Electrocatalytic hydrogenation of acetophenone and benzophenone using palladium electrodes

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ABSTRACT

We have studied the electrocatalytic hydrogenation of acetophenone and benzophenone using a) potentiometric titration of adsorbed hydrogen by the organic reactant in excess, b) electrochemical impedance spectroscopy at a potential at the onset of hydrogen evolution and c) electrolysis at constant potential at high adsorbed hydrogen coverage. The rate of reactions between adsorbed hydrogen and adsorbed ketones and the respective alcohols intermediates of hydrogenation have been obtained from the titration curves at different organic reagent concentrations. Both the reaction rate and the charge transfer resistance, R_{ct}, for the H^+/H_{ads} reaction follow a concentration dependence that can be interpreted by a Langmuir adsorption isotherm for the organic molecules and also a blockage of the palladium surface for the hydrogen adsorption. From the results of electrolysis at controlled potential under high hydrogen coverage, the faradaic yield and the product distribution, namely 1-phenylethanol, ethylbenzene, diphenylmethanol, diphenylmethane have been obtained.

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1. Introduction

Pharmaceutical and agrochemical synthesis has been focused on selective preparation of hydrogenated products due to their high economical/commercial impact. However, control conditions to obtain single products remain a challenge. For this purpose, electrosynthesis arises as an interesting, inexpensive and safe alternative which includes ketones, aldehydes, nitro compounds, nitriles, aromatic hydrocarbon and olefins as reagents [1–10].

In this context, highly active electrocatalysts for proton discharge (low overpotential materials) shift the working potential to moderate values and reduce electrical consumption. Thus, the chemisorbed hydrogen formed on electrocatalysts can react with coadsorbed organic molecules at different reaction rates [3], in analogy to heterogeneous catalysts. Nevertheless, formation of molecular hydrogen via Volmer–Heyrovsky or Volmer–Tafel reactions (see Eqs. (1),(2) and (1), (3) respectively) becomes dominant when the applied potential is cathodically shifted and the hydrogen-reaction with the organic molecule is thermodynamically or kinetically unfavorable.

Platinum and metals of the platinum group have an exceptional catalytic activity for the hydrogen evolution reaction (HER) and are widely used as catalysts in electrocatalytic hydrogenation

reactions (ECH). In particular, palladium can also absorb hydrogen previously electrosorbed (H_{ads}), from acid aqueous solutions [11–13], which makes it an attractive material for hydrogen storage. In the absence of chemical or electrochemical driving forces, the limited regeneration of H_{ads} is a consequence of its expulsion from the inner metal. The exchange process is governed by a thermodynamic equilibrium constant which is a function of temperature and hydrogen species proportion inside/outside the material. Soluble scavengers in the surface neighborhood unbalance the equilibrium ratio by hydrogen abduction [14].

On the other hand, the ECH of a carbonyl group conjugated to one or two phenyl rings yields more than one possible product, the alcohol and the hydrocarbon. Specifically, two mechanisms have been proposed in the literature for the formation of these two products: parallel reactions, one leading to the alcohol and the other one giving the hydrocarbon directly [15], or sequential reactions involving first the formation of the alcohol followed by hydrogenolysis of the alcohol to the hydrocarbon [16]. In addition, the last mechanism was also suggested for the hydrogenation of nitrobenzene [17] and benzaldehyde [18] at Cu electrodes.

This work aims at determining whether the formation of phenyl alcohols and phenyl alkanes results from parallel or consecutive processes in ECH reactions using acetophenone and benzophenone as reactants. Moreover, we deduce quantitative kinetic expressions for a model reaction sequence to improve hydrogenation selectivity in future works.

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2. Experimental

2.1. Chemicals

In this study acetophenone, benzophenone, 1-phenylethanol, diphenilmethanol, ethylbenzene, diphenylmethane (Aldrich), Sulfuric acid 98% (Merk) and Sintorgan ethanol were used without further purification. Milli Q water (>18 MΩ) was employed.

A palladium wire cathode was used and all potentials were referred to the Ag/AgCl; 3 M KCl reference electrode, separated by a Luggin capillary in order to minimize the ohmic drop. A large surface platinum mesh was employed as counter electrode. Sulfuric acid 0,5 M was used as proton and electrolyte sources in ethanol–water, (60–40) mixture. The temperature was kept at 298 ± 2 K and all solutions were mechanically stirred and permanently deoxygenated with Ar.

Electrochemical hydrogen titration [19,20] was carried out in an undivided O_2 free cell, with special tightly cavities for the electrodes and the Hamilton syringe containing the organic substrate. The electrolytic solution and the headspace were flushed with Ar during 10 minutes, so that the gas pressure was close to 1 atm. Initially, the palladium electrode was charged with 1C at a $-0,5$ V step potential, in the absence of organic compounds. Then, the potential transients at zero current were recorded from the open circuit potential (OCP), with increasing concentrations of ketones and alcohols.

