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Cathodic Electrochemical Detection of Sonochemical Radical Products

Peter R. Birkin,*[†] John F. Power,[†] Timothy G. Leighton,[‡] and Aurore M. L. Vinçotte[†]

Department of Chemistry and Institute of Sound and Vibration Research, University of Southampton, Southampton, SO17 1BJ, U.K.

This paper reports on an electrochemical technique for the detection of oxidizing radical species, produced as the result of cavitation induced by ultrasound. A study of two example reactions is reported: the Weissler reaction and the Fricke reaction. In both cases, redox-active materials trap oxidative radicals. Electrochemical detection within a flow cell system is then used to sense redox-active products of the reactions between a chosen trapping agent and radicals produced within an ultrasonically irradiated aqueous solution. A demonstration of the sensitivity of electrochemical detection of radical products is presented. An equivalent dose of the ultrasonic reactor is reported.

The generation of transient and localized high temperatures and pressures within a liquid has been the basis of the phenomenon termed sonochemistry. Sonochemistry has its origin in the process known as cavitation. The exposure of a liquid to intense ultrasound under appropriate physical conditions can produce transient voids or bubbles.[1] These cavitation bubbles can collapse to produce extreme conditions within the liquid. Suslick et al. reported inferred temperatures and pressures of the order of 5000 K and 500 atm, respectively, as a result of cavitation bubble collapse.[2,3] These extreme conditions are thought to bring about breakdown of the solvent matrix, which populates the solution with radical species. Evidence for the creation of radicals has been gained from a variety of sources. Trapping experiments using either ESR detection or chemical trapping agents have successfully reported a variety of different target radicals present within a cavitating solution.[4−7] Indeed, it has been proposed[8] that the local concentration of radicals generated around a single cavitation event can reach the order of 4 mmol dm^{-3}. Similarly the buildup of radical byproducts, for example, hydrogen peroxide, within the bulk solution gives further evidence for radicals produced within a medium.[9,10] However, the detection of radical species using electrochemical detection methods has received limited attention. Compton et al. reported that direct electrochemical detection of radical species within a cavitation cloud produced by high-intensity ultrasound was possible.[11] In this technique, a stable radical species, generated through the reduction of fluorescein, was produced in the cavitation plume in front of an operating ultrasonic horn. The detection of a current increase in excess of that produced by mass transfer alone was taken to be evidence for the presence of radicals. In this respect, a *sono-EC′* mechanism was proposed. However, few other examples of direct electrochemical detection of radicals produced by cavitation can be found within the literature.

A new electrochemical method for the detection of radicals within a cavitating liquid is presented here for the first time. In this system, the solution is constantly pumped from an acoustically well-characterized chamber irradiated with ultrasound into a flow cell. Electrochemical detection of the products of reactions between radicals and suitable chemical traps is subsequently performed. This new method has several clear advantages when compared to direct detection of radicals within the liquid under irradiation with ultrasound. It is known that radical species themselves have relatively short lifetimes within solution and as such are difficult to sense directly with electrochemical techniques. Additionally, the chaotic nature of the bubbly fluid within a cavitation plume inhibits the detection of these radical species through many forms of spectroscopy. However, the addition of chemical species with the ability to react with radicals produced within the cavitating solution circumvents the short lifetime problem. The reaction, if facile, between the radicals produced from the cavitation process and the redox-active material, leaves within the solution a chemical memory of the presence of the radical. To electrochemically detect these reactions, an electroactive product, ideally with a redox state different from that initially in the solution, is required. This is relatively easy task to achieve as many traps for radicals involve a straight redox reaction between the radical and the trapping agent. As examples of this, the Fricke reaction and the Weissler reaction are among many different redox systems used to detect radicals.[8,12−14] In both cases, a redox change is initiated by the production of oxidizing radicals

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[†] Department of Chemistry.

[‡] Institute of Sound and Vibration Research.

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(thought to involve the generation of OH$^\bullet$). In the Weissler reaction, I_3^- ions are produced through the oxidation of iodide ions.[15] However, direct electrochemical detection of the products of these types of reaction (e.g., iodine in the form of I_3^- ions) has not, to the knowledge of the authors, been reported.

