

# Catalytic Hydrogenation of Organic Compounds without H<sub>2</sub> Supply: An Electrochemical System

Daniela Maria do Amaral Ferraz Navarro and Marcelo Navarro\*

Departamento de Química Fundamental - CCEN, Universidade Federal de Pernambuco, Cidade Universitária 50740-901, Recife (PE), Brazil; \*navarro@ufpe.br

Modern organic chemistry wants to combine the search for new reactions with the goal of optimizing the efficiency of known synthetic procedures. Economical as well as environmental concerns have led chemists to attempt to increase the selectivity of chemical reactions, while trying to avoid the formation of polluting products and using the simplest possible reaction conditions (1).

Electrochemistry meets these requirements and has been applied to several industrial procedures. The principal advantages of electrochemistry are that the electrons are inexpensive to generate and the system may be controlled by charge passage in a clean way, since the process may be regulated by potential scale (2). However some constraints are imposed by the technique. For example, most frequently reductive electrolysis is carried out in divided cells to avoid secondary reactions that occur on the auxiliary electrode. This requires membranes that are stable in organic solvents. The use of organic aprotic solvents would necessitate the use of a supporting electrolyte, usually an expensive quaternary ammonium salt at a concentration as high as that of substrate. Electrolysis is frequently performed under a controlled current condition that requires complex electrochemical apparatus (3).

The electrocatalytic hydrogenation (ECH) of organic compounds is a simple and interesting procedure that may exemplify the advantages of electrochemistry. Although this technique has been known since the beginning of the 19th century (4), it had not been used much in organic chemistry as compared to traditional catalytic hydrogenation. The experiment described here was developed for an undergraduate organic chemistry laboratory course and can be used to introduce the catalytic hydrogenation reaction, catalysis, electrochemical principles, and gas chromatography (used as analytical technique).

## Experimental Procedure

### Electrochemical Cell

A 50-mL glass flask with two capped orifices was used as the electrochemical cell. One orifice was used to connect the nickel foil<sup>1</sup> (or bar) anode and the other to connect the iron bar (0.1-dm diameter). The latter functioned as the working electrode (cathode). The potential was monitored by a multimeter (Figure 1). Both electrodes can be reused several times (Ni electrode after cleaning with 6.0 M hydrochloric acid solution followed by washing with distilled water and the Fe electrode after removing the nickel deposit by polishing). Electrodes should not be allowed to touch each other during electrolysis. The cathode must be immersed ~0.5 dm in solution, allowing a reasonable current intensity of 30 mA and a current density of ~180 mA dm<sup>-2</sup> (5). Nickel was chosen because it could work both as a sacrificial anode and as a catalyst. Iron was chosen because it is inexpensive and strongly

adsorbs H• (6), reducing the loss of H• by evolution of hydrogen gas. The Fe/Ni pair works as a good catalyst for hydrogenation reactions (5). If Ni is used in place of Fe, the electrochemical efficiency decreases.

### ECH Solution, Electrolysis, and Analysis

The organic compounds hydrogenated by the ECH process were styrene, benzaldehyde, and acetophenone. The organic compound, 0.5 mmol, was dissolved in 10 mL of methanol and added to 40 mL of 0.25 M ammonium chloride. The positive pole of the battery (1.5 V) was connected to the Ni electrode and the negative pole to the iron electrode. Vigorous stirring with a magnetic stir bar was necessary. The potential of the electrochemical system was monitored by using a multimeter (Figure 1). The hydrogenation reaction was stopped after three hours. The hydrogenation product yields were determined by gas chromatography with injection of an authentic sample in a Varian GC 3380 using 30-m capillary CP-SPL5CB Chrompack column and 60–200 °C temperature range (20 °C min<sup>-1</sup>). The chromatographic organic samples were obtained from 2-mL reaction aliquots extracted with 1 mL of diethyl ether.

### Hazards

Use disposable gloves when handling organic solvents and reagents. Skin contact with irritant reagents like styrene, benzaldehyde, acetophenone, and ammonium chloride must be avoided. Handling of concentrated hydrochloric acid should be done in the fume hood using gloves to prepare the 6.0 M solution. The toxic methanol solvent used in ECH solution may be replaced by ethanol, but the electrochemical efficiency of the ECH process will be reduced (5).

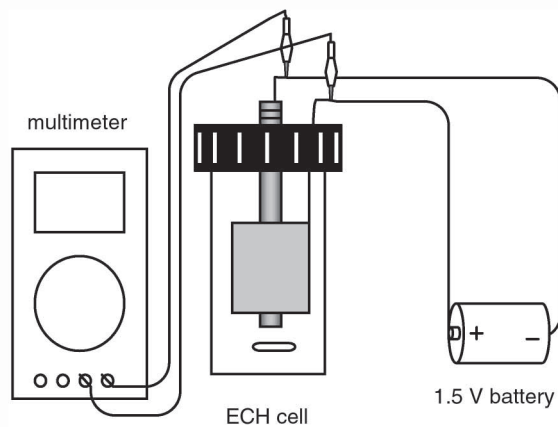
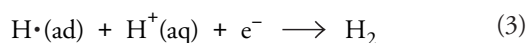
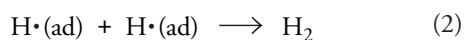
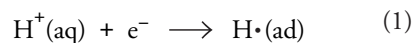


Figure 1. Apparatus for ECH experiment.