Also the electrochemical impedance spectroscopy (EIS) was carried out in a Teflon cell in order to minimize the current lines distortion. The cell was totally isolated from the environment and was continuously purged by Nitrogen flow. The potential selected for this experiment was $-0,1$ V in order to minimize hydrogen absorption ($R_{abs}^{-1} \approx 0$) and evolution ($R_{ev}^{-1} \approx 0$). It should be noticed that all three processes (Eqs. (1)–(6)) may occur and an equilibrium between absorbed an adsorbed H is established at each potential. However, under the experimental conditions in these experiments, i.e. applied potential, one expects a very low H_{ads} coverage and low driving force for H absorption, thus the recombination rate is expected also to be negligible from comparison with the adsorption isotherm of hydrogen on palladium in sulfuric acid solution [21,22]. The frequency was scanned between 10 kHz–10 mHz interval.
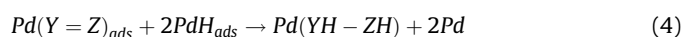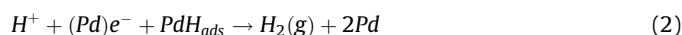
On the other hand, the quantitative electrocatalytic hydrogenation of the organic molecules was carried out in a two-compartment Teflon divided cell [23] with a Nafion® 324 membrane. The working electrode was polarized at $-0,5$ V in solutions containing the organic compound. It was necessary to apply a potential lower than that used in EIS in order to reduce the length of time of the experiment. The initial reagent concentration was 0,06 M whereas the end of the experiment was attained at 90–80% reagent conversion. The composition of the cathodic compartment was periodically sampled and the reaction mixtures were analyzed by high performance liquid chromatography with UV/vis detection, using a Merck LiChrospher 100 RP-8 column. The identification and yield of each reaction product were obtained by HPLC against previously calibrated with standards of reactants and products.

All experiments were performed with an Autolab PGSTAT 30 potentiostat (Autolab, Ecochemie, Holland) with Nova 1.10 software. In order to obtain high intensities values, the electrochemical active area was estimated by PdO reduction peak according to Fang, L.-l. et al. [24] and was equal to 20 cm^2.
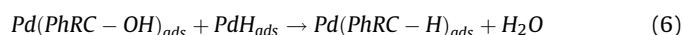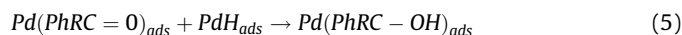
3. Results and discussion

The heterogeneous hydrogenation of unsaturated bonds in organic molecules can be achieved either by chemical gas catalysis (CH) or by electrocatalysis (ECH). In both cases hydrogen atoms adsorbed on metal surfaces are the reactive species. While gas catalysis needs high temperature and pressure to dissociate H_2 molecules, in ECH adsorbed hydrogen is produced from the electro-reduction of protons at the electrode surface with the advantage of *in situ* generation of atomic hydrogen readily available to react at ambient pressure and low temperature with no need to pre-dissociate molecular hydrogen. The respective reactions are depicted in Eqs. (1)–(4), where PdH_{ads} represents an ad-atom of hydrogen on the Pd surface, Pd(H) hydrogen atoms within the metal lattice, H_2 (g) the gaseous hydrogen evolved at electrode surface and Y=Z and YH–ZH the unsaturated and saturated organic molecule respectively [16]:

$$H^+ + (Pd)e^- \rightarrow PdH_{ads} \rightleftarrows Pd(H) \tag{1}$$

$$H^+ + (Pd)e^- + PdH_{ads} \rightarrow H_2(g) + 2Pd \tag{2}$$

$$2PdH_{ads} \rightarrow H_2(g) + 2Pd \tag{3}$$

$$Pd(Y = Z)_{ads} + 2PdH_{ads} \rightarrow Pd(YH - ZH) + 2Pd \tag{4}$$

In the present work we have investigated the multistep hydrogenation reaction of acetophenone and benzophenone and the reduction of the respective intermediate alcohols, and Eq. (4) becomes:

$$Pd(PhRC = 0)_{ads} + PdH_{ads} \rightarrow Pd(PhRC - OH)_{ads} \tag{5}$$

$$Pd(PhRC - OH)_{ads} + PdH_{ads} \rightarrow Pd(PhRC - H)_{ads} + H_2O \tag{6}$$

The reaction mechanism for the electrocatalytic hydrogenation of ketones (C=O) to the corresponding secondary alcohols (C—OH) 1-phenylethanol or diphenylmethanol, and further reduction to ethylbenzene and diphenylmethane respectively, involves adsorbed reactants. In Reaction (5) and (6) we should consider the adsorption/desorption equilibrium and diffusion into the bulk electrolyte. Besides, Reactions (2) and (3) must be considered as competing processes at the cathodic potential applied in the electrolyses (-0.5 V) but neglected at the higher potentials, $-0,1$ V, monitored in the OCP titrations.

