Electrochemical evidence of H· produced by ultrasound

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Electrochemical evidence of H· produced by cavitation as the result of ultrasonic irradiation of an aqueous solution is presented.

The production of radical species[1] through the generation of high temperatures and pressure created in the interior of a collapsing cavitation bubble is one of the fundamental pieces of evidence for the phenomena classed as sonochemistry. These high temperature and pressures (estimated† to be around 5000 K and 500 atm)[2,3] are thought to break down the solvent matrix according to reaction (1).
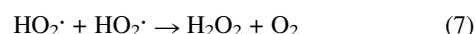
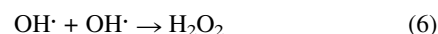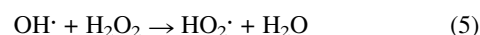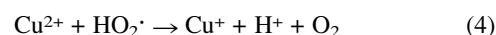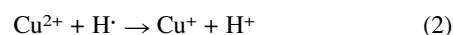$$H_2O \rightarrow OH^{\cdot} + H^{\cdot} \quad (1)$$

The radical species generated, which have been detected in a number of ways including spin trapping experiments performed by Riesz and coworkers,[1,4] have been suggested as possible pollutant destruction agents owing to their extremely high redox potential (*e.g.* OH· radicals,[5] $E^{\circ} = +2.8$ V). However, less evidence is available for the use and detection of H· even though in principle it is generated in equivalent quantities when compared to OH· in the primary solvent degradation step [see reaction (1)]. The chemical nature of these two radical species is quite different.[6–9] As an example, the OH· radical is known to initiate a number of different reactions within solution[10–12] while in contrast the H· atom can be rapidly consumed directly by molecular oxygen.[13] Indeed less attention has been placed on H· perhaps due to these quenching reactions.

Electrochemical evidence for the production of radical species is limited. Compton and coworkers provided evidence for OH· through a *sono*-EC' reaction involving the electrochemical generation of a radical species (from the electroreduction of fluorescein) which in turn was re-oxidised by OH· produced by ultrasound.[14] However, to the knowledge of the authors, no direct electrochemical evidence for H· appears in the literature. We present here for the first time an electrochemical method for the detection of H· produced by cavitation as the result of ultrasonic irradiation of an aqueous electrolyte solution.

Hart and Heinglein showed that it was possible to detect H· production[15] [measuring HO$_2$·, see reaction (4)] using a system containing Cu^{2+}. In the electrochemical system reported here, a Cu^{2+} solution is also employed. Reaction (2) is thought to be the main process occurring as the H· diffuses into the liquid phase of the mixture employed. The rate constant for the above reaction was determined to be 9.1×10^7 dm^3 mol^{-1} s^{-1}.[16] There are several competing reactions.[3–7] Cu$^+$ can also be produced by reaction (4). However, the production of HO$_2$· can also be attributed to H· generation [see reaction (3)]. HO$_2$· can be generated from both products of reaction (1). However, in the absence of a scavenger for OH·, reaction (6) dominates and the geminate recombination product is preferentially formed.[16] In addition reaction (5) requires the presence of significant H$_2$O$_2$ concentrations and if this reaction was very important a non-linear response in Fig. 1 would be expected. Also HO$_2$· can be consumed by reaction (7). Under these considerations it is

expected that the dominant reaction pathway leading to the formation of Cu$^+$ will involve the generation of H·.

$$Cu^{2+} + H^{\cdot} \rightarrow Cu^+ + H^+ \quad (2)$$

$$H^{\cdot} + O_2 \rightarrow HO_2^{\cdot} \quad (3)$$

$$Cu^{2+} + HO_2^{\cdot} \rightarrow Cu^+ + H^+ + O_2 \quad (4)$$

$$OH^{\cdot} + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (5)$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2 \quad (6)$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \quad (7)$$

