_6)]_2$ (Aldrich) were used as catalysts. Citral (*trans* and *cis*, purity 95%) was purchased from Aldrich and toluene, poly(ethylene glycol) (PEG), isopropanol, K_2CO_3, $HCOONa{\cdot}2H_2O$, HCOOK, $HCOONH_4$ and HCOOH from Beijing Chemical Reagent Company.

2.2. General procedures for the reduction of citral with microwave irradiation

The reduction of citral was carried out in a quartz tube (10 mL) under microwave irradiation. The order of addition of the reagents plays an important role in the reactions [27]. We selected the following standard protocol. Hydrogen donor was first dissolved in a solvent in the reactor, catalyst was then added, and finally the substrate was added. Then, the reaction vessel was sealed and the reaction was carried out under microwave irradiation at 300 W with a stirring speed of 900 r/min. The reaction time was started to count when the reaction mixture reached the desired temperature. After the reaction, the mixture was extracted with *n*-hexane and the resulting solution was analyzed with gas chromatography (GC-Shimadzu-14C, FID, Capillary column Rtx-Wax 30 m-0.53 mm-0.25 mm) and gas chromatography/mass spectrometry (GC/MS, Agilent 5890). The gas phases were analyzed by Shimadzu GC-14C with TCD and a TDX-01 packed column. The reactions in the autoclave (50 mL) were also carried out in a water-bath with the same procedures.

2.3. The hydrogen formation and consumption during the reaction

2.3.1. Demonstration of the production of hydrogen

The reaction gas phase was analyzed by GC and the conventional test. After reaction, the gas phase was collected and analyzed by GC using the TCD detector, the results show that hydrogen was formed. Moreover, the collected gas can be kindled in the air and so it was confirmed to be hydrogen again.

2.3.2. Estimation of the quantity of hydrogen produced

The hydrogen produced during the reaction in the presence of HCOONa has been collected by water removing method and calculated by the ideal gas equation. We carried out the test under the reaction conditions with Pd/C catalyst, water, and HCOONa, but without the reactant citral. After the pressure goes to the unchanged level, the reactor was cooled to room temperature then the gas was transferred to a volumetric cylinder immersed into water and then the volume of the gas produced was calculated by sum volume of $V_1 + V_2$, V_1 volume of reactor excluding the volume of reaction solution; V_2 volume of the amount of removing water. Finally, the hydrogen amount was calculated by ideal gas equation $pV = nRT$.

When the selective reduction of citral (2 mmol) were carried out with HCOONa aqueous solution (1.2 M, 5 mL) as hydrogen donor over 10% Pd/C catalyst at 80 °C in 30 min, the conversion of citral reached 68%, citronellal (hydrogenation of conjugated C=C bond) and dihydrocitronellal (hydrogenation of conjugated C=C bond and isolated C=C bond) were produced as the main products with selectivity of 86% and 9%, respectively, and traces of isopulegol, menthol, citronellol and verbenol were also detected. So consumption of hydrogen during the reaction is about $n = 2\,\text{mmol} \times 68\% \times (86\% + 9\% \times 2) = 1.41\,\text{mmol}$. The pressure of the system after the reaction is 3.7 bar, while vapor pressure of the mixture of citral (0.6 mmol) and citronellal (1.4 mmol) in 5 mL H_2O is 3 bar under the reaction conditions. So the quantity of hydrogen left after reaction is $n = pV/RT = (3.7 - 3.0)\,\text{bar} \times 10^{-5} \times 5\,\text{mL} \times 10^{-6}/8.314472\,\text{J K}^{-1}\,\text{mol}^{-1} \times 353\,\text{K} = 0.12\,\text{mmol}$. So the total quantity of hydrogen produced in the presence of acceptor (2 mmol citral) $n = (0.12 + 1.41)\,\text{mmol} = 1.53\,\text{mmol}$, which is in agreement to the quantity of hydrogen calculated by the amount of removing water suggesting there are no CO_2 formation during the reaction. Therefore, we can say that the present reaction is mainly going through the pathway of hydrogen production and then hydrogenation with hydrogen molecules.