There is a branching point at the hydrogen adsorbate with a competition for H_{ads}. Under OCP conditions, the H_{ads} is involved in three competing processes: recombination of two H_{ads} to give H_2 (Eq. (3)), insertion into the palladium lattice (Eq. (1)), and reaction with the adsorbed organic molecule (Eqs. (5) and (6)). Under the constant-potential electrolysis conditions, the electroreduction of H_{ads} to H_2 is an additional competing process (Eq. (2)).

3.1. Titration of H_{ads} by organic molecules

The surface concentration of adsorbed hydrogen atoms will be determined by the electrode potential, the concentration of the organic molecules and the diffusion of H atoms into the palladium lattice. The Pd–hydrogen system is a pseudo-reference electrode [12] and its OCP in the absence of oxygen is fixed by the $H^+/Pd(H)$ fast equilibrium and is independent of the hydrogen content in the solid α and β-Pd phases for atomic fraction between 0.03 and 0.36 [12,25,26]. In absence of hydrogen acceptor molecules (such as unsaturated organic molecules or traces of oxygen) at the Pd–H equilibrium potential, the superficial H_{ads} concentration depends on the recombination rate and insertion rate into the Pd lattice. On

the other hand, in the presence of unsaturated organic molecules, the adsorbed hydrogen can also be depleted by direct hydrogenation. During the hydrogenation process at the electrode surface, the OCP will evolve as the reaction consumes the hydrogen ad-atoms until complete titration of surface H_{ads} occurs. The time evolution of the open circuit potential is indicative of the amount of organic molecules available and of the rate of the hydrogenation reaction (Eq. (4)) [14], which depends on the particular functional group being hydrogenated [27,28].

We have studied the electrochemical hydrogenation of acetophenone, benzophenoe and the respective secondary alcohols, 1-phenylethanol and diphenylmethanol, by redox titration following the time evolution of the OCP of palladium which was previously charged with hydrogen at −0.5 V as shown in Fig. 1 for different concentrations of the reactive organic molecules.

Initially the OCP exhibits fairly constant values close to that observed in the absence of the organic scavenger and is given by the Pd/H_{ads} equilibrium. Then, a sharp shift to positive OCP potentials is observed as adsorbed hydrogen is progressively consumed by the reaction and reaches a final constant value set by other reactions.

The potential-time S-shaped curves show a characteristic mid-point time, τ, which decreases upon increasing the organic molecule concentration and therefore 1/τ is a measure of the reaction rate. By inspection of the τ values in Fig. 1, we conclude that the ketones react faster with the electrochemically generated hydrogen than the secondary alcohols which are the hydrogenation intermediate products (see the scales in Fig. 1A-B and C-D). Comparison of Fig. 1A-C and B-D show that the hydrogenation kinetics is more sensitive to the concentration of the organic molecule for the acetophenone and 1-phenylethanol than for benzophenone and diphenylmethanol. Furthermore, the molecules with two aromatic rings react with H_{ads} at a lower rate than those with a single phenyl ring at α position. This may be due to steric effects or more probably to the different surface mobility of the target organic molecules, Pd(Y = Z)$_{ads}$, to react with PdH$_{ads}$. The lower the mobility, the less frequent are the encounters between Pd(Y = Z)$_{ads}$ and PdH$_{ads}$, and, therefore, the higher is the probability of the competing process conversion of PdH$_{ads}$ into H$_2$: thermal desorption (Eq. (3)) under OCP conditions and thermal desorption (Eq. (3)) and electrochemical reduction (Eq. (2)) under

potentiostatic electrolysis conditions. On the other hand, the adsorption must not be too weak, otherwise the amount of Pd (Y = Z)$_{ads}$ would be too low to ensure efficient and frequent surface bimolecular collisions between Pd(Y = Z)$_{ads}$ and PdH$_{ads}$.

