

Electrolyte free electro-organic synthesis: The cathodic dimerisation of 4-nitrobenzylbromide in a micro-gap flow cell

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Received 20 May 2005; accepted 15 June 2005

Available online 8 August 2005

Abstract

The electrochemical reduction of 4-nitrobenzylbromide is studied in *N,N*-dimethylformamide solution in the presence and in the absence of intentionally added supporting electrolyte. By conventional voltammetry it is shown that an ECE-type reaction occurs with formation of the dimer 4,4'-dinitrodibenzyl irrespective of the presence of supporting electrolyte. Next, a micro-gap flow cell is characterised and employed for the preparative electro-reduction in the absence of supporting electrolyte. Excellent yields of the dimer are obtained and explained based on a self-propagation mechanism.

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Keywords: Micro-flow cell; 4-Nitrobenzylbromide; Electro-reduction; Platinum

1. Introduction

Preparative electrochemistry can provide a clean and versatile method for the synthesis of organic compounds as the addition of electrons to or the removal of electrons from neutral organic substrates can be activated under relatively mild reaction conditions. As the electrons are not bound to a reagent, the pollution of the environment by spent reagents can be minimised. However, the common use of supporting electrolytes in electro-synthesis has been a problem in realizing such clean processes because the recovery of the supporting electrolyte may create problems and can be costly. Whilst solid polymer electrolyte membranes [1] have been developed for electrolyte-free electrolysis, an approach based on micro-fluidic systems could prove particularly attractive for electro-organic synthetic methods [2a]. Indeed industrial processes do already employ cells with relative

small interelectrode gap (~ 1 mm) [21] in order to minimise energy losses.

Recently, micro-gap flow cell devices have received significant research interest [2] because of the small anode–cathode gap, high electrode surface area to volume ratio, a uniform current distribution, and the continuous production of products. In the thin-gap flow cell geometry, working and counter electrodes can be placed facing each other and the inter-electrode gap is typically in the range of a few tens up to approximately 500 μm . This electrode geometry reduces the total value of the ohmic resistance of a cell by orders of magnitude compared to those observed in conventional cells. Therefore, it is possible to eliminate the need for supporting electrolyte depending on the residual intrinsic conductivity of the organic solvents. Electrode processes which by definition involve charge carrier formation and transport may be regarded as “self-supported” as long as the inter-electrode distance is similar to the diffusion layer thickness. The elimination of supporting electrolyte in turn reduces costs and in some cases simplifies the chemistry. This methodology also opens up the possibility to couple processes at anode

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and cathode to give new reaction pathways in “paired” organic electro-syntheses [2b]. The control of reaction conditions can be readily achieved via the reaction parameters potential, current density, and residence time.

Many types of thin-gap flow cells have been proposed for electro-organic synthesis including the segmented thin-gap flow cell [2c], multisectioned porous electrode flow-through cell [2f,2g,2i,2j], the coplanar interdigitated micro-band electrode cell [2k], and the miniaturized parallel channel electrochemical reactor [2d,2h]. However, all of these approaches have involved the use of supporting electrolytes or relatively low conversion without intentionally added supporting electrolyte [2d,2h]. Recently, Yoshida and coworkers [2a] reported a flow-through porous thin-gap electrode micro-reactor permitting operation without supporting electrolyte. The control of the applied potential in this reactor was however a problem due to the ohmic drop in the current flow direction which results in a natural tendency for current density to be concentrated in the portion of the porous electrode nearest the counter electrode [2g]. This non-uniformity in the current distribution can have a considerable impact on the process feasibility and performance. Marken and coworkers [2e] reported a micro-gap flow cell for the reduction of tetraethylethylenetetra-carboxylate also allowing operation without supporting electrolyte. Relatively low flow rates (1.9 $\mu\text{l}/\text{min}$) were necessary to obtain high yields of the product. Whilst the electro-synthesis approach in the absence of intentionally added supporting electrolyte has received only limited attention to date, its ability to deliver clean electro-organic syntheses is attractive in terms of green chemical methodology and timely in view of the recent surge in micro-reactor synthesis applications.