3. Results and discussion

3.1. Hydrogen evolution

Citral was hydrogenated in a sealed microwave reactor with HCOONa as a hydrogen donor with 10 wt% Pd/C catalyst in water at 80 °C. The total conversion of citral was 68% under the conditions used. In the organic liquid phase, citronellal and dihydrocitronellal were detected in the selectivity values of 86% and 9%, respectively, along with such very minor products as isopulegol, menthol, citronellol, and verbenol. The system pressure was continuously measured with a pressure sensor during the reaction. Fig. 1 (line (a)) shows that the pressure increased sharply to 9.6 bar within an initial 30 s and decreased gradually to 4 bar in about 30 min. After the reactor was cooled down to room temperature, the pressure was still 1 bar (relative to atmospheric pressure). The pressure increase should be caused by the production of molecular hydrogen but not by vaporization of water and organic compounds with an increase in the temperature (Fig. 1B).

To examine the implication of the above-mentioned observations, we further measured the changes of pressure and temperature with time for several selected reaction mixtures (Fig. 1). When only water was used (line (b)), the pressure increased but less sharply, compared with the above-mentioned line (a), up to 4.5 bar, this pressure maintained unchanged during 30 min, and it decreased to atmospheric pressure after the reactor was cooled to room temperature. When organic compounds of citral and/or citronellal were added, similar pressure changes were seen (lines (c) and (d)) but the increased pressure (3.5 bar) was smaller than that observed in water alone. Note that such a large pressure increase as observed during the reaction (line (a)) did not appear for the mixtures of water and/or organic compounds. The addition of catalyst into water did not influence the pressure change of the water alone (lines (b) and (e)). But, for the mixture containing water, HCOONa, and Pd/C catalyst, the pressure increased promptly up to 13.8 bar in a few seconds and then maintained unchanged (line (f)). After the reactor was cooled, the gas phase was collected and analyzed by GC, only hydrogen gas was detected as we expected, and moreover, the gas phase sample is flammable and could burn in air, confirming again it was hydrogen gas. In previous works, however, the formation of hydrogen was not detected in the TH reactions, whenever it occurred in open or closed reactors under either conventional oil or microwave heating [28–33]. The aqueous phase indicated a pH value of 8.9–9.3, which was between $NaHCO_3$ solution (pH 8.3)

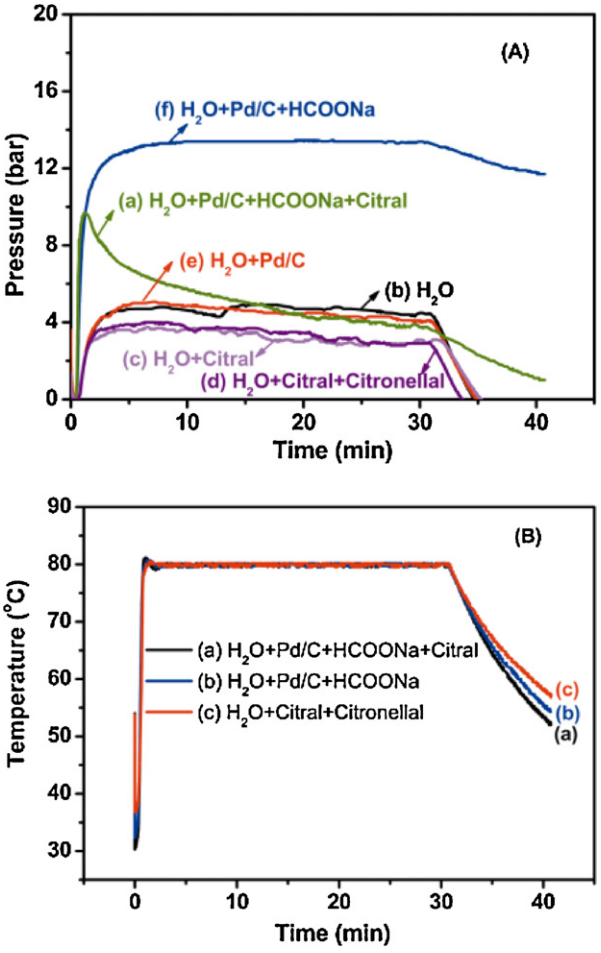
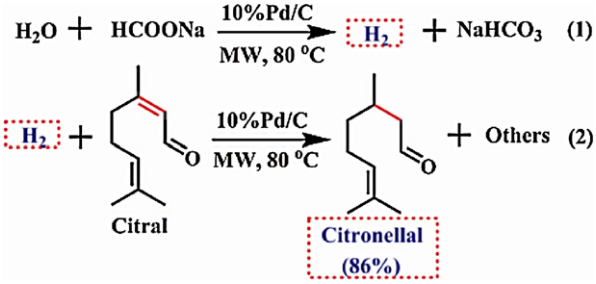