The open circuit potential of −0.20 V observed in the present study is close to the value reported for Pd(H)/H$^+$ in 0.5 M H$_2$SO$_4$ [12]. When one half of the surface hydrogen has been consumed, the Nernst equation predicts a half-wave potential equal to −0.16 V. This corresponds to the value reached for τ in Fig. 1 (dashed line), which we associate to the inverse of the observed kinetic constant, i.e. τ = 1/k$_{obs}$. We are interested in relative kinetics of the ECH reaction for different reactants, not in absolute values. Therefore, in excess of organic reactant, the OCP evolves as a titration curve, the midpoint of which corresponds to the consumption of half the adsorbed hydrogen. Therefore, we have taken this characteristic time as a reciprocal of an operational kinetic coefficient to assess the relative reaction rate. As we see in EIS experiments, the adsorbed organic molecules react with the PdH$_{ads}$ surface (R$_{ct}$ increases upon increasing the reagent concentration in solution). Fig. 2 shows the dependence of k$_{obs}$ = 1/τ as a function of the concentration of the organic molecules for both ketones and alcohols.

The shape of all curves in Fig. 2 suggests surface saturation at high reactant concentrations which would correspond to saturation of the adsorbed reactant. For the bimolecular reaction of adsorbed hydrogen atoms with the organic molecules, assuming Langmuir adsorption isotherm for the organic reagent in excess, the pseudo-first order reaction rate can be estimated from the half-life time:

$$k_{obs} = 1/\tau = k.\theta_H^2 \frac{K_L.C_{org}}{K_L.C_{org} + 1} \qquad (7)$$

where K_L is the Langmuir adsorption constant for the organic molecule, k is the hydrogenation reaction constant and θ_H is the initial surface concentration of H_{ads} under those conditions. This equation was directly derived from the kinetic law equation assuming that both adsorbed reactants react in a bimolecular reaction. From the best non-linear fit of the experimental data in Fig. 2 to Eq. (7) we obtain values for the pseudo-first order rate constant and the Langmuir adsorption constant as compiled in Table 1.
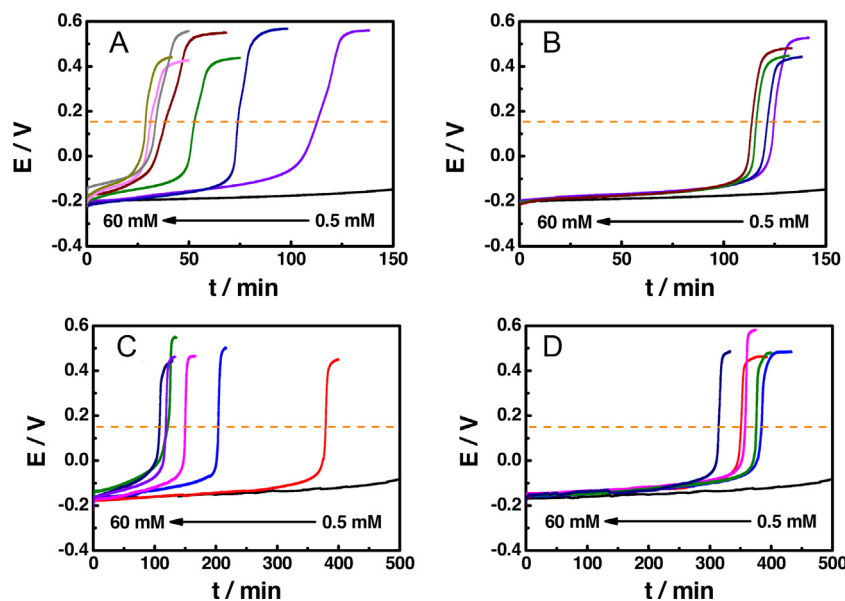

Fig. 1. Potential transients at open circuit (*I* = 0 A) of palladium charge with 1C electrode and increasing concentration of acetophenone (A), benzophenone (B), 1-phenylethanol (C) and diphenylmethanol (D). Concentrations: 0.5, 1, 5, 10, 20, 40 and 60 mM, and dashed lines represent the half-wave potential of the H+/Pd(H) system.
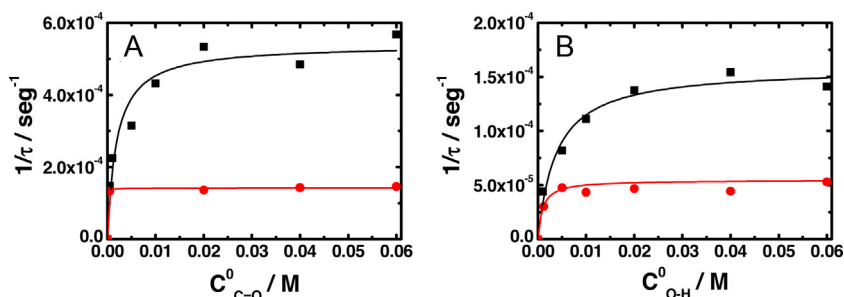
Fig. 2. Reaction rates at half-life potential (−0.15 V) as function of concentration for acetofenone (Squares in A), benzophenone (Circles in A), 1-phenylethanol (Squares in B) and diphenylmethanol (Circles in B). Continuous line depicts best fitting curves for each reagents of Eq. (6).

