



ELECTROCHEMICAL REDUCTION OF BENZYL CHLORIDE ON SILVER, GRAPHITE AND SILVER/GRAPHITE POWDER MACROELECTRODES



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ABSTRACT

Benzyl chloride reduction was studied in a powder macroelectrode (PME) made of silver, graphite or silver/graphite mixtures (1:3, 1:1 and 3:1) in absence of solvent, or using a very low amount of DMF as solvent (PhCH₂Cl/DMF 3:1). A 0.1 mol L⁻¹ KCl aqueous solution was used as anolyte. A competitive hydrogenation and dimerization process was observed, affording the respective toluene and bibenzyl products. The well-known electrocatalytic effect of silver on reduction of the C–Cl bond was confirmed by a significant positive shift of the benzyl chloride reduction potential in comparison with pure graphite powder. The products distribution was analysed after linear sweep voltammetries at low scan rate (0.1 mV s⁻¹), indicating high yields of bibenzyl produced on Ag/graphite-PME. Pure graphite-PME was not selective towards dimer formation. The best results for bibenzyl production occurred at more positive potentials, in the presence of silver. A small amount of solvent (DMF) play an important role on the electrode surface desorption and diffusion of intermediary species.

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1. Introduction

Modern organic synthesis, and more especially organic electro-synthesis, aims to achieve simple, selective, efficient and clean processes, taking into account economic and environmental constraints. From this point of view, electrochemical processes use the electron, which does not need additional reactants, is cheap and easy to handle.

In the perspective to improve these processes and make them more eco-friendly, a large effort was put into the replacement of classical molecular solvents (N,N-dimethylformamide (DMF), N-methylpyrrolidone (NMP), propylene carbonate (PC), etc) by light alcohols [1], water [2,3] and ionic liquids [4], accepted as less toxic.

From a similar viewpoint, another approach we develop consists in the use of three-dimension (3D) electrodes. So we have settled on a cell with a powder electrode (as cathode) for electro-synthesis, using an aqueous anolyte, and applied it, for the first time, to the Reformatsky reaction [5]. The divided state of the powder confers a large material/substrate interface that allows the complete or near absence of solvent, while keeping high chemical and faradaic yields. This electrode is inspired by the

graphite paste electrode, usually used for the study of insoluble or slightly soluble compounds and will be named the powder macroelectrode (PME).

Electrochemical reduction of organic halides is an important topic that finds applications in electrosynthesis [6] and in the remediation of hazardous compounds [7–9]. The direct reduction of some organic halides presents high overvoltages restricting their use in electrosynthesis. To remedy this drawback, two main answers are put forward: an indirect reduction implying homogeneous catalysis by transition metal [10–12] or a reduction on cathodic materials such as silver based electrodes that presents a particular affinity towards organic halides and reduces this overvoltage [7,13–15] in comparison with other electrode materials, particularly in the case of benzyl halides [16,17]. It has been shown that the electrocatalytic effect of silver depends on several factors such as the type of halogen atom [13], the molecular structure [14], the solvent [18], the adsorption effect of the halide ion X⁻ [19] and the electrode surface morphology [17,20]. Elsewhere, the study of a silver micrometric powder in a cavity microelectrode (CμE) for CHCl₃ reduction showed a high electrocatalytic effect of the powder in comparison with electrodeposited films, indicating the presence of extremely active sites [21].

In a recent paper [22], we performed coupling reactions of benzyl halides in a PME on graphite powder and 2% silver electrochemically doped graphite in potentiostatic conditions

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without any addition of solvent in the cathodic powder. It was shown that yields of the reduction or coupling products (dimerization or carbonyl addition) depend on the nature of the halide, the potential and the presence or not of silver. In the case of benzyl chloride reduction, the higher yield of dimer obtained was only 64% on the silver doped material and the conversion of the reactant was not complete. The results suggest that both yield and conversion rate could be improved by increasing the percentage of silver in the cathodic powder. The effect of addition of solvent was not examined. Thus, the present work involves a voltammetric study of the benzyl chloride reduction on a PME, using silver/graphite powder mixtures in several proportions, in the presence and absence of solvent (DMF). It is compared to the voltammetric behavior of the silver powder towards benzyl reduction in a usual organic medium at a C μ E. Voltammetry characteristics and quantification of reaction products were examined in order, to determine the optimum material composition for obtaining the higher conversion rate and dimer yield with the PME and for understanding the role of the solvent.

2. Experimental conditions

2.1. Materials

Silver powder and silver oxide were purchased from Aldrich. The silver powder was stated to consist of grains between 2.0 and 3.5 μm . According to the manufacturer, graphite KS44 (from Lonza) consists of crystallites with minimum and maximum sizes, respectively, of 0.1 and 50 μm ; its specific area is 9 $\text{m}^2 \text{g}^{-1}$. Mixtures of silver/graphite in different mass proportions were prepared (x% silver + 100 – x% graphite with x = 25, 50 and 75%) and were mixed with a Heidolph vibrator during 15 min. DMF (SDS) and benzyl chloride (Aldrich) were used as received. Tetra-n-butyl ammonium tetrafluoroborate (Bu_4NBF_4) (Aldrich) was dried in an oven at 100 °C before experiments.

2.2. Electrode implementation

2.2.1. Powder macroelectrode (PME)

The PME (Fig. 1) was already described, and details about the cell can be found in the literature [5,22]. 0.15 g of the cathodic

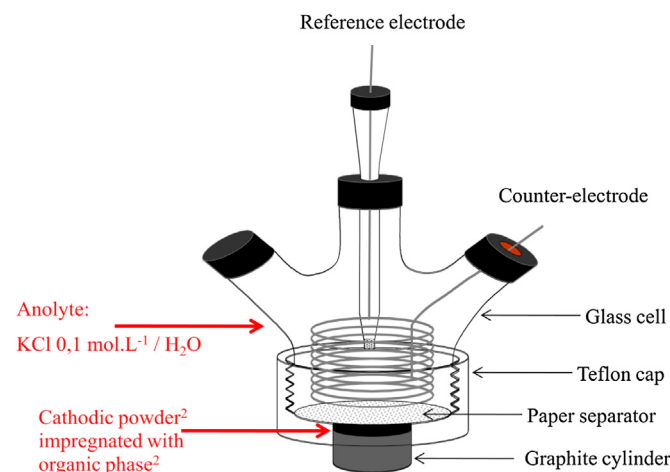


Fig. 1. Scheme of the Powder MicroElectrode (PME). ¹ the cathodic powder is graphite, silver or a graphite/silver mixture, ² the organic phase is either 60 μL of PhCH_2Cl , either 60 μL of PhCH_2Cl with 20 μL of DMF.

powder material (silver, graphite or silver-graphite mixtures in different proportions as described in Section 2.1) was put in a Teflon[®] cavity (13 mm diameter and 2 mm depth) the bottom of which is a graphite cylinder serving as current collector and pressed under a 3 Kg weight during 10 min. The pressed powder was then impregnated with a mixture of 60 μL of the reactant PhCH_2Cl (0.52 mmol) and 20 μL of DMF. A filter paper disk allows keeping the powder in the cavity. In voltammetric experiments with the PME, the curves are designated by the material composition (pure graphite: 100% G, pure silver: 100% Ag or Ag-PME; mixtures silver/graphite: 25% Ag + 75% G; 50% Ag + 50% G; 75% Ag + 25% G).

2.2.2. Cavity microelectrode (C μ E)

The C μ E was obtained by etching a planar platinum electrode with *aqua regia* according to a protocol already described [23,24]. The cavity is a cylinder of 50 μm diameter and 20 μm depth; the depth was determined with an optical microscope Olympus BX30. It was filled with the material to study using the electrode as a pestle. The C μ E filled with silver or silver oxide are respectively denoted Ag-C μ E and Ag_2O -C μ E.

2.3. Electrochemical studies

Voltammetries were performed with an Autolab PGSTAT 30 potentiostat, using two types of three-electrode cell:

- A classical glass cell for voltammetric measurements was equipped with a C μ E as working electrode, an Ag/AgCl electrode in KCl as reference, and a platinum wire as auxiliary electrode. The cell was filled with 15 mL of solvent (DMF) containing 0.1 mol L^{-1} tetra-n-butyl ammonium tetrafluoroborate (TBABF_4) as supporting electrolyte. Solutions of electroactive PhCH_2Cl at different concentrations were prepared by addition of a precise volume of pure reactant with a micropipette.
- A PME cavity cell was previously described [5,22]. A PME working electrode described in paragraph 2.2.1 was used as cathode. It was assembled with a glass cell filled with 15 mL of a 0.1 mol L^{-1} KCl aqueous solution as anolyte. The device was completed with a reference Ag/AgCl electrode in KCl and a counter electrode (platinum wire). The separator between anodic and cathodic compartment was the filter paper added for retaining the cathodic powder. In such an undivided device, the organic compounds are nevertheless kept trapped due to their immiscibility with the aqueous phase and the adsorbing properties of the cathodic materials. The anodic reactions are the oxidation of chloride ions and of water.

Voltammograms recorded with the PME were obtained at very low scan rate (0.1 mV s^{-1}) for limiting contributions of ohmic drop and double-layer capacitance, due to high surface electrode. After voltammetry, the not-consumed reagents and formed products contained in the cathodic powder material were quantified according to the following procedure: the aqueous phase was eliminated from the PME cavity cell and the device was dismantled. The cathode powder and the paper were transferred to a flask containing 1 mL of 6.0 mol L^{-1} HCl and 5 mL of dichloromethane. After stirring, the liquid was separated from the powder by filtration on filter paper. Products extracted by dichloromethane were identified and quantified by GC with a chromatograph Varian CP-3300 using internal reference (phenylbenzene, usually called diphenyl). Product characterization was confirmed with mass spectrometry (ThermoFisher) coupled to GC.

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