Fig. 1. In situ pressure (A) and temperature (B) changes for various mixtures on microwave heating at 80 °C. Conditions: H_2O 5 cm^3, 10% Pd/C 40 mg, HCOONa·$2H_2O$ 6 mmol, citral 2 mmol, 0.6 mmol citral + 1.4 mmol citronellal.

and Na_2CO_3 solution (pH 11.6) under the same conditions. Those results indicate that HCOONa decomposes to H_2 and $NaHCO_3$ in the aqueous phase assisted by 10 wt% Pd/C.

3.2. A case study of reaction pathway

We calculated and compared the amount of H_2 evolved with that of citral consumed for the reaction of citral (2 mmol), HCOONa (6 mmoL), H_2O (5 mL), and 10% Pd/C catalyst (21 mg) operated at 80 °C for 30 min under the microwave irradiation. The results of lines (a) and (f) in Fig. 1 strongly suggested that the H_2 formed was consumed for the hydrogenation of citral, because that the system pressure kept a stable level in the absence of citral, indicating that hydrogen was produced (a) and it decreased smoothly with the progress of the reaction in the presence of citral, suggesting the hydrogen formed was consumed during the reaction (f). The present reaction gave a total citral conversion of 68% and produced citronellal in a selectivity of 86% and dihydronellal in 9%, as mentioned above. The quantity of H_2 needed for these conversion and selectivity values was 1.41 mmol as calculated in Section 2. Considering the 0.12 mmol hydrogen left in the system after reaction, the total quantity of H_2 formed was estimated to be 1.53 mmol from the results of line (a) of Fig. 1. That is similar to the results of line (f), in which 1.56 mmol H_2 was formed through the decomposition of HCOONa in water over Pd catalyst in the absence of citral. Therefore, for the present reaction using HCOONa as a hydrogen donor, the reaction should mainly take place with gaseous



Scheme 1. Reaction pathways for the reduction of citral over 10%Pd/C in H_2O with HCOONa as a hydrogen donor under the microwave assistance.

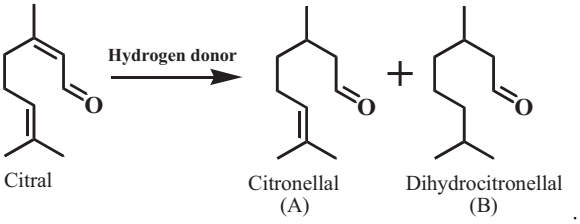
H_2 formed through the decomposition of HCOONa and both the decomposition and the hydrogenation are promoted by Pd/C catalyst as shown in Scheme 1. The TH should also occur but less significant in the present reaction system. Such a decomposition reaction of HCOONa with noble metal catalysts was reported, but no hydrogen was detected to form in the presence of acceptor in the literature [34]. In addition, some researchers suggested that the acceptor could not or less be reduced with the produced hydrogen under the conditions, even though hydrogen was produced in their experiments [35,36]. For example, it was observed that formic acid decomposed to H_2 and CO_2 to a larger extent during Ru^{II}-catalyzed asymmetric TH of ketones; however, the gaseous hydrogen was claimed to contribute very less to the formation of alcohols [35]. In another example, hydrogen was reported to be released from *p*-menthane and decalin in xylene at 144 °C but no hydrogenation reaction occurred [36].

No hydrogen was detected in the most TH reactions over Pd/C, this may be ascribed to (1) the hydrogenation of hydrogen acceptor is much faster than the decomposition of hydrogen donor, (2) the quantity of hydrogen, if produced, is so small that it cannot be detected, which may be significant for open systems (in the present work, a closed reaction system was used). HCOONa decomposes rapidly under the microwave irradiation, yielding molecular hydrogen. Then, the formed hydrogen was consumed for the hydrogenation of citral in a lower rate; so, some hydrogen remains un-reacted in the gas phase and can be detected in the present work.