Note that for the benzophenone/diphenylmethanol systems, saturation is observed at a lower reactant concentration than for the acetophenone/1-phenylethanol system, implying a stronger adsorption of the former molecules. The hydrogenation rate at saturation concentration is larger for acetophenone than for benzophenone, therefore the stronger adsorption would result in a lower hydrogenation rate probably due to a lower mobility of the organic reagent on the catalysts surface and the steric hindrance of an additional phenyl ring. at α position. The less frequent are the encounters between H_{ads} and the adsorbed organic substrate, the higher is the production of H_2 (g), the lower are the reaction and current efficiencies. Pletcher et al. [29] reported slower electron transfer kinetics in hexanophenone as compared to acetophenone.

Furthermore, the ketones exhibit higher reaction rates compared to their corresponding alcoholic derivatives 1-phenylethanol and diphenylmethanol. According to the mechanism proposed in the literature [16,30], the hydrogenation of carbonyl compounds is faster than that of their respective alcohols. In the present study, we indeed found that the hydrogenation of 1-phenylethanol and diphenylmethanol is slower than that of the respective ketones (see product distribution and efficiency below).

3.2. Electrochemical impedance spectroscopy

The H^+/H_{ads} electrochemical reaction was studied by electrochemical impedance spectroscopy (EIS) at constant potential, c.a. −0.1 V, at the onset of the hydrogen evolution reaction. Fig. 3 depicts the Nyquist plots, Z'' vs. Z', for different concentrations of acetophenone, benzophenone, 1-phenylethanol and diphenylmethanol, respectively. Additionally, in Fig. 4 we show the Nyquist plots for the end products ethylbenzene and diphenylmethane which cannot undergo further hydrogenation.

The imaginary-real impedance plots in Figs. 3 and 4 have been fitted with the EIS equivalent circuit proposed by Birry and Lasia [22] for hydrogen sorption into Pd in the presence of crystal violet. The model used to describe the adsorption, absorption and hydrogen evolution reactions is presented in Fig. 5. The circuit is comprised of the charge transfer resistance, R_{ct}, in series with the next subsystem: parallel connection of (i) the hydrogen evolution resistance, R_{ev}, (ii) pseudo-capacitance of adsorbed hydrogen, C_{Hads}, and (iii) a series connection of the hydrogen absorption resistance, R_{ab}, and finite length Warburg impedance, Z_W. However the relevant parameters to consider in the present study are are R_{ct}, for the H^+/H_{ads} electrochemical reaction and the double layer capacitance represented by an almost capacitive constant phase element (CPE), with $\gamma = 0.95$–0.96. Both parameters depend on the concentration of organic molecules as can be seen in Fig. 6.

While the R_{ct} values increase in all cases upon increasing the soluble organic compound concentration and reaches a plateau, the double layer capacity decreases and levels off. This can be interpreted by a competitive adsorption of hydrogen at the palladium surface blocked by the organic molecules. This poisoning effect becomes more pronounced at higher surface concentration of the organic reactant. Notice in these Figures that the final reaction products that cannot undergo further hydrogenation also block the surface, i.e. increase of R_{ct} and decreace of C_{dl} at higher concentrations. This behavior is consistent with the dependence of the hydrogenation rates on the concentration of organic species obtained from titration experiments.

The exponential parameter of the CPE related frequency dispersion was found close to unity, i.e. 0,98–0,99, therefore the C_{dl} can be approximated to CPE values. Besides, the coverage of individual organic molecule can be estimated from C_{dl} values by assuming Parsons' approximation [31] and from the corresponding adsorption isotherms shown in Fig. 1 SI. It is worth mentioning that the ketones and alcohols reach surface saturation at lower concentrations than the organic alkanes. Also, the presence of phenylaryl and diphenyl-compounds seems to inhibit the electrogeneration of H_{ads} and establishes Volmer–Heyrovsky mechanism [7] for HER at higher concentrations than 1 mM as it is depicted in Fig. 2 SI at high surface coverage. These results are analogous to the poisoning effect of inorganic cations [32] (i.e. Cu^{2+} or Pb^{2+}) and organic coatings [33].

3.3. Electrolysis at constant potential

Continuous electrolysis at constant potential, c.a. −0.5 V under high H_{ads} coverage was performed in order to study the

Table 1
Comparison of reaction rates, determination of Langmuir constant and quantification of reaction mixture plus their faradaic yield for electrocatalytic hydrogenation of phenylalkyl and diphenyl ketones and of the corresponding alcohols.

