



## Hydrogenation of chalcones using hydrogen permeating through a Pd and palladized Pd electrodes

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### ABSTRACT

The hydrogenation of benzalacetone and benzalacetophenone was carried out using atomic hydrogen permeating through a palladium membrane. A two-compartment cell separated by a Pd sheet or a palladized Pd (Pd/Pd black) sheet electrode was employed. The reduction products were identified by (GC) gas chromatography, UV–vis absorption spectroscopy and NMR spectroscopy. The carbon–carbon double bond was hydrogenated and the benzylacetone and benzylacetophenone were obtained as products using palladium catalyst. The current efficiency for hydrogenation reaction increases when the current density for water electrolysis decreases and depends on the initial chalcone concentration. It is over 90% at the concentration of 10 mmol L<sup>-1</sup>. The hydrogen absorption and diffusion into and through a palladium membrane electrode has been studied by using an electrochemical impedance spectroscopy method. The impedance results would indicate that the hydrogen permeated through the membrane is consumed by the chalcone during the hydrogenation process keeping as the permeable boundary condition in the outer side of the Pd membrane the hydrogen activity almost zero. The hydrogen entering the metal through an adsorbed state and the rate of hydrogen absorption is diffusion-controlled.

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### 1. Introduction

Chalcones are  $\alpha,\beta$ -unsaturated ketones, which have four possible substituents: R1, R2, R3 and R4. R1 is the substituent in the C $\alpha$ , in the C $\beta$  and R4 is directly bound to the carbonyl group (Fig. 1). In benzalacetone, the substituent R1 is a phenyl (C<sub>6</sub>H<sub>5</sub>) group and R<sub>4</sub> a methyl group; while, in benzalacetophenone both R1 and R4 are C<sub>6</sub>H<sub>5</sub> groups. Some chalcones are open chain flavonoids whose basic structure includes two aromatic rings connected by an  $\alpha,\beta$ -unsaturated carbonyl group. They are usually obtained from natural products with extractive techniques [1–3] or by several homogeneous [4,5] and heterogeneous [6,7] synthetic methods. The importance of these chalcones is due to their wide range of biological and chemical properties.

Reduction reaction of  $\alpha,\beta$ -unsaturated carbonyl compounds [8] can occur in different ways. It may lead to different products such as (a) an allylic alcohol, resulting from the attack of an hydride the carbonyl group, (b) a saturated carbonyl compound, resulting from the hydrogenation of the carbon–carbon double bond and (c) a saturated alcohol resulting from the reduction of the

carbon–carbon double bond as well as the carbonyl group [9]. The most common hydrogenation catalysts are transition metals. On metals the reactivity of isolated C=C bond is always higher than that of C=O bonds and this behavior is likely related to the bond adsorption strength [10]. Palladium is a very good catalyst for the C=C hydrogenations, but a very bad catalyst for hydrogenation of carbonyl compounds. It is known that this is due to a too weak adsorption of carbonyls under reaction conditions. On the other hand, the selective hydrogenation of the  $\alpha,\beta$ -unsaturated ketones to obtain the corresponding unsaturated alcohols need the activation of the carbonyl group which is less reactive than the olefinic bond. Modified metal with cation [11], single crystals [12], polycrystalline nanoparticles and orientated nanoparticles supported on carbon are employed for the hydrogenation of  $\alpha,\beta$ -unsaturated compounds [13]. Santori et al. [14] investigated the behavior of Pt/SiO<sub>2</sub> and tin-modified Pt catalysts, in the hydrogenation of aromatic ketones such as acetophenone, 3,4-dimethoxyacetophenone, benzophenone and chalcone. The different catalysts used led to high selectivity values of the desired products.

The electrocatalytic hydrogenation (ECH) is one of those methods which have been used since the beginning of the last century [15]. The active hydrogen is produced in powdered cathodes, particularly on Raney-nickel or palladium over carbon catalysts. The outset is similar to the catalytic hydrogenation (CH) where unsaturated molecules as well as hydrogen atoms are adsor-

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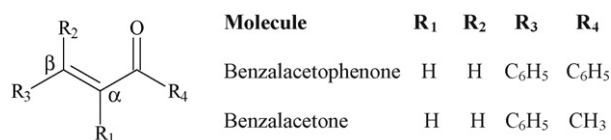


Fig. 1. Scheme of chalcones.

bed on the catalyst surface. However, the catalytic hydrogenation frequently needs high temperature and pressure to sustain the process. In the electrocatalytic method, the  $H_{ads}$  is produced by the proton discharge onto surface sites. Thus, the advantage of the electrocatalytic method is the *in situ* generation of atomic hydrogens on the surface of the electrode, which can be directly used for the envisaged hydrogenation. Several techniques were developed to improve the electrocatalytic hydrogenation [16]. The electrocatalytic method was also employed on the chalcone reduction reaction in early research performed by a Russian group [17]. They studied the reduction of benzalacetophenone at a platinized platinum (Pt/Pt) electrode in dioxane-sulfuric acid solution. Chromatographic analysis disclosed that dihydrochalcone was formed during electrolysis. Recently, Calvo et al. demonstrated the good agreement between electrocatalytic hydrogenation method and heterogeneous catalysis [18]. They performed the hydrogenation of ethyl pyruvate to yield S-ethyl lactate over palladium supported on carbon felt electrodes modified with cinchonidine. Their results were in good agreement with previously reported heterogeneous enantioselective hydrogenation on Pd/C catalyst using molecular hydrogen at high pressure. The ECH limitation is the requirement of a large surface of the catalyst employed as working electrode and the need of adding a supporting electrolyte that often leads to difficulties with subsequent product purification procedures.