3.3. Reaction with different hydrogen donors

In the TH reactions with hydrogen donors, it is still not clear how does the hydrogen transfer. For example, formic acid was proposed as a hydrogen donor to give a proton and a hydride or two hydrogen atoms [3]. Until now, the mechanisms are still contradictory. Earlier, Wieland suggested that the donor reacted initially with palladium catalyst to form a palladium hydride intermediate, which was added to the acceptor, and then decomposed [22]. Herein the influence of hydrogen donor was studied also. Note that, in the presence of HCOONa and Pd/C catalyst, citral was hydrogenated mainly to citrenollal and dihydrocitonellal along with the formation of molecular hydrogen. Further we considered the significance of two kinds of hydrogen donors, H_2 gas and HCOONa, and measured and compared with the reactions conducted in an autoclave (50 mL) under conventional heating because the decomposition of HCOONa to hydrogen was quite fast (less than 30 s) under microwave irradiation. The results are shown in Table 1, implying that when H_2 gas was used as hydrogen donor, the TOF (turnover frequency) was 14.0 mmol g^{-1} min^{-1} (entry 1). The reaction was also run with an adjusted amount of HCOONa (6 mmol) in which the quantity of H atoms included was very similar as that in H_2 (4 bar in entry 1), and a smaller TOF of 0.04 mmol g^{-1} min^{-1} was obtained for the reaction with HCOONa (entry 3). That is, the TOF of the

Table 1
Comparison of the results of citral reduction with H_2 gas or HCOONa as hydrogen donor under the conventional heating mode.



Entry	Hydrogen donor	Additive	Catalyst	Time (min)	Conversion (%)	Selectivity (%)			TOF (mmol g^{-1} min^{-1})
						A	B	C	
1	H_2 (4 bar)	-	10 wt% Pd (5 mg)	10	35	72	6	22	14
2	H_2 (1 bar)	$NaHCO_3$	10 wt% Pd (5 mg)	10	45	93	2	5	18
3	HCOONa (6 mmol)	-	10 wt% Pd (40 mg)	240	20	56	13	31	0.04

Citral 2 mmol; $NaHCO_3$ 6 mmol; H_2O 5 mL, 80 °C. C: citronellol, 3,7-dimethyloctanol, geraniol, nerol, and menthol.

reaction with H_2 was about 350 times larger than that of the reaction with HCOONa in spite of the similar quantities of H atoms involved. According to the result of Fig. 1 (line (a)), about 26% of the initial amount of HCOONa used was decomposed to H_2 and $NaHCO_3$. So, we conducted another reaction in the presence of H_2 and $NaHCO_3$ in the quantities corresponding to the extent of HCOONa decomposition of 26% and a TOF of 18.0 mmol g^{-1} min^{-1} was observed (entry 2). These results show that the direct hydrogenation of citral with H_2 should be faster than the TH with HCOONa under the conditions used, and such results should be suitable to the reactions under the microwave assistance. Note that little amount of hydrogen was left in the system after reaction (as calculated and discussed above), and, in addition, the hydrogenation with hydrogen gas was much faster than the TH. Therefore, the reduction of citral with the HCOONa hydrogen donor should mainly go through the hydrogenation with the produced hydrogen. Furthermore, Table 1 also indicates that the product distribution depends on the reaction systems and the selectivity to citronellal is larger in the presence of H_2 and $NaHCO_3$ (entry 3); the selectivity to citronellal is 93%, which is comparable to 86% observed in the above-mentioned microwave-assisted reaction in the presence of HCOONa. This can also suggest that the hydrogenation is predominating reaction in the presence of HCOONa under the microwave irradiation, but the TH should not be ignored under the reaction conditions used.