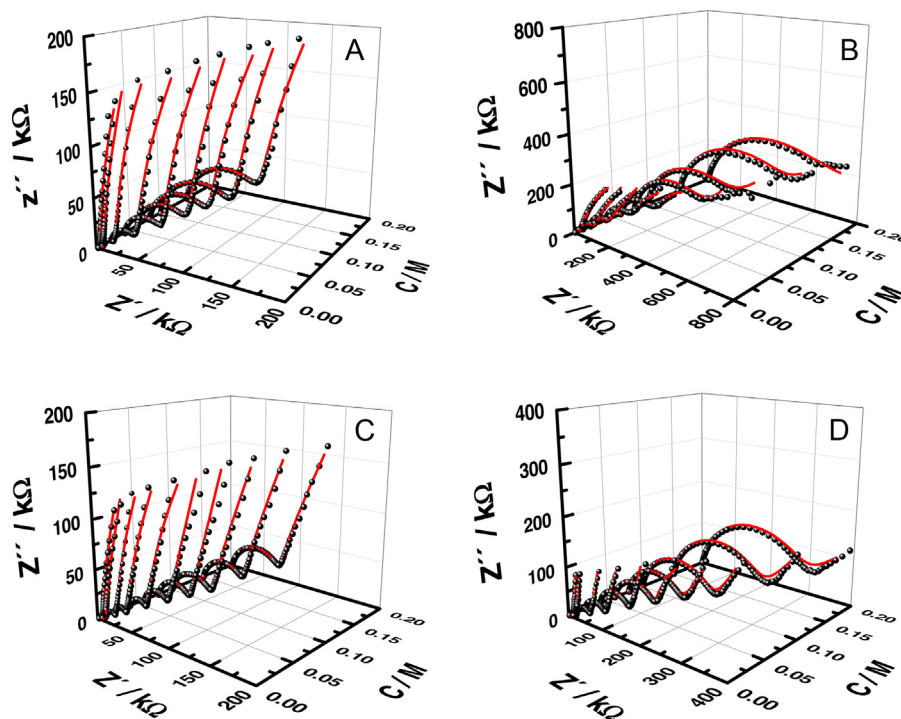| Reagents	Method	k_{Hyd} (−0,5 V) (sec^{-1})	K_L (M^{-1})	Starting Reagent %	2H product %	4H hydrogen %	FY %
Acetophenone	Titration	$5,4.10^{-4}$	524	–	–	–	
	Electrolysis	$1,6.10^{-4}$	–	9	76	15	30
Benzophenone	Titration	$1,4.10^{-4}$	2934	–	––	–	
	Electrolysis	$5,1.10^{-5}$	–	22	61	17	26
1-phenyl ethanol	Titration	$1,6.10^{-4}$	263	–	–	–	
	Electrolysis	$7,8.10^{-5}$	–	27	73	–	9
Diphenyl methanol	Titration	$5,0.10^{-5}$	1450	–	–	–	
	Electrolysis	$1,2.10^{-5}$	–	69	31	–	4

Fig. 3. Nyquist plots of palladium electrodes at −0.1 V in hydro alcoholic solution of 0.5 M sulfuric acid for different concentration of acetophenone (A), benzophenone (B), 1-phenyl etanol (C) and diphenil methanol (D) respectively and the best fit to equivalent circuit in Fig. 5.
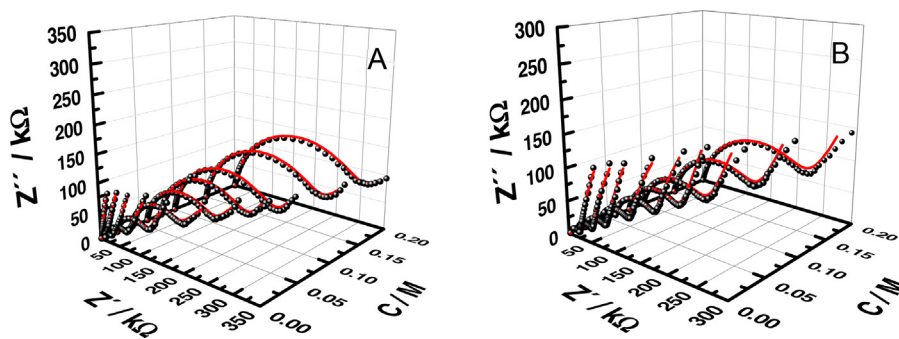