An additional complication to the electrochemical detection of radical species lies in the chaotic nature of the solution in the presence of cavitation. Each cavitation event produces efficient enhancement of mass transfer to an electrode.[15–17] This enhancement in mass transfer must be taken into account by calibrating at a particular electrode/ultrasonic source arrangement before conventional detection methods can be employed. This calibration process must be particularly accurate considering the low overall concentrations of radicals produced by cavitation bubble collapse. To circumvent this problem, a flow cell was employed here. This essentially removes a small quantity of material from the ultrasonic reactor and relatively rapidly pumps it into a flow cell where electrochemical detection, away from the chaotic cavitation process, can be performed. The solution is then pumped back into the ultrasonic reactor. This method does not change the volume and hence the acoustics of the ultrasonic reactor but enables electrochemical detection of trace species with relative ease. In addition, the symmetry of the cell is largely unperturbed by the presence of the sampling and return piping, an advantage when compared to the insertion of electrodes within conventional sonochemical experiments. The results of this study are now reported.

EXPERIMENTAL SECTION

Sonoelectrochemical Equipment. All electrochemical measurements were made using a three-electrode arrangement comprising a working electrode sealed in glass (a disk either 0.5-mm-diameter platinum for the Weissler reaction or a 3-mm-diameter glassy carbon disk for the Fricke reaction). A steel counter electrode and a homemade saturated calomel reference electrode (SCE) were also employed. Electrochemical measurements were made using an electrochemical workstation and recorded on a PC using an ADC card (Computer Boards CIO DAS08 PGL) programmed using in-house-written software. The flow cell was fabricated out of PMMA. The flow cell was kept in a Faraday cage to minimize electrical noise. The solution was pumped from the ultrasonic reactor through the flow cell and back to the reactor using a peristaltic pump (Pharmacia Fine Chemicals, P-1). Cavitation was generated within a thermostated glass cylindrical cell using a piezoelectric transducer (Morgan Matroc resonant frequency ~27 kHz). The electrical signal that drove the piezoelectric transducer was generated by a Thurlby Thandar TG1010 function generator and amplified by a Bruel & Kjear 2713 power amplifier. The voltage amplitude to the piezoelectric transducer was recorded on a Tektronix TDS 224 digital oscilloscope. The cell had an inner diameter of 5.8 cm and a height of 12 cm. The transducer was attached to the cell using slow-drying epoxy resin (Struers Epofix). The temperature of the solutions within the cell was fixed at 25 °C by thermostating the cell with a water jacket (see Figure 1). The frequency of the ultrasound employed was kept constant at a value reported in the appropriate figure legend. Figure 1 shows a schematic representation of the experimental rig employed. An Avantes UV 100-2 spectrometer with an Avantes mini D2 UV−visible−NIR light source was used to record UV−visible spectrums (Anglia Instruments). The piping for the flow cell (PTFE, ~50 cm, 1.6-mm outside diameter, 0.8-mm internal diameter) was positioned so that the inlet remained at the base of the sonochemical reactor for all experiments. The flow cell and piping had a volume of ~6 cm^3. The flow cell system was primed with the appropriate solution used in each experiment. This ensured that the volume within the reactor remained constant (100 cm^3) throughout the experiment as a closed-loop system was employed.

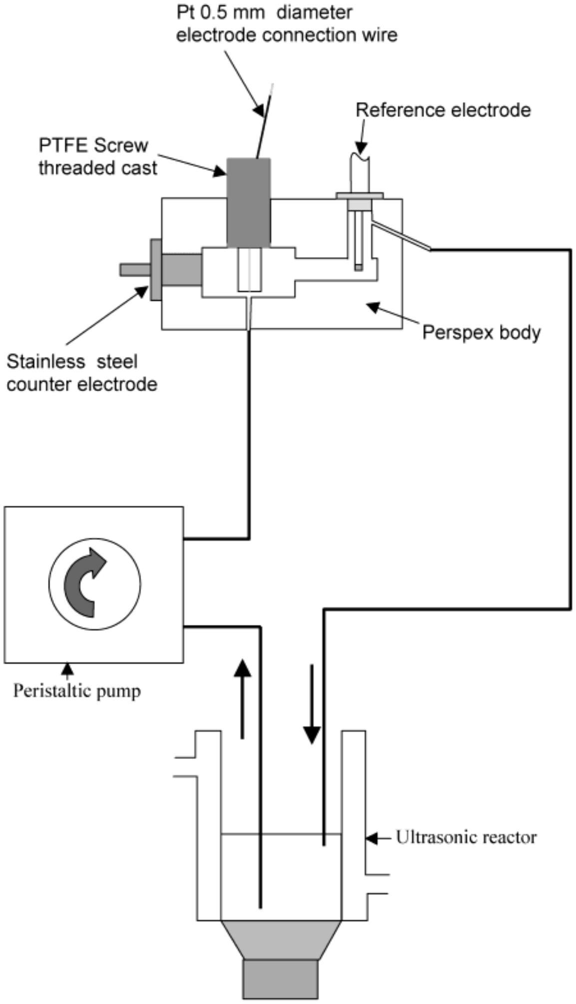

Figure 1. Schematic showing the flow cell and sonochemical reactor used for electrochemical measurements of radical production. The solution is pumped to and from the ultrasonic reactor via a peristaltic pump into the flow cell during the ultrasonic irradiation of the test liquid.

