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ELECTROCATALYTIC HYDROGENATION OF DIETHYL FUMARATE. A SIMPLE SYSTEM DEVELOPMENT.

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Abstract: Diethyl fumarate was chosen as a model in search for better conditions to achieve selective electrocatalytic hydrogenation. In addition to carbon felt, several catalytic cathode surfaces have been examined, including Fe, Pt, Ni, Pb, Al, Cu, Zn, and stainless steel. Other variables like current density (58 to 285 mA.dm^{-2}), supporting electrolyte (NaCl, KBr, NaBr, NaI, NaF), solution pH* (3.0 to 9.0) and co-solvent (CH_3CN, t-BuOH, MeOH and THF) were tried. The majority of the reactions were carried out at constant current in an undivided cell fitted with the chosen working electrode and DSA® (RuO_2/TiO_2) as the auxiliary electrode, in H_2O/co-solvent (4:1). The best results for hydrogenation (84 % chemical yield) were obtained using Fe as cathode, a current density of 175 mA.dm^{-2}, in H_2O/CH_3CN (4:1) at pH* 5.5. NaBr and KBr are also useful electrolytes for hydrogenation. pH* variation does not seem to affect product ratio. THF as co-solvent and NaF as supporting electrolyte should be avoided, as well as carbon felt and Ni as electrodes. © 1999 Elsevier Science Ltd. All rights reserved.

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Introduction

Catalytic hydrogenation is one of the most widely used reactions in organic chemistry. Noble metals are generally used as heterogeneous catalysts in reduction of organics, including alkenes, ketones, nitro- and aromatic compounds.[1,2] Homogeneous catalysts like Rh and Ru complexes may be applied in enantioselective hydrogenation reactions.[1,2] The electrocatalytic process, in which hydrogen is generated *in situ*, is very attractive for industrial scale reductions, since the experimental conditions are simple, cathode materials are made of single metals as Fe, Ni, Zn or Cu and the supply of hydrogen gas is avoided. Fundamental features of water reduction over several cathode materials have been described.[3-5] Several electrocatalytic procedures involving the metals Pt, Pd and Ni, in deposits or in surface modifications, have been studied with the aim of performing efficient electrocatalytic hydrogenations, using several organic compounds as substrates.[6-11] Ni and Cu cathodes are of interest because of their low cost and the possibility of surface modifications such as Raney nickel or Devarda copper deposits, or simply deposits that allow an increase of the electrode surface area and consequent increase in hydrogenation efficiency.[12-14]

Polypyrrole modified electrodes containing Pt, Rh and Pd particles, or Rh and Ir complexes immobilized on film, have been described as alternative materials for hydrogenation studies. These studies use polypyrrole

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conductive properties and the H_2 generation ability of the immobilized metal particles or complexes to obtain stable composite electrodes. For instance, cyclohexenone was selectively hydrogenated to cyclohexanone with 100% current efficiency. The stability of the film permits turnovers in the order of 10^3.[15-18]

In general, the mechanism consists of generation of atomic hydrogen [$H^{\bullet}$] at the catalyst surface by electrochemical reduction of water:

$$H^{+}_{(aq)} + e^{-} \longrightarrow H^{\cdot}_{(ad)} \qquad (1)$$

$$H^{\cdot}_{(ad)} + H^{\cdot}_{(ad)} \longrightarrow H_2 \qquad (2)$$

$$H^{\cdot}_{(ad)} + H^{+}_{(aq)} + e^{-} \longrightarrow H_2 \qquad (3)$$

The retention of [$H^{\bullet}$] at the electrode surface is characteristic of each metal and depends on the adsorption energy (step 1), which is of fundamental importance since it regulates the catalytic hydrogenation mechanism. A secondary reaction is the formation of H_2 that suffers desorption from metal surface and is lost as a gas (steps 2 and 3), which can lead to low efficiency for the electrocatalytic system.[3,4,13]

α,β-Unsaturated diesters such as diethyl fumarate (DEF) and maleate (DEM), and other activated olefins[19] are easily reducible at water reduction potentials. The major competing reactions in this system is formation of H_2, olefin hydrogenation and/or reduction.[3,4,13] DEF and DEM afford diethyl succinate (DES). Electrohydrodimerization may occur following the same mechanism proposed for the reduction of acrylonitrile in protic media,[20-22] furnishing tetraester derivative (TET) (steps 4-6).