Fig. 4. Nyquist plots of palladium electrodes at −0.1 V in hydro alcoholic solution of 0.5 M sulfuric acid of ethylbencene (A) and diphenylmethane (B) with increasing concentrations and the best fit to equivalent circuit in Fig. 5.
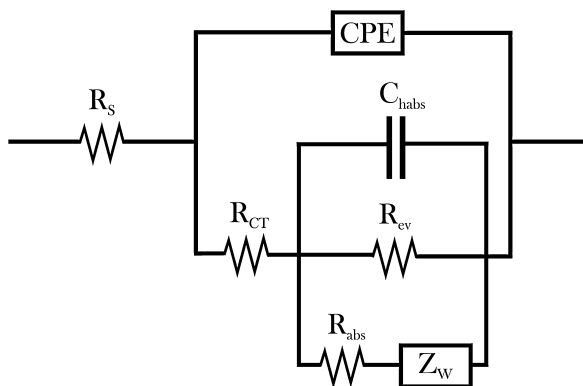

Fig. 5. An electrical equivalent circuit for hydrogen adsorption, absorption and evolution at palladium electrodes in acidic solutions.

distribution of reaction products, the reaction efficiency and the reaction kinetics. For the ketones, the electrolysis was stopped at 80–90% of the theoretical conversion. Due to the slower kinetics of the hydrogenation of the alcohols, the electrolysis was stopped at the same length of time as that of the hydrogenation of the corresponding ketones.

The time evolution of the reactants, intermediates and products concentrations is depicted in Fig. 7 for acetophenone/1-phenyl-ethanol in panels A, C and for benzophenone/diphenylmethanol in panels B, D.

It should be noticed that, while 90% of the acetophenone reacts with PdH$_{ads}$ in 5 hours, the same conversion for benzophenone required twice as much time (see time axis), in agreement with the titration results. The reactant decay can be described by:

$$C_{org} = C_{Org}^0 . e^{-k't} \tag{8}$$

where C_{Org}^0 is the initial concentration of organic molecule and k' is pseudo-first order rate constant in excess of adsorbed hydrogen atoms of each particular reagents. The best fit of the experimental
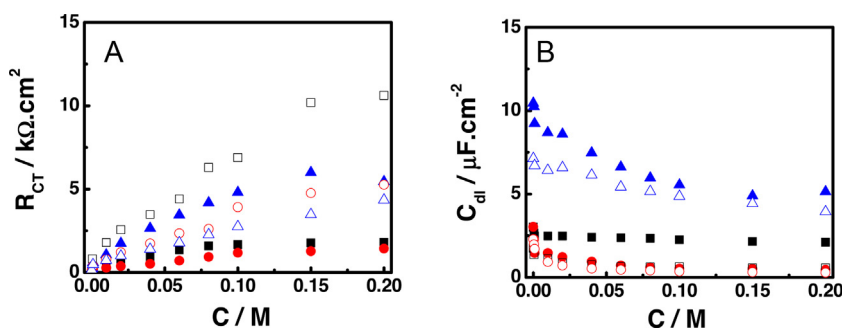
Fig. 6. A) Charge transfer resistance and B) double layer capacity obtained from equivalent circuit in Fig. 5 at high frequencies interval acetofenone (fill black squares), benzophenone (open black squares), 1-phenylethanol (fill red circles), diphenylmethanol (open red circles), ethylbencene (fill blue triangles) and diphenymethane (open blue triangles). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

data for all reactants and intermediates to Eq. (8) yield kinetic data also collected in Table 1.

In Fig. 7 we observe a buildup of a very small fraction of the final alkane product while there still is a growing trend in the intermediate compound concentration in solution, which can be taken as a parallel process. However, the evidence shown in the paper is that the intermediate alcohol can be hydrogenated under those conditions, therefore a sequential path is possible.

The yields of 1-phenylethanol and diphenylmethanol in panels A, B are always larger than those of ethylbenzene and diphenylmethane, which can be explained by the lower reactivity of the alcohols towards electrochemical hydrogenation as seen in panels C and D, the reactivity of diphenylmethanol being the lowest. The 1-phenylethanol and diphenylmethanol, resulting from the addition of two H, have a relatively weak C–O bond because they are benzylic alcohols (sigma bond conjugated with the phenyl ring(s) and this C–O bond is weak enough to be hydrogenolysed by ECH.

Table 1 summarizes the results of titration and electrolysis experiments for the rate of hydrogenation, the adsorption constant, product distribution and faradaic yield. "2H product %"