Chemicals. All solutions were made using water purified through either a USF Elga Elect 5 or a Vivendi Purelab Option

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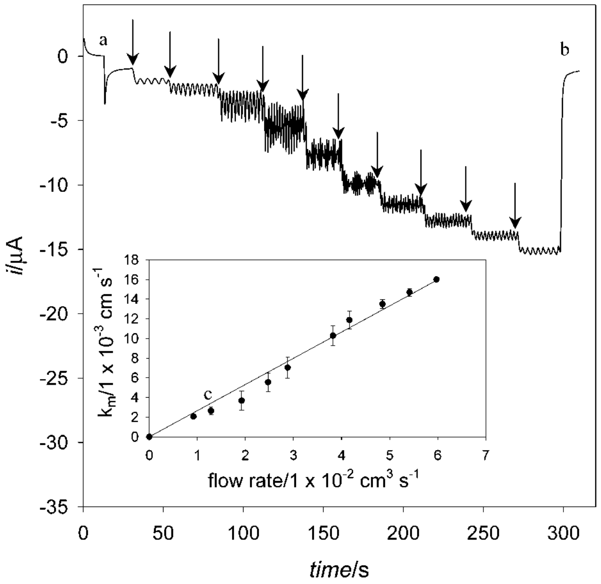

Figure 2. Current recorded as a function of time for the flow cell employed in this study as the flow rate was increased sequentially (indicated by the arrows). The figure shows how the mass transport to the electrode surface varies with flow rate. The calibration was performed employing 5 mmol dm^{-3} $Ru(NH_3)_6Cl_3$ in 0.1 mol dm^{-3} KCl at 25 °C using a 0.5-mm-diameter Pt electrode. The potential was stepped to −400 mV vs SCE at (a). The pump was stopped at (b). The inset in the figure illustrates the relationship between the mass-transfer coefficient (calculated from the average current at each pump rate; see, for example, $t = 55-85$ s for point c on the calibration inset) and the volumetric flow rate of the system.

10 water purification system. These systems produced pure water with a resistivity of typically >15 MΩ cm. Potassium iodide (Aldrich, 99%), ruthenium(III) hexaamine trichloride (Strem, 99%), potassium fluoride (Sigma, 99%), potassium sulfate (BDH 99%), potassium chloride (BDH 99%), sulfuric acid (BDH, 98%), and iron(II) sulfate heptahydrate (Aldrich, 99%) were used as received.

RESULTS

Figure 2 shows a calibration plot of the steady-state current recorded for a 5 mmol dm^{-3} solution of $[Ru(NH_3)_6]Cl_3$ in 0.1 mol dm^{-3} KCl as a function of flow rate. In this experiment, the platinum electrode was held at −0.4 V versus SCE, which corresponds to a mass-transfer limiting potential for this redox system. Figure 2 shows that as the pump rate of the liquid through the flow cell was raised the steady-state current increased. It is apparent that some noise on the signal can be seen. This corresponds to pressure fluctuations caused by the peristaltic pump and can be seen to change over the course of the experiment. This was due to aliasing through the sampling routine employed in the acquisition software. However, this does not effect the acquisition of the experimental data, as the signal produced by the generation of chemical species within the cell results in a relatively slow dc component. The mass-transfer coefficient of the electrode cell arrangement was calculated from the average steady-state current and is plotted as an inset in Figure 2 as a function of flow rate. The flow rate was determined by measuring the volume output of the flow system as a function of the pump setting over a fixed known period of time. The mass-transfer coefficient obtained depended on the electrode/jet arrangement employed within the flow cell. In the case shown in Figure 2, a 0.5-mm-diameter platinum electrode was employed. Mass-transfer coefficients of the order of 0.02 cm s^{-1} were obtained. This calibration experiment was repeated if any of the components of the flow system were changed. In all subsequent results, the actual mass-transfer coefficient of the flow cell at that time was used to calculate the rate of the reactions reported.