$$\mathrm{DEF} + e^{-} \longrightarrow \mathrm{DEF}^{\cdot-} \qquad (4)$$

$$2\,\mathrm{DEF}^{\cdot-} \xrightarrow{k_1} \mathrm{TET}^{2-} \qquad (5)$$

$$\mathrm{TET}^{2-} + 2\,H^{+} \longrightarrow \mathrm{TET} \qquad (6)$$

$$\mathrm{DEF}^{\cdot-} + H^{+} \xrightarrow{k_2} \mathrm{DEFH}^{\cdot} \qquad (7)$$

$$\mathrm{DEFH}^{\cdot} + e^{-} \longrightarrow \mathrm{DEFH}^{-} \qquad (8)$$

The electrochemical hydrogenation may occur if protonation (step 7) precedes step 5, followed by a second electron transfer (step 8). Studies performed with fumaronitrile showed that this mechanism is pH dependent.[3,23,24]

The purpose of this work is to find the best electrochemical reaction conditions to achieve selectivity toward hydrogenation of DEF, as a model, with emphasis in the generation of hydrogen [$H^{\bullet}$] adsorbed on the cathode surface, capable of reducing the substrate. In order to maximize hydrogenation, experimental parameters like electrode material, electrolyte, cell design, co-solvent and current density have been varied, and their effects on the product ratio analysed, mainly through GC.

Experimental Section

Diethyl fumarate and diethyl maleate were prepared as described in the literature.[25] Supporting electrolytes KBr, NaBr, NaCl, NaF and NaI were purchased from Aldrich. Co-solvents acetonitrile (Merck) methanol (Merck), tetrahydrofuran (Vetec), *tert*-butyl alcohol (Aldrich), all HPLC grade solvents, were used as received. Water was Mille-Q® grade. Hydrochloric acid and sodium hydroxide used for pH* variations were obtained from Merck.

The controlled current preparative electrolyses were carried out with a Princeton Applied Research (PAR) 173 or PAR 273A potentiostat/galvanostat, with a digital coulometer connected in series within the auxiliary circuit. An undivided cell with a 50 mL compartment was used. Initial experiments were also performed with a two-compartment glass H-cell (volume of each compartment 50 mL), with sintered glass as a separator. The counter electrode used in all the cases was a home built DSA® (dimensionally stable anode, type $Ti/Ru_{0,3}\ Ti_{0,7}O_2$). The potential of the working electrode was monitored by a reference electrode Ag/AgCl, NaCl 0.1 M, placed in parallel and separated from the solution by Vycor®. The working electrodes studied were: Ni and Pb, from Aldrich; Fe, Cu, Zn, Al, from Goodfellow; Pt/Ir (9:1) gauze, from Degussa, carbon felt RVC 2000 from Le Carbone Lorraine and stainless steel gauze ($Fe/Cr_{18}/Ni_{10}$) from Goodfellow. Electrodes were polished (except carbon felt and gauzes), immersed in glacial acetic acid for 1 hour and washed with water. Electrode areas were calculated from geometric surface. Values of pH* were measured at the begining and the end of electrolysis (pH* corresponds to apparent pH, since the medium is not entirely aqueous). After consumption of 4 $F.mol^{-1}$, the reaction products were extracted with 3 portions of ethyl ether and dried with anhydrous sodium sulfate. The organic solutions were evaporated under reduced pressure and the mass of the crude product determined. The product ratios and yields were obtained by gas liquid chromatography (GC), using Varian 3400 equipment, fitted with a 5 m capillary CP-SPL5CB Chrompack column using 50 to 250 °C temperature range (6 $°C.min^{-1}$) program. Peak integrals were recorded and determined with a Merck 2000 integrator. Products were identified by comparison of retention times with those of standard solutions using an internal standard. ^1H-NMR spectra were recorded on a Varian EC 360 (60 MHz) spectrometer using CCl_4 as solvent and tetramethylsilane (TMS) as internal standard. Mass spectra (electron impact) were obtained on a Finnigan ITD 800 spectrometer coupled to a Varian 3300 chromatograph with a SIL – 5 CP capillary column.