The reduction of citral was further studied with other common hydrogen donors to compare with HCOONa. Many studies demonstrate that formate salt as a hydrogen donor is superior to formic acid in the TH. Formate salt is usually utilized as a universal hydrogen carrier and the decomposition mechanism of formate acid/salt to produce hydrogen has attracted increasing interest as hydrogen is the cleanest energy source [37–40]. Table 2 gives the results with different hydrogen donors. When HCOOK was used, the total conversion and the selectivity to citronellal were 62% and 76%, respectively, which were both lower than those with HCOONa (entries 1 and 2). However, Wiener et al. observed that HCOOK was more effective than HCOONa and HCOOH in TH of nitrotoluene over 10 wt% Pd/C [34]. They suggested that the $KHCO_3$ produced from HCOOK was more soluble than $NaHCO_3$ from HCOONa and did not cover the surface of catalyst, leading to the higher activity. The results with $HCOONH_4$ were quite different from those with HCOONa and HCOOK (entry 3). This is because it can supply molecular hydrogen (decomposing to hydrogen, ammonia and carbon dioxide) even in the absence of H_2O [27,41–43]. However, the total conversion was small (44%) and the selectivity to citronellal was only 53% due to that NH_3 reacted with aldehydes (citral and citronellal) to produce corresponding hydroxylamines and imines. HCOOH was practically inactive for hydrogenation of citral but effective for acid catalyzed reactions (entry 4). The system pressure (4.8 bar) did not change during the whole course of reaction (Fig. 2d), which indicated that HCOOH did not decompose to hydrogen. Similarly, when a mixture of HCOONa and HCOOH was used (entries 5 and 6), the main product came from acid-catalyzed reactions rather than the hydrogenation. So, the presence of HCOOH might retard the decomposition of HCOONa and HCOOH could not be activated over Pd/C as reported in transfer hydrogenolysis of 2-chlorotoluene [43].

In addition, isopropanol was tested for the reduction of citral with a heterogeneous catalyst of 10 wt% Pd/C and a homogeneous one of $[RuCl_2(C_6H_6)]_2$ (entries 7 and 8). Very similar pressure changes were seen in the both cases (Fig. 2, lines (g) and (h)). It was confirmed that isopropanol produced hydrogen and acetone and then citral was hydrogenated with the in situ released hydrogen, in the same manners as for the other hydrogen donors. But, the conversion was quite low (12%) over 10 wt% Pd/C and the selectivity to hydrogenation was low due to the aldolization reaction between citral and isopropanol. It was also found that no reaction occurred in the absence of K_2CO_3 base. For $[RuCl_2(C_6H_6)]_2$ catalyst, the conversion was enhanced up to 57% and the selectivity to citronellal increased to 54%. Those results indicate that the selective reduction of citral mainly goes through consecutive reactions of hydrogen

Table 2
Results of citral reduction with different hydrogen donors.[a]

Entry	Hydrogen donor	Conversion (%)	Selectivity (%)		
			A	B	C
1	HCOONa	68	86	9	5[f]
2	HCOOK	62	76	13	11[f]
3	$HCOONH_4$	44	53	6	4[g]
4	HCOOH	91	-	-	100[h]
5	HCOOH/HCOONa[b]	13	17	8	75[h]
6	HCOOH/HCOONa[c]	7	16	4	80[h]
7	Isopropanol[d]	12	6	3	91[i]
8	Isopropanol[e]	57	54	1	45[i]

A: citronellal; B: dihydrocitronellal; C: others.

[a] Citral 2 mmol, formic salt or formic acid 6 mmol, 10% Pd/C 21 mg, H_2O 5 mL, 80 °C, 30 min, microwave heating 300 W.

[b] The mol ratio of HCOOH to HCOONa is (1:1).

[c] The mol ratio of HCOOH to HCOONa is (1:5).

[d] Isopropanol 5 mL, K_2CO_3 0.1 g, without H_2O.

[e] Isopropanol 5 mL, $[RuCl_2(C_6H_6)]_2$ 10 mg, without H_2O.

[f] Traces of citronellol, 3,7-dimethyloctanol, geraniol, nerol, and menthol.

[g] 3,7-Dimethylocta-2,6-dienylidene hydroxylamine, 3,7-dimethylocta-2,6-dienylidene imine and others formed through the reaction between NH_3 and aldehydes.

[h] Benzene, ethylbenzene, isopropylbenzene, and others formed through acid-catalyzed reactions.

[i] 3,7-Dimethyl-2,6-octadienal diisopropanol acetal.