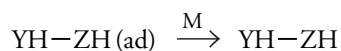
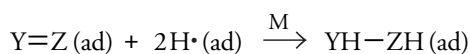
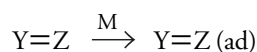
## Discussion

### Mechanism

A combination of two mechanisms is responsible for the success of the ECH: the electrochemical generation of atomic hydrogen and the catalytic hydrogenation mechanism. The first mechanism is known as the hydrogen evolution reaction (7) and occurs on the cathode surface. The first step of the hydrogen evolution reaction gives atomic hydrogen that remains adsorbed on the electrode surface; this is called the Volmer reaction, eq 1. The second step may be either a recombination reaction of the adsorbed atomic hydrogen, the Tafel reaction, eq 2, or an ion reduction plus atom reaction (electrochemical desorption), the Heyrovsky reaction, eq 3. The prevalence of either of the latter reactions depends on the electrode material (8):



The ECH process is completed by the traditional catalytic hydrogenation reactions (9),



adsorption, hydrogenation, and desorption, respectively.

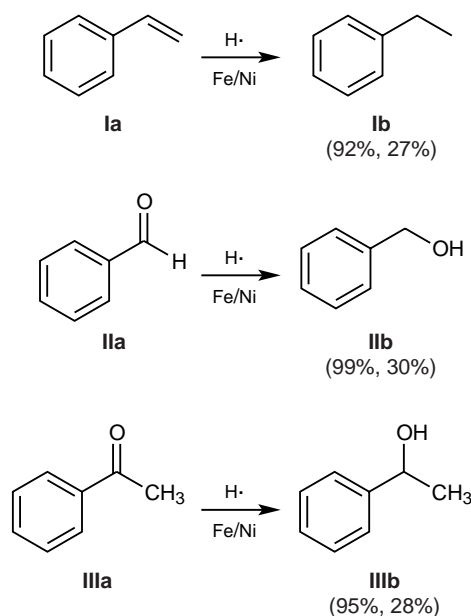


Figure 2. Yields and electrochemical efficiency of ECH reactions of styrene, **Ia**, benzaldehyde, **IIa**, and acetophenone, **IIIa**.

### Efficiency

The electrochemical efficiency of the process, that is, the relation between charge passed and hydrogenated product yield, depends on the electrode material choice (eqs 2 or 3 should be the rate-determining step) and reaction conditions (current density, supporting electrolyte, etc.) (8). At the same time the catalyst (electrode) should hydrogenate the organic substrate avoiding the loss of hydrogen in the gas form. While traditional catalytic hydrogenation of functional groups, such as olefins and ketones, requires a hydrogen supply and noble metal catalysts, the ECH technique gives the same results using a simpler apparatus involving an inexpensive technique. The ECH also introduces students to the concept of hydrogenation of organic compounds at the same time that a physical chemistry technique is applied to generate hydrogen in situ.

### Results

Styrene, benzaldehyde, and acetophenone were successfully hydrogenated (Figure 2), giving the respective products in good yields: 1-phenylethane (92%), benzyl alcohol (95%), and 1-phenylethan-1-ol (99%). The electrochemical system is very simple and uses a 1.5 V battery (alkaline) as power supply, an iron cathode, and a nickel anode as described in Figure 1. The experiments were monitored by gas chromatography and the progress of the hydrogenation reaction was verified by taking 0.5-mL aliquots every 30 minutes and extracting with diethyl ether. Hydrogenation products were identified by injection of an authentic sample, as shown in Figure 3 for the hydrogenation of benzaldehyde.

In most cases, an electrochemical system using Ni as catalyst can hydrogenate the double bond conjugated to an un-

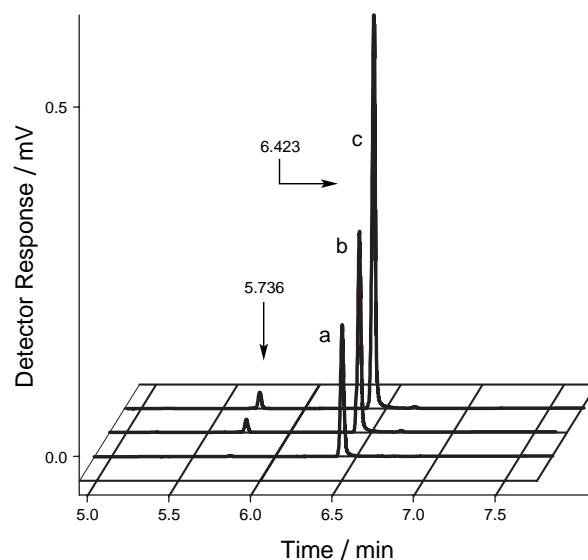


Figure 3. Gas chromatograms obtained from the ECH of benzaldehyde: (a) 0.01 M benzyl alcohol solution in diethyl ether, (b) product extracted from ECH of benzaldehyde, and (c) co-injection of a and b.