Results and Discussion

The electrocatalytic hydrogenation of DEF to diethyl succinate (DES) under different conditions using several metal electrodes was investigated. As described above, competitive dimerization can occur at the electrode surface. DEM was used in only one experiment to observe possible differences in the system.

The electrolyses were examined in divided and undivided cells. Due to a high ohmic drop in the divided cell, very high overpotentials were necessary to keep a desirable current density and the reduction occurred in a non-selective way. In an undivided cell, the solution resistance was better controlled and so it was used for all the experiments reported here. Table 1 summarizes the results obtained. Since the main goal of the work was reaction selectivity, with complete consumption of the substrate, a charge of 4 $F.mol^{-1}$ was used for all the experiments. When 2 F.mol^{-1} was used (data not included in Table 1) incomplete substrate conversion was observed.

Table 1: Conditions and Results from Electrolyses using Diethyl Fumarate (DEF).

Entry	Cathode Metal	Supporting Electrolyte	Co-Solvent	pH*	J mA.dm^{-2}	E *vs* Ag/AgCl in./ final (V)	Cell ΔE in./final (V)	Yields (%) DEF/DES/DEA
1	Fe	NaCl	CH_3CN	5.5	265	-1.58/ -1.92	2.86/ 3.01	3/ 74/ 9
2	Pt/Ir					-1.66 / -1.93	2.87/ 3.21	0/ 50/ 30
3	C/ felt					-1.16 / -1.51	2.48/ 2.69	1/ 30/ 51
4	Ni					-1.58/ -1.70	2.81/ 2.86	17/ 8/ 18
5	Pb					-1.54/ -2.02	2.66/ 3.16	0/ 52/ 34
6	Al					-1.31/ -1.41	2.47/ 2.51	0/ 44/ 28
7	Cu					-1.12/ -1.44	2.44/ 2.64	0/ 40/ 35
8	Zn					-1.38/ -1.75	2.51/ 2.95	0/ 53/ 14
9	S. Steel^a				175	-1.26/ -1.25	2.66/ 2.47	18/ 42/ 10
10	Fe^a					-1.21/ -1.54	2.41/ 2.71	3/ 84/ 5
11		KBr				-1.16 / -1.26	2.06/ 2.25	5/ 76/ 5
12		NaBr				-1.18 / -1.32	2.28/ 2.58	7/ 77/ 4
13		NaF				-1.19/ -1.27	3.05/ 2.88	4/ 36/ 20
14		NaI				-1.52/ -1.50	1.94/ 2.04	0/ 50/ 8
15		NaCl	MeOH			-1.10 / -1.06	2.50/ 2.76	0/ 65/ 0
16			t-BuOH			-1.24/ -1.30	2.90/ 2.96	9/ 61/ 12
17			THF			-0.96/ -0.60	0.84/ 0.75	88/ 0/ 0
18			CH_3CN	3.0		-1.49/ -1.59	2.63/ 2.94	0/ 67/ 7
19				4.0		-1.12/ -1.39	2.62/ 2.90	0/ 66/ 17
20				7.0		-1.35/ -1.91	2.54/ 3.09	0/ 68/ 4
21				9.0		-1.61/ -1.89	2.49/ 2.82	0/ 70/ 7
22				5.5	58	-1.07/ -1.50	1.98/ 2.46	0/ 67/ 7
23					285	-1.74/ -2.01	2.95/ 3.25	0/ 48/ 12
24^b					175	-1.62/ -1.87	2.69/ 2.83	8/ 70/ 0

Electrolysis conditions: 23.2 mM solution of substrate, H_2O/co-solvent (4/1, v/v), 0.1 M supporting electrolyte, room temperature, electrode geometric area: 0.113 dm^2 and (^{a}) 0.171 dm^2. Charge passed: 4 F.mol^{-1}. (^{b}) Reaction performed with DEM.