Table 3
Results for the reduction of citral in different solvents.[a]

Solvent	Catalyst	Time (min)	Conversion(%)	Selectivity (%)		
				A	B	C
H_2O	10% Pd/C (40 mg)	30	68	86	9	5[d]
H_2O/toluene[b]	10% Pd/C (40 mg)	30	75	87	7	6[d]
Toluene	10% Pd/C (40 mg)	30	9	59	2	39[e]
PEG[c]	10% Pd/C (21 mg)	20	9	96	-	4[f]
H_2O/PEG[c]	10% Pd/C (21 mg)	20	90	2	-	98[f]
H_2O	$[RuCl_2(C_6H_6)]_2$ (20 mg)	30	15	49	-	5[g]
H_2O/PEG[c]	$[RuCl_2(C_6H_6)]_2$(5 mg)	5	82	16	-	84[h]

A: citronellal; B: dihydrocitronellal; C: others.
[a] Citral 2 mmol, solvent 5 mL, $HCOONa{\cdot}2H_2O$ 6 mmol, 80 °C, microwave heating 300 W.
[b] H_2O 3 mL, toluene 2 mL.
[c] H_2O 3 mL, PEG-400 2 mL, 180 °C.
[d] Citronellol, 3,7-dimethyloctanol, geraniol, nerol, menthol, and 6-methyl-5-hepten-2-one.
[e] Citronellol, 3,7-dimethyloctanol, geraniol, nerol, menthol, 3,7-dimethyloctanol and some other unidentified products.
[f] 6-Methyl-5-hepten-2-one.
[g] Citronellol.
[h] Unsaturated alcohols of geraniol and nerol.

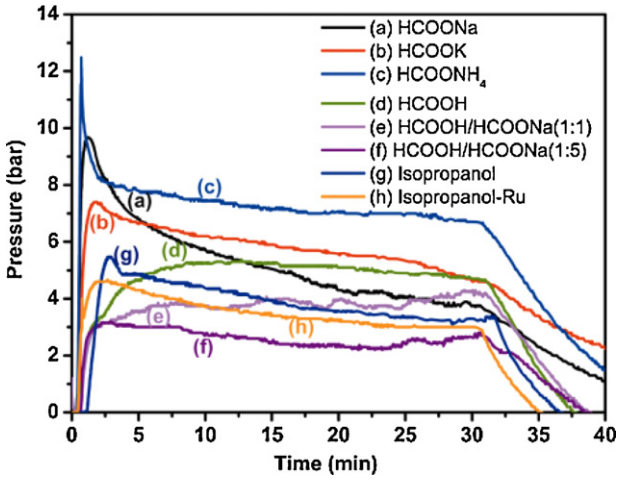


Fig. 2. In situ pressure changes for the reduction of citral with different hydrogen donors on microwave heating. Reaction conditions: citral 2 mmol, formic salt/formic acid 6 mmol, 10% Pd/C 21 mg, H_2O 5 mL, 80 °C, 30 min, microwave heating 300 W. (a) Mixture hydrogen donor and the mol ratio of HCOOH and HCOONa is 1:1; (b) mixture hydrogen donor and the mol ratio of HCOOH and HCOONa is 1:5; (c) isopropanol 5 mL, K_2CO_3 0.1 g, without H_2O; (d) isopropanol 5 mL, $[RuCl_2(C_6H_6)]_2$ 10 mg, without H_2O.

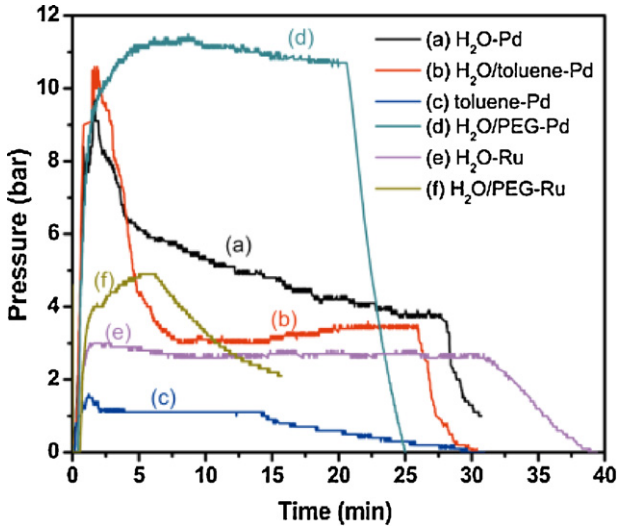
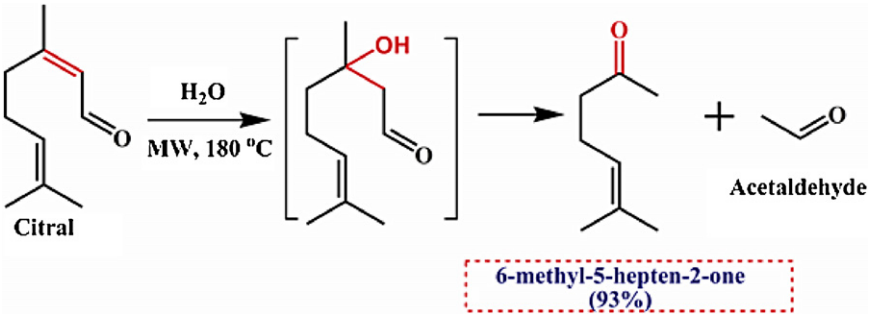


