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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

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* 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)