

Sonovoltammetric measurement of the rates of electrode processes with fast coupled homogeneous kinetics: making macroelectrodes behave like microelectrodes

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Voltammetric measurements of the rates of fast homogeneous chemical reactions coupled to heterogeneous electron transfer at macroelectrodes are demonstrated for two systems, the reductive dehalogenations of *ortho*-bromonitrobenzene and of 3-bromobenzophenone, by the use of power ultrasound to confer fast mass-transport properties so giving the electrodes the kinetic timescale of microelectrodes.

The exposure of electrode processes to power ultrasound^{1,2} leads to a variety of benefits including surface activation³ and the initiation of novel coupled chemical processes.⁴ However the dominant effect⁵ is the dramatic increase in the rates of mass transport to the electrode surface: the conventional cyclic voltammetric response is no longer characterized by current peaks but by sigmoidal shaped current–voltage responses.⁵

In acetonitrile† solution the effect of power ultrasound on mass transport has been quantified.⁶ The electrode diffusion layer, even for millimetre sized electrodes, is planar with a dimension, δ , approximately in the micrometre scale [eqn. (1)]:

$$I_{\text{lim}} = nFAD [\text{substrate}]/\delta \quad (1)$$

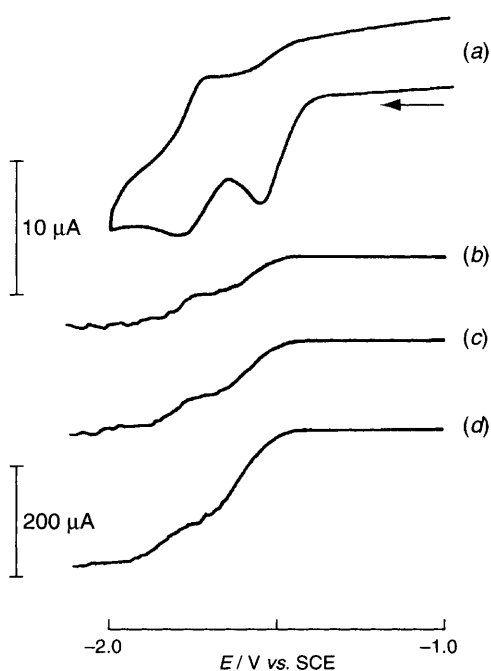
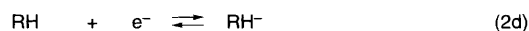
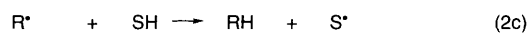
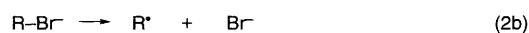
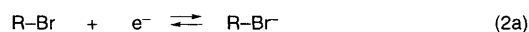


Fig. 1 (a) Cyclic voltammogram (scan rate 50 mV s^{−1}, $T = 25 \pm 2^\circ\text{C}$) for reduction of 0.5 mmol dm^{−3} 3-bromobenzophenone in dimethylformamide (0.1 mol dm^{−3} NBu₄ClO₄) at a 3 mm diameter glassy carbon disk electrode. (b)–(d) Sonovoltammograms obtained with 25 W cm^{−2} power (scan rate 50 mV s^{−1}) and (b) 27, (c) 15, (d) 8 mm horn-to-electrode distance.

where I_{lim} is the limiting current, F the Faraday constant, A the electrode area and $[\text{substrate}]$ the concentration of the substrate which undergoes an n -electron process at the electrode surface. Hitherto such a small average diffusion layer thickness has only been attainable under steady-state conditions by using microelectrodes, that is, electrodes with at least one surface dimension approaching the micron scale or less.

One enormous merit of microelectrodes which arises directly from their unusually huge rates of mass transport is their ability to probe the kinetics of fast homogeneous chemical processes coupled to heterogeneous electron-transfer events. For electrodes of conventional dimension (\approx mm) fast homogeneous reactions are masked by transport control and are therefore beyond the scope of voltammetric detection. In particular the use of microdisk electrodes, which has recently been reviewed,⁷ has successfully been shown to probe rapid kinetic data. Microdisk electrodes when operated under steady-state conditions can probe processes with first-order rate constants comparable to D/a^2 (a denotes the electrode radius). This implies that processes with first-order rate constants in the range 10²–10⁴ s^{−1} are accessible with radii of μm size. The purpose of this communication is to explore whether the use of power ultrasound in connection with macroelectrodes can also permit the inference of fast kinetics and associated mechanisms.

The electrochemical reduction of many halogenated organic compounds is followed by bond cleavage and loss of a halide anion.⁸ In the case of the reduction of *ortho*-bromonitrobenzene and 3-bromobenzophenone the overall process follows an ECE mechanism [eqn. (2)]:



After loss of the halide anion in a rate-determining reaction step (2b) the radical species R^\bullet undergoes H-atom transfer (probably from the supporting electrolyte) and the product RH is detected at the electrode by a second one-electron transfer step (2d).