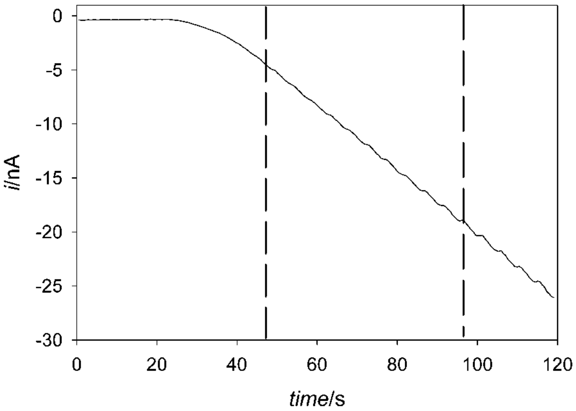

Figure 3. Variation of current as a function of time as the reactor was irradiated with ultrasound. The cell contained 100 cm^3 of aerobic 0.1 mol dm^{-3} $KI_{(aq)}$ thermostated at 25 °C. The 0.5-mm-diameter Pt electrode was held at +200 mV vs SCE. The irradiation of the liquid at 125 kHz was initiated at time $t = 0$. The segment of the graph between the two dashed lines was used to calculate the slope (di/dt), which was required to determine the rate of the reaction.

Figure 3 shows an example of the detection of radical products using this technique. The potential of the working electrode was maintained at +0.2 V versus SCE. This potential was chosen as it avoided oxygen reduction but allowed mass-transfer-limited reduction of I_3^- produced within the ultrasonic reactor. In this case, a 10 mmol dm^{-3} solution of potassium iodide containing 90 mmol dm^{-3} potassium chloride solution was pumped through the flow cell from the ultrasonic reactor. Ultrasonic irradiation of the solution was initiated at about time $t = 0$. After a period of ~20−30 s (the time required for circulation of the liquid from the ultrasonic reactor to the flow cell), the current recorded at the electrode was seen to proceed cathodically. This corresponds to the electrochemical reduction of I_3^- produced from the sonochemical oxidation of iodide within the ultrasonic reactor.

$$I^- + OH^\bullet \rightarrow OH^- + I^\bullet \tag{1}$$

$$I^\bullet + I^- \rightleftarrows I_2^{\bullet -} \tag{2}$$

$$2I_2^{\bullet -} \rightarrow I_2 + 2I^- \tag{3}$$

$$I_2 + I^- \rightleftarrows I_3^- \tag{4}$$

$$I_3^- + 2e \rightleftarrows 3I^- \tag{5}$$

Reactions 1−4 depict the primary reactions thought[18] to occur within the ultrasonic cell while reaction 5 represents the reactions occurring at the working electrode surface. Figure 3 shows that

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a linear region in the current time trace was observed. This enables the rate of triiodide production to be calculated using eq 6, where i represents the current, t the time, n the number of

$$\mathrm{d}i/\mathrm{d}t = -nFAk'k_\mathrm{m}(\mathrm{d}c/\mathrm{d}t) \tag{6}$$

electrons involved in the electrode reaction (in the Weissler case $n = 2$), A the electrode area, k' the ratio of the diffusion coefficient of the sonochemical product to $[Ru(NH_3)_6]^{3+}$ (9×10^{-6} cm^2 s^{-1}), k_m the mass-transfer coefficient, and c the concentration of the sonochemical product. In the case of the Weissler reaction, the diffusion coefficients of I_3^- was required. This was calculated by employing a solution of known I_3^- concentration and measuring the steady-state reduction current at a 25-μm-diameter Pt microelectrode under the same physical conditions. The diffusion coefficient of I_3^- was found to be 7.62×10^{-6} cm^2 s^{-1} under the conditions employed. This is in approximate agreement with literature[19] values for I_3^- (8×10^{-6} cm^2 s^{-1}), and hence, k' was calculated to be 0.85 in this case. The initial linear gradient of the current time transient was measured and the rate of I_3^- production calculated using eq 7.

