Electrolysis in the presence of ultrasound: cell geometries for the application of extreme rates of mass transfer in electrosynthesis

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Two types of sonoelectrochemical reactors for preparative synthetic work are suggested and characterized by their performance in the reversible one electron reduction of cobalticenium cations in acetonitrile solution. The dominant effect of ultrasound is to strongly agitate the liquid phase and the corresponding parameters (mass transport coefficients) for the transport at the electrode surface are reported. An upper limit for ultrasound induced mass transport at macroelectrodes an order of magnitude beyond that achieved in conventional electrolysis is described. Further, for a synthetic scale reaction, the reductive ring opening of the α,β-epoxyketone isophorone oxide to yield the corresponding β-hydroxyketone, an improved current efficiency (3 F for a direct two electron reduction) and a clean conversion (yields up to 80% isolated) are demonstrated. The extremely high rates of mass transport achieved in the presence of ultrasound considerably enhance the performance and current efficiency in electrosynthesis by selectively increasing the rates of the mass transport controlled processes.

Introduction

Preparative electrochemical methodology has been employed in organic chemistry for a long time.[1] In addition to the use in synthetic scale work electrochemistry offers powerful tools for the analytical dissection of redox processes[2] and the measurement of reaction rates. The use of ultrasound in electrochemistry, or 'sonoelectrochemistry', began with experiments by Moriguchi[3] as early as 1934. Although a few applications of sonoelectrochemistry in metal plating,[4] polymer deposition[5] and analytical electrochemistry[6–9] have been suggested and many fundamental aspects of sound and cavitation in electrochemical systems have been resolved[10–13] the widespread use of this technique still appears to be limited.

In synthetic organic electrochemistry a series of studies[14–20] and a comprehensive review[21] concerning the application and effects of power ultrasound have been published. Authors commonly employ ultrasonic cleaning baths in which the electrochemical cell may be immersed without further characterization and optimization. Matsuda *et al.*[17] employed an immersion horn system placed directly into a H-type electrolysis cell and Durant *et al.*[20] reported the use of the titanium horn tip itself as the working electrode. Several possible benefits have been identified. First, ultrasound very efficiently agitates liquids[6] and is therefore extremely helpful in electrolysis.[22] In fact, depending on the equipment and cell used, levels of mass transport can be achieved which compare only to those observed at ultramicroelectrodes under silent conditions. Second, cavitation induced by ultrasound[23] as well as shear forces can cause cleaning of electrode surfaces[24,25] or prevent precipitation processes. Further, ultrasound allows multiphase systems (liquid/liquid, liquid/solid or liquid/gas) to be efficiently homogenized[26] and examples for solid particles being fused into the electrode material[7] or electrolysed *in situ*[15] have been reported. Finally, new processes involving highly reactive intermediates generated in violent cavitation events in the solution phase are possible.[27]

In this study two types of sonoelectrochemical cells for synthetic work are suggested: a small scale cell (20–50 cm^3) and a preparative scale cell (200–500 cm^3) both of which use an immersion horn transducer as an efficient and reproducible source of high intensity ultrasound. The reduction of cobalticenium in acetonitrile is used to characterise these electrolysis cells. As an example of the analytical tool 'sonovoltammetry' and of a synthetic scale transformation the reductive ring opening of the α,β-epoxyketone isophorone oxide[28–30] is used in order to demonstrate the positive effects of ultrasound promoting the electrochemical process.

Experimental

Reagents and instrumentation

Cobalticenium hexafluorophosphate (Aldrich), NBu_4PF_6 (electrochemical grade, Fluka), isophorone oxide (Aldrich) and potassium *tert*-butoxide (Aldrich) were of the highest commercially available purity and were used as received. The solvent for electrochemical reactions was acetonitrile (dried and distilled, Fisons) which was additionally dried by passing through a column of alumina (neutral, Brockmann activity I, Aldrich) and degassed with Argon for at least 15 min prior to electrochemical experiments.

Voltammetric and bulk electrolysis experiments were carried out using an Oxford electrodes bipotentiostat or a PAR 173A potentiostat/galvanostat controlled by an Oxford Electrodes programmer and connected to a Lloyd P3 recorder. A VCX400 model sonic horn (Sonics and Materials, USA) was employed with an extended titanium tipped horn probe (diameter 13 mm) and operated at a frequency of 20 kHz. The ultrasound intensity was variable up to 65 $W\ cm^{-2}$ and determined calorimetrically.[31] The horn tip inserted in the electrochemical system was either controlled *via* a bipotentiostat[32] or electrically insulated by inserting a thin layer of Teflon (0.15 mm) and a Delrin ®

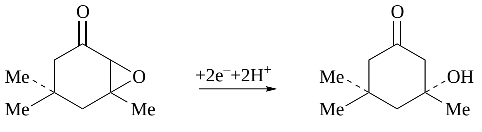
screw connection between horn and transducer unit. Analyses by GC/MS were carried out on a Trio-1000 (Fisons Instruments). Proton NMR spectra were recorded on a Bruker WH-300 spectrometer using [$^2H_3$]-acetonitrile as a solvent.

Electrodes

For voltammetric and sonovoltammetric experiments 3 mm diameter glassy carbon disc electrodes (BAS, Lafayette, USA) were used. For bulk electrolysis experiments a platinum gauze (52 mesh, Aldrich), a glassy carbon plate (type 1, Johnson Matthey, Hertfordshire) and a carbon cloth electrode (graphite tape, Johnson Matthey) were employed. Damage to the electrode material during treatment with high intensity ultrasound was insignificant for the very hard glassy carbon material and platinum. The carbon cloth electrode slowly released fragments of carbon fibres into the solution but retained its geometry and electrochemical activity. The distance between transducer horn tip and electrode has in all experiments been kept constant at 10 ± 2 mm. The reference electrode used was a Saturated Calomel Electrode (SCE) (Radiometer) which in acetonitrile/ 0.2 mol dm^{-3} NBu_4PF_6 allowed the reversible ferrocene redox couple to be detected at $E_{\frac{1}{2}}(Fc^+/Fc) = +388 \pm 3$ mV *vs.* SCE.

Electrolysis of isophorone oxide (1)

A solution of 0.2 mol dm^{-3} NBu_4PF_6 and 50 mmol dm^{-3} diethyl malonate in acetonitrile (250 cm^3) was placed in electrolysis cell 'B' equipped with a carbon cloth working electrode and a titanium wire counter electrode. After degassing, isophorone oxide (620 mg; 4 mmol) was added into the cathode compartment and electrolysed in the presence of ultrasound ($E_{app} = -2.45$ V *vs.* SCE, 30 W cm^{-2} ultrasound, charge passed 3 F). The progress of the reduction process was monitored by cyclic voltammetry using a 3 mm diameter glassy carbon disc electrode. After completion the solution volume was reduced *in vacuo* to give a white residue. Extraction with diethyl ether (4 × 50 cm^3), removal of the diethyl ether *in vacuo* and column chromatography following the procedure of Inokuchi *et al.*[29] afforded 3-hydroxy-3,5,5-trimethylcyclohexanone **2** in good yield (80%, 520 mg).



1 **2**

Scheme 1

Results and discussion

Introduction of a source of ultrasound into an electrochemical cell is achieved efficiently[13] by placing an immersion horn transducer probe into a conventional thermostatted electrolysis cell. Fig. 1 shows two suitable cells which have been used in this study. First the small volume cell 'A' (20–50 cm^3), of a type similar to a 'Rosette' reaction vessel,[33] immersed in a thermostatted bath was used. The horn probe is placed in the centre of this sonoelectrolysis cell and induces a very fast circulation of the liquid through the arms of the upper cell compartment. The counter electrode compartment is separated by a fine frit and equipped with a gas outlet. Second, in cell 'B' the immersion horn is surrounded by the counter electrode compartment and a stainless steel cooling coil connected to a thermostatted bath used to keep the temperature stable at 25 ± 2 °C. At the cell floor the exchangeable working electrode is located, which is usually a plate or gauze of *ca.* 50 mm diameter made of platinum, glassy carbon, a carbon cloth or a pool of mercury. A very similar cell has been employed previously[34] in the study of the voltammetry of electrochemical processes in the presence of ultrasound and therefore effectively the same cell may be used for analytical and bulk electrolysis purposes.

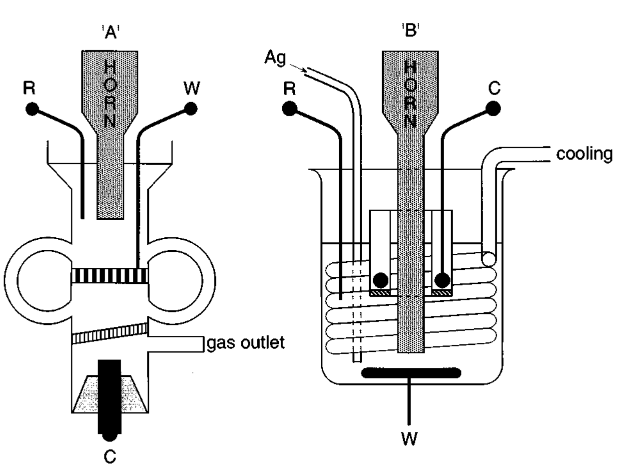


Fig. 1 Small volume cell 'A' and preparative cell 'B' for bulk electrolysis in the presence of high intensity ultrasound

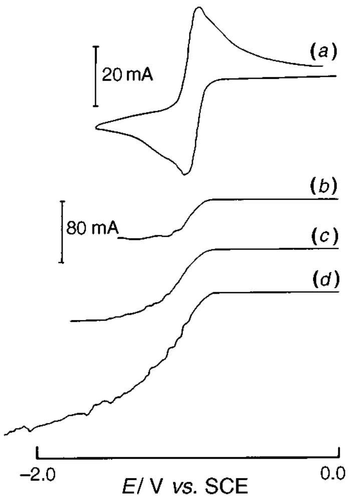


Fig. 2 Voltammograms for the reduction of 5 mmol dm^{-3} cobalticenium hexafluorophosphate at a 23.8 cm^2 area glassy carbon plate electrode in acetonitrile/0.1 mol dm^{-3} NBu_4PF_6 at 25 °C. (*a*) Cyclic voltammograms obtained with a scan rate of 100 mV s^{-1} under silent conditions. (*b*–*d*) Sonovoltammogram obtained with a scan rate of 100 mV s^{-1} using 20 kHz ultrasound of an intensity (*b*) 6, (*c*) 18, (*d*) 30 W cm^{-2}.

The properties of the sonoelectrolysis cells were characterized by using a model system: the reversible one electron reduction of cobalticenium in an acetonitrile solution [eqn. (1)].

$$Co(\eta^5\text{-}C_5H_5)_2^+ + e^- \rightleftharpoons Co(\eta^5\text{-}C_5H_5)_2 \qquad E_{\frac{1}{2}} = -935 \pm 3\ \text{mV}\ \textit{vs.}\ \text{SCE} \quad (1)$$

A reversible one electron reduction occurs[35] with a product, cobaltocene, which is chemically stable during the course of the experiment. In Fig. 2(*a*) a cyclic voltammogram obtained for the reduction of 5 mmol dm^{-3} cobalticenium cations at a glassy carbon electrode in cell 'B' is shown. Due to the high magnitude of the currents and the presence of solution resistance, IR compensation has to be applied to control the potential of the working electrode. In the presence of ultrasound a considerably enhanced current is observed and a sigmoidal shaped response results [Fig. 2(*b*)]. Analysis of this type of sonovoltammetric response is possible using eqn. (2) as described previously.[36]

$$I_{lim} = \frac{nFDAc}{\delta} \qquad (2)$$

In this equation the limiting current, I_{lim}, is related to the number of transferred electrons, n, the Faraday constant, F, the diffusion coefficient, D, the concentration, c, and the average

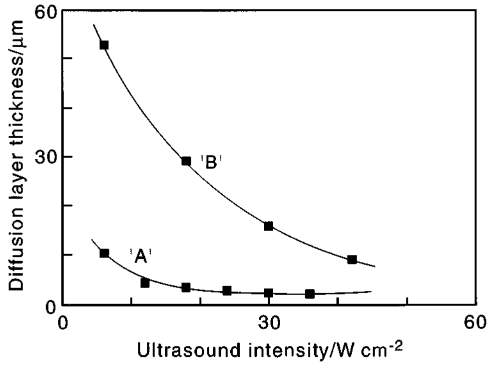


Fig. 3 Plot of the average diffusion layer thickness *versus* ultrasound intensity calculated from the limiting currents [eqn. (2)] observed for the reduction of cobalticenium cations in acetonitrile at various ultrasound intensities and in cells 'A' and 'B'

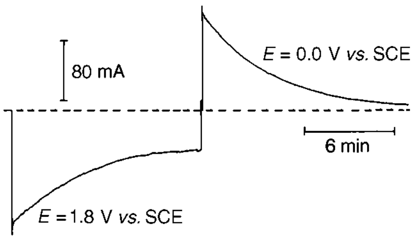


Fig. 4 Chronoamperogram observed for the reduction of 5 mmol dm^{-3} cobalticenium hexafluorophosphate at a 23.8 cm^2 area glassy carbon plate electrode at 25 °C when ultrasound with 30 W cm^{-2} intensity is applied

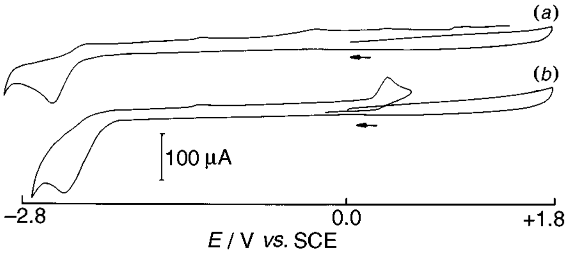


Fig. 5 Cyclic voltammograms obtained for the reduction of 2 mmol dm^{-3} isophorone oxide in acetonitrile/0.2 mol dm^{-3} NBu_4PF_6 at a 3 mm diameter glassy carbon electrode using a scan rate of 500 mV s^{-1} (*a*) in the absence and (*b*) in the presence of 20 mmol dm^{-3} diethyl malonate

Table 1 Electrochemical data[a] for the reduction of 2 mmol dm^{-3} isophorone oxide in acetonitrile/0.2 mol dm^{-3} NBu_4PF_6

E_p^{red}/V^b	$I_p^{red}/\mu A^b$	$\Delta E_p^{red}/mV^c$	$\ln(I_p^{red})/\ln(\nu)^d$
No diethyl malonate			
−2.54	100	150	0.26
With 20 mmol dm^{-3} diethyl malonate			
−2.44	155	150	0.42

[a] Conventional cyclic voltammograms recorded using a 3 mm diameter glassy carbon disc electrode at 25 °C. [b] Scan rate 500 mV s^{-1}. [c] Per decade change in scan rate. [d] For a diffusion controlled process a value of 0.5 is expected.

diffusion layer thickness, δ. The use of the diffusion layer thickness implies a simple physical model which has been justified by previous experimental observations.[37,38] Parameters such as the diffusion layer thickness as well as the concentration of reactants determine the pathway of the electrochemical process and should therefore be carefully controlled. By analysing the sonovoltammetric responses shown in Fig. 2(*b*)–(*d*) average diffusion layer thicknesses of between $\delta = 50$ and 15 µm at ultrasound intensity between 6 and 30 W cm^{-2} were calculated. The values at higher intensities are very low compared to those achievable by conventional stirring: typically 50–100 µm. Furthermore, in a plot shown in Fig. 3 the effect of the increase in ultrasonic power can be seen to improve the rate of transport yet further by thinning of the diffusion layer at higher intensities.

The small volume cell 'A' is equipped with a platinum gauze electrode which is located on glass indentations directly in front of the transducer horn tip. The surface area of this electrode, $A = 15.1\ cm^2$, was determined by measuring and comparing the capacitance of the Pt gauze electrode and a conventional 4 mm diameter Pt disc electrode. This experimental arrangement allows very low values for diffusion layer thicknesses to be achieved (Fig. 3) even at moderate ultrasound intensity. Due to the flow of liquid through the electrode in this cell a high degree of uniformity in the diffusion layer thickness and therefore in the current density is possible. It can be seen that a limit of the diffusion layer thinning at very high intensities with *ca.* 2 µm results. This effect has been attributed to a limit of agitation which can be achieved by ultrasound.[13] The higher the ultrasound intensity the more energy is dissipated in processes other than agitation.

For a bulk electrolysis experiments the current–time or chronoamperometric response for a simple transport limited *n*-electron transfer reaction follows a simple exponential law,[2] eqn. (3). The parameters $A = 23.8\ cm^2$, $D = 2.4 \times 10^{-9}\ m^2\ s^{-1}$[39]

$$I(t) = I(0) \exp\left(\frac{-nDAt}{\delta V}\right) \qquad (3)$$

and $\delta = 15$ µm for the reduction of a solution of cobalticenium cations in acetonitrile at a glassy carbon plate electrode in the cell 'B' are known as well as the total cell volume $V = 150\ cm^3$. The resulting time estimate for the conversion of half of the starting material, $t_{\frac{1}{2}} = 4.5$ min, is slightly higher than that observed in the electrolysis experiment, $t_{\frac{1}{2}} = 3.0$ min (Fig. 4, an additional current due to background processes causes an offset of the reduction current).

'Silent' voltammetry for the reduction of isophorone oxide

The reductive ring opening of α,β-epoxyketones is a synthetically useful transformation performed chemically by using reducing reagents such as chromous ions,[40] aluminium amalgam[41] or SmI_2.[42] The electrochemical reduction has been performed as a direct as well as an indirect or catalysed reaction. The first direct reduction by Shapiro *et al.*[28] was achieved at a mercury pool electrode using multifunctional steroid systems. An extended study based on the electrochemical ring opening of a steroid derivative was reported by Kamernitskii and coworkers.[43] The detailed voltammetric study of the reduction of three phenyl substituted α,β-epoxyketones by Bencharif *et al.*[44] examined the mechanism, side reactions and the effect of added acid. Finally, Inokuchi *et al.* published a series of papers[29,30] in which they employed direct and by selenium or tellurium compounds mediated electrochemical reduction procedures for a range of α,β-epoxyketones including isophorone oxide in different types of media using divided as well as undivided cells.

In this study isophorone oxide **1** (Scheme 1) was chosen as a model system which is electrochemically closely related to a wide range of α,β-epoxyketones. A voltammetric characterization of these compounds has hitherto not been described and is given first. Cyclic voltammograms obtained for the reduction of 2 mmol dm^{-3} isophorone oxide in acetonitrile/0.2 mol dm^{-3} NBu_4PF_6 at a 3 mm diameter glassy carbon electrode are shown in Fig. 5. Reduction occurs at $E_p = -2.54$ V *vs.* SCE as a chemically irreversible process [Fig. 5(*a*)]. On the reverse scan several small product signals were detected. Electrochemical data is summarized in Table 1 and—especially the observed change of the peak current with scan rate—suggests more complex kinetics. The addition of diethyl malonate as a source of protons changes the appearance of the voltammograms [Fig. 5(*b*)]

Table 2 Yields and conditions for the bulk electrochemical reduction of isophorone oxide under various conditions

	Solvent	Supporting electrolyte	Proton donor[a]	Charge passed	Yield[b]	Ref.
	Indirect[c]					
1	methanol	$NaClO_4$	DMM	3.5 F	86%	29
	Direct					
2	THF/H_2O (9:1)	NBu_4BF_4	DEM	6.3 F	65%	29
3	DMF	NEt_4OTs	DEM	7.0 F	63%	29
4	acetonitrile	NBu_4PF_6	DEM	3.0 F	80%	this work

[a] DEM = diethyl malonate, DMM = dimethyl malonate. [b] Yields after isolation of the product. [c] The redox mediator diphenyl diselenide was employed.

so that a chemically irreversible reduction at $E_p = -2.44$ V *vs.* SCE and one well defined chemically irreversible product response on the reverse scan at $E_p = +0.36$ V *vs.* SCE are detected. This chemically irreversible product response can be attributed to the oxidation of the diethyl malonate anion formed in the vicinity of the electrode surface after proton loss: addition of the strongly basic reagent $KOBu^t$ into a solution of 2 mmol dm^{-3} diethyl malonate in acetonitrile/0.2 mol dm^{-3} NBu_4PF_6 immediately causes an identical oxidation response to occur in cyclic voltammograms.

It is interesting to note that the product, β-hydroxyketone **2**, is sensitive to dehydration in the presence of acids and reagents such as $KOBu^t$. Upon reduction in the presence of diethyl malonate, however, no such side reaction occurred due to the buffer effect of diethyl malonate. In experiments in which substrates without β-substitution are reduced in the absence of a buffer system a base induced retro-aldol condensation has been observed instead.[44] More detail concerning the mechanism of the reduction of isophorone oxide in the presence of diethyl malonate was gained from rotating disc voltammetry studies at a 3 mm diameter glassy carbon electrode. The diffusion coefficient for isophorone oxide in acetonitrile at 25 °C as estimated by the empirical Wilke–Chang expression,[45] $D = 1.8 \times 10^{-9}$ m^2 s^{-1}, is in good agreement with the observed limiting current in the absence of diethyl malonate being associated with a one electron reduction process. Inokuchi *et al.*[29] determined the products of this process under bulk electrolysis conditions and a dimeric species as well as isophorone, the dehydration product of the β-hydroxyketone, were isolated. As a second limiting case in the presence of excess diethyl malonate the reduction follows an overall two electron mechanism consistent with the reduction mechanism which yields the β-hydroxyketone. The presence of sufficient amounts of diethyl malonate is therefore necessary both to act as a buffer environment and to prevent the formation of side products.

Sonovoltammetry and electrolysis of isophorone oxide

In order to analyse the voltammetric characteristics of the α,β-epoxyketone reduction at a glassy carbon electrode in the presence of ultrasound sonovoltammograms for a solution of 2 mmol dm^{-3} isophorone oxide in acetonitrile/0.2 mol dm^{-3} NBu_4PF_6 with varying amounts of diethyl malonate added were recorded. In Fig. 6(*b*) it can be seen that a very drawn out response for the reduction of isophorone oxide is obtained in the presence of ultrasound. The same is true for sonovoltammograms obtained after addition of diethyl malonate [Fig. 6(*c*,*d*)]. Under conditions of fast mass transport the process appears to proceed rather sluggishly and a defined limiting current was not observed. Therefore, it is not possible to directly compare the mechanistic features of the reduction processes in the presence and in the absence of ultrasound. Nevertheless, bulk electrolysis experiments under conditions of high mass transport can be carried out successfully. Recent studies of other types of electrode reactions[37,38] strongly support the assumption that under the conditions applied, mass transport effects dominate the electrode process. A very high rate of mass transport will increase the current efficiency as well as lowering the amount of electricity lost in the background process. It should be pointed out that in the case of the reduction of isophorone oxide in the presence of ultrasound an upper limit for the increase of the efficiency is reached because both the reduction of the substrate as well as the background process are not purely mass transport controlled.

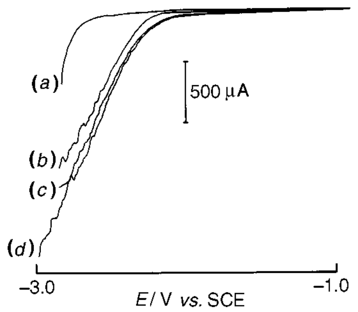


Fig. 6 Sonovoltammograms for the reduction of 2 mmol dm^{-3} isophorone oxide in acetonitrile/0.2 mol dm^{-3} NBu_4PF_6 obtained at a 3 mm diameter glassy carbon disc electrode (scan rate 100 mV s^{-1}, intensity 30 W cm^{-2}, $T = 25$ °C) in the presence of (*b*) 0, (*c*) 2, (*d*) 4 mmol dm^{-3} diethyl malonate [in (*a*) the solvent background is shown].

The electrolysis of a 20 mmol dm^{-3} solution of isophorone oxide in acetonitrile containing 0.2 mol dm^{-3} NBu_4PF_6 and 50 mmol dm^{-3} diethyl malonate at a carbon cloth electrode in the cell ‘B’ described above gave a clean and rapid conversion of isophorone oxide. A potential of −2.45 V *vs.* SCE was applied and by monitoring the reduction process voltammetrically the decrease in the peak current observed for isophorone oxide and the parallel increase of the peak current for the diethyl malonate anion were detected. A good yield of the β-hydroxyketone was achieved after passing a charge of 3 F mol^{-1}. In control experiments it was established that degradation of the starting materials due to side reactions in the presence of high intensity ultrasound were not observed. A comparison of results obtained by bulk electrolysis of isophorone oxide under various conditions is shown in Table 2.

Conclusions

A source of high intensity ultrasound such as an immersion horn probe is readily incorporated in an electrochemical cell and generates exceptionally high levels of mass transport comparable only to conditions achieved at ultramicroelectrodes. Therefore, one considerable advantage introduced by ultrasound is the gain achieved for mass transport controlled processes over background processes. Further, it is now possible to undertake bulk electrolysis experiments under conditions directly comparable to microelectrode voltammetry. For the special case of the reduction of isophorone oxide an improved yield and efficiency for the direct reduction has been demonstrated. In general, ultrasound should be regarded as a very useful tool in preparative electroorganic synthesis.

Acknowledgements

We wish to thank the EC for financial support (contract no. CHRX CT94 0475) under the Human Capital and Mobility Scheme.

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Paper 7/01004D
Received 11*th February* 1997
Accepted 16*th June* 1997