Inoue et al. have developed a new hydrogenation system using a two-compartment cell separated by a Pd sheet with a thickness of 50  $\mu\text{m}$  [19]. This system was composed of three processes, which were the following: (i) the electrochemical production of atomic hydrogen by water electrolysis on one side of the Pd sheet, (ii) permeation of the atomic hydrogen through the Pd sheet and (iii) hydrogenation on the other side. The water electrolysis and the hydrogenation reaction proceed on different sides of the metal sheet. As a consequence, it is not necessary to separate the supporting electrolyte from the products. The method was used for hydrogenation of styrene [19], 4-methyl styrene [20], in the hydrogenolysis of the azo dye amaranth [21] and in the dechlorination of 4-chlorotoluene [22]. To the best of our knowledge, this system has never been assayed with chalcones.

The hydrogenation process would be described as follows [22]: in the electrolytic reduction of water at one side of the Pd sheet electrode in alkaline solution, one-electron reduction of the water molecule occurs



where  $\text{MH}_{\text{ad}}$  represents an hydrogen atom adsorbed on the Pd sheet. Most of  $\text{H}_{\text{ad}}$  atoms diffuse into the Pd sheet at a velocity proportional to their concentration gradient to reach the other side of the Pd sheet.



where  $\text{H}_{\text{ab}}$  represent the absorbed hydrogen. Permeated hydrogen atoms via an adsorption step at the other side are utilized as the hydrogen source for the hydrogenation of organic molecules.



In the present work the hydrogenation of benzalacetophenone and benzalacetone is performed using atomic hydrogen permeating through a Pd and modified palladized Pd sheet electrode. The objective is to optimize the hydrogenation method using simple chalcones to obtain exclusively dihydrochalcones as reaction products. After that, the optimized permeating method will be assayed with more complex molecules as naringin chalcone and neohesperidine chalcone. They are glycosilated flavanons and their corresponding dihydrochalcones present important properties as sweeteners [23]. Neohesperidin dihydrochalcone (NHDC) is a safe semi-synthetic low-calorie sweetener, bitterness blocker, and flavor enhancer with unique properties and applications for the food, beverage, pharmaceutical, and animal feed industries.

## 2. Experimental

### 2.1. Chalcone preparation

The benzalacetophenone (1,3-diphenyl-2-propen-1-one) and the benzalacetone (4-phenyl-3-buten-2-one) were obtained by the condensation of acetophenone or acetone with benzaldehyde in the presence of aqueous alcoholic alkali (method of Claisen-Schmidt) [24]. An aliquot corresponding to 1.1 mol of acetone was mixed with 0.4 mol of benzaldehyde. An aliquot of 10% NaOH aqueous solution was added and the temperature was controlled with a cold bath in the range of 25–31 °C. Hydrochloric acid was added up to neutralization and the aqueous layer was extracted with benzene. The product formed was recrystallized from ethanol. The benzalacetophenone was prepared using a similar method. The corresponding moles of acetophenone and benzaldehyde were added to a NaOH water-ethanol solution previously cooled on an ice bath. The temperature was controlled in a range between 15 and 30 °C.

The melting point of the purified benzalacetophenone obtained was 54–56 °C and the benzalacetone melting point was 40–42 °C. Both ranges are in good agreement with the literature values [24]. These chalcones were also characterized by using UV-vis and <sup>1</sup>H and <sup>13</sup>C NMR analysis. The spectra obtained are described in Section 3 of the present paper. The benzalacetophenone and benzalacetone solutions for hydrogenation reactions were prepared using ethanol as solvent.

### 2.2. Cell and equipment

The cell used for the catalytic hydrogenation was composed of two compartments separated by a Pd sheet (geometric area: 3.14 cm<sup>2</sup>, thickness: 50  $\mu\text{m}$ ) which served as a cathode for water electrolysis in 1 mol L<sup>-1</sup> KOH aqueous solution to produce atomic hydrogen [25]. A platinum sheet was used as a counter electrode. The galvanostatic electrolysis was carried out at various applied currents between 25 and 150 mA.

No supporting electrolyte was needed by using this hydrogenation method and the benzalacetone and benzalacetophenone solutions were prepared in ethanol solvent and the concentration range was from 0.1 to 10 mmol L<sup>-1</sup>. As chalcones are photo-sensitive compounds, their degradation induced by light was prevented. The cell compartment containing the chalcone solution was protected from light action with aluminum foil and adequately closed to prevent solvent evaporation and the consequent concentration changes. Chalcones remained un-reacted in the absence of the hydrogenation conditions. Their stability was monitored for 25 h, a time period equivalent to that used in the experiments. This stability was verified by GC and by UV spectrophotometry.

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