In order to stabilise the Cu$^+$ species a solution containing a high Cl$^-$ concentration was employed. The complex that forms (CuCl$_2^-$) is stable and can be electrochemically detected as shown in reaction (8) (Cu^{2+}/CuCl$_2^-$, $E_{1/2} = +231$ mV *vs.* SCE as measured under similar conditions).

$$CuCl_2^- \rightarrow Cu^{2+} + 2Cl^- + e^- \quad (8)$$
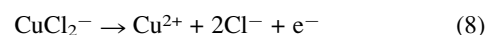
In order to detect the generated product (CuCl$_2^-$) a pump was used to remove small quantities of liquid from the reactor and then pass this solution through a flow cell where electrochemical detection of the products could be achieved. This method has a number of advantages when compared to employing electrochemical detection of sonochemically generated products directly within the reactor. First, the mass transfer characteristics of the flow cell can be well characterised. Second, employing electrochemistry within an ultrasonic reactor, although producing efficient mass transfer close to the cavitation phenomena, leads to non-steady state mass transfer characteristics (particularly for microelectrodes) or mass transfer characteristics that require careful calibration. These two problems are avoided by employment of a flow cell.
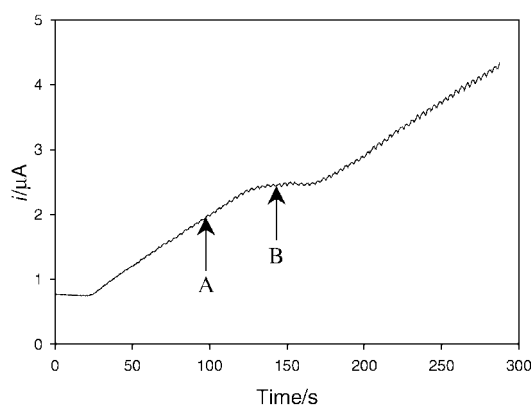

Fig. 1 Plot showing the current as a function of time for the electrochemical detection of Cu$^+$ produced by H· capture. The solution contained 10 mmol dm^{-3} CuSO$_4$ in 1.5 mol dm^{-3} NaCl. The experiment was performed under aerobic conditions at 25 °C. The electrode (0.071 cm^2) was held at +1 V *vs.* SCE. The solution in the reactor was exposed to 125 kHz ultrasound. The applied drive voltage amplitude was 100 V (corresponding to a measured pressure amplitude of 421 kPa).‡ Ultrasonic irradiation of the liquid was initiated at time $t = 0$ s, terminated at 'A' and re-started at 'B'.