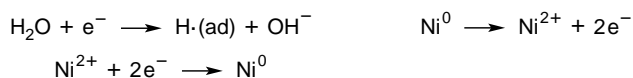
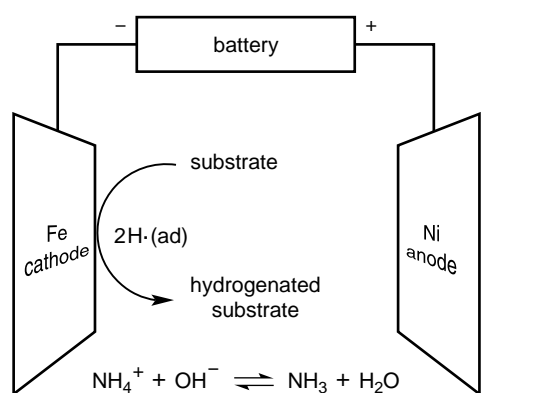


Figure 4. Reactions occurring in the electrocatalytic hydrogenation process using a sacrificial anode of nickel.

saturated group (5, 8). Isolated double bonds (5) and aromatic (10) systems are more difficult to hydrogenate, but it may occur at elevated temperature or pressure.

It is important to use the sacrificial anode because it simplifies the electrochemical system and allows the use of an undivided cell. Nickel is also necessary to activate the iron cathode surface (5). The reactions occurring in the ECH system are shown in Figure 4. Nickel metal is oxidized, working as a sacrificial anode. The electrochemical generation of atomic hydrogen occurs on the cathode surface at the same time that the reduction of  $\text{Ni}^{2+}$  takes place. The reduction of water also generates hydroxide ions that are neutralized by ammonium chloride present as supporting electrolyte, avoiding  $\text{Ni}(\text{OH})_2$  precipitation. The organic substrate is hydrogenated on the Fe/Ni cathode surface.

It is possible to reduce the reaction time by increasing the surface area of cathode, maintaining approximately the same current density ( $\sim 180 \text{ mA dm}^{-2}$ ). Electrochemical effi-

ciency of the process may be calculated by equations relating current ( $I$ ), time ( $t$ ), charge ( $Q$ ), electrons ( $e^-$ ) involved, and mol number of hydrogen ( $n$ ) promoted in the process,

$$Q = I(\text{A}) \times t(\text{s}) = e^- \times n \times F,$$

where  $F = 96,487 \text{ C mol}^{-1}$ .

## Acknowledgments

We wish to thank Rajendra Mohan Srivastava for fruitful discussions and correcting the manuscript and FINEP/CTPETRO/PETROBRAS for financial support.

## Note

1. Both Ni foil and Ni foam electrodes were used and both types of electrode worked in this experiment.

## Literature Cited

1. Chaussard, J.; Folest, J. C.; Nédélec, J. Y.; Périchon, J.; Sibille, S.; Tropel, M. *Synthesis* **1990**, 369.
2. Schäfer, H. J. In *Organic Electrochemistry: An Introduction and Guide*, 3rd ed.; Lund, H., Baiser, M. M., Eds.; Marcel Dekker: New York, 1991; pp 233–249.
3. Nédélec, J. Y.; Périchon, J.; Tropel, M. *Curr. Top. Chem.* **1997**, 185, 141.
4. Haber, F. *Physik. Chem.* **1900**, 32, 193. Fokin, S. Z. *Elektrochem.* **1906**, 12, 749. Haber, F. *Physik. Chem.* **1900**, 32, 193.
5. Santana, D. S.; Lima, M. V. F.; Daniel, J. R. R.; Navarro, M. *Tetrahedron Lett.* **2003**, 44, 4725. Santana, D. S.; Lima, M. V. F.; Daniel, J. R. R.; Navarro, M. *J. Electroanal. Chem.* in press.
6. Trasatti, S. *J. Electroanal. Chem.* **1972**, 163, 39.
7. Marin, D.; Mendicuti, F.; Teijeiro, C. *J. Chem. Educ.* **1994**, 71, A277.
8. Moutet, J. C. *Org. Prep. Proced. Int.* **1992**, 24, 309.
9. Landgrebe, J. A. *J. Chem. Educ.* **1995**, 72, A220.
10. Pintauro, P. N.; Bontha, J. R. *J. Applied Electrochem.* **1991**, 21, 799. Menini, R.; Martel, A.; Ménard, H.; Lessard, J.; Vittori, O. *Electrochim. Acta* **1998**, 43, 1697.