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -\frac{(\mathrm{d}i/\mathrm{d}t)}{nFAk'k_\mathrm{m}} \tag{7}$$

It is interesting to note that because of the subsequent reactions in the Weissler system, it is theoretically possible that the followup reactions (in the scheme above reactions 2−4) may not be complete before the solution reaches the flow cell (note reaction 1 is known[18] to be virtually diffusion controlled, $k = 1.1 \times 10^{10}$ mol^{-1} dm^3 s^{-1}). However, in the experiments performed, no evidence for this followup effect was observed. If one expects that this is indeed the case, then it would be expected that, on termination of ultrasonic irradiation of the solution, a slow relaxation transient to a steady-state value would be observed. However, the current time behavior indicates a reasonably sharp "off" response (see Figure 5). This implies that the following reactions are likely to be complete before the solution reaches the flow cell (after the 20−30 s flow delay). Hence, the quantity of I_3^- measured is expected to be the total yield of reaction 1 considering the equilibria in the scheme shown (reactions 2−4).

Figure 4 shows the concentration dependence of the rate on the production of I_3^-. In this experiment, the ionic strength of the solution was maintained by adding potassium chloride to the solution. This was necessary to ensure that the acoustic properties of the cell remained constant. Initially, the rate increases linearly with concentration up to 10 mmol dm^{-3} KI. In excess of this concentration, the rate appears to plateau out. It should be noted that the rate is still dependent on the KI concentration. This dependence in rate was noted by Heinglein et al.[8] They proposed that this was due to competition between the I^- ion to capture $OH^\bullet$ and formation of H_2O_2 through self (geminate) capture. In addition, the measurement performed in the absence of KI (100 mmol dm^{-3} KCl) demonstrated a small but significant response of the system under the conditions stated. This response of the electrode is believed to be due to the presence of Cl^- in electrolyte solution. The production of $OH^\bullet$ radicals within a cavitating medium has been well documented. Hydroxyl radicals are extremely powerful oxidizing agents with a formal potential[20] of 2.8 V. This is in excess of the formal potential for Cl^- (+1.328 V), and it can be expected that free Cl_2 could be generated. In aqueous solution, free chlorine reacts readily to form HOCl and Cl^-.[21] The HOCl species is known to be electrochemically active on platinum.[22] Hence it is suspected that this signal, in the absence of I^-, represents oxidation of the chloride within the electrolyte. This assumption is further supported by a control experiment performed in 100 mmol dm^{-3} potassium fluoride. In this case, no signal was obtained. Further discussion of this background reaction is beyond the scope of this paper.

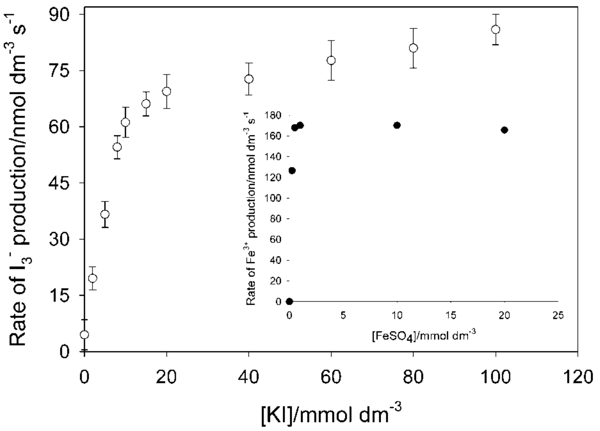

Figure 4. Variation in the rate (○) of the Weissler reaction as a function of KI concentration. The ionic strength of the solution was maintained at 0.1 mol dm^{-3} by adding an appropriate amount of KCl. The error bars represent ±1 standard deviation of three repeat measurements. The inset shows a plot of the effect of $[Fe^{2+}]$ on the rate of the Fricke reaction (●). The irradiated solution contained 1 mmol dm^{-3} NaCl in 0.4 mol dm^{-3} H_2SO_4. The sum of the $FeSO_4$ and K_2SO_4 concentrations was equal to 0.1 mol dm^{-3} in each case. The potential of the 3-mm-diameter glassy carbon electrode was held at −400 mV vs SCE. The frequency was fixed at 125 kHz and the drive voltage amplitude was 100 V in both cases. The temperature of the aerobic solution was maintained at 25 °C for both experiments.

To verify that the rate of iodine production determined electrochemically was indeed accurate, an independent measurement of final triiodide concentration was made using spectrophotometric means. Figure 5 shows a current time transient recorded in the manner described above. Figure 5 also shows the predicted final current determined by measuring the absorbance of 350-nm light using a UV−visible spectrometer (see inset in Figure 5). The concentration of I_3^- predicted by the spectrophotometric method was 8.73×10^{-9} mol cm^{-3}, assuming an extinction coefficient of 26 000 M cm^{-1}.[23] The current expected for this quantity of I_3^- can be calculated as -4.412×10^{-8} A. The actual current change (i_predict) was -4.389×10^{-8} A (taking into account the background current in both cases). This experiment shows an excellent agreement between the electrochemical detection of I_3^- and the spectrophotometric method (0.5% difference).

