Organic sonoelectrochemistry. Reduction of fluorescein in the presence of 20 kHz power ultrasound: an EC′ reaction

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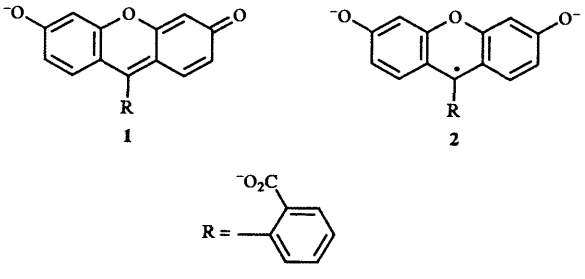
The electro-reduction of the dye fluorescein at mercury electrodes in basic aqueous solution is known to produce the stable semi-fluorescein radical. When the electrolysis is exposed to power ultrasound of intensity up to *ca.* 65 W cm^{-2} the radicals are shown to be re-oxidised by means of hydroxyl radicals formed through the sonochemical decomposition of the aqueous solvent. The electrode process adopts the mechanistic characteristics of a 'sono-EC" or 'sono-catalytic' reaction and this constitutes, to the author's knowledge, the first ever mechanistic assignment of this type.

Various workers have demonstrated beneficial results from exposing electrochemical reactions to the effects of power ultrasound. Specific areas of application include electroplating,[1,2] the deposition of polymer films[3,4] and electrosynthesis.[5,6] However whilst the value of ultrasound in these contexts is undisputed, prior work has been of an essentially applied and/or empirical nature. Our present work is aimed at appreciating the fundamental physical mechanisms by which ultrasound might modify electrode processes. Several possible mechanisms may be identified including the following, (*i*) the enhancement of mass transport to and from the electrode surface resulting from cavitation in solution,[7,8] (*ii*) the continuous activation of the electrode surface,[9] (*iii*) the formation of ions, radicals and other high energy intermediates during transient cavitation[10] and (*iv*) the ultrasonic mediation of chemical processes associated with heterogeneous electron transfer steps.[11]

Examples of these various possibilities have been addressed in previous papers.[7–11] In the present paper we seek to illustrate how hydroxyl radicals, OH•, formed during the insonation of aqueous solutions, can qualitatively change the nature of an electrode reaction mechanism from that observed under silent conditions. To this end we employ the thermostatted cell shown in Fig. 1, which has well characterised transport properties (*vide infra*) and in which an ultrasonic horn is immersed in the solution of interest at a known distance above the working electrode under investigation. This arrangement is used to investigate the influence of ultrasound on the electro-reduction of fluorescein **1** at mercury-plated solid electrodes. Under silent conditions this is known to undergo a one electron reduction in aqueous solution at pH *ca.*[12,13] forming the semi-fluorescein radical, **2**, which is stable on the voltammetric timescale.[12,13]



Background theory

In this section the mass transport characteristics of the sonoelectrochemical cell depicted in Fig. 1 are briefly reviewed. As reported elsewhere[10,11] substantially larger currents are

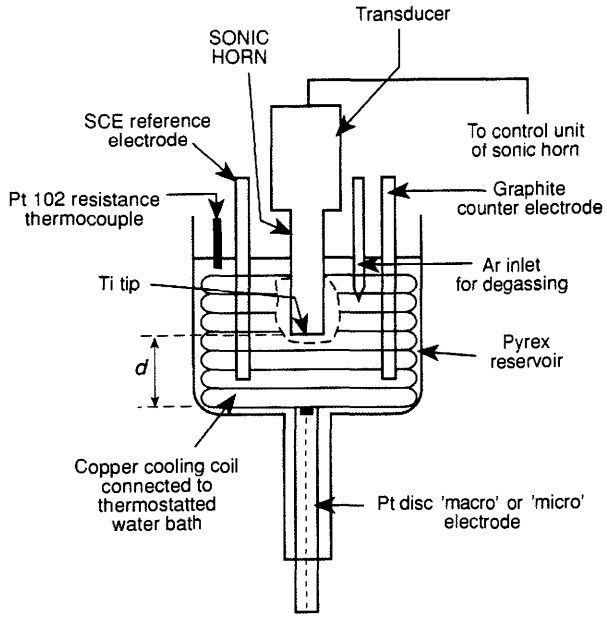


Fig. 1 Sono-electrochemical cell used for the voltammetric studies described

observed than in the absence of ultrasound and a clearly defined transport limited current, I_{lim}, is attained at sufficiently negative voltages (in the case of electro-reductions) implying that a steady flux of the electroactive species towards the electrode from bulk solution is promoted by the ultrasonically induced agitation of the solution. This effect has been discussed in detail elsewhere;[7,8,10,11] for the purposes of this work it suffices to note that mass transport to macroelectrodes insonated as shown in Fig. 1 is characterised by a thin diffusion layer immediately adjacent to the electrode of thickness, δ_d, so that I_{lim} is given by eqn. (1), where D is the diffusion coefficient of

$$I_{lim} = nFAD[X]_{bulk}/\delta_d \quad (1)$$

the electroactive molecule, n is the number of electrons transferred in the electrochemical process, F is the Faraday constant, A the electrode area and $[X]_{bulk}$ is the bulk concentration of the electroactive species, X. The average diffusion layer thickness was shown to depend on both the power of the ultrasound and on the electrode radius. δ_d was appreciably smaller for microelectrodes than for electrodes of

conventional dimensions,[8,10,11] although for both cases the diffusion layer thickness in the presence of ultrasound was significantly less than in the absence. Eqn. (1) was used to infer the thickness of the diffusion layer of macroelectrodes in the presence of ultrasound (20 kHz, 64 W cm^{-2}) for different sized unplated platinum electrodes using the cell shown in Fig. 1 with d = 32 mm and the reduction of the ferricyanide anion.[10] The results are summarised in Table 1.

Experimental

The sonic horn employed in this work was a VCX400 model supplied by Sonics and Materials (USA) and had titanium-tipped horn probes (of diameter 13 mm) which were extended by 127 mm and operated at 20 kHz. Power levels up to and including 55 W cm^{-2} were employed and calibrated calorimetrically according to the procedure of Margulis and Mal'tsev.[14] Thermostatting of the electrochemical cell was accomplished by means of a copper cooling coil inserted in the solution through which water was circulated from a constant temperature bath. By limitation of the sonication time to less than one minute this arrangement enabled the voltammetric measurements to be conducted at approximately constant temperature (to within 2 °C). A platinum resistance thermometer (RS Components Ltd, UK) was used to record the exact temperature (to within 0.5 °C) for each experimental run.

A microdisc of radius 60 μm was obtained from Bioanalytical Systems (West Lafayette, USA). Macroelectrodes of radii between 0.05 and 0.30 cm were mounted in an insulating teflon sheath. All electrodes were carefully polished before use using diamond lapping compounds (Kemet, Kent, UK) of decreasing size down to 0.25 μm. Mercury-plated platinum electrodes were prepared using the procedure reported previously.[8]

Voltammetric measurements were carried out using a Solartron 1286 electrochemical interface three-electrode potentiostat under computer control or an Oxford electrodes potentiostat. A carbon rod served as a counter-electrode and a saturated calomel reference electrode was located close to the working electrode surface as shown in Fig. 1.

Fluorescein and potassium ferricyanide were used as received from Aldrich and BDH, respectively. Aqueous solutions were made up using Elgastat (High Wycombe, Bucks) UHQ grade water of resistivity 18 MΩ. Sodium hydroxide (98%, BDH) served as the background electrolyte. Solutions were thoroughly purged of oxygen prior to electrolysis by outgassing with pre-purified argon.

The fluorescence experiments were conducted using a Perkin-Elmer Luminescence Spectrometer LS50.3.7.

Supporting theory was generated from programs written in FORTRAN 77 using double precision on a Sun IPC workstation.

Results and discussion

Experiments were conducted using mercury-plated macrodisc electrodes in conjunction with the cell shown in Fig. 1 to study solutions of **1** in aqueous 0.1 mol dm^{-3} NaOH. Fig. 2(*a*) shows a typical cyclic voltammogram recorded under silent conditions. The voltammetric response originates from a one electron reduction of **1** to the semi-fluorescein radical anion, **2**, as has been observed elsewhere under analogous conditions.[12,13,15] Using a 60 μm mercury-plated platinum microdisc electrode the half-wave potential for the reduction of **1** was found to be −1.19 V (*vs.* SCE) in good agreement with the literature value.[12] Mass transport corrected Tafel analysis showed the reduction to be electrochemically reversible (Tafel slope of 65 mV per decade) and a diffusion coefficient of 4.0 (±0.4) × 10^{-6} cm^2 s^{-1} was calculated from the steady-state microdisc current using eqn. (2), where r is the radius of the microdisc electrode.

$$I_{lim} = 4FD[X]_{bulk}r \quad (2)$$

Table 1 Variation in diffusion layer, δ_d, with electrode radius

Electrode radius/cm	δ_d/μm	Error/μm
0.05	4.2	±0.4
0.10	5.0	±0.5
0.21	6.0	±0.6
0.30	6.2	±0.6

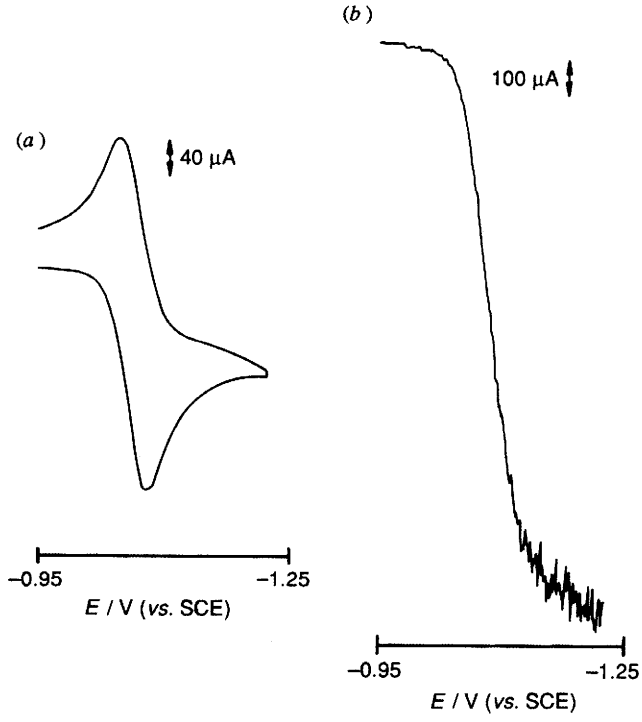


Fig. 2 Cyclic voltammograms for the reduction of **1** (1 mmol dm^{-3} in 0.1 mol dm^{-3} aqueous NaOH) at a mercury-plated platinum disc electrode (radius 0.30 cm) under (*a*) silent and (*b*) sonicated conditions using an ultrasound power of 64 (±7) W cm^{-2}. In each case the voltage scan rate used was 20 mV s^{-1}.

Next the reduction of **1** was examined in the presence of ultrasound (20 kHz, 64 W cm^{-2}) using the sonoelectrochemical cell shown in Fig. 1. Fig. 2(*b*) depicts a representative voltammogram; the 'peak-shaped' voltammogram of Fig. 2(*a*) is replaced by a sigmoidal-shaped wave indicative of a sustained rate of mass transport to the electrode surface. Additionally the limiting current in the presence of ultrasound was more than 10 times greater than the peak current seen in its absence. These observations are consistent with the thinning of the diffusion layer thickness, δ_d, as proposed above and elsewhere.[8–11] The mass transport limited current under sonication, I_{sono}, was then measured as a function of concentration of **1** in the range $0.5 < [\mathbf{1}]/\text{mmol dm}^{-3} < 5.0$, maintaining the ultrasound power at its previous value. It was found that I_{sono} scaled linearly with concentration in this range as shown in Fig. 3. This is consistent with the predictions of eqn. (1).

In order to determine whether any processes additional to the simple one-electron reduction of fluorescein were occurring the diffusion layer, δ_d, was quantified using independent measurements on the reduction of the ferricyanide anion as described above and summarised in Table 1. The values of I_{sono} observed for the reduction of **1** at the mercury-plated disc

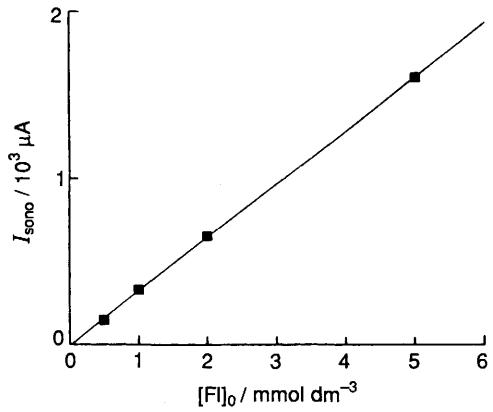


Fig. 3 Plot of I_{sono} *vs.* [**1**] recorded using mercury-plated platinum disc of radius 0.30 cm and a 20 kHz ultrasound power of 64 W cm^{-2}

electrodes were then compared with those calculated from eqn. (1) above, using a knowledge of the diffusion coefficient of **1** and the values from Table 1. It was seen that rather greater than one electron, but less than two electrons, were transferred on the reduction of **1** in the presence of ultrasound ($1 < n < 2$). The mechanistic origin of this extra current is considered next.

Various possible mechanisms can be proposed for the reduction of **1** in the presence of power ultrasound. First, we note that it is well established that sonolysis of water produces significant amounts of hydroxyl radicals, OH$^{\bullet}$, through cavitation and that this species can interact with and modify electrode processes.[10] The following catalytic (EC′) mechanism

$$H_2O \longrightarrow H^{\bullet} + OH^{\bullet}$$

may therefore be proposed in which **2** is oxidised by OH$^{\bullet}$ back to **1** which undergoes further heterogeneous electron transfer so producing the observed extra current. If the C′ step is assumed

$$\text{E} \qquad \mathbf{1} + e^- \rightleftharpoons \mathbf{2}$$

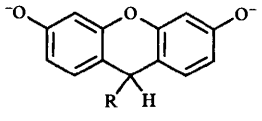
$$\text{C}' \qquad \mathbf{2} + OH^{\bullet} \longrightarrow \mathbf{1} + OH^-$$

to be pseudo-first order then the voltammetric data recorded in the presence of ultrasound may be analysed by means of eqn. (3),[16] where $k_{EC'}$ is the rate of the C′ step which is

$$I_{sono} = \frac{AFD[Fl]_0}{\delta_d}\left[\frac{1.65 + k_{EC'}\delta_d^2/D}{\sqrt{3.10 + k_{EC'}\delta_d^2/D}}\right] \qquad (3)$$

assumed to be irreversible and [Fl]$_0$ is the bulk concentration of fluorescein.

An alternative to the above EC′ mechanism would be a disproportionation mechanism in which the two electron reduction product leuco-fluorescein, **3**, is formed. Two



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possibilities are likely. The first is a DISP1 mechanism, where

$$\text{E} \qquad \mathbf{1} + e^- \rightleftharpoons \mathbf{2}$$

$$\text{C} \qquad \mathbf{2} + H^+ \longrightarrow SH^{\bullet +}$$

$$\text{DISP} \qquad SH^{\bullet +} + \mathbf{2} \longrightarrow \mathbf{3} + \mathbf{1}$$

$SH^{\bullet +}$ is protonated semi-fluorescein and the C step is rate limiting. The other possibility is a DISP2 mechanism analogous

$$\text{E} \qquad \mathbf{1} + e^- \rightleftharpoons \mathbf{2}$$

$$\text{DISP} \qquad \mathbf{2} + \mathbf{2} \longrightarrow \mathbf{1} + L^{2-}$$

$$\text{C} \qquad L^{2-} + H^+ \longrightarrow \mathbf{3}$$

to that observed under photolysis,[17] where L^{2-} is deprotonated leuco-fluorescein and the DISP step is rate limiting.

The DISP2 possibility may be ruled out immediately since I_{sono} was directly proportional to the concentration of **1** as was shown in Fig. 3. This would not be the case for a mechanism in which the additional current resulted from a kinetically second-order contribution. This leaves the DISP1 possibility as the only likely disproportionation-type mechanism for which I_{sono} is given by eqn. (4),[16] where k_{DISP1} is the rate of the C step in

$$I_{sono} = \frac{AFD[Fl]_0}{\delta_d}\left(2 - \frac{\tanh\,(\delta_d^2 k_{DISP1}/D)^{\frac{1}{2}}}{(\delta_d^2 k_{DISP1}/D)^{\frac{1}{2}}}\right) \qquad (4)$$

the DISP1 mechanism above. The above expression for I_{sono} assumes that any difference between ECE and DISP1 processes is too small to be experimentally visible as is recognised to be the case for most electrode types.[18,19]

In order to pursue the mechanistic analysis implicit in the previous paragraph quantitative experiments were conducted using a 2 mmol dm^{-3} aqueous/0.1 mol dm^{-3} NaOH solution of **1** using the cell design shown in Fig. 1 with $d = 32$ mm. Reductive voltammograms were recorded in the presence of ultrasound of power 64 W cm^{-2} as a function of electrode size using discs of radii 0.05, 0.10, 0.21 and 0.30 cm, respectively. The experimental values of I_{sono} were fitted against the electrode area using eqns. (3) and (4) with a least squares fitting procedure to optimise the rate constants, $k_{EC'}$ and k_{DISP1}. The result of this exercise is shown in Fig. 4 from which it can be seen that both models predict behaviour in respectable agreement with the measured experimental data. This exercise was repeated for different concentrations of **1** and the best fit rate constants are collected in Table 2. It can be seen that whereas the EC′ analysis gives rise to a set of rate constants close to a mean of $k_{EC'} = 20.5$ ($\pm$ 3) s^{-1}, and which show no systematic dependence of [**1**] for the DISP1 analysis, the analysis gives a set of values with $k_{DISP1} = 35$ ($\pm$ 13) s^{-1}. The DISP1 analysis has both a much greater variation about the mean and also shows some systematic dependence on [**1**] suggesting that the catalytic mechanism is possibly to be preferred.

The conclusion of the mechanistic analysis was tested by attempting an exhaustive sonoelectrolysis of the substrate, **1**, to see if the final product was regenerated **1**, which is highly fluorescent, or **3** which is colourless in aqueous solution.[15] Initially a small scale cell was set up which consisted of a small glass tube (of length 12 cm and diameter 2.4 cm) containing a mercury-plated platinum disc electrode of radius 0.30 cm, a platinum foil counter electrode (4 × 4 mm), a silver wire pseudo-reference electrode and a sonic horn. The latter was positioned *ca.* 5 mm from the disc surface and provision was made for degassing the electrolyte. A solution of volume 10 cm^3 containing 0.5 mmol dm^{-3} **1** was sonoelectrolysed using ultrasound of power 35 W cm^{-2} for *ca.* 1 h with an ice bath surrounding the cell to minimise heating. A period of 1 h was calculated, in the light of the observed currents, as being of sufficient time for a substantial conversion of **1** into **3** if a DISP1 mechanism were to operate. Fluorescence spectra recorded before and after sonication of the solution both showed emission peaks at 510 nm (as expected for **1**[15]), for an

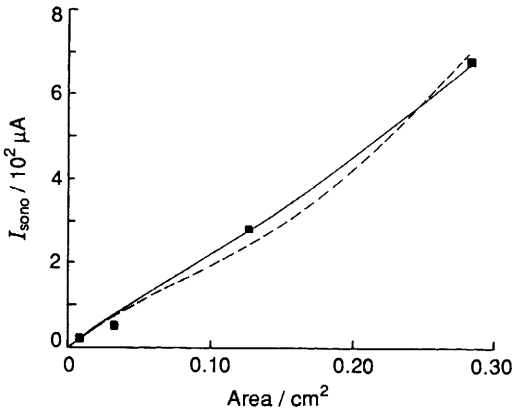

Fig. 4 Plot of I_{sono} *vs.* electrode area for the reduction of **1** (2 mmol dm^{-3} in aqueous 0.1 mol dm^{-3} NaOH). The solid squares represent experimental data points and the two lines are those generated from (*i*) eqn. (3) for an EC′ process with $k_{EC'} = 23$ s^{-1} and (*ii*) from eqn. (4) for a DISP1 process with $k_{disp1} = 34$ s^{-1}.

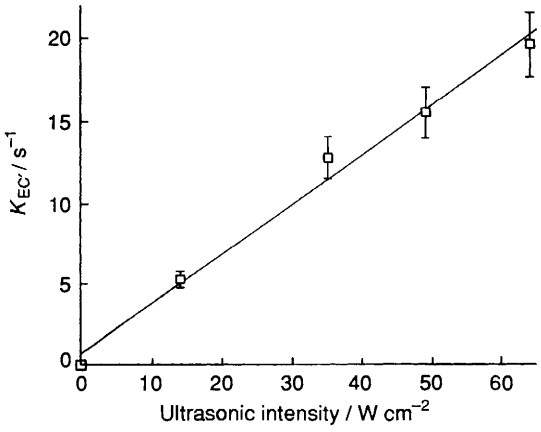

Fig. 5 Plot of $k_{EC'}$ *vs.* ultrasound power for the reduction of 2.0 mmol dm^{-3} fluorescein in aqueous 0.1 mol dm^{-3} NaOH as inferred from measurements made using mercury-plated platinum disc electrodes

Table 2 Variation in the rate constants $k_{EC'}$ and k_{DISP1} with fluorescein concentration

$[F1]_0$/mmol dm^{-3}	$k_{EC'}$/s^{-1}	k_{DISP1}/s^{-1}
0.50	17	48
1.00	23	33
2.00	23	34
5.00	19	23

excitation wavelength of 490 nm, but the fluorescence intensity of the pre- and post-sonicated solutions were identical (to within 10%). These results were reproduced using the standard sonoelectrochemical cell (see Fig. 1), with $d = 20$ mm, employing 100 cm^3 of a 0.5 mmol dm^{-3} solution of **1** in aqueous 0.1 mol dm^{-3} NaOH. Sonoelectrolysis was pursued for 4 h with cooling coil thermostatting being used to keep the cell temperature close to 20 °C. Fluorescence spectroscopy again suggested negligible net consumption of **1** and this was confirmed by the essential constancy of I_{sono} during the experiment. The results of the attempted exhaustive sonoelectrolyses thus support the mechanistic conclusion made above and suggest that an EC′ process is operative which regenerates **1** from **2**.

Last, experiments were conducted to study I_{sono} as a function of the ultrasound power level. Voltammograms were again recorded as a function of electrode size, fixing on a concentration of 2 mmol dm^{-3} for **1** dissolved in the same medium as above. Analysis was pursued in terms of the EC′ process inferred above and Fig. 5 shows the dependence of $k_{EC'}$ on the power. The excellent linear dependence seen may be taken as further confirmation of the veracity of the deduced mechanism.

In conclusion we have shown that the sonoelectrolysis of **1** proceeds *via* an EC′ mechanism in which the initial product of the reductive electrolysis (**2**) is re-oxidised to the parent material **1** by means of hydroxyl radicals formed by the sonochemical decomposition of the aqueous solvent. This example represents the first known case of a 'sono-EC" mechanism and complements assignments of 'sono-EC'[10] and 'sono-DISP' mechanisms[11] made elsewhere for other substrates.

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