The first parameter to be varied was the electrode materials. Cathode metal effects were evidenced using controlled parameters: NaCl, pH* 5.5, current density of 265 mA.dm^{-2} and charge of 4 F.mol^{-1} (Table 1, entries 1 to 8). Electrode materials Pt, Pb, Al, Cu and Zn showed lower selectivities. With Ni electrode, a mixture of starting material, hydrogenated product and dimer in the lowest yields of the series were obtained (Table 1, entry 4). Carbon felt favored dimerization, due to known high hydrogen evolution overpotential (Table 1, entry 3). Stainless steel gauze was also tested (Table 1, entry 9). Low yields were observed, perhaps due to the presence of Ni (10%) and Cr (18%). The Fe electrode showed the best selectivity for hydrogenation (Table 1, entry 1), and it was the electrode of choice for the rest of the experiments. This selectivity may be improved with an increase of the surface area. H_2 evolution at Fe cathodes occurs at medium potentials, perhaps because of high adsorption energy of [H$^•$] at the metal surface.[4] This characteristic leads to the observed higher selectivity, i.e, adsorbed hydrogen remains at the metal surface at high potentials, preventing dimerization.

NaCl, NaBr, KBr, NaF and NaI were tested (Table 1, entries 10 to 14). DSA® anode, normally used as a catalyst in oxidation of halides,[4] may promote I_2, IOH, Br_2 and BrOH evolution, in the presence of NaBr or

NaI. With these two electrolytes, a low overpotential was required to obtain the current density of 175 $mA.dm^{-2}$. A drawback is related to the possible anodic oxidation of Br^- and I^-, when the reactions are carried out in an undivided cell. These species may attack olefins giving dihalogenated derivatives, halohydrins or epoxides, as described by Torii.[26] Good yields, however, were obtained in the present case (Table 1, entries 11 and 12). Bromine evolution is observed, but no addition to DEF occurs, possibly due to the olefin conjugation with electron-withdrawing groups which disfavors electrophilic addition.[26] The use of fluoride ion led to DES in low yield (Table 1, entry 13). Chloride anion was considered the best one since, at low concentrations, only small amounts are oxidized at the anode surface, simultaneously with water (Table 1, entry 10).

The solubilization of DEF or DEM in water requires a co-solvent. The minimum proportion was 20% (v/v). CH_3CN, t-BuOH, methanol and THF were tested (Table 1, entries 10, 15 to 17). No hydrogenation was observed using THF as co-solvent, probably due to preferential solvent reduction. DEF is recovered unchanged (88%) (Table 1, entry 17). CH_3CN gave better yields, is inert and is the co-solvent of choice (Table 1, entries 1-14, 18-24).

The pH* of the solutions was measured in the beginning and end of reactions, and for all cases, an expected pH* increase is observed due to hydrogen consumption. Some initial pH* variations were tested. High pH values should be avoided due to the possibility of ester hydrolysis and carboxylate formation. Oxidation of the carboxylates, by Kolbe reaction, gives hydrocarbons with low molecular weight, and product loss by evaporation during extraction process. Several experiments were carried out at different initial pH*s (3 to 9) and no relevant variations in product yields were observed (Table 1, entries 10, 18-21). An increase of proton activity would have favored electrochemical hydrogenation over dimerization and a change in product ratio might be expected, but was not observed.

Current density higher than the chosen value of 175 $mA.dm^{-2}$ led to a decrease in selectivity (Table 1, entries 1, 10, 22, 23). When very low current densities were used, the amount of product is also lowered. This fact has a direct relationship with extended reaction time and pH* increase, which can cause ester hydrolysis. The ideal reactional conditions were also used for DEM, (Table 1, entry 24). Lower DES yields was obtained due to lower DEM solubility. No dimerization was observed probably due to its higher reduction potential.[19]

Conclusion

A simple system was developed for hydrogenation of DEF that can be used for similar activated olefins. Metal electrode dependent competition between hydrogenation and dimerization occurs. Among cathode metals tested, iron showed the best selectivity for the hydrogenation reaction, and carbon felt for dimerization. The chosen reaction parameters that led to optimization of the hydrogenation products were supporting electrolyte (NaCl, 0,1 M), co-solvent (acetonitrile), current density (175 $mA.dm^{-2}$), pH* 5.5 and charge of 4 $F.mol^{-1}$. No dependence on the initial pH* was observed. The key reaction steps are related to adsorption and desorption of the species evolved at the electrode surface, leading to differences in product yields.

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