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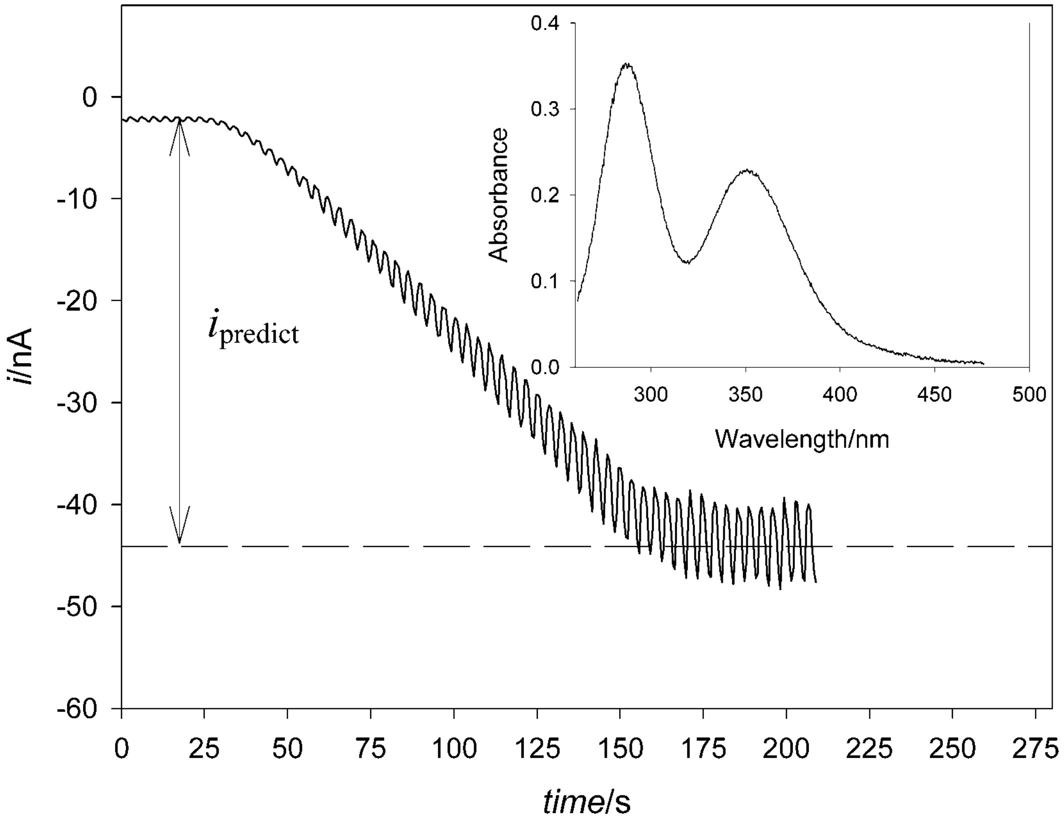

Figure 5. Comparison between the electrochemical technique and spectrophotometry. The conditions employed are the same as described in Figure 3. The dashed line represents the predicted current (see text). The inset shows the absorbance of the solution after irradiation of the liquid with ultrasound had been terminated. The background was the preirradiated solution. Note that under the conditions employed the maximum acoustic pressure amplitude in the reactor was 3.16 atm measured with a calibrated hydrophone.

It is also possible to extend the technique reported here to other systems. The Fricke reaction has been used extensively in the assessment of ionizing radiation. In this system, an acidified solution of Fe^{2+} is irradiated with ionizing radiation, which is thought to produce hydroxyl radicals. These hydroxyl radicals oxidize Fe^{2+} to Fe^{3+}. The concentration of the Fe^{3+} can then be determined analytically and the equivalent dose exposed to the test solution calculated. Several authors have used the Fricke reaction to measure the production of radical species as the result of acoustic cavitation.[12,13] In these reports, UV−visible absorption spectroscopy was used to measure the production of Fe^{3+}. It is possible to use the same methodology, as reported here, to measure the production of Fe^{3+} as a function of time. In this case, the electrochemical reduction of Fe^{3+} at an electrode surface was performed within the flow cell while the production of Fe^{3+} form the cavitation-induced oxidation of Fe^{2+} occurs within the ultrasonic reactor. Reactions 8−11 depict the primary reactions thought to occur inside the ultrasonic reactor while reaction 12 represents the electrochemical reaction occurring at the electrode surface.