A 3 mm diameter glassy carbon electrode was held at +1 V *vs.* SCE§ (a potential sufficient to oxidise any $CuCl_2^-$ produced by the reaction of H· with Cu^{2+} present within the solution). Fig. 1 shows the current time response for the glassy carbon electrode employed within the flow cell. The solution contained Cu^{2+} in a high $[Cl^-]$ media. Ultrasonic irradiation of the solution was initiated at time $t = 0$. A *ca.* 25 s lag time was observed before any $CuCl_2^-$ was detected at the electrode. This corresponds to the time taken for the solution to pass through the piping to the flow cell. The current at $t = 25$ s is seen to deviate anodically from its initial steady state condition. This is due to the electrochemical oxidation of the $CuCl_2^-$ produced by the radical trap reaction. The gradient of the current time plot at this point is constant indicating a steady production of $CuCl_2^-$ and therefore H· within the ultrasonic reactor. If the ultrasonic irradiation of the solution was terminated (at time $t = 100$ s) then, after the lag time produced by the piping, the current time trace was observed to plateau out. This indicates that in the absence of ultrasonic irradiation of the solution, no significant background reactions could be observed. If the ultrasonic irradiation of the solution was repeated (time $t = 145$ s) then the current was observed to deviate anodically, indicating that it was possible to produce further quantities of $CuCl_2^-$ and hence H· within the ultrasonic reactor. The gradients of the two current–time anodic deviations were the same indicating that the rate of Cu^+ production was identical in both cases. It is possible to determine the rate of $CuCl_2^-$ production from the slope of these current time transients.[17] In the example shown in Fig. 1 the rate of $CuCl_2^-$ production was 320 nmol dm^{-3} s^{-1}. This procedure can be repeated under a variety of different conditions. Fig. 2 shows how the rate of $CuCl_2^-$ production can vary as a function of $CuSO_4$ concentration. Below *ca.* 20 mmol dm^{-3} $CuSO_4$ it is apparent that the rate of production of $CuCl_2^-$ is dependent on the concentration of Cu^{2+}. Above 20 mmol dm^{-3} the rate of $CuCl_2^-$ production appears to be independent of Cu^{2+} concentration. This is consistent with other measurements (*e.g.* the Fricke reaction, known to be sensitive to OH· radical production, showed Fe^{3+} productions rates up to *ca.* 250
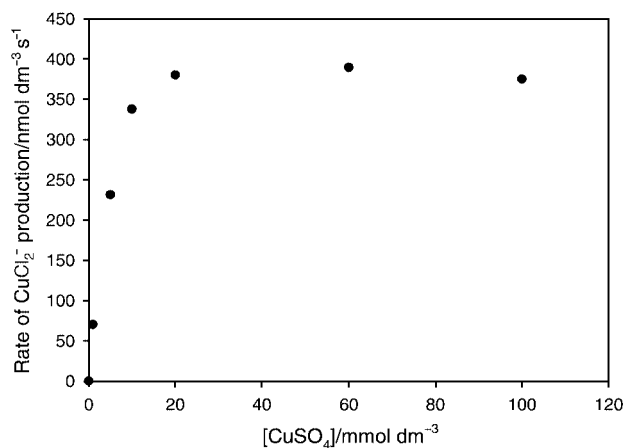
nmol dm^{-3} s^{-1}) performed on other electrochemical trapping systems.[17]

The results shown here demonstrate that it is possible to detect the sonochemical production of H· electrochemically using a coupled chemical reaction. The criteria for this detection method are that the products of the trapping reaction are stable over the experimental timescale (as ensured by the presence of high $[Cl^-]$) and that a product of the trapping reaction is electrochemically active.

The sensitivity of the electrochemical flow system enables very small quantities of sonochemically generated products to be detected. This method enables electrochemically active radical trap generation rates within the nmol dm^{-3} s^{-1} range to be measured. This method can be extended to a number of different products of sonochemical reactions.[17]

Notes and references

† The estimates of the conditions within the interior of a collapsing cavitation bubble are a matter of some debate.[18] The estimation presented by Flint and Suslick relied on the measurement of sonoluminescent emission from silicone oil. The spectra obtained were fitted to a rotation vibration model for a C_2 diatomic molecule.[2] Other authors have assigned differing single value temperatures to the interior of a sonoluminescing bubble.[19,20] However, if the collapse is sufficiently rapid, the pressure and temperature within the bubble will be spatially non-uniform,[21] in which case assignment of a single value temperature is inappropriate.

‡ This pressure was measured with a Bruel & Kjaer 8103 hydrophone placed within the cell. Note that, owing to the modal nature of the sound field the pressure will vary throughout the cell depending on the particular mode excited under the physical conditions within the system.

§ This high potential was employed as it avoided unwanted electrochemical interference presumably from other sonochemical products.

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Fig. 2 Plot showing the variation in the rate of $CuCl_2^-$ production as a function of $[CuSO_4]$. The irradiated solution contained 1.5 mol dm^{-3} NaCl. The ionic strength of the solution was maintained at 1.6 mol dm^{-3} using Na_2SO_4. The frequency was fixed at 125 KHz and the drive voltage amplitude was 100 V. The aerobic solution was thermostated at 25 °C.