represent the amount of the product obtain by 2 electrons and 2 protons transfer while "4H product %" indicates the amount of the product produce by 4 electrons and 4 protons transfer. As it was previously anticipated by titration and electrolysis experiments, the hydrogenation rate for acetophenone and benzophenone are 3 times higher than that of 1-phenylethanol and diphenylmethanol, respectively. Polcaro et al. [34] have reported a reaction rate of $3,09.10^{-4}\,M\,s^{-1}$ for the reaction of acetophenone with adsorbed hydrogen, which is in good agreement with our results. It should be noticed that the hydrogenation rate values obtained by two different methods for a particular organic molecule are highly consistent and present the following trend: acetophenone > benzophenone > 1-phenylethanol > diphenylmethanol. Conversely, the surface association constants for the system benzophenone/diphenylmethanol extracted from Eq. (6) are 6 times higher than for the system acetophenone/1-phenylethanol, as described by electrode surface saturation below 5 mM concentrations. The product yields of acetophenone and benzophene hydrogenation reactions are 76% of 1-phenylethanol and 61% of diphenylmethanol, respectively, and a similar alkane proportion is observed for
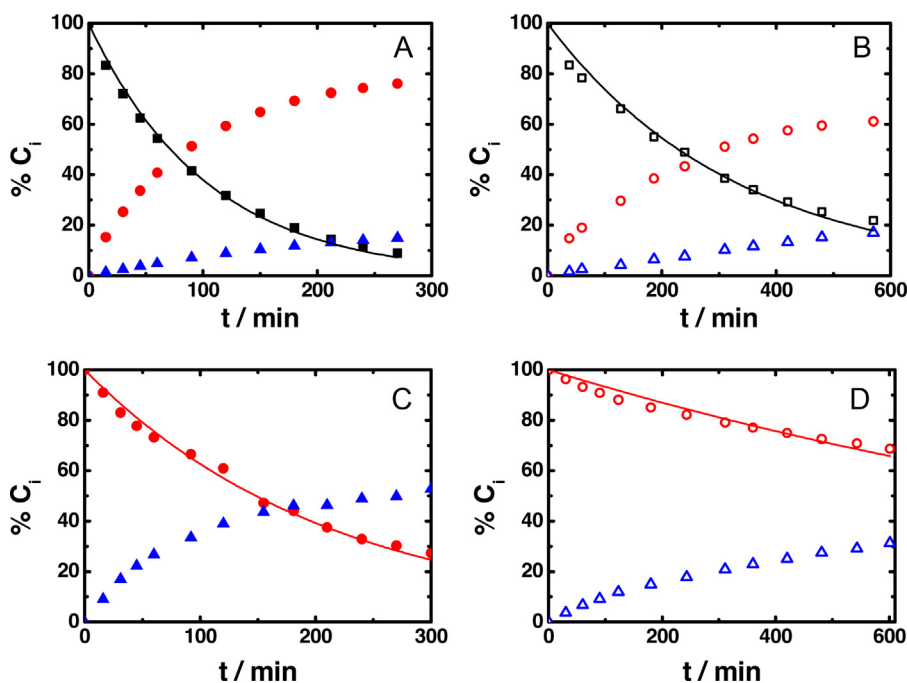

Fig. 7. Evolution of reagents and products proportion for electrocatalytic hydrogenation of acetophenone (A), benzophenone (B), 1-phenylethanol (C) and diphenylmethanol (D) as fuction of time at −0.5 V.Acetophenone: fill black squares; benzophenone: open black squares; 1-phenylethanol: fill red circles; diphenylmethanol: open red circles; ethylbencene: fill blue triangles; diphenylmethane: open blue triangles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

both ketones. When the reagent injected is the intermediate product, nearly 70% of the original 1-phenylethanol is converted to ethylbenzene along a similar time interval required by its carbonyl precursor. An analogous comparison between diphenylmethanol and diphenylmethane shows that the latter percentage drops down by proximately a 31%.

The intensity of the step potential was almost invariant (40–60 mA, see Fig. 3 in SI) along the interval of the experiment which suggests that it is a PdH$_{ads}$ mediated reaction. Also, the non-linear relation between alcohol/alkane concentration seems to suggest an ECH sequential mechanism (see Fig. 4 in SI).

4. Conclusions

A sequential pathway for acetophenone and benzophenone electrocatalytic hydrogenation via their corresponding alcohols as intermediate species was established from different experimental approaches: OCP potentiometry and bulk electrolysis. The kinetics expressions reflect the surface mobilities of adsorbed phenyl ketones and phenyl alcohols on the palladium substrate and their reactivity towards adsorbed hydrogen. It was shown that the ECH efficiency depends on the strength of adsorption of the organic substrate, which is modulated by the number of phenyl rings. Indeed, the ECH of benzophenone/diphenylmethanol with two phenyl rings is less efficient than that of acetophenone/1-phenyl-ethanol with only on phenyl ring because the formers are adsorbed more strongly and are less mobile on the surface, which results in a lesser probability of collision between H$_{ads}$ and the adsorbed organic substrate.

The computed values of the rate of hydrogenation are in agreement with the experimental yields and the distribution of products. The number of phenyl rings is the main factor influencing the efficiency and the selectivity of the ECH of aryl ketones.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.electacta.2015.02.113.

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