$$Fe^{2+} + OH^{\bullet} \rightarrow Fe^{3+} + OH^{-} \tag{8}$$

$$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet} \tag{9}$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{-} \tag{10}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \tag{11}$$

$$Fe^{3+} + e \rightarrow Fe^{2+} \tag{12}$$

It should be noted that in this system it is theoretically possible to produce a number of Fe^{3+} ions from the ionization of one water molecule in the presence of oxygen. However, it was found that the electrochemical reduction of Fe^{3+} within the flow cell occurred more reproducibly if, instead of a platinum electrode, a glassy carbon electrode was employed.

Figure 6 shows a typical current time transient for the Fricke reaction with electrochemical detection. Again, at time $t = 0$ the irradiation of the solution commenced. The delay due to the time required to pump solution from the ultrasonic reactor to the flow cell is again ~20−30 s. The cathodic deviation of the current was due to the electrochemical reduction of the sonochemically produced Fe^{3+}. The rate of production of Fe^{3+} determined from the initial slope of the current time transient shown in Figure 6 can be calculated using eq 6. The mass-transfer coefficient of the system was recalculated using the steady-state current recorded for Fe^{3+} at the pump flow rate employed in the experiments. In this case, the k_m value was 6.6×10^{-3} cm s^{-1}. The rate of the reaction can then be determined. Figure 6 also shows a second burst of ultrasonic irradiation of the liquid within the ultrasonic irradiation. The current time transient shows a corresponding second deviation (see time $t = 200-250$ s). In the absence of ultrasonic irradiation of the liquid, the current remains constant. This indicates that, in the absence of ultrasound, no background reactions perturb the system.

The inset in Figure 4 shows how the rate of Fe^{3+} production varies as a function of Fe^{2+} concentration. Figure 4 shows a rapid

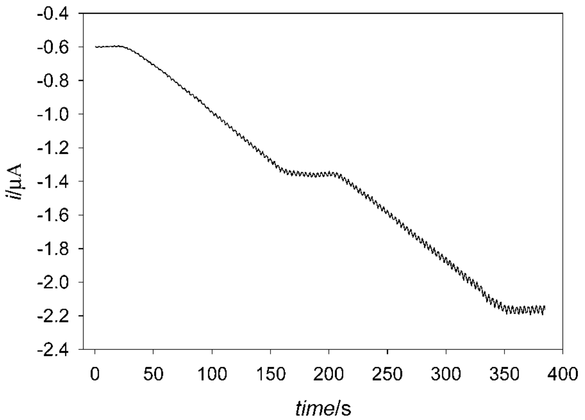

Figure 6. Variation of current as a function of time for the Fricke reaction. The current time plot was obtained by employing a 3-mm glassy carbon working electrode. The solution contained 1 mmol dm^{-3} $FeSO_4$, 99 mmol dm^{-3} K_2SO_4, and 1 mmol dm^{-3} NaCl in 0.4 mol dm^{-3} H_2SO_4. The potential of the electrode was held at -400 mV vs SCE. The frequency was 125 kHz, and the drive voltage amplitude maintained at 90 V. The temperature of the aerobic solution was maintained at 25 °C.

linear increase up to an Fe^{2+} concentration of 1 mmol dm^{-3} before the rate becomes independent of concentration. This is in agreement with previous studies.[12,13,25] The Fricke reaction can be used to calculate an equivalent dose of radiation exposed to the solution. To calculate these quantities, it is necessary to employ eq 13, which has been adapted from radiochemical dose equivalent