Fig. 3. In situ pressure changes for the reduction of citral in different solvents on microwave heating. Reaction conditions: citral 2 mmol, microwave heating 300 W, $HCOONa{\cdot}2H_2O$ 6 mmol, (a) H_2O 3 mL, 10% Pd/C 5 mg; (b) H_2O 3 mL, toluene 2 mL, 10% Pd/C 5 mg; (c) toluene 2 mL, 10% Pd/C 5 mg; (d) H_2O 3 mL, PEG-400 2 mL, 10% Pd/C 5 mg; (e) H_2O 3 mL, $[RuCl_2(C_6H_6)]_2$ 5 mg; (f) $[RuCl_2(C_6H_6)]_2$ 5 mg, PEG-400 2 mL, H_2O 3 mL.

production and hydrogenation with the formed hydrogen gas irrespective of the hydrogen donors and the catalysts used under the present conditions.

3.4. Reaction in different green media

The reduction was further studied with different media using green solvents of water and poly(ethylene glycol) (PEG) with a molecular weight of 400. Fig. 3 and Table 3 show the results obtained at 80 °C. When a H_2O/toluene mixture was used, the pressure increased rapidly to 10.5 bar in an initial 2 min and dropped to 3 bar in the following 7 min (Fig. 3, line (b)). The pressure drop was much faster than that observed with pure H_2O (line (a)). With pure toluene, in contrast, the pressure change was very small (line (c)). The reaction results in these different media are presented in



Scheme 2. Reaction pathway of H_2O and citral in H_2O/PEG solvent with microwave assistance at elevated temperature.

Table 3. The mixed solvent medium of H_2O/toluene gave a total conversion of 75% and a selectivity to citronellal of 87%, which were larger and similar to those obtained with H_2O alone, respectively. In contrast, very smaller conversion of 9% and selectivity of 59% were obtained in toluene alone. The low conversion in this medium should result from the absence of one of two components of H_2O giving molecular hydrogen (Scheme 1). Furthermore, PEG was also checked because of its lower vapour pressure and good absorption of microwave [44]. It was observed that no reaction occurred at temperatures <120 °C; at 180 °C, a small conversion of 9% was obtained. When H_2O was also added, the total conversion increased significantly but 6-methyl-5-hepten-2-one was produced in a selectivity of 93%, through the addition–elimination reaction of citral and H_2O, as shown in Scheme 2. It was reported that H_2O could behave differently at elevated temperatures; the bond angle widens and its dielectric properties become similar to those of organic solvents [45]. It is thus assumed that H_2O is activated at 180 °C and added to the citral molecule, yielding 6-methyl-5-hepten-2-one and acetaldehyde (Scheme 2).

4. Conclusion

Under the microwave irradiation, the reaction pathway for the selective reduction of citral under typical transfer hydrogenation (TH) conditions over a heterogeneous 10 wt% Pd/C catalyst was studied. The system pressure increased promptly within the first 3 min, the GC analysis indicated the production of a large amount of hydrogen from HCOONa in aqueous phase over Pd/C catalyst. The results suggest that the reaction mainly goes through consecutive pathways of hydrogen production and then hydrogenation reaction, rather than those commonly considered of TH reactions. Moreover, the proposed reaction pathway was also demonstrated for other catalysts under TH conditions like a homogeneous catalyst of $[RuCl_2(C_6H_6)]_2$, and typical hydrogen donors such as formate salts and isopropanol. However, acid-catalyzed reaction took place when formate acid was used as hydrogen donor, and addition–elimination reaction of citral and H_2O occurred at high temperature in the case of H_2O/PEG mixed solvent was used.

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