In the present study, the electrochemical reduction of 4-nitrobenzylbromide [3a,3b] is chosen to demonstrate the utility of the proposed methodology. This reaction is studied first by cyclic voltammetry in the presence and in the absence of intentionally added electrolyte and then at conventional and micro-gap flow cell electrodes. Electro-synthetic reactions under optimised conditions in *N,N*-dimethylformamide (DMF) in the absence of intentionally added supporting electrolyte are shown to give very high yields of the dimeric product, 4,4'-dinitrobenzyl. The reaction was carried out in a preparative micro-gap flow cell by simply pumping the starting material 4-nitrobenzylbromide dissolved in DMF through the cell and isolation of the product by solvent evaporation.

2. Experimental

The cyclic voltammetric (CV) experiments were carried out with an Autolab PGSTAT30 system (Eco Chemie, The Netherlands) in both a conventional

three-electrode cell and in micro-gap flow cells. In this work electrolyte (0.1 M *n*-Bu₄NBF₄) was added to assist in interpreting the voltammograms produced. For the conventional cell, either a Pt disc (diameter 0.5 mm) or a Pt micro-disc (diameter 0.025 mm) were used as the working electrode, a Pt wire and silver wire (both diameter 0.1 mm) were used as the counter and the reference electrode, respectively. In some experiments an Ag|AgCl (3 M KCl) electrode (Cypress Systems, USA) was used as the reference electrode and externally placed upstream near the inlet of the micro-gap flow cell. For the micro-gap flow cell, two equally sized Pt foils (squares of 5 mm width and length, 0.05 mm thickness) were used for the working and the counter electrodes. A Harvard PHD 2000 syringe pump was used to pump solution flow through the cell system at controlled flow rate. The diffusion coefficients in DMF (at $22 \pm 2^\circ\text{C}$) for ferrocene, 4-nitrobenzyl bromide and 4,4'-dinitrobenzyl were determined independently by steady state micro-electrode voltammetry at a 25 micrometer diameter Pt disc electrode [2e] (estimated error $\pm 5\%$) and by comparison with the literature value for ferrocene in DMF [4]. The diffusion coefficients were found to be $1.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for ferrocene, $1.0 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for 4-nitrobenzyl bromide, and $0.83 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for 4,4'-dinitrobenzyl.

The micro-gap flow cells were easy and convenient to build by simply clamping all components together with a suitable spacer. As shown in Fig. 1, the cell consisted of two glass plates (3 cm length, 2 cm width, 6 mm thickness) forming the bottom and top with two holes connecting PEEK tubes (i.d. 0.24 mm) which acted as the flow inlet and outlet. Two equally sized Pt foils (5 mm width and length, 50 μm thickness, Goodfellow Cambridge Limited, purity 99.99%) were used as working and counter electrodes and a PTFE spacer (BOHLENDER GmbH, Germany) with rectangular window (3 mm width and 19 mm length) generated the reaction flow cell. A small amount of silicone adhesive sealant (Ambersil Ltd., UK) was used for sealing the outside area around glass and the Pt foil to avoid leakage. PTFE spacers with thicknesses of 120 and 250 μm were employed. After assembly, the cell height was calibrated by flowing a solution of 1 mM ferrocene in 0.1 M NBu₄BF₄-DMF and analysing the limiting current I_{lim} with the expression $I_{\text{lim}} = 0.925nFc \left(\frac{DA}{h}\right)^{2/3} (V_f)^{1/3}$. In this expression, n is the number of electrons transferred per reacting molecule, D denotes the diffusion coefficient, A is the electrode area, V_f is the volume flow rate, and h is the cell half height. For the two spacers the inter-electrode distance was found to be $2h = 160 \mu\text{m}$ and $2h = 320 \mu\text{m}$.

The electrochemical reduction of 4-nitrobenzyl bromide was chosen to test the proposed micro-gap flow cell configuration in the presence and absence of supporting electrolyte. During typical reaction runs,

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