$$D_{\text{rad}}' = \frac{(dc/dt)[9.64 \times 10^8]}{G(X)\rho} \qquad (13)$$

calculations.[25] Here D_{rad}' represents the equivalent dose of rads exposed to the test solution per second, $G(X)$ the chemical yield expressed as a number of molecules or ions liberated per 100 eV of equivalent radiation, and ρ the density of the test solution. In the case of the Fricke reaction, $G(X)$ was assumed to be 15.6 and ρ measured at 1.1 g cm^{-3}. The value of $G(X)$ of 15.6 was chosen as we wished to make an analogy with radioactive dosimetry. Dosimetry applied to cavitation has been suggested by a number of authors. As an example, von Sonntag et al. quoted a number of $G(X)$ values depending on the gas content within their reactor.[12] The values given by von Sonntag et al. indicate that the efficiency of the cavitation process may change by altering the gas content. However, it is also important to point out that although the approach of von Sonntag et al. is thorough in its handling of the complex combination of sonochemistry with radical chemistry, the authors assumed that by employing calorific measurements it is possible to relate the energy input to the cavitation dynamics within the solution of a reactor. Cavitation is a nonlinear threshold technique and as such equating the power in to the yield of products is not realistic. Hence, it is unlikely that the $G(X)$ values quoted are generally accurate but may give a representation of the results obtained with varying gas content. Considering that the reactor geometry and frequency was different from the one reported here, employing the $G(X)$ values suggested in the paper by von Sonntag et al. would be in error. With these difficulties in mind, our employment of $G(X) = 15.6$ is physically realistic as it enables us to make a direct comparison to radiation dosimetry, which does not suffer from these problems.

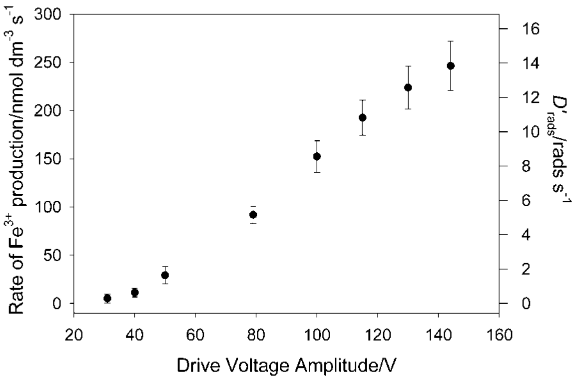

Figure 7. Effect of drive voltage on the rate of the Fricke reaction. All other conditions are the same as those reported in Figure 6. Error bars were calculated using three repeat measurements and they represent ± one standard deviation.

Figure 7 shows the rate of Fe^{3+} production and the equivalent dose exposed to the solution as the result of radicals produced through cavitation action. It is interesting to note that the equivalent dose values are relatively low. This emphasizes the sensitivity of the electrochemical detection of the products of radical reactions. This is in contrast to previous electrochemical studies employing a cerium system which was shown to be a useful dosimeter at high doses (e.g., 10−40 kGy range).[24] Figure 7 also shows that as the drive voltage to the ultrasonic cell was increased the production of radicals (and hence the equivalent dose) increased. This is understandable considering that increasing the drive voltage will ultimately increase the acoustic pressure amplitude within the cell and hence increase the amount of cavitation of the solution. In turn, it should be expected that the amount of radical produced would increase. Below a drive voltage amplitude of 30 V, the detection of sonochemical products appears not to be possible. This represents a relatively low equivalent dose (<1 rad s^{-1}). It is also interesting to note that irradiation levels of this magnitude are usually difficult to measure using chemical dosometers.[25] This is because the change in absorbance at this level of absorbed dose is relatively small. As an example for the Fricke reaction 0.28 rad of radiation should produce a concentration of Fe^{3+} of the order of 4.98×10^{-9} mol dm^{-3}. This corresponds to a absorbance change of 1.09×10^{-5} (assuming a 1-cm path length and $\epsilon_{304\text{ nm}} = 2196$ M^{-1} cm^{-1}).[25] This level of sensitivity is difficult to achieve. However, the electrochemical system presented here is able to detect this level of absorbed dose and perhaps could be extended to lower levels using more sensitive electrochemical technology (for example, hydrodynamic voltammetry) or an improved mass-transfer coefficient.

CONCLUSIONS

It has been shown that electrochemical detection of sonochemically generated products can be applied as a sensitive real-time technique for the monitoring of radical production. A novel flow cell technique has been shown to be successful with a number of direct advantages when compared to both in situ electrochemical

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detection techniques and conventional spectroscopic assaying of the solution. The Weissler and Fricke reactions were studied successfully using this electrochemical technique. Rate constants of 6.12×10^{-6} ($[I^-] = 10$ mmol dm^{-3}) and 2.5×10^{-4} s^{-1} ($[Fe^{2+}] = 1$ mmol dm^{-3}) were measured for the Weissler and Fricke reaction, respectively, under the conditions employed by assuming first-order kinetics. The concentration dependence of both reactions were measured and found to be in agreement with previous reports. An equivalent dose of up to 13.8 rad s^{-1} from the sonochemical reactor was calculated. Electrochemical detection levels in the nmol dm^{-3} s^{-1} range were shown to be possible.

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