A cyclic voltammogram† obtained for the reduction of 0.5 mmol dm^{−3} 3-bromobenzophenone in *N,N*-dimethylformamide at a 3 mm diameter glassy carbon electrode is compared to the corresponding sonovoltammogram in Fig. 1. The first chemically irreversible reduction process is followed by a second reduction process assigned to the reduction of benzophenone. Whereas peak-shaped responses are observed under silent conditions, sigmoidal-shaped voltammograms with much higher currents result in the presence of power ultrasound. The variation of the distance between electrode and the horn tip of the ultrasound transducer¹¹ allows the alteration of the diffusion layer thickness, δ , and so of the limiting current [eqn. (1)]. The

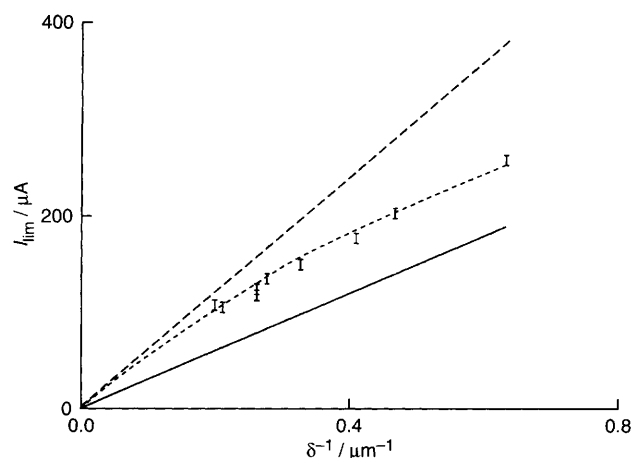


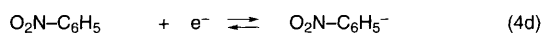
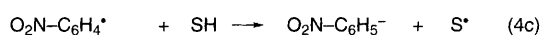
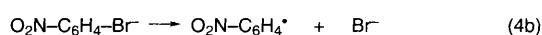
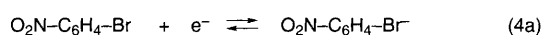
Fig. 2 Plot of sonovoltammetrically obtained limiting currents vs. the reciprocal diffusion layer thickness for reduction of 0.5 mmol dm⁻³ 3-bromobenzophenone in dimethylformamide at a 3 mm diameter glassy carbon disk electrode. The theoretically predicted curves for $k \rightarrow \infty$ (dashed line) and for $k = 6 \times 10^2$ s⁻¹ (dotted line) are also shown.

ratio of the limiting currents for the second- and the first-reduction process corresponds to the effective number of electrons transferred, n_{eff} , given for an ECE process by eqn. (3):¹²

$$n_{\text{eff}} = \frac{I_{\text{lim}}}{I_{\text{lim}}^0} = 2 - \frac{\tanh(\delta^2 k/D)^{0.5}}{(\delta^2 k/D)^{0.5}} \quad (3)$$

In Fig. 2 a plot of the measured limiting currents for the reduction of 3-bromobenzophenone vs. δ^{-1} together with the expected values [eqn. (3)] for $k = 600$ s⁻¹ (see Table 1) and for a simple two-electron process (dashed line) are shown. The corresponding rate constant reported in the literature,¹³ $k = 800 \pm 200$ s⁻¹, measured in dimethylformamide (0.1 mol dm⁻¹ NEt₄ClO₄) at 20 °C is in good agreement. We conclude that sonovoltammetry allows the determination of fast electrode processes at macroelectrodes placed in an ultrasonic sound-field.

The reduction of *ortho*-bromonitrobenzene in *N,N*-dimethylformamide is known to follow an ECE reaction scheme.¹⁴ [eqn. (4)].



The product after dehalogenation, nitrobenzene (O₂N-C₆H₅), is reduced at more positive potentials compared to the starting material and therefore the diffusion layer thickness with respect to the electrode-to-horn separation has to be calibrated. This was accomplished by monitoring the one-electron oxidation of ferrocene. The analysis of the obtained limiting currents yields data with $1 < n_{\text{eff}} < 2$ for diffusion-layer thicknesses ranging from 1 to 6 μm and the corresponding rate constant, $k = 200 \pm 50$ s⁻¹, also agrees closely with known literature values¹⁴ (Table 1).

Table 1 Sonovoltammetrically^a determined rate constants for reduction of 3-bromobenzophenone and *ortho*-bromonitrobenzene

	Diffusion coeff./ 10 ⁻⁹ m ² s ⁻¹	k_{exp} /s ⁻¹	k_{lit} /s ⁻¹
3-bromobenzophenone	0.92	600 ± 100	800 ± 200 ¹³
<i>ortho</i> -bromonitrobenzene	0.88	200 ± 50	250 ¹⁴

^a Measurements at 25 ± 2 °C of 0.5 mmol dm⁻³ solutions in dimethylformamide (0.1 mol dm⁻³ NBu₄ClO₄).

In the case of the sonovoltammetric reduction of 4-bromobenzophenone in dimethylformamide a very fast chemical step is involved and only a two-electron transfer could be detected. The known rate constant,⁸ $k = (8 \pm 2) \times 10^4$ s⁻¹, is considerably higher and exceeds the sonovoltammetrically accessible range of rate constants from 10 to 10⁴ s⁻¹.

The use of conventional electrodes to measure the rate of fast chemical reactions which are usually accessible only by microelectrode voltammetry is possible in the presence of power ultrasound.

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Footnotes

† This model may also be appropriate for solvents such as *N,N*-dimethylformamide, but could fail in other cases.

‡ The well characterised electrochemical cell used for voltammetric and sonovoltammetric experiments has been described⁹ previously. An Oxford Electrodes bipotentiostat with IR compensation (manually set to 90%) was employed to control the potential applied at the working electrode and at the ultrasound transducer (titanium tip).¹⁰ Electrodes (3 mm diameter glassy carbon, BAS, West Lafayette, IN) were polished using diamond lapping compound (Kemet, Kent, UK). Solutions were prepared from HPLC grade *N,N*-dimethylformamide and degassed with high purity argon prior to measurements. Low substrate concentrations (0.5 mmol dm⁻³) were used in order to prevent electrode